

**Compiling Triplets:
An Integrated Transient-Absorption Framework
Unravels Triplet Generation and Relaxation**

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Natura in minima maxima

Abstract

Over the past decades, transient absorption (TA) spectroscopy has matured into a routine, broadband femto- to microsecond probe for photoinduced dynamics. It is uniquely powerful to disentangle photo-physical pathways, including the generation and relaxation of triplet states that govern efficiencies in applications ranging from light-emitting diodes and solar cells to photodynamic therapy and sensing. However, turning TA experiments into quantitative insight often remains a bottleneck since it demands global modeling and substantial coding expertise, while existing workflows too often lack statistical robustness, transparency and flexibility.

This cumulative thesis, based on four research papers, addresses these limitations in TA data handling and modeling by developing a software framework covering the full TA workflow from import and preprocessing to analysis and visualization. This workflow is then applied to investigate the nature, generation and relaxation of triplets in oxygen-sensitive tungsten iodide clusters and heptacenes.

First, I developed TAPAS (Transient Absorption Processing and Analysis Software) as a fully integrated graphical user interface. Leveraging a modern machine-learning compiler ecosystem, substantial speedups

in the computationally intensive fitting engine were achieved when compared to conventional packages. I implemented methods to estimate parameter confidence intervals and correlations via automatic differentiation, effective-sample-size scaling, and Bayesian posterior analysis. These capabilities were validated on multiple TA datasets and complementary measurements of rose bengal, yielding a single, self-consistent kinetic model. The analysis also exposed parameter correlations and weak identifiability in smaller datasets or local fits, which is often not captured by conventional software, resulting in a misleading impression of model robustness. This clearly emphasizes the advantage of the TAPAS engine for jointly fitting multiple datasets and complementary information, as well as the value of the implemented statistical methods for a more reliable assessment of model and parameter uncertainties and identifiability.

Second, I established TA spectroscopy to monitor triplet generation and relaxation of a novel cationic tungsten iodide cluster under varied conditions, correlating the results with time-resolved emission measurement. By globally modeling multiple TA datasets spanning different temporal windows, I characterized the excited-state properties including intersystem crossing (ISC)

rates, triplet-emission lifetimes and oxygen quenching. The cationic cluster undergoes ultrafast ISC within about 2 ps into a hot triplet state, which further relaxes to the emissive triplet and then decays on microsecond timescales.

Building on this, in the third study on two general anionic tungsten iodide clusters, I combined TA with time- and temperature-resolved emission spectroscopy and relativistic time-dependent density functional theory to explore the ultrafast triplet-state generation and the unusual broad and temperature-sensitive emission characteristics. Tracking the dynamics from 200 fs to 400 μ s shows that both clusters populate triplet states within 6 ps, which subsequently decay either via bimolecular oxygen quenching or phosphorescence. Extracted emission lifetimes and oxygen-quenching rates agree with complementary time-resolved emission measurements. Further, temperature-dependent emission measurements from 4 to 340 K of the clusters dispersed in a polymer matrix reveal systematic shifts in both spectra and lifetimes. Using a group-theoretical model with three distinct emissive spin sublevels yields satisfactory simulations, contrasting earlier reports on molybdenum-based clusters that invoked four sublevels. Relativistic calculations further indicate substantial excited-state geometric relaxation, challeng-

ing a purely group-theoretical description and motivating a relativistic model with three thermally accessible excited-state geometries, each possessing three triplet sublevels.

Finally, the photophysics of a novel photochemically stable heptacene derivative were investigated using comprehensive steady-state absorption, emission, and TA measurements. These studies show that the lowest excited state is an electric-dipole-forbidden (dark) transition, in contrast to shorter acenes. In this context, I performed broadband TA experiments which reveal rapid triplet formation and relaxation, plausibly facilitated by this dark singlet state. These results were used to discuss the underlying triplet-generation pathway, considering both ISC and singlet fission as viable mechanisms.

In summary, this thesis delivers an open-source software providing the whole TA processing-, analysis-, modeling- and visualization- workflow with comprehensive statistical treatment essential for complex models and uses this framework to elucidate triplet-state population, configuration and relaxation in tungsten iodide clusters and heptacenes.

Zusammenfassung

In den vergangenen Jahrzehnten hat sich die transiente Absorptionsspektroskopie (engl. *Transient Absorption*, TA) zu einer routinemäßig eingesetzten, breitbandigen Methode entwickelt, mit der photoinduzierte Dynamiken auf Zeitskalen von Femto- bis Mikrosekunden untersucht werden können. Sie ist besonders geeignet, photophysikalische Prozesse einschließlich der Erzeugung und Relaxation von Triplettzuständen aufzuklären, welche die Effizienz in Anwendungen von Leuchtdioden und Solarzellen bis hin zu photodynamischer Therapie und Sensorik bestimmen. Die Gewinnung quantitativer Erkenntnisse aus TA-Experimenten bleibt jedoch häufig eine Herausforderung, da sie globales Modellieren und erhebliche Programmierkenntnisse erfordert, während es vorhandenen Softwarelösungen oft an statistischer Robustheit, Transparenz und Flexibilität mangelt.

Diese kumulative Dissertation, die auf vier Forschungsarbeiten basiert, befasst sich mit diesen Einschränkungen in der Behandlung und Modellierung von TA-Daten durch die Entwicklung einer Software, die den gesamten Prozess der TA-Datenauswertung von Import und Aufbereitung bis hin zu Analyse und Visualisierung abdeckt. Dieser Ansatz wird anschließend eingesetzt, um die Natur, Bildung und Relaxation von Triplett-

zuständen sauerstoffsensitiver Wolframiodid-Cluster und Heptacene zu untersuchen.

Zunächst entwickelte ich TAPAS (*Transient Absorption Processing and Analysis Software*) als vollständig integrierte Software mit grafischer Benutzeroberfläche. Durch die Nutzung eines modernen Compiler-Ökosystems, wie es im maschinellen Lernen eingesetzt wird, konnten deutliche Geschwindigkeitsgewinne der rechenintensiven Simulationen im Vergleich zu herkömmlichen Softwarepaketen erzielt werden. Hierbei implementierte ich Methoden zur Abschätzung von Konfidenzintervallen und Parameterkorrelationen mithilfe automatischer Differenzierung, effektiver Stichprobengrößen-Skalierung und Bayescher Posterior-Analyse. Diese Verfahren wurden an mehreren TA-Datensätzen sowie durch komplementäre Messungen an Bengalrosa validiert und führten zu einem einheitlichen, selbstkonsistenten kinetischen Modell. Die Analyse legte zudem Parameterkorrelationen und eingeschränkte Identifizierbarkeit in kleineren Datensätzen oder lokalen Fits offen, die von konventioneller Software häufig nicht erfasst werden und fälschlich den Eindruck eines robusten Modells vermitteln. Dies unterstreicht klar die Vorteile der TAPAS-Algorithmen für das gemeinsame Fitten mehrerer Datensätze und komplemen-

tärer Informationen sowie den Nutzen der implementierten statistischen Methoden für eine verlässlichere Beurteilung von Modell- und Parameterunsicherheiten sowie der Identifizierbarkeit.

Im zweiten Teil setzte ich TA-Spektroskopie ein, um die Triplettbildung und -relaxation eines neuartigen kationischen Wolframiodid-Clusters unter verschiedenen Bedingungen zu messen, und korrelierte die Ergebnisse mit zeitaufgelösten Emissionsmessungen. Durch globales Modellieren mehrerer TA-Datensätze, die unterschiedliche Zeitfenster abdecken, charakterisierte ich die angeregten Zustände, einschließlich Interkombinationsraten (engl. *Intersystem Crossing*, ISC), Triplet-Emissionslebensdauern und Sauerstofflöschungseffekten. Der kationische Cluster durchläuft innerhalb von etwa 2 ps einen ultraschnellen ISC-Prozess in einen heißen Tripletzustand, der weiter in den emissiven Tripletzustand relaxiert und anschließend auf Mikrosekunden-Zeitskalen zerfällt, wobei der emissive Zustand effizient durch molekularen Sauerstoff gelöscht wird.

Anhand dieser Ergebnisse kombinierte ich in der dritten Studie zu zwei repräsentativ anionischen Wolframiodid-Clustern TA-Spektroskopie mit zeit- und temperaturlösender Emissionsspektroskopie sowie relativistischer zeitabhängiger Dichtefunktionaltheorie, um die ultraschnelle Triplettbildung und die ungewöhnlich breite und temperaturabhängige Emission zu untersuchen. Zeitaufgelöste Messungen im Bereich von 200 fs bis 400 ps zeigen, dass beide Cluster innerhalb von 6 ps Tripletzustände besetzen, die anschließend entweder über bimolekulare Sauerstofflöschung oder Phosphoreszenz zerfallen. Die extrahierten Emissionslebensdauern und Sauerstoffquench-Raten stimmen mit komplementären zeitaufgelösten Emissionsmessungen überein. Darüber hinaus zeigen temperaturabhängige Emissionsmessungen zwischen 4 und 340 K an dispergierten Clustern in einer Polymermatrix systematische Verschiebungen sowohl in

Spektren als auch in Lebensdauern. Die Modellierung unter Verwendung eines gruppentheoretischen Ansatzes mit drei unterschiedlichen emissiven Spin-Unterniveaus liefert gute Übereinstimmung mit den Messungen und steht damit im Gegensatz zu früheren Arbeiten an molybdänbasierten Clustern, in denen vier Unterniveaus angenommen wurden. Relativistische Rechnungen weisen zudem auf erhebliche geometrische Relaxation im angeregten Zustand hin, was eine rein gruppentheoretische Beschreibung infrage stellt und ein relativistisches Modell mit drei thermisch zugänglichen angeregten Geometrien nahelegt, von denen jede drei Tripletunter-niveaus aufweist.

Abschließend wurde die Photophysik eines neuartigen, photochemisch stabilen Heptacen-Derivats mittels umfassender Absorptions-, Emissions- und TA-Messungen untersucht. Diese Studien zeigen, dass der niedrigste angeregte Zustand im Gegensatz zu kürzeren Acenen ein elektrisch dipolverbotener („dunkler“) Übergang ist. In diesem Zusammenhang führte ich breitbandige TA-Experimente durch, die eine schnelle Bildung und Relaxation von Tripletzuständen offenlegen, was plausibel durch diesen dunklen Singulettzustand begünstigt wird. Diese Ergebnisse dienen als Grundlage für die Diskussion des zugrunde liegenden Tripletbildungsmechanismus, wobei sowohl ISC als auch Singulettspaltung als mögliche Pfade in Betracht gezogen wurden.

Zusammenfassend stellt diese Dissertation eine quelloffene Software zur Verfügung, die den vollständigen Prozess der TA-Datenauswertung, von Verarbeitung, Analyse, Modellierung und Visualisierung bis hin zu einer umfassenden statistischen Behandlung komplexer Modelle, unterstützt und deren Architektur nutzt, um Tripletpopulation, -konfiguration und -relaxation in Wolframiodid-Clustern und Heptacenen aufzuklären.

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Contents

Abstract	i
Zusammenfassung	iii
Acknowledgments	v
List of Figures	xiii
List of Schemes	xix
List of Charts	xxi
List of Tables	xxiii
Abbreviations	xxv
Symbols	xxvii
1 Introduction	1
1.1 Motivation	1
1.1.1 Triplet States and Their Importance	1
1.1.2 Transient Absorption for Triplet Photophysics	2
1.1.3 The Bottleneck is not (Only) Data	2
1.2 Objective	3
1.3 Structure of the Work	4
2 Theoretical and Scientific Fundamentals	7
2.1 Photophysical Background	7
2.1.1 Photons and Their Energies	8
2.1.2 Energies in Boxes: The Schrödinger Equation	8
2.1.3 When Spins Align	9
2.1.4 The Geometry of Intensity	9
2.1.5 Mapping Excited-State Pathways	10

2.2	Fates of the Excited States	11
2.2.1	Excited States and Excitons	12
2.2.2	Nonradiative Spin-Conserving Relaxation	12
2.2.3	Nonradiative Spin-Conversion Processes	13
2.2.4	Radiative Emission Pathways	14
2.2.5	Bimolecular and Multi-State Interactions	15
2.2.6	Photochemical Transformations	16
2.3	Photophysical Observables	17
2.3.1	Steady-State Absorption	17
2.3.2	Steady-State Emission	18
2.3.3	Time-Resolved Emission Spectroscopy	18
2.3.4	Time-Resolved Absorption Spectroscopy	20
2.3.5	Variable-Parameter Spectroscopy	22
2.4	Transient Absorption Instrumentation	24
2.4.1	Femtosecond Light Sources	24
2.4.2	Nonlinear Frequency Conversion	26
2.4.3	Pump-Probe Synchronization	27
2.4.4	Experimental Conditions	28
2.5	Modeling Transient-Absorption Data	29
2.5.1	Raw Data and Preprocessing	29
2.5.2	Dispersion and Artifacts	30
2.5.3	Kinetic Models	31
2.5.4	Model and Parameter Selection	35
2.5.5	Uncertainty Quantification	36
2.5.6	Algorithmic Implementation for Global Kinetics	38
2.6	Investigated Material Systems	39
2.6.1	Reference System: Xanthene Dyes	39
2.6.2	Octahedral Metal Halide Clusters	41
2.6.3	Acenes	44
3	TAPAS: Transient Absorption Processing and Analysis Software	49
3.1	Abstract	50
3.2	Introduction	50
3.3	Design and Implementation of TAPAS	52
3.3.1	User Interface	52
3.3.2	Background Architecture	52
3.4	Algorithms and Theoretical Background	54
3.4.1	Global Analysis Algorithm	54
3.4.2	Kinetic Models	54
3.4.3	Fit Metrics	57
3.5	Results: Case Study Rose Bengal	57
3.5.1	NIR Exploration and Sequential Kinetic Modeling	58
3.5.2	Comprehensive Target Analysis	59
3.6	Discussion	62
3.7	Conclusion	64
4	Preparation, Photoluminescence and Excited State Properties of the Homoleptic Cluster Cation $[(W_6I_8)(CH_3CN)_6]^{4+}$	65
4.1	Abstract	66

4.2	Introduction	66
4.3	Results and Discussion	67
4.3.1	Electron Localization Function	70
4.3.2	Photoluminescence Studies	70
4.3.3	Excited-State Studies	72
4.4	Experimental Section	74
4.4.1	Synthetic Procedures	74
4.4.2	Single-Crystal X-ray Diffraction	75
4.4.3	Luminescence Studies	75
4.4.4	Density Functional Theory	75
4.4.5	Transient Absorption Spectroscopy	76
4.4.6	NMR studies	76
4.4.7	IR Studies	76
4.4.8	Elemental Analyses	76
4.5	Conclusion	76
5	Time- and Temperature-Resolved Triplet Dynamics in Tungsten Iodide Clusters	79
5.1	Abstract	80
5.2	Introduction	80
5.3	Experimental Section	82
5.3.1	Sample Preparation and Containers	82
5.3.2	Spectroscopic Measurements	83
5.3.3	Emission Spectroscopy	83
5.3.4	Cryogenic Emission Spectroscopy	83
5.3.5	Transient Absorption Measurements	83
5.3.6	TDDFT Calculations	84
5.3.7	Model Fitting and Software	84
5.4	Results and Discussion	85
5.4.1	Steady-State Properties	85
5.4.2	Ultrafast Spectroscopy of Excited States	85
5.4.3	Excited Triplet State Properties and Oxygen Quenching	86
5.4.4	T-Dependent Emission Characteristics in Solution	89
5.4.5	T-Dependent Emission Properties in PMMA	89
5.4.6	T-Dependent Emission Lifetime Model in PMMA	91
5.4.7	T-Dependent Emission Spectrum Model in PMMA	92
5.4.8	TDDFT Computations	93
5.5	Conclusion	94
6	The Lowest Excited State of Heptacenes Is Dark	97
6.1	Abstract	98
6.2	Introduction	98
6.3	Results and Discussion	99
6.4	Conclusion	107
7	Conclusion & Outlook	109
7.1	TAPAS in Practice	109
7.2	Tungsten Iodide Clusters: From ISC to Sublevels	111
7.3	Heptacene: Between Singlet Fission & ISC	112

A	Supplementary Information for Chapter 3	115
A.1	Detailed Information on the Workflow Tabs	116
A.2	CDF or EMG for Analytical Convolving the IRF	118
A.3	Time-Zero Definition	121
A.4	Formulas Used to Calculate Fit Metrics	123
A.5	Tutorial: Case Study Rose Bengal	125
A.5.1	Experimental Section	125
A.5.2	Step-by-Step Guide: NIR Exploration and Sequential Kinetic Modeling	126
A.5.3	Step-by-Step Guide: Comprehensive Target Analysis	143
A.5.4	Define and Integrate a new Kinetic Model	151
A.6	Comparison TAPAS, Glotaran and KiMoPack	153
A.6.1	NIR Dataset: Performance and Fit Statistics	153
A.6.2	Vis Dataset: Performance and Fit Statistics	158
A.6.3	Discussion	162
B	Supplementary Information for Chapter 4	163
C	Supplementary Information for Chapter 5	171
C.1	Additional Experimental Information	172
C.2	Transient Absorption Data	173
C.2.1	Analysis of 2	173
C.2.2	Analysis of the IRF and Solvent Response	173
C.2.3	Fitting Model and Variability	174
C.2.4	Analysis of the long-lived Component with ns-TA	175
C.3	Emission Data at 295 K and Oxygen Quenching	176
C.4	Analysis of the T-Dependent Emission Data of 1 in Solution	178
C.5	T-Dependent Emission Data of 1 and 2 in PMMA	180
C.5.1	Variability of the Lifetime Fits	180
C.5.2	Fitting Results of the Spectral Emission Fits	185
C.5.3	Variability of the Spectral Emission Fits	185
C.6	Additional Information on the φ_n/ϕ_n model	190
C.6.1	Model Assumptions and Comparison	190
C.6.2	Derivation of the Spectral Fit	190
C.7	TDDFT Analysis	192
C.7.1	Optimized Geometries for the SOC2 and SOC3 states of 1	192
C.7.2	Eigenvectors of the SOC0-3 matrices of 1	193
C.7.3	Optimized Geometries for the S_0 and T_1 states of 2	198
D	Supplementary Information for Chapter 6	203
D.1	General	204
D.2	Synthesis	204
D.2.1	Heptacene-6,8,15,17-diquinone (1)	204
D.2.2	Tetra-6,8,15,17-TIPS-ethinyl Heptacene (Tetrol 2)	204
D.2.3	Tri-8,15,17-TIPS-ethinyl Heptacene-6-one (Triol 3)	205
D.2.4	Tetra-6,8,15,17-TIPS-ethinyl Heptacene (TIPS4Hep)	205
D.2.5	Monocarbonyl Heptacene COHep	206
D.3	Crystallography	207
D.3.1	Tetra-6,8,15,17-TIPS-ethinyl Heptacene (TIPS4Hep)	207
D.4	Additional Information	208

D.4.1	Literature-Known Spectra of Heptacene Derivatives	210
D.4.2	Steady State Absorption Spectroscopy	212
D.4.3	Fluorescence Spectroscopy	214
D.4.4	Transient Absorption Spectroscopy (TAS)	215
D.4.5	Matrix Isolation	217
D.4.6	EPR	218
D.5	Computations	219
D.5.1	TD-UDFT	219
D.6	Experimental Spectra	224
D.6.1	NMR	224
D.6.2	Mass Spectrometry	228
E	List of Publications & Scholarly Contributions	233
E.1	List of Publications	233
F	Declaration of Authorship & Contribution	235
F.1	Declaration of Authorship	235
F.2	Publication Contributions	236
	Bibliography	239

List of Figures

2.1	Franck-Condon principle energy diagram.	10
2.2	Comparison of measured absorption, fluorescence and phosphorescence with a corresponding Jabłoński diagram	11
2.3	Molecular structure of fluorescein derivatives.	14
2.4	Schematic of an absorption experiment.	17
2.5	Simplified schematic of a steady-state emission experiment.	18
2.6	Simplified schematic of a time-resolved emission experiment with TCSPC.	19
2.7	Simplified measurement principle of a TA experiment.	20
2.8	Schematic origin of the differential absorption spectrum.	21
2.9	Photoinduced changes in absorption and their spectral contributions to the differential spectrum.	23
2.10	Simplified schematic of the TA apparatus used in this work	25
2.11	Schematic representation of the optical parametric amplification step in a non-centrosymmetric crystal.	27
2.12	Raw and preprocessed TA data of a tungsten iodide cluster system in acetonitrile upon excitation at 350 nm.	30
2.13	Kinetic trace of a TA experiment (dark blue) and parallel model (red).	32
2.14	Kinetic trace of a TA experiment (dark blue) and sequential model (red).	33
2.15	Kinetic trace of a TA experiment (dark blue) and a parallel (top) and sequential (bottom) model (red) convolved with the Gaussian IRF.	34
2.16	Kinetic trace of a TA experiment (dark blue) and a parallel (top) and sequential (bottom) model (red) convolved with the Gaussian IRF. CAs are modeled with the zeroth- (CA ₀ , green) and first-order (CA ₁ , purple) derivatives of the IRF.	35
2.17	Molecular structure of xanthene	40
2.18	Schematic illustration of the [(M ₆ X ₈)L ₆] ²⁻ cluster core	41
2.19	Excited triplet state spin sublevel models of octahedral metal halide clusters	44
2.20	General molecular structure of acenes	45
2.21	Molecular structure of heptacene α -diketone	45

3.1	Sequential fit and posterior analysis of the 1200 nm kinetic trace for Rose Bengal.	59
3.2	Global sequential fit of the Rose Bengal TA NIR dataset.	60
3.3	Broadband sequential analysis of Rose Bengal TA data.	61
3.4	Global target analysis of Rose Bengal TA data.	63
4.1	Structure of $[(W_6I_8)I(CH_3CN)_5]^{3+}$ (I) (left) and $[(W_6I_8)(CH_3CN)_6]^{4+}$ (II) (right) cluster cations.	68
4.2	Projection of the crystal structure of II in the ab plane.	70
4.3	Projection of the crystal structure of III	70
4.4	ELF of III and $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$ (left side) and an illustration of the view on one of the clusters depicted in the ELF (right side).	71
4.5	Excitation (black) and emission (red, blue, green) spectra of crystalline $[(W_6I_8)(CH_3CN)_6](BF_4)_4 \cdot 2(CH_3CN)$ (III) powder.	72
4.6	Temperature-dependent photoluminescence spectra of III in the temperature range of 100 K to 300 K.	73
4.7	EADS resulting from the global analysis of III in acetonitrile after excitation at 300 nm.	74
4.8	Kinetic trace of III , measured at the ESA feature at 470 nm after excitation at 390 nm in acetonitrile.	74
5.1	Optical properties of 1 (red) and 2 (blue).	85
5.2	TA-hyperspectrum, kinetic trace at 500 nm and EAS of 1	87
5.3	Kinetic traces and fits of ns-TA and emission measurements at different oxygen concentrations of 1 (red) and 2 (blue) as well as the proposed Jabłoski diagram.	88
5.4	Intensity spectra, extracted lifetimes and zero-field splitting of 1 (upper panel) and 2 (lower panel) at different temperatures.	90
5.5	Simulated and observed temperature-dependent emission spectra of 1 and 2 based on ϕ_n and the φ_n model.	92
5.6	Calculated absorbance spectrum, requesting 50 states of 1 with a 0.5 eV line width from SOC0 geometry (dark).	93
6.1	Absorption spectrum (1×10^{-5} M, rt) of TIPS4Hep in C_6F_6	100
6.2	Absorption spectroscopy experiments of TIPS4Hep	101
6.3	Fluorescence and excitation spectra of TIPS4Hep	103
6.4	Optical properties of Hep	104
6.5	Transient absorption spectra of TIPS4Hep in C_6F_6 ($\lambda_{exc} = 900$ nm).	106
A.1	Comparison of the transient absorption response for six decay time constants computed with an IRF.	119
A.2	Analysis of the kinetic trace of Rose Bengal at 1100 nm using different time zero definitions for the local fit.	122
A.3	Used 2 mm cuvette with custom-built opening.	125
A.4	Menu, toolbar and workflow tabs of TAPAS.	126
A.5	Import widget for importing 2D TA data.	126
A.6	Metadata widget of the Import Tab.	127

A.7	Preprocessing Canvas showing ΔA spectral slices (top) and kinetic traces (bottom right) at the current position of the cross-hair in the 2D hyperspectrum (bottom left).	128
A.8	Widget to trim the dataset.	128
A.9	Widget to resample or regularize the dataset.	129
A.10	Chirp-correction widget in TAPAS.	130
A.11	Canvas during chirp correction. The points and the fitted 4th order polynomial are displayed.	130
A.12	Background correction widget.	131
A.13	Time-zero correction widget.	131
A.14	Averaging and filtering widget	132
A.15	Preprocessing Canvas after trim, chirp and background correction.	132
A.16	Workspace of the <i>Component Analysis</i> tab.	133
A.17	Input mask of the <i>Local Fit</i> Tab.	134
A.18	Full output after a successful local fit in TAPAS including the results of the (unbound) posterior analysis.	135
A.19	Fitting List widget, where the user selects a presaved fit for the MCMC parameter space evaluation which can be defined in the lower widget.	136
A.20	Plot properties for the visualization of the local fit kinetic traces.	137
A.21	Figure style panel used for the visualization and export of data and fit results.	138
A.22	Plot properties for the visualization of the parameter posteriors.	139
A.23	Local sequential analysis of Rose Bengal in the NIR at 1200 nm (unbound)	140
A.24	Section of TAPAS Global Fit Tab during fitting of the RB NIR data.	141
A.25	Global sequential analysis of Rose Bengal in the NIR.	142
A.26	Widgets of the Combine Projects tab.	144
A.27	Fitting settings and parameters used for the global sequential fit.	145
A.28	Fitting settings and parameters used for the target fit.	146
A.29	SVD of the target-fit residuals.	147
A.30	Full output after the target global fit in TAPAS including the results of the posterior analysis.	148
A.31	Corner plot of the MCMC posterior for the target model.	149
A.32	HDF5 container generated for the combined data set.	150
A.33	Analysis scheme from Glotaran used for fitting of the NIR dataset.	154
A.34	Script used for NIR sequential fitting and error estimation using KiMoPack .	154
A.35	Fitting parameter widget of TAPAS used for the NIR sequential fit.	155
A.36	Glotaran overview output after a successful fit.	157
A.37	Console output of KiMoPack after analyzing the NIR dataset with a confidence interval of 0.68 using the consecutive model.	157
A.38	Console output of KiMoPack after analyzing the NIR dataset with a confidence interval of 0.68 using the full-consecutive model.	157
A.39	Analysis scheme from Glotaran used for fitting of the vis dataset including a weight and CA parameter (CohSpec).	158
A.40	Script used for sequential fitting and error estimation using KiMoPack .	159
A.41	Fitting parameter widget of TAPAS used for the NIR sequential fit.	159
A.42	Glotaran overview output after a successful fit of the vis dataset.	160
A.43	Console output of KiMoPack after analyzing the vis dataset with a confidence interval of 0.68 using the consecutive model.	161

A.44	Console output of KiMoPack after analyzing the vis dataset with a confidence interval of 0.68 using the full-consecutive model.	161
B.1	Crystals of III under VIS (left side) and UV (right side) irradiation.	164
B.2	Decay measurement of solid III	164
B.3	Decay measurement of solid $(\text{TBA})_2[\text{W}_6\text{I}_8(\text{CO}_2\text{C}_3\text{F}_7)_6]$	165
B.4	Excitation and emission spectra of solid $(\text{TBA})_2[\text{W}_6\text{I}_8(\text{CO}_2\text{C}_3\text{F}_7)_6]$ under nitrogen, air and oxygen atmosphere.	165
B.5	Decay measurement of III in acetonitrile.	166
B.6	Emission spectra of solid $(\text{TBA})_2[\text{W}_6\text{I}_8(\text{CO}_2\text{C}_3\text{F}_7)_6]$ at different temperatures.	166
B.7	Selected ΔA spectra (A-F) of III at different time delays (blue) after excitation at 300 nm and kinetic trace at 450 nm (G).	167
B.8	Selected ΔA spectra of III at different delay times after excitation at 300 nm.	168
B.9	Section of the ^1H -NMR of III in CD_3CN showing the signal for the CH_3 -group at 2.77 ppm and a signal of H_2O at 2.13 ppm.	168
B.10	Greater section of the ^1H -NMR of III in CD_3CN between 0.0 and 10 ppm.	168
B.11	Infrared spectrum of III in black and of acetonitrile in red.	169
C.1	PMMA film of 1 under UV light.	172
C.2	Microcuvette with homebuilt opening to control the atmosphere within the cuvette.	172
C.3	Analysis of the fs TA-hyperspectrum of 2 after excitation at 350 nm.	173
C.4	Analysis of the fs TA-hyperspectrum of acetonitrile after excitation at 350 nm.	174
C.5	All emission lifetime traces + fits of 1 (right column red) and 2 (left column blue) at different oxygen concentrations.	176
C.6	Emission Spectra of 1 and 2 at different oxygen concentrations.	177
C.7	Biexponential and average lifetimes of 1 in MeCN extracted at different temperatures and corresponding emission spectra.	178
C.8	(A) Lifetimes of 1 in solution at room temperature (upper panel) and 77 K (lower panel) as a function of equivalents of (TBA)I. (B) Corresponding emission spectra.	179
C.9	Emission maximum (A) and FWHM (B) of 1 and 2 at every temperature step	180
C.10	Corner Plots of the MCMC posterior parameter distribution of the lifetime fits of 1 using the φ_n model.	181
C.11	Corner Plots of the MCMC posterior parameter distribution of the lifetime fits of 2 using the φ_n model.	182
C.12	Corner Plots of the MCMC posterior parameter distribution of the lifetime fits of 1 using the ϕ_n model.	183
C.13	Corner Plots of the MCMC posterior parameter distribution of the lifetime fits of 2 using the ϕ_n model.	184
C.14	Corner Plots of the MCMC posterior parameter distribution of the spectral emission fits of 1 using the φ_n model.	186
C.15	Corner Plots of the MCMC posterior parameter distribution of the spectral emission fits of 2 using the φ_n model.	187
C.16	Corner Plots of the MCMC posterior parameter distribution of the spectral emission fits of 1 using the ϕ_n model.	188

C.17	Corner Plots of the MCMC posterior parameter distribution of the spectral emission fits of 2 using the ϕ_n model.	189
D.1	Molecular structure of TIPS4Hep in the solid state.	208
D.2	Absorption spectrum of the formation of heptacene Hep via mono carbonyl photo precursor COHep in 2-MeTHF at 77 K inside a J.-Young tube. . .	208
D.3	Distances of vibrational progression of absorption and emission of TIPS4Hep in <i>n</i> -hexane compared to each other.	209
D.4	Absorption spectra of 7,16-silylethynylheptacene.	210
D.5	Absorption spectra of two heptacene derivatives reported by Wudl et al. . .	210
D.6	Absorption spectra of heptacene	211
D.7	Optical properties of the products obtained from MPV reduction of 7,16-heptacenequinone	211
D.8	Cuvette and various solvents in the Vis and NIR region.	212
D.9	Various solvents in the Vis and NIR region.	213
D.10	Red coloring of a solution of TIPS4Hep in CCl_4 after attempted fluorescence spectroscopy.	214
D.11	NIR transient absorption spectra at selected delay times of TIPS4Hep in C_6F_6	215
D.12	Kinetic traces at 620 nm and 635 nm and their corresponding fits.	216
D.13	Calculated vertical electronic absorption spectrum of the T_1 state of TIPS4Hep	216
D.14	UV-Vis spectrum measured in solid argon at 7 K, showing the formation of heptacene generated from COHep	217
D.15	EPR spectrum of radical cation of TIPS4Hep , oxidized by $\text{Ag}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ at rt in C_6F_6	218
D.16	^1H NMR of TIPS4Hep (700.29 MHz, C_6D_6).	224
D.17	^{13}C NMR of TIPS4Hep (176.09 MHz, C_6D_6).	225
D.18	^1H NMR of heptacene-6,8,15,17-diquinone 1 (400.16 MHz, D_2SO_4). . . .	225
D.19	^1H NMR of tetra-6,8,15,17-TIPS-ethynyl heptacene tetrol 2 (400.16 MHz, CDCl_3).	226
D.20	^{13}C NMR of tetra-6,8,15,17-TIPS-ethynyl heptacene tetrol 2 (400.16 MHz, CDCl_3).	226
D.21	^1H NMR of tri-8,15,17-TIPS-ethynyl heptacene-6-one triol 3 (400.16 MHz, CDCl_3).	227
D.22	^{13}C NMR of tri-8,15,17-TIPS-ethynyl heptacene-6-one triol 3 (400.16 MHz, CDCl_3).	227
D.23	HRMS (APCI) of TIPS4Hep	228
D.24	HRMS (ESI) of tetra-6,8,15,17-TIPS-ethynyl heptacene tetrol 2	229
D.25	HRMS (ESI) of tri-6,8,15-TIPS-ethynyl heptacene-6-one triol 3	230
D.26	HRMS (APCI) of heptacene-6,8,15,17-diquinone 1	231

List of Schemes

3.1	Typical workflow for processing and analyzing TA data.	51
3.2	An overview of TAPAS MVC-Architecture consisting of a View layer (green), the Controller layer (orange) and the Model layer (grey).	55
6.1	Synthesis of TIPS4Hep Starting from Heptacene-6,8,15,17-diquinone 1 . .	99

List of Charts

5.1	Structure of Octahedral Hexanuclear M(II) Clusters of the Type $[(M_6X_8)L_6]^{2-}$.	80
5.2	Lowest-Lying Excited Triplet State Spin Sublevel Models of M(II) Clusters	81
5.3	Distortions Found in the SOC1 Geometry (W = Purple, I = Green) Compared to SOC0 Geometry (W = Red, I = Yellow).	94
5.4	Sublevel Splitting of the Three Lowest-Lying SOC Geometries According to TDDFT Calculations.	94
C.1	Distortions found in the SOC2 (A) and SOC3 (B) geometry (W = purple, I = green) compared to SOC0 geometry (W = red, I = yellow.	192
C.2	Distortions found in the T_1 geometry (W = purple, I = green, C = light gray, O = pink) compared to S_0 geometry (W = red, I = yellow, C = dark gray, O = orange).	198

List of Tables

2.1	General relationship of quantum numbers.	8
2.2	Photophysical properties of xanthene derivatives.	14
2.3	Representative bimolecular and multi-state pathways.	16
2.4	Spectral ranges of white-light continua generated by self-phase modulation in different materials.	27
2.5	Wavelength coverage of the different nonlinear processes inside an optical parametric amplifier (Apollo-T, Ultrafast Systems)	28
2.6	Names of the first smaller acenes and their number of rings.	45
3.1	Overview of the TAPAS workflow tabs.	53
3.2	Modules and responsibilities in the TAPAS framework.	56
3.3	Optimization algorithms and their key characteristics used by TAPAS. . .	56
4.1	Crystal data for $[(W_6I_8)I(CH_3CN)_5](I_3)_2(BF_4)$ I , $[(W_6I_8)(CH_3CN)_6](I_3)(BF_4)_3 \cdot H_2O$ II , and $[(W_6I_8)(CH_3CN)_6](BF_4)_4 \cdot (CH_3CN)_2$ III	69
4.2	Interatomic W–W and W–N distances (pm) for compounds III	69
5.1	Photophysical properties of 1 and 2 at 297 K in acetonitrile and PMMA. .	86
5.2	Temperature-dependent parameters for 1 and 2 (4–300 K).	90
A.1	Comparison of parameter estimates and correlations for the two settings. .	121
A.2	Preprocessing metadata of the vis fs-TA data created by TAPAS.	143
A.3	Preprocessing metadata of the vis ns-TA data created by TAPAS.	143
A.4	Runtimes for optimization and uncertainty estimation in five replicate fits of the NIR data set.	156
A.5	Parameter estimates and 1σ uncertainties ($\approx 68\%$ confidence interval) calculated by different software.	156
A.6	Runtimes for optimization and uncertainty estimation in five replicate fits of the vis data set.	160
A.7	Parameter estimates and 1σ uncertainties ($\approx 68\%$ confidence interval) calculated by different software.	160

C.1	Parameter uncertainties and parameter–parameter correlations of the local (500 nm) and global fits of the TA data.	174
C.2	Monoexponential fits of 1 and 2 at different oxygen concentrations corresponding to Figure 5.3 A in the main manuscript. Errors are estimated to be within 10 %.	175
C.3	Table S3.1. Monoexponential lifetime fits of 1 and 2 at different oxygen concentrations. Errors are estimated to be within 5%.	177
C.4	Parameter uncertainties of the T-dependent lifetime fit estimated from the covariance matrices for 1 and 2	180
C.5	Fitting results of the T-dependent spectral measurements for 1 and 2 . Parameter names refer to equations Equations C.1 to C.4	185
C.6	Fitting results of the T-dependent spectral measurements for 1 and 2 . E_n refers to the emission maximum, and FWHM_{xK} represents the temperature-dependent broadening according to Equation C.4	185
C.7	Parameter uncertainties of the T-dependent spectral fit estimated from the covariance matrices for 1 and 2	185
C.8	Degree of degeneracy for the sublevels according to the geometry assumed by the φ_n and ϕ_n models.	190
C.9	Eigenvectors of the SOC0 matrices for 1	193
C.10	Eigenvectors of the SOC1 matrices for 1	194
C.11	Eigenvectors of the SOC2 matrices for 1	194
C.12	Eigenvectors of the SOC3 matrices for 1	195
C.13	Cartesian coordinates in Å of the optimized SOC0 geometry of 1	195
C.14	Cartesian coordinates in Å of the optimized SOC1 geometry of 1	196
C.15	Cartesian coordinates in Å of the optimized SOC2 geometry of 1	196
C.16	Cartesian coordinates in Å of the optimized SOC3 geometry of 1	197
C.17	Structural parameters in Å of the optimized SOC0, SOC1, SOC2 and SOC3 geometries of 1	197
C.18	Cartesian coordinates in Å of the optimized S_0 geometry of 2	199
C.19	Cartesian coordinates in Å of the optimized T_1 geometry of 2	200
C.20	Structural parameters in Å of the optimized S_0 and T_1 geometries of 2 . . .	201

Abbreviations

AIC : Akaike information criterion	ESA : excited-state absorption
BBO : β -barium borate	FAIR : Findable, Accessible, Interoperable, Reusable
BGR : band-gap renormalization	FFT : fast Fourier transform
BIC : Bayesian information criterion	FRET : Förster resonance energy transfer
CA : coherent artifact	FWHM : full width at half maximum
CB : conduction band	GS : ground state
CDF : Gaussian cumulative distribution function	GSB : ground-state bleaching
CI : confidence interval	GUI : graphical user interface
CrI : credible interval	HDF : Hierarchical Data Format
CT : charge transfer	Hep : heptacene
d.o.f : degree of freedom	IAC : integrated autocorrelation time
DAS : decay-associated spectrum	IC : internal conversion
DFT : density functional theory	IR : infrared
DMF : dimethylformamide	IRF : instrument response function
DMSO : dimethyl sulfoxide	ISC : intersystem crossing
EAS : evolution-associated spectrum	JIT : just-in-time
ELF : electron localization function	LED : light-emitting diode
EMG : exponentially-modified Gaussian	MAE : mean absolute error
	MCMC : Markov chain Monte Carlo

MLCT : metal-to-ligand charge transfer	TA : transient absorption
NIR : near-infrared	TAS : transient absorption spectroscopy
NMR : nuclear magnetic resonance	TBA : tetra- <i>n</i> -butylammonium
ODE : ordinary differential equation	TBAI : tetra- <i>n</i> -butylammonium iodide
OPA : optical parametric amplifier	TCSPC : Time-Correlated Single Photon Counting
OTs : tosylate	TDDFT : time-dependent density functional theory
PDF : Gaussian probability density function	TFA : trifluoroacetate
PDT : photodynamic therapy	Ti:Sapphire : titanium-sapphire
PET : photo induced electron transfer	TIPS : triisopropylsilyl
PIA : photo-induced absorption	TIPS4Hep : 6,8,15,17-tetrakis((triisopropylsilyl)-ethynyl)heptacene
PL : photoluminescence	TRES : time-resolved emission spectra
PMMA : poly(methyl methacrylate)	TTA : triplet-triplet annihilation
RB : rose bengal	UV : ultraviolet
RMSE : root-mean-square error	VB : valence band
rt : room temperature	Vis : visible
SAS : species-associated spectrum	VR : vibrational relaxation
SF : singlet fission	WLC : white-light continuum
SOC : spin-orbit coupling	XLA : Accelerated Linear Algebra
SQL : Structured Query Language	YAG : yttrium aluminum garnet
SSR : sum of squared residuals	ZFS : zero-field splitting
SST : sum of squares total	
SVD : singular value decomposition	

Symbols

A : absorbance	ϵ : molar absorption coefficient
A^* : excited-state absorbance	ϵ_e : vacuum permittivity
A^{gs} : ground-state absorbance	ε_i : spectrum of component i
A_{ij} : Einstein coefficients	f : oscillator strength
α : amplitude	g : Gaussian function
c : concentration	h : Planck constant
c_0 : speed of light in vacuum	$\hbar$: reduced Planck constant
χ^2 : chi-squared	H_{SO} : spin-orbit matrix element
χ_{red}^2 : reduced chi-squared	I : intensity
χ_1 : electric (linear) susceptibility	I_0 : incident intensity
$\otimes$: convolution	J : total angular momentum quantum number
d : optical path length	J_{rot} : rotational quantum number
Δt_P : pulse duration	k : rate constant
$\Delta \nu_P$: spectral bandwidth	k_B : Boltzmann constant
ΔA : differential absorbance	k_q : quenching constant
ΔE : energy difference	$\vec{k}$: wavevector
E : energy	L : total orbital quantum number
E_F : electric field	l : single-electron azimuthal quantum number

λ : wavelength	res : residuals
m_l : single-electron magnetic quantum number	ρ : density of states
μ : transition-dipole moment	S : total spin quantum number
n : single-electron principal quantum number	s : measured signal
n_{comp} : number of components	SE(θ_k) : standard error of optimized parameter k
N_e : number of electrons	σ : standard deviation
ν : vibrational quantum number	$\hat{\sigma}$: residual standard deviation
Φ : quantum yield	t : (delay) time
ϕ_n : four triplet state spin sublevel model	τ : lifetime
φ_n : three triplet state spin sublevel model	θ : parameter vector
ψ : electron wavefunction	V : volume
r^2 : coefficient of determination	v : frequency
	V_{if} : matrix element of a perturbation
	Z : atomic number

Introduction

1.1 Motivation

Photoactive materials are an important research and development field for applications such as light-emitting diodes (LEDs) and displays, solar cells, photosensitizers for medical therapy and biosensors.^{1–4} For technical progress, it is crucial to understand excited-state behavior and loss channels, as this knowledge enables both higher efficiency and improved durability of the active material.⁵

1.1.1 Triplet States and Their Importance

In many of these materials, the energetically lowest-lying excited state is a long-lived and often dark state with a characteristic electronic configuration, the triplet state.^{6,7} Even when the triplet population rate is low, triplets can sensitize the formation of singlet oxygen, which can subsequently degrade the molecule.⁸ Moreover, the slow, long-lived accumulation of triplets can also induce degradation and substantially reduce device efficiency.^{9,10}

On the other hand, organic semiconductors or clusters with high triplet generation do not need to reduce the overall performance, often the opposite is true: In LED appli-

cations, triplet emitters can achieve much higher internal efficiencies because there are statistically more microstates available for radiative recombination (3 vs. 1).^{1,11} In solar cells, combining a conventional semiconductor with a material that produces triplet states via a process called singlet fission (SF), can increase the theoretical power-conversion efficiency from about 33 % to 44 %.^{12–14}

Moreover, the ability to generate singlet oxygen can not only be unfavorable in terms of photobleaching, but also a feature for oxygen sensing and photodynamic therapy (PDT), where reactive oxygen species can be used to initiate cancer cell death.¹⁵ Finally, triplet emitters typically have a low-energy emission in the far red, making them well-suited for bioimaging within the optical transparency window of biological tissues.⁵

An example for the aforementioned photophysical properties are transition metal halide clusters: They exhibit long-lived and bright triplet emission which can be quenched efficiently via singlet oxygen formation.^{15–19} Despite decades of study, the population pathways and nature of the underlying triplet states remain under active debate, particularly for tungsten-iodide clusters, whose excited-state properties are still only scarcely characterized.^{20–22}

An important class of materials that can undergo SF are acenes. These organic semiconducting materials consist of linearly fused benzene rings which have already proven effective in organic LEDs and acene-based photovoltaics.^{23–25} However, as ring number increases, the molecules become more reactive and their electronic structure more complex, so relatively little is known about triplet-state generation in higher acenes like heptacene.^{26–29}

Understanding when and how triplets are generated and how they relax or emit is essential for both fundamental photophysics and applications. At the same time, triplet manifolds are intrinsically multidimensional. Their complex electronic structure and environmental sensitivity, combined with their occurrence over broad energy and time scales, make quantitative and mechanistic investigations challenging.^{7,30} Extracting reliable rate constants and triplet-level splittings require not only sensitive and high-resolution measurements but also models capable of distinguishing true physical structure from parameter cross-talk.³¹ A measurement technique proven to be valuable for probing triplet dynamics is transient absorption (TA) spectroscopy.³²

1.1.2 Transient Absorption for Triplet Photophysics

TA spectroscopy, which is the central method of this thesis, tracks the excited-state population of a material in real time across broad spectral and temporal windows, revealing the formation of triplets and other transient species as well as their subsequent relaxation pathways.^{31,33,34} This method is based on pump-probe spectroscopy which was developed in 1949 by Eigen, Norrish and Porter, and was further recognized with the Nobel Prize in 1967.³⁵ Ahmed Zewail extended this approach to ultrafast femtosecond pump-probe experiments and TA spectroscopy in the narrower sense and received the Nobel Prize in 1999 for this develop-

ment of femtochemistry.³⁶ One femtosecond (10^{-15} s) bears the same relation to a second as a second does to 32 million years and it is on this time scale where photo-physical and photochemical reactions typically begin.³⁶ Over the last decades, TA spectroscopy has become far more accessible due to advances in laser amplification (Nobel Prize in 2018), improved stability as well as computer-controlled and automated tuning of optical components, moving TA from specialized laboratories toward wider adoption.^{37–42}

In contrast to time-resolved emission experiments, the key strength of TA spectroscopy is its sensitivity to both radiative *and* nonradiative transient states or products. With modest adjustments of the setup, TA experiments can typically cover temporal delays from a few hundred femtoseconds to many microseconds and spectral regions from the ultraviolet (UV) to the near-infrared (NIR), making this technique especially well-suited for monitoring triplet dynamics.^{32,43,44}

1.1.3 The Bottleneck is not (Only) Data

Paradoxically, this ability to "see everything" across broad temporal and spectral windows is also its main complication. Kinetic and spectral signatures from various excited states, photoproducts, their mutual or environmental interactions as well as setup artifacts can overlap the same spectral and temporal regions. Disentangling these contributions typically requires complementary observables (e.g., time-resolved emission and temperature-dependent measurements) to constrain assignments, careful data modeling and an explicit treatment of uncertainty so that conclusions reflect what the data support.^{31,33,34,45}

In practice, complex TA models are often reported with limited provenance (preprocessing choices, constraints, priors), without statistical diagnostics and use closed and

"blackbox" software or private scripts, making it difficult for the broader community to reproduce or extend results. Thus, the limiting factor is less about acquisition and more about transparent analysis.

The need and development of more open science and data management was summarized in 2016 by the Findable, Accessible, Interoperable, Reusable (FAIR) principles.⁴⁶ In essence, the principles serve as guidelines to describe, store and publish data by using rich, standardized and persistent (meta)data, shared formats, vocabulary and clear provenance, so that the data are interoperable and reusable by humans and machines. This growing awareness in open and transparent data management is also reflected in the "Guidelines for Safeguarding Good Research Practice" by the German Research Foundation (German: *Deutsche Forschungsgemeinschaft, DFG*) from 2019, which explicitly encourage implementation of the FAIR principles.⁴⁷ Given the complexity and multidimensionality of TA data, their kinetic models and the various preprocessing steps involved, FAIR practices and the use of advanced statistical methods are particularly important for TA spectroscopy.

Having outlined the importance of triplet phenomena, the suitability of TA spectroscopy for probing these transient contributions, and the need for careful, transparent and reproducible data management and analysis of TA data, the next section states the specific objectives of this thesis.

1.2 Objective

This cumulative thesis has two main aspects: First to develop and validate an accessible, FAIR, and statistically rigorous workflow for TA spectroscopy implemented in an open-source graphical user interface (GUI) and

second, to apply that workflow to resolve previously unanswered questions about triplet generation and relaxation in two archetypal systems: oxygen-sensitizing tungsten iodide clusters and a stabilized heptacene derivative in which the electronic structure and potential triplet state population has not yet been analyzed experimentally.

In this context, the present work addresses the following issues:

1. TA Analysis Software Combining FAIR Principles & Uncertainty Quantification

A TA analysis software covering the whole workflow (import, preprocessing, fitting, visualization) should ideally be free and open-source, intuitive via a GUI, transparent with automated, FAIR-compliant (meta)data, extendable, and equipped with fast, customizable fitting routines and rigorous uncertainty analysis. For our laboratory and within the context of this work, it is further essential that complementary experiments and TA measurements covering different temporal or spectral regions can be combined into a single project and analyzed jointly to increase statistical robustness.

Because no software met all these requirements at the start of this work, their development and implementation became a primary goal of this work. The performance of the software with focus on parameter and model identifiability was evaluated on the literature-known dye rose bengal.

2. Triplet Generation and Nature in Tungsten Iodide Clusters

Although the emission properties of molybdenum and tungsten halide clusters have attracted interest since the 1980s, many aspects of their photoluminescence remain unresolved, especially for the less investigated tungsten

iodide subfamily. Although competing models exist for the molybdenum-based cluster emission, their comparison and applicability to tungsten halide clusters have not been systematically tested, resulting in a lack of important key figures like triplet population rates, triplet splitting energy and number of emissive triplet states. Further, the structural, photoluminescent and oxygen-quenching changes when moving to cationic tungsten iodide species have not been explored in detail.

Thus, a first aim was to characterize the excited-state properties of a novel cationic tungsten iodide cluster by establishing TA spectroscopy to monitor triplet population and decay under varied conditions and to compare with complementary emission experiments. In a comprehensive follow-up study on two general tungsten iodide clusters, TA spectroscopy was combined with temperature- and time-resolved emission to quantify triplet-population and quenching rates, as well as the splitting of emissive triplet sublevels. In doing so, the overarching question of the nature of the triplet states in tungsten iodide clusters was addressed by integrating TA and emission results with theoretical calculations and literature on related Mo-based clusters.

3. Electronic Configuration & Triplet-Formation Mechanism in a Heptacene Derivative

While the photophysics of shorter acenes (e.g. tetracene, pentacene) are well studied, investigations of higher acenes such as heptacene remain scarce due to their low stability.

For this reason, the aim of this study was to fully analyze a new, stable heptacene derivative using steady-state and TA spectroscopy to reveal its electronic structure and triplet-state population and compare the findings with theoretic-

cal predictions. Beyond guiding future applications, this provides insight into the acene family as a whole and tests the applicability of advanced theoretical models.

In summary, this thesis pursues the development of FAIR-compliant TA software covering the full analysis workflow with detailed uncertainty estimation, and the investigation of triplet-state nature, generation and relaxation in tungsten iodide cluster systems and a novel heptacene derivative. The following section outlines the structure of the cumulative thesis and how each chapter contributes to these objectives.

1.3 Structure of the Work

This cumulative thesis is organized as follows:

In **Chapter 2**, the scientific and conceptual background required for this work are introduced. The first two sections cover the theoretical and photophysical fundamentals of light-matter interaction and excited-state dynamics. The general spectroscopic methods used in this work are then outlined with a focus on their accessible observables, followed by a detailed description of the implementation of a TA setup and the fundamentals of TA data analysis and modeling. Finally, the investigated material systems are introduced with emphasis on their photophysical properties.

Chapter 3 treats the development, implementation and design choices of the free and open-source software TAPAS (Transient Absorption Processing and

Analysis Software). The graphical interface, the underlying modular architecture and the numerical and theoretical algorithms employed for fitting and error analysis are

described. The complete analysis workflow is then demonstrated on multiple TA datasets of the model dye rose bengal. Practical aspects of the analysis and detailed assessments of error and parameter identifiability are discussed and compared with existing TA software. This chapter is based on the publication "TAPAS: Transient Absorption Processing and Analysis Software", published in *ChemPhotoChem*. Supplementary information on this chapter can be found in **Appendix A**.

In **Chapter 4**, the preparation as well as the structural and photophysical characterization of a novel cationic tungsten iodide cluster is reported. TA spectroscopy reveals, for the first time for tungsten halide clusters, an ultrafast transition within ≈ 2 ps, assigned to triplet state population as well as the subsequent decay of the long-lived triplet via emission or oxygen quenching, consistent with complementary measurements. This chapter is based on the publication "Preparation, photoluminescence and excited state properties of the homoleptic cluster cation $[(W_6I_8)(CH_3CN)_6]^{4++}$ ", published in *Dalton Transactions*. Supplementary information on this chapter can be found in **Appendix B**.

In **Chapter 5**, the insights from handling and analyzing oxygen-sensitive tungsten iodide clusters with TA spectroscopy from **Chapter 4** are extended to two prototypical tungsten iodide clusters. These are investigated comprehensively by TA and by time- and temperature-resolved emission spectroscopy, enabling application and testing of triplet-state models from related systems and yielding key parameters such as triplet-population and decay rates, quenching rates, and triplet sublevel splittings.

Together with theoretical calculations, this chapter evaluates existing models based on molybdenum clusters and proposes a refined quantum-theoretical framework for the triplet nature and optoelectronic properties. This chapter is based on the publication "Time- and Temperature-Resolved Triplet Dynamics in Tungsten Iodide Clusters", published in *Inorganic Chemistry*. Supplementary information on this chapter can be found in **Appendix C**.

Chapter 6 addresses the lowest excited state of a novel and stable heptacene derivative, allowing a broadband TA analysis from the UV to the NIR over the full temporal range. The results support a different electronic structure compared with shorter acenes, consistent with theory and complementary spectroscopy. Further, TA reveals triplet-state population and decay, whose possible mechanisms are discussed. This chapter is based on the publication "The Lowest Excited State of Heptacenes Is Dark", published in *The Journal of Physical Chemistry Letters*. Supplementary information on this chapter can be found in **Appendix D**.

In **Chapter 7**, the main results of this work are summarized and discussed, followed by an outlook and concluding remarks.

Theoretical and Scientific Fundamentals

This chapter provides the conceptual foundation for the experimental and analytical investigations that follow. I begin in **Section 2.1** with the photophysical and photochemical fundamentals governing light-matter interactions, followed by outlining the cascade of processes triggered by photoexcitation in **Section 2.2** and the spectroscopic observables that make them accessible in **Section 2.3**. **Section 2.4** then turns to TA spectroscopy, detailing femtosecond laser technology, light conversion and setup geometry as well as the accompanying experimental workflow. Building on this, **Section 2.5** outlines data processing and data analysis strategies for kinetic modeling of TA data that underpins the framework developed in this work. Finally, in **Section 2.6**, I survey the material families investigated to elucidate energy transfer and triplet-generation dynamics throughout this thesis. Together, these sections supply the theoretical and methodological scaffolding necessary to interpret the TA data and photophysical pathways discussed in subsequent chapters.

2.1 Photophysical Background

Generally, optical phenomena can be approached from three complementary perspectives: Geometrical optics describe the light as straight-line rays, which can be a useful approximation for describing optical images or beam paths. However, this view cannot describe interaction of light and matter such as scattering, diffraction, interference or polarization. These effects fall under wave optics which understands light as a periodic oscillation of electromagnetic fields in time and space, first anticipated by Faraday in 1831 and rigorously formulated by Maxwell in 1865.^{48–50} In the beginning of the 20th century, quantum optics emerged, describing light as a stream of discrete quanta, so-called photons without abandoning its underlying wave nature and thereby explaining photoabsorption, emission and related processes.⁵¹

Together, these perspectives embody the particle-wave duality of light.^{6,50,52} I will invoke each of them in the following sections as required.

2.1.1 Photons and Their Energies

Spectroscopy refers to a group of techniques that study the energy-dependent interaction between matter and electromagnetic radiation. In 1900, Planck modeled a black-body radiator as an ensemble of oscillating and emitting molecules or oscillators and showed that absorption and emission are not continuous but occur in discrete quanta. Building on this insight, Einstein unified the particle- and wave models of light by relating the energy E of a radiation quantum (a photon) to its frequency ν given by **Equation 2.1**.⁵³

$$E = h\nu = h \frac{c_0}{\lambda}, \quad (2.1)$$

with the Planck constant $h = 6.626 \cdot 10^{-34}$ Js. Since the speed of light is a constant $c_0 = 2997925 \frac{m}{s}$, frequency ν can be replaced by the wavelength λ . (**Equation 2.1**).

A stream of photons with a very narrow energy distribution (or ideally a single energy) is termed monochromatic. Real light sources, however, exhibit a finite bandwidth that can be characterized, for example, by a maximum and their full width at half maximum (FWHM).

Across the electromagnetic spectrum from long waves and radio waves ($\approx 10^2$ Hz) to γ - and cosmic rays ($\approx 10^{23}$ Hz), photons can interact with matter and chemical processes in distinct ways.⁵⁰ Low-energy photons in the microwave region induce rotational transitions, NIR photons drive vibrational modes, visible (Vis) to UV photons promote electrons between electronic states and higher energies can ionize atoms by ejecting core electrons.^{51,54} Since the present work mainly investigates the electronic transitions in the UV-Vis-NIR range, the following discussion mainly focuses on the related processes.

2.1.2 Energies in Boxes: The Schrödinger Equation

The center of spectral analysis is the measurement of energy differences ΔE either

through absorption (the uptake of a photon that promotes an electron from a lower to a higher energetic state), or conversely through emission (photon release accompanied by a transition to a lower energetic state). These processes are formally described by the Schrödinger equation formulated in 1926 which I will reference conceptually below.⁵⁵

Much as the classical wave equation governs the vibration of a stretched string, the Schrödinger equation relates an electron's wavefunction ψ to the system's kinetic and potential energy. The probability of finding the electron within a volume dV is given by the squared modulus $\psi^2 dV$. Each discrete (eigen)solution carries a definite energy and is labeled by three quantum numbers analogous to the single mode index in the one-dimensional string problem: principal- n , azimuthal- l and magnetic quantum number m_l . Additionally, the spin quantum number m_s accounts for the electron's intrinsic angular momentum and can be derived taking the temporal fourth dimension into account.^{6,50,56} The allowed values of these quantum numbers are mutually constrained, as summarized in **Table 2.1**.

Table 2.1: General relationship of quantum numbers.

Quantum Number	Symbol	Values
Principal	n	1, 2, ... n
Azimuthal	l	0, 1, 2, ... ($n-1$)
Magnetic	m_l	$-l, -l+1 \dots l-1, l$
Spin	m_s	$\pm 1/2$

From the Schrödinger equation, the atomic orbitals and their energies can be derived and defined by the three main quantum numbers. For a given l , there are $2l + 1$ orbitals only diverging in their spatial orientation. Since they share the same energy in a spherically symmetric field, these orbitals are degenerate. The degeneracy can be lifted for example by applying an external magnetic field

resulting in a splitting of the spectral features (Zeeman effect).^{57–59}

2.1.3 When Spins Align

In the following discussion, I omit explicit operator and bra-ket notation, describing all angular momenta in the vector-model framework. A rigorous operator-based derivation can be found in the standard quantum-mechanics literature.^{6,56} I treat each electron as carrying a spin vector $\vec{s}_i$ and an orbital vector $\vec{l}_i$. Vector addition over all electrons N_e yield the total spin vector $\vec{S}$ and the total orbital vector $\vec{L}$, whose allowed lengths are characterized by their quantum number S and L respectively in **Equations 2.2 and 2.3**.

$$\vec{S} = \sum_{i=1}^{N_e} \vec{s}_i \quad |\vec{S}| = \sqrt{S(S+1)}\hbar \quad (2.2)$$

$$\vec{L} = \sum_{i=1}^{N_e} \vec{l}_i \quad |\vec{L}| = \sqrt{L(L+1)}\hbar \quad (2.3)$$

Further, the total angular momentum vector $\vec{J}$ is characterized by the quantum numbers J (magnitude) and M_J (its z -component) in **Equation 2.4**, while the spin multiplicity is defined in **Equation 2.5**.^{6,60}

$$\vec{J} = \vec{S} + \vec{L} \quad |\vec{J}| = \sqrt{J(J+1)}\hbar \quad (2.4)$$

$$\text{spin multiplicity} = 2S + 1 \quad (2.5)$$

If every electron is spin-paired, the total spin is $S = 0$ giving a spin multiplicity of 1 and defining a singlet state. When $S = 1$, the multiplicity rises to 3, producing a triplet state whose three sublevels separate in an external magnetic field. It is worth noting, that in the above case, LS (Russell-Saunders) coupling is assumed, which is a valid approximation for light atoms (atomic number $Z \lesssim 40$) where electron-electron Coulomb interactions dominate spin-orbit coupling (SOC).^{50,61} In heavier atoms SOC scales roughly as Z^4 and mixes $\vec{L}$ and $\vec{S}$ making the orbital angular momentum L

and the spin S lose their status as good quantum numbers. In this case, jj coupling is used, where the single electron angular momentum $\vec{j}_i$ is formed first and then vector added to build the total angular momentum vector $\vec{J}$.⁶

For electric-dipole transitions in LS-coupled atoms the main rules are

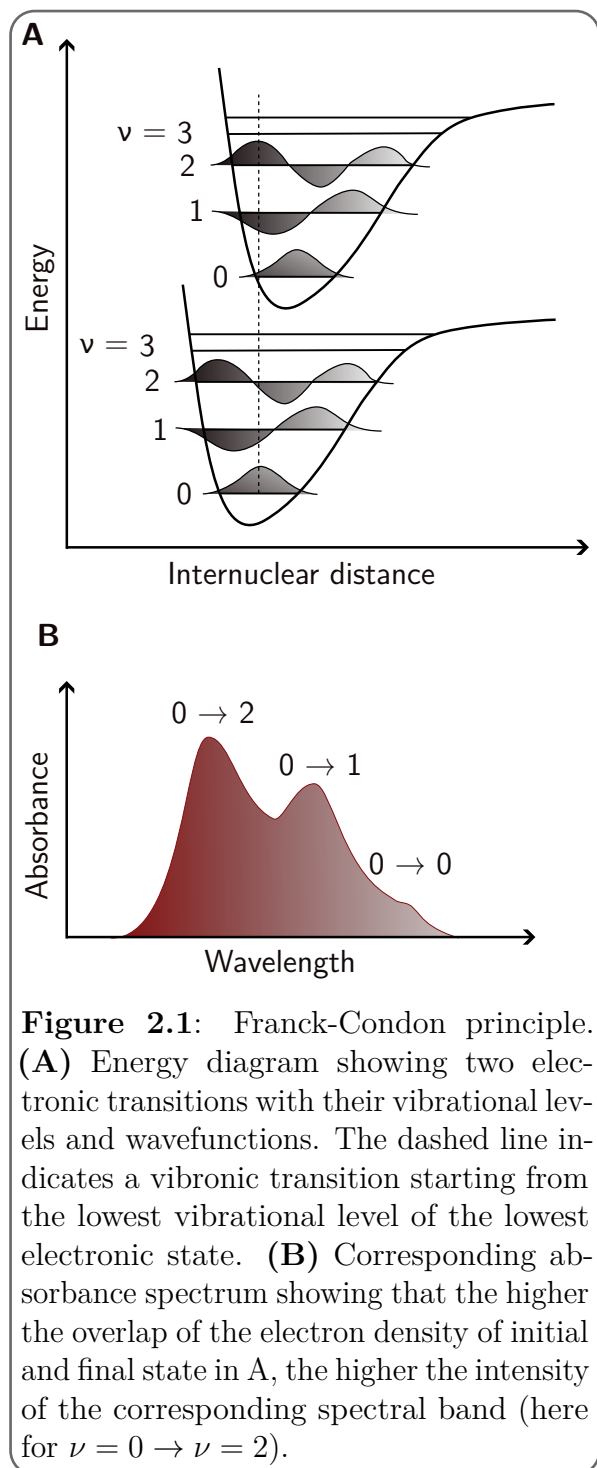
- **Pauli exclusion principle:**⁶² all electrons need to differ in at least one quantum number.
- **Hund's rules:**⁶³ the configuration with the maximum total angular momentum L and the maximum total spin S has the lowest energy.
- **Dipole selection rules:**⁶
 - $\Delta S = 0$
 - $\Delta L = 0, \pm 1 (L = 0 \nleftrightarrow 0)$
 - $\Delta J = 0, \pm 1 (J = 0 \nleftrightarrow 0)$
 - $\Delta M_J = 0, \pm 1$

For molecules, these strict atomic selection rules relax since molecular vibrations and rotations add extra, quantized degrees of freedom. By invoking the Born–Oppenheimer approximation, the fast electronic motion can be separated from the slower nuclear motion.⁶⁴ Treating the nuclei alone then reduces the Schrödinger equation to an (an)harmonic oscillator for vibrations and a rigid rotor for rotations, yielding the vibrational quantum number ν and the rotational quantum number J_{rot} with discrete energy values. Because molecules can exchange energy among electronic, vibrational, and rotational modes, spin-forbidden electronic transitions, for example, can gain intensity via spin-orbit and vibronic coupling.^{6,51,56}

2.1.4 The Geometry of Intensity

The Franck-Condon principle offers a more intuitive picture of the intensity of transitions.^{50,51,54,65,66} It states that during

an ultrafast electronic transition, the nuclei are effectively frozen and therefore, the transition probability is governed by the overlap of the initial and final vibrational wavefunctions. In other words, the strongest spectral lines occur where the two vibrational modes overlap most closely as sketched in **Figure 2.1**.



In addition to the vibrational structure superimposed on every electronic level, rotational transitions are also overlaid which can broaden the spectrum even more. Extrinsic factors like solvent properties, temperature and aggregation state damp vibrations and rotations leading to changes in the spectral resolution of transitions. Further, solvent interactions can stabilize or destabilize some excited states translating the entire band to higher or lower energy.^{50,54,67,68}

Electronic states and their transitions can be classified in several ways. Notations based on molecular orbitals following Kasha (e.g. $n \rightarrow \pi^*$),⁶⁹ group theoretical symmetry classes (e.g. $^1A_1 \rightarrow ^1A_2$), or the older Mulliken system (e.g. $N \rightarrow V$)⁷⁰ all appear in the literature. In the following, I will mainly use an enumerative ordering based on spin multiplicity (e.g. $S_0 \rightarrow S_2$).

2.1.5 Mapping Excited-State Pathways

A Jabłński diagram, named after the scientist who first proposed it in 1933,⁷¹ is the standard way to illustrate the electronic and vibrational manifolds in a material together with their transitions. In contrast to a molecular orbital diagram, it arranges states vertically according to the energy spacings measured spectroscopically. In line with the enumerative ordering of states, the ground state is typically the S_0 state, while S_1 and T_1 denote the lowest excited singlet and triplet states, respectively. **Figure 2.2** shows a typical Jabłński diagram alongside the corresponding electronic spectrum. The electronic states are displayed by thick vertical lines while the vibrational and some rotational levels are indicated by thin lines.

Transitions between states through excitation or relaxation are displayed by arrows whereby a distinction is made between radiative (straight) and radiationless transitions (wavy).⁷² A nonradiative transition from an excited state to its lowest vibrational level is termed VR.⁵² When the excess energy is

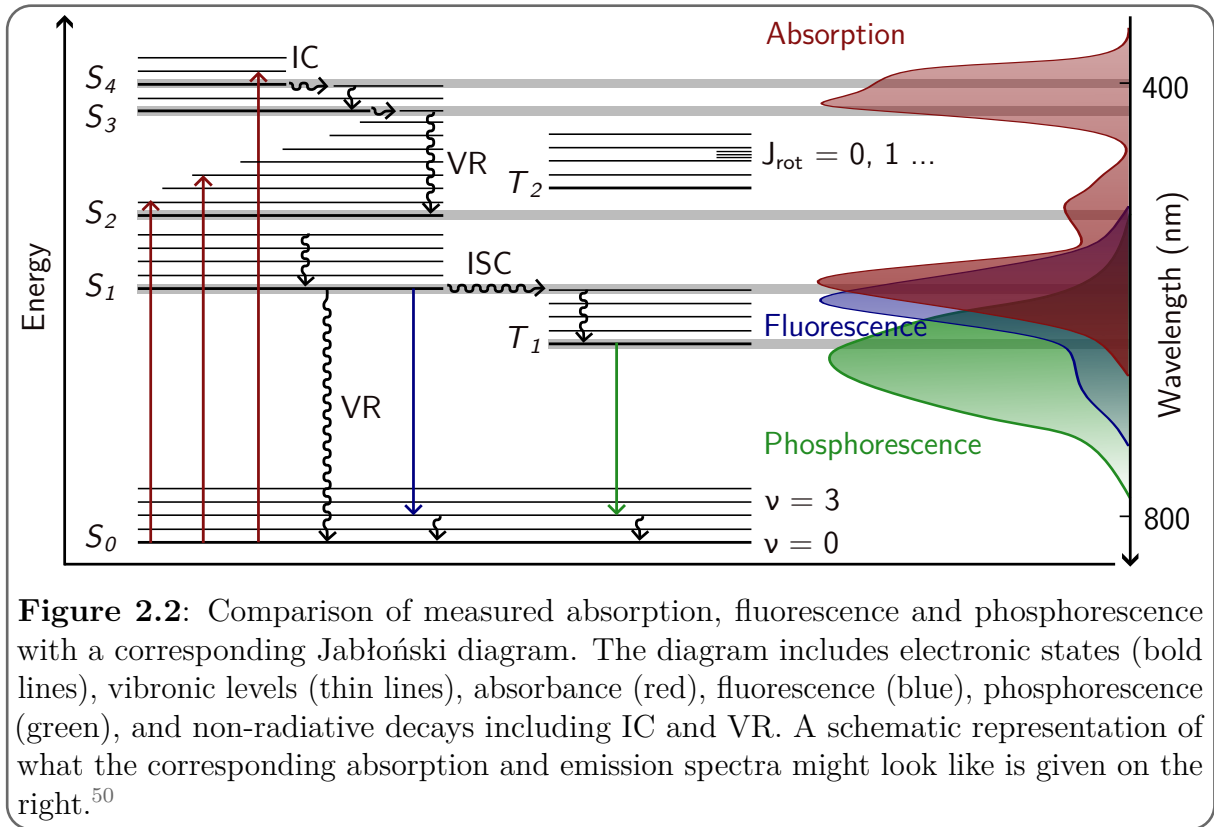


Figure 2.2: Comparison of measured absorption, fluorescence and phosphorescence with a corresponding Jablonski diagram. The diagram includes electronic states (bold lines), vibronic levels (thin lines), absorbance (red), fluorescence (blue), phosphorescence (green), and non-radiative decays including IC and VR. A schematic representation of what the corresponding absorption and emission spectra might look like is given on the right.⁵⁰

passed from the vibrational manifold of an excited electronic state to that of a lower electronic state of the same spin multiplicity, the process is called IC. If the nonradiative transition involves a change in spin multiplicity, it is known as ISC. Radiative relaxation is collectively referred to as photoluminescence and is subdivided into fluorescence which conserves spin multiplicity and phosphorescence which involves emission from a triplet to a singlet state.

Having identified the radiative and non-radiative pathways available to an excited molecule, I now examine these processes in more detail from a time-resolved perspective, introducing the characteristic lifetimes that govern each pathway.

2.2 Fates of the Excited States

The excited state j of N free atoms or molecules has an intrinsic lifetime or radiative decay τ given by

$$\begin{aligned}
 -\frac{dN_j}{dt} &= N_j \sum_{i < j} A_{ji} \\
 k_r &\equiv \sum_i A_{ji}, \quad \tau_j \equiv \frac{1}{k_j} \\
 \curvearrowright \Leftrightarrow \int_{N_j(0)}^{N_j(t)} \frac{dN'_j}{N'_j} &= -k_j \int_0^t dt' \\
 \Leftrightarrow N_j(t) &= N_j(0) e^{-\frac{t}{\tau_j}}, \quad (2.6)
 \end{aligned}$$

where A_{ji} are the so-called Einstein coefficients for spontaneous emission and k_r being the corresponding radiative rate constant from the excited state j to the ground state i .^{50,73} Excited states may also relax through nonradiative channels, each described by ordinary first-order rate constants k_{nr} . The experimentally observed population therefore decays with the total rate k_{tot} given by

$$k_{tot} = k_r + k_{nr} = \sum_i A_{ji} + \sum_m k_{j-m,nr} \quad (2.7)$$

$$\tau_{tot} = \frac{1}{k_{tot}}. \quad (2.8)$$

The ratio of radiative to total decay defines the emission quantum yield Φ

$$\Phi = \frac{k_r}{k_{tot}} = \frac{\tau_{tot}}{\tau_r}, \quad (2.9)$$

which quantifies the fraction of excited molecules that return to the ground state by emitting a photon.

The same light-matter coupling can be expressed as an Einstein B coefficient (absorption / stimulated emission), as the dimensionless oscillator strength f or as the transition-dipole moment μ . These quantities are in essence different rescalings of the matrix element that controls the probability, lifetime and intensity of the transition.^{6,73}

A quantum mechanical prediction based on perturbation theory about the transition rate k from one initial state i to the final state f can be given with Fermi's Golden Rule in **Equation 2.10**.⁷⁴

$$k_{i \rightarrow f} = \frac{2\pi}{\hbar} |V_{if}|^2 \rho(E_f) \quad (2.10)$$

with the matrix element of the perturbation V between the final and initial state and the density of states ρ at the energy of the final state E_f .

2.2.1 Excited States and Excitons

Although this work centers on organic molecules and transition-metal clusters behaving like inorganic molecular emitters in solution, the scope occasionally extends to solid-state, semiconductor or quantum-confined systems. Throughout this chapter, the term excited state denotes an electronic excitation whether it is localized on a single organic molecule, weakly delocalized across

a cluster or dimer, or a bound electron-hole pair (exciton) confined within a quantum dot or molecular crystal. While the fundamentals described in the preceding and following sections apply in all cases, there can be differences in terminology and efficiency of mechanisms due to exciton-phonon coupling, dielectric screening, quantum confinement and surface or defect trapping. For detailed discussions of the optoelectronic characteristics specific to semiconductor and quantum-confined systems, see the recent reviews in the literature.^{75–79}

In the following, the different radiative and nonradiative relaxation processes from the excited state to the ground state are discussed. Where solid-state-specific channels become important, they are explicitly highlighted.

2.2.2 Nonradiative Spin-Conserving Relaxation

Upon excitation with sufficient energy, a molecule is promoted to a higher-lying vibrational level of an excited electronic state (see the Franck-Condon diagram in **Figure 2.1**). The resulting excess vibrational energy within the same electronic state can be redistributed intramolecularly among other vibrational, rotational or kinetic modes (intramolecular VR) or transferred intermolecularly to surrounding molecules via collisions which is often loosely called "cooling".^{52,80,81}

By contrast, IC is an isoenergetic transition from an excited electronic state to a highly vibrational ("hot") level of a lower electronic state driven by vibronic coupling. As outlined in **Section 2.1.1**, transitions within the same spin manifold are spin-allowed and therefore fast. Since both VR and IC conserve spin, they are ultrafast, typically occurring on comparable time scales of a few hundred femtoseconds.^{52,54,82}

Within the framework of Fermi's Golden Rule (compare **Equation 2.10**),⁷⁴ a high density of vibronic states (e.g. in large

molecules) accelerates intramolecular VR. In the same theoretical context, the energy-gap-law predicts that the internal conversion rate k_{IC} decreases exponentially with the electronic energy gap ΔE (**Equation 2.11**) in the weak coupling limit.^{83–85}

$$k_{\text{IC}} \propto e^{-\alpha \Delta E} \quad (2.11)$$

The properties of the surrounding solvent such as polarity, hydrogen-bonding ability and viscosity primarily modulate intermolecular VR in a complex way.^{81,86}

In quantum dots and molecular crystals, the excess energy is not translated to discrete intramolecular modes but rather into lattice vibrations (so-called phonons) which is why VR is often termed "phonon-assisted cooling", "hot-exciton cooling" or "carrier thermalization" in those cases.^{87,88} Surface defects or dangling bonds, especially significant for nanocrystals, can lead to an additional relaxation pathway which is often called trap-assisted recombination or Shockley-Read-Hall recombination. In short, the exciton is captured by a defect-derived, sub-gap state and then relaxes to the ground state, usually via multi-phonon and sometimes via photon emission. Although this process competes with the other intrinsic relaxation mechanisms, this pathway is driven by lattice or surface defects rather than by the host electronic manifold and is therefore extrinsic.^{75,89}

2.2.3 Nonradiative Spin-Conversion Processes

ISC is an isoenergetic transition where the spin multiplicity changes. Since it is spin-forbidden, it is expected to be slow and out-competed by faster spin-allowed processes such as VR, IC and fluorescence. However, the ISC rate k_{ISC} can be increased by various effects, which will be outlined in the following.

Equation 2.12 partitions the overall ISC

rates k_{ISC} into three kinetically distinct contributions, including direct coupling ($k_{\text{ISC}}^{\text{direct}}$), a sequential pathway via an intermediate triplet ($k_{\text{ISC}}^{\text{seq}}$) and a spin-vibronic channel ($k_{\text{ISC}}^{\text{SV}}$).³⁰

$$k_{\text{ISC}} = k_{\text{ISC}}^{\text{direct}} + k_{\text{ISC}}^{\text{seq}} + k_{\text{ISC}}^{\text{SV}} \quad (2.12)$$

Direct ISC The first term $k_{\text{ISC}}^{\text{direct}}$ is accounting for the direct SOC between the S_1 and T_1 states and can be expressed using Fermi's Golden Rule with **Equation 2.13**

$$k_{\text{ISC}}^{\text{direct}} = \frac{2\pi}{\hbar} |H_{\text{SO}}|^2 \rho(\Delta E_{\text{ST}}), \quad (2.13)$$

where H_{SO} is the spin-orbit matrix element scaling roughly as $H_{\text{SO}} \propto Z^4$, and $\rho(\Delta E_{\text{ST}})$ is the Franck-Condon-weighted density of accepting vibrational states evaluated at the energy difference between the specific singlet and triplet level in question.^{30,90} For weak-coupling molecules, $\rho(\Delta E_{\text{ST}})$ follows the exponential energy-gap-law in **Equation 2.11**, thus a larger singlet-triplet separation reduces the number of near-resonant vibronic states and, therefore, ρ and the overall rate.^{83–85} H_{SO} is responsible for the so-called *heavy atom effect* predicting larger SOC and therefore faster ISC with increasing atomic number Z . The xanthene dye family (compare **Figure 2.3**) provides a clear illustration.

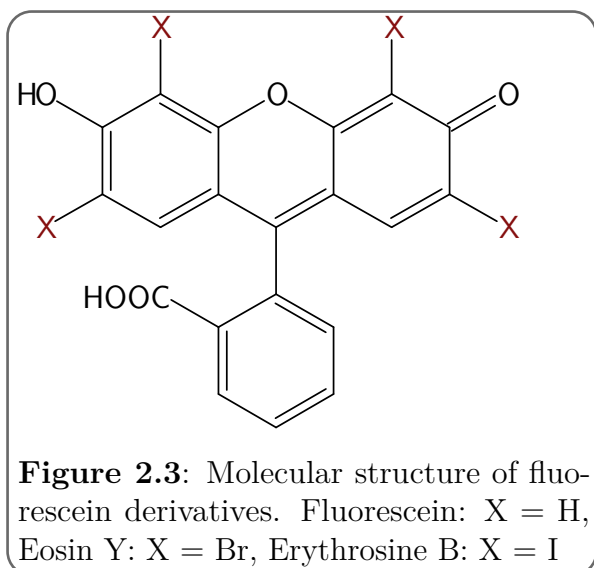
As illustrated in **Table 2.2**, introducing bromine and iodine substituents raise H_{SO} and shifts the dominant decay channel from fluorescence to ISC, exactly as predicted by the heavy-atom effect.^{91–93}

However, the matrix element H_{SO} does also depend on the character of two states i and f involved. This is qualitatively described by the El-Sayed rule stating that k_{ISC} increases if a change of orbital type is involved (e.g. $^1\pi\pi^* \rightarrow ^3n\pi^*$).^{72,90,94}

Sequential ISC The second term $k_{\text{ISC}}^{\text{seq}}$ in **Equation 2.12** describes a two-step process, $S_1 \rightarrow T_2 \rightarrow T_1$, involving an energetically close-lying intermediate state T_2 . This

Table 2.2: Photophysical properties of xanthene derivatives.

Dye (MeOH)	Heavy Atoms	Φ_{fl}	Φ_{ISC}
Fluorescein	none	≈ 0.97	≈ 0.03
Eosin Y	4 Br	≈ 0.67	≈ 0.25
Erythrosine B	4 I	≈ 0.13	≈ 0.58



can become an important contribution to the overall k_{ISC} , especially if T_2 has a different orbital parentage and therefore being El-Sayed-allowed.³⁰ Time-dependent density functional theory (TDDFT) calculation on xanthene dyes showed that this mechanism is in fact the main driving force of the high ISC yields in eosin and erythrosine, boosting the $S_1 - T_2$ spin-orbit matrix element by nearly two orders of magnitude relative to fluorescein.⁹¹ The organic dye hypericin offers a second example, where a $S_1 \rightarrow T_2$ ISC is expected to be the main driving force. Without any heavy atoms and El-Sayed-forbidden lowest singlet and triplet states of mainly $\pi\pi^*$ character, the molecule still exhibits a remarkably high ISC quantum yield of $\Phi_{ISC} \approx 0.5$.^{95,96} Current computational and spectroscopic evidence points to a quasi-degenerate $S_1 \rightarrow T_2$ ISC followed by a rapid $T_2 \rightarrow T_1$ IC as the dominant deactivation route.^{95,97}

Spin-Vibronic ISC When a molecule is conformationally flexible and its electrons are highly delocalized, electronic-, spin- and nuclear dynamics can couple giving rise to vibration-induced SOC described by the third term k_{ISC}^{SV} in **Equation 2.12**.^{30,90} Free-base porphyrin exemplifies such a spin-vibronic coupling mechanism. Despite lacking heavy atoms, near-degenerate triplets or El-Sayed-allowed channels, it shows an enhanced ISC rate. TDDFT calculations attribute the effect to out-of-plane S_1 vibrations that admix a small $\sigma\pi^*$ component into the $\pi\pi^*$ framework causing a significant increase of the H_{SO} matrix elements by roughly two orders of magnitude and correspondingly accelerating k_{ISC} .^{90,98}

The mechanism of ISC can differ greatly, and the kinetics reflect that diversity. Molybdenum- and tungsten-halide complexes complete ISC in just a few picoseconds, rose bengal crosses in 70 to 500 ps depending on the solvent, and terrylene takes several microseconds.^{99–101}

2.2.4 Radiative Emission Pathways

Fluorescence Radiative emission pathways or spontaneous emission include fluorescence, a spin-allowed process characterized by nanosecond lifetimes and emission spectra that mirror the absorption profile in accordance with the Franck-Condon principle.⁵¹ Since the energy difference between the excited states within the same multiplicity are generally smaller compared to the $S_1 \rightarrow S_0$ ground state transition, VR and IC usually outcompete fluorescence from higher excited states (see the energy-gap-law in **Equa-**

tion 2.11). Kasha's rule summarizes this empirical observation, stating that fluorescence normally originates from $S_1 \rightarrow S_0$.⁶⁹

However, "hot" fluorescence from higher vibrational or electronic state can appear if IC between $S_2 \rightarrow S_1$ is slow due to a high energy gap e.g. in aromatic thioketones or if the $S_1 \rightarrow S_0$ transition is sufficiently slow to allow thermal population of the energetically close S_2 state, leading to dual emission from S_1 and S_2 .^{102,103} Delayed fluorescence may arise via thermally activated reverse ISC ($T_1 \rightarrow S_1$) or via triplet-triplet annihilation (TTA), a bimolecular process discussed in **Section 2.2.5**.^{5,104}

Phosphorescence Spontaneous emission from an excited triplet state is termed phosphorescence ($T_1 \rightarrow S_0$). Because the transition is spin-forbidden, its radiative rate is much slower, around microseconds to seconds.⁵¹ As T_1 lies lower in energy than S_1 , phosphorescence is strongly red-shifted yielding a large Stokes shift.¹⁰⁵ The extended excited-state lifetime also often produces a richer vibronic structure or even emission from multiple triplet states, resulting in broader bands.^{7,51,54,106,107}

In semiconductor nanocrystals and molecular crystals this $S_1 \rightarrow S_0$ fluorescence or $T_1 \rightarrow S_0$ phosphorescence picture translates directly to radiative recombination of a confined exciton which can be either "bright" and spin-allowed or "dark" and spin-forbidden.¹⁰⁸

2.2.5 Bimolecular and Multi-State Interactions

Beyond the intrinsic relaxation pathways, excited molecules can interact with their surroundings or with one another, opening additional decay channels. Because the triplet state is usually long-lived, multiple processes can compete with the spin-forbidden $T_1 \rightarrow S_0$ transition. Monomolecular thermally activated reverse ISC which can lead to delayed fluorescence, has already been addressed in the previous section.

Collisional Quenching Another channel is collisional triplet quenching, most prominently by dissolved molecular oxygen. The ground state of O_2 is a triplet with two unpaired electrons (3O_2), allowing efficient coupling to other triplet manifolds and a shortening of phosphorescence lifetimes. If the donor triplet energy exceeds ≈ 1 eV, energy transfer can promote molecular oxygen to its first excited singlet state (1O_2), which is a cytotoxic species of great interest for photodynamic therapy.^{109–111} Octahedral transition-metal halide cluster complexes provide a clear example of this bimolecular quenching mechanism. Owing to the heavy-atom effect (see **Section 2.2.3**), these clusters possess very fast ISC and bright phosphorescence of multiple microseconds.^{17,19,112,113} Nevertheless, due to their geometry and energy alignment, molecular oxygen efficiently quenches their triplet state, giving 1O_2 quantum yields close to 100 % and reducing the triplet-state lifetime by several orders of magnitude when the atmosphere is switched from oxygen-free to oxygen-saturated conditions.^{18,114} These aspects are discussed in greater detail in **Section 2.6.2**. The different bimolecular processes are summarized in **Table 2.3**.

Triplet-triplet Annihilation TTA is a second-order process in which two molecules in their triplet configuration collide to form one excited singlet state S_1 and one ground-state molecule, thereby annihilating both triplet states and generating delayed fluorescence.¹¹⁵ The conversion proceeds through an intermediate spin-correlated triplet-pair state, often written as (TT^*), whose exact electronic nature remains a matter of active debate.^{5,32,116}

Singlet Fission SF is a process, in which an excited singlet molecule transfers its energy to a ground-state molecule, yielding a spin-correlated triplet pair that can subsequently dissociate into two individual triplet states. It can therefore be understood as the microscopic reverse of TTA.^{14,32} Like TTA,

Table 2.3: Representative bimolecular and multi-state pathways. An asterisk (*) denotes an electronically excited species, superscripts give the spin multiplicity.

Process	Representative Elementary Step
Self-Quenching	$A^* + A \rightsquigarrow A + A$
Oxygen Quenching	$^3A^* + ^3O_2 \rightarrow A + ^1O_2^*$
TTA	$^3A^* + ^3A^* \rightarrow (TT)^* \rightarrow ^1A^* + A$
SF	$^1A^* + A \rightarrow (TT)^* \rightarrow ^3A^* + ^3A^*$
Photo induced electron transfer (PET)	$^3A^* + A \rightarrow A^{\bullet-} + A^{\bullet+}$
Exciplex	$A^* + B \rightleftharpoons [A \cdots B]^* \xrightarrow{h\nu} A + B$
Förster resonance energy transfer (FRET)	$A^* + B \rightarrow A + B^*$

SF is spin-allowed and can occur on picosecond time scales, but only when the energy of each triplet is at most half that of the originating singlet ($S_1 \geq 2T_1$).¹¹⁷ As a bimolecular process SF requires close contact, which is typically found in aggregates, molecular crystals, or covalently linked dimers. The acene family provides classic examples with the ability of SF satisfying the energy requirement.^{29,118–121} Further details are given in **Section 2.6.3**.

Photo-induced Electron Transfer

A long-lived triplet might also undergo PET with a ground-state donor or acceptor, generating a spin-correlated radical-ion pair. A representative example is dianionic rose bengal, whose triplet state transfers an electron to a ground-state molecule to form the redox pair ($^3RB^{2-*} + RB^{2-} \rightarrow RB^{\bullet-} + RB^{\bullet3-}$).^{122,123}

Exciplex Transient formation of an excited dimer (excimer) or an excited heteronuclear complex (exciplex), where one fragment is electronically excited while the other remains in its ground state, opens yet another decay pathway. These complexes typically relax quickly, either nonradiatively or through a broad, structureless emission band. The attractive interaction exists only in the excited configuration and is often endowed with charge transfer (CT) character.^{124,125}

FRET FRET is a long-range ($\approx 1 - 10$ nm) nonradiative energy transfer from the excited singlet state of a donor molecule to an acceptor via dipole-dipole coupling. The rate falls off with the inverse sixth power of donor-acceptor distance and requires spectral overlap between donor emission and acceptor absorption.^{126,127} Dexter energy transfer is a short-range (< 1 nm) two-electron exchange process demanding direct orbital overlap. Its rate decays exponentially with distance and can transfer either singlet or triplet energy, making it the operative mechanism in triplet-sensitized reactions such as singlet-oxygen generation.^{128–130}

In quantum-confined semiconductors, Auger or biexciton recombination can occur, where a multi-exciton state transfers its energy nonradiatively to a third charge carrier, ultimately limiting the brightness at high excitation densities.^{79,131}

2.2.6 Photochemical Transformations

Beyond the photophysical and bimolecular deactivation pathways outlined above, excited states can also drive covalent transformations. Photobleaching, an often unwanted photochemical transformation, irreversibly destroys the chromophore and is especially pronounced in the presence of 1O_2 .^{132,133} Other photochemical pathways include α -cleavage of triplet carbonyls or triplet-

sensitized cycloadditions and photoredox cycles initiated by triplet metal-to-ligand charge transfer (MLCT) complexes.^{134–139} A comprehensive survey is beyond the scope of this thesis, but these examples illustrate that excitation energy may be channeled into permanent chemical change rather than dissipated as light or heat.

In summary, photoexcited materials exhibit multiple, competing decay pathways with characteristic rates that depend on their electronic structure, on environmental factors and on the nature of the transition. Although these processes can overlap in energy or time, they can be disentangled by combining complementary spectroscopic techniques and by systematically varying external parameters such as concentration, temperature, and excitation conditions. The following section outlines these strategies used in this work.

2.3 Photophysical Observables

There are various and often complementary spectroscopic techniques to decipher the excitation and relaxation pathways of a material outlined in the previous chapter. Any spectrum, lifetime trace or a 2D map is essentially a measurable projection of those pathways whose purpose is to convert raw optical signals into quantitative parameters. Absorption and emission recorded under continuous illumination provide an ensemble-averaged picture of the excited-state manifold including transition energies, oscillator strengths, and quantum yields, whereas time-resolved methods slice the same landscape along the time axis, revealing rate constants for ISC, radiative decay, and charge or energy transfer.^{51,72}

In the pages that follow, the discussion therefore proceeds from linear (steady-state)

observables, through time-resolved observables, to variable-parameter and multidimensional measurements employed in this work.

2.3.1 Steady-State Absorption

Absorption spectroscopy measures how the transmitted light intensity varies with photon energy i.e. how transmissive a sample is at a given energy or wavelength. The basic measuring geometry is shown in **Figure 2.4**.

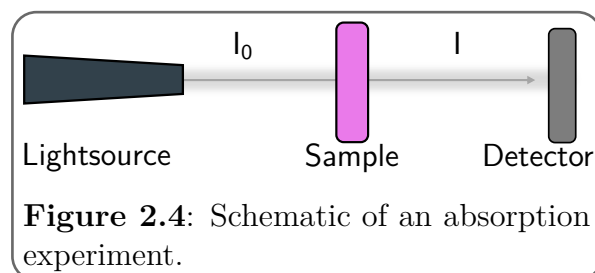


Figure 2.4: Schematic of an absorption experiment.

The transmitted fraction $T(\lambda)$ as a function of energy or wavelength λ is defined as the ratio of detected I and incident I_0 light given by **Equation 2.14** while the decadic absorbance A is defined in **Equation 2.15**.^{50–52}

$$T(\lambda) = \frac{I}{I_0} \quad (2.14)$$

$$A(\lambda) = -\log_{10}(T(\lambda)) \quad (2.15)$$

It is worth noting that the measurable quantity is the attenuation of the light intensity. Interpreting this as absorbance is only valid when reflection, scattering, luminescence etc. is negligible. Some authors therefore refer to attenuation or extinction (the latter discouraged by IUPAC) when such additional losses are present.⁷²

The Beer-Bouguer-Lambert law empirically relates absorbance to concentration c and optical path length d , given in **Equation 2.16**^{140–142}

$$A(\lambda) = -\log_{10}\left(\frac{I}{I_0}\right) = \epsilon(\lambda) c d, \quad (2.16)$$

where ϵ is the (decadic) molar absorption coefficient. Because $A \propto c$, absorption spectroscopy is the standard method for concentration determination. Due to the already mentioned differences of absorbance and the measured attenuated intensity, the linear relationship fails when absorbers interact, scatter strongly, are inhomogeneously distributed, or when the excitation is polychromatic or induce saturation, bleaching or other nonlinear processes.^{50,143}

As discussed in **Section 2.1** and **Figures 2.1 and 2.2**, the position (energy), intensity and width of an absorption band reveal the nature of the quantum-mechanical transition involved. Bands in the microwave region arise from rotational changes, those in the NIR from vibrational transitions, and bands in the UV to Vis from electronic excitations. The integrated intensity reflects the underlying transition's oscillator strength and the sample concentration (see **Equation 2.16**), while the width depends on the instrumental resolution, the underlying vibronic structure (Franck-Condon envelope) and the intrinsic homogeneous and inhomogeneous broadening mechanisms (e.g. natural broadening, thermal Doppler broadening and pressure broadening).^{144–147} Solvent, aggregation state, temperature, and other environmental factors can further modulate both the energy and width of absorption bands in complex ways.^{148–150}

2.3.2 Steady-State Emission

Emission spectroscopy analyzes the fluorescence or phosphorescence of a sample and thus complements absorption spectroscopy, with the main limitation that the analyte must be emissive. After excitation at a fixed wavelength, the emitted photon intensity as a function of emission wavelength generally reports the $S_1/T_1 \rightarrow S_0$ transition and the associated vibrational manifold of the ground state. The simplistic design of a steady-state emission spectroscopy setup is depicted in **Figure 2.5**.

The gap between absorption and emission

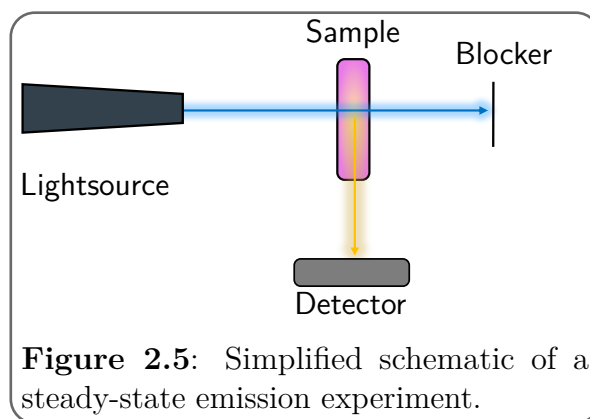


Figure 2.5: Simplified schematic of a steady-state emission experiment.

maxima (Stokes Shift) encodes how much the excited state and its solvent shell relax after photoexcitation and depend among others on solvent polarity, analyte polarizability and temperature.^{50–52}

As in absorption spectroscopy, band position and shape are sensitive to homogeneous/inhomogeneous broadening mechanisms and to environmental factors revealing aggregation tendencies, solvent interactions, energy transfer pathways (e.g. exciplex formation, FRET, collisional quenching) or other excited-state properties. To suppress inner-filter effects and reabsorption of the emitted light, the concentration of the analyte must be sufficiently low.^{148–150}

In excitation spectroscopy, by contrast, the emission wavelength is held fixed while the excitation wavelength is scanned, typically resulting in a spectrum that mirrors the absorption profile when the system follows Kasha's rule.

Steady-state emission measurements also provide emission quantum yields, obtained either absolutely with an integration sphere or relatively against a calibrated reference system. From quantum yields, emission rate constants can be derived (see **Equation 2.9**) and thereby quantify the competing relaxation pathways.^{151,152}

2.3.3 Time-Resolved Emission Spectroscopy

Time-resolved emission techniques record the intensity of the emitted light as a func-

tion of the delay t after a short excitation pulse. After photoexcitation, the population resides in S_1 (or T_1 in case of phosphorescence) and the ensuing emission intensity $I(t)$ can be described as a sum of exponentials in **Equation 2.17**¹⁵³

$$I(t) = \sum_i \alpha_i \exp\left(\frac{-t}{\tau_i}\right), \quad (2.17)$$

where each component i represents a distinct emissive sub-population with amplitude α_i and lifetime τ_i which shares a common environment, electronic state or kinetic history. The observed lifetime τ_i or reciprocal rate k_i represents the sum of all first-order relaxation channels available to that population i . In the special case of a single monoexponential decay, the radiative (k_r) and nonradiative (k_{nr}) rates follow directly from the observed lifetime and the quantum yield via **Equations 2.7 to 2.9**.^{50,73}

Detection Types There are several detection schemes, each optimized for a particular timescale and sensitivity. For micro- to millisecond phosphorescence decays, a gated integrator could be used, where the detector integrates the photons within a gate window and subsequently shifts the gate for the next excitation pulse, resulting in a step-by-step reconstruction of the decay.¹⁵⁴

For faster processes in the pico- to nanosecond regime a streak camera can be used capturing the entire temporal profile per shot. In this case, each photon is converted into an electron on a photocathode which is subsequently deflected by a rapidly sweeping electric field so that its landing height on the phosphor screen encodes the arrival time.^{155,156} Another method uses Time-Correlated Single Photon Counting (TCSPC), where each detected photon stops a high-resolution "stopwatch" that started with the excitation trigger. Repeating the cycle builds a histogram of arrival times representing the overall decay dynamics.^{153,157,158} This is schematically illustrated in **Figure 2.6**.

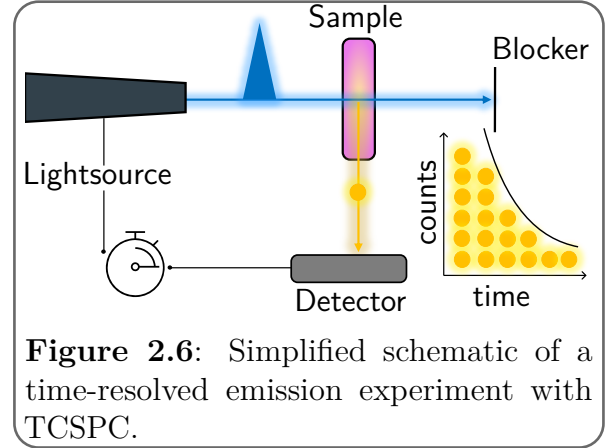


Figure 2.6: Simplified schematic of a time-resolved emission experiment with TCSPC.

Instrument response function (IRF)

The achievable time resolution is limited by multiple factors which also depend on the detection method. Generally, it includes the pulse width of the excitation source, precision of the timing reference signal, the timing accuracy of registering a photon and electronic jitter. Together they form the instrument response function (IRF) which is a convolution of every individual response function g_i given in **Equation 2.18**.^{34,153}

$$\text{IRF} = g_{\text{source}} \otimes g_{\text{detector}} \otimes g_{\text{jitter}} \otimes \dots \quad (2.18)$$

If each contribution is approximated by a Gaussian in the time domain, the FWHM of the overall IRF or resolution is the geometrical sum of the FWHM of each component:^{153,158}

$$\text{FWHM}_{\text{IRF}} = \sqrt{\sum_i \text{FWHM}_{g_i}^2} \quad (2.19)$$

Besides the approximated prediction of the IRF using **Equation 2.19**, the IRF can be measured directly by recording the scattered excitation pulse from a nonemissive medium. Because the experimental decay trace is the convolution of the true kinetics with the IRF, reconvolution or deconvolution techniques are required to recover the underlying dynamics.^{153,158} The mathematical details, particularly applied to TA data, are discussed in **Section 2.5**.

2.3.4 Time-Resolved Absorption Spectroscopy

The following paragraphs outline the basic principles of TA spectroscopy and show how the spectral and temporal evolution of its signals can be used to map relaxation pathways in photoexcited materials. Instrumentation details are given in **Section 2.4**, while strategies for modeling the full data cube are described in **Section 2.5**.

Time-resolved absorption spectroscopy records changes in absorbance or transmittance as a function of delay between an initial excitation and a subsequent probe. Typically, the sample is excited by a pulsed laser, the pump, which initiates photophysical processes. A weak white-light continuum, the probe, then monitors the resulting absorption changes across many wavelengths simultaneously. The method is therefore a form of pump-probe spectroscopy, historically called flash photolysis.¹⁵⁹ Because it resolves the full temporal evolution of the transient species produced, it is commonly referred to as transient absorption (TA) spectroscopy. The basic principle is illustrated in **Figure 2.7**.^{33,160}

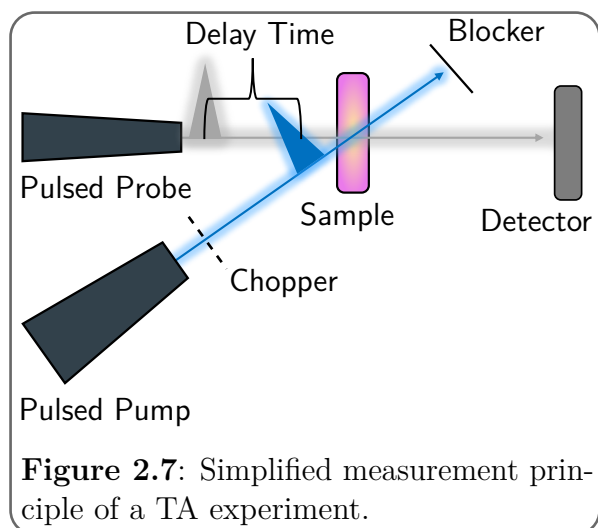


Figure 2.7: Simplified measurement principle of a TA experiment.

Differential Absorption The quasi-monochromatic pump pulse passes through the sample, promoting only a few percent of the molecules within the illuminated volume

to an excited state. After a controlled delay, the broadband probe pulse traverses the same region. Increasing the pump fluence would indeed raise the excited-state population, but it would also introduce nonlinear processes such as multiphoton absorption and increase the risk of photodamage, so the pump intensity is usually kept moderate.³³ As a result, the ensemble absorbance deviates only slightly from the ground-state absorbance measured in a conventional steady-state spectrum, because most molecules remain unexcited (compare **Figure 2.8, A and B**). The differential absorbance ΔA is therefore defined as

$$\Delta A(t) = A^*(t) - A^{gs}, \quad (2.20)$$

where $A^*(t)$ is the absorbance of the excited ensemble at delay time t and A^{gs} is the ground-state absorbance recorded without the pump by using a mechanical chopper (**Figure 2.8 C**). Using **Equations 2.14 and 2.15**, this can be rewritten in **Equation 2.21**

$$\begin{aligned} \Delta A(t) &= \log \left(\frac{I_0^*(t)}{I^*(t)} \right) - \log \left(\frac{I_0^{gs}}{I^{gs}} \right) \\ I_0^*(t) &= I_0^{gs} \\ \Delta A(t) &= \log \left(\frac{I^{gs}}{I^*(t)} \right), \end{aligned} \quad (2.21)$$

because the incident intensity I_0 is constant throughout the experiment and therefore cancels out. Here, I denotes the detected intensity, and I_0 the incident intensity on the sample.^{31,33,160}

After an averaged ΔA spectrum at a fixed delay time has been recorded, the experiment is repeated for a range of delays, yielding a three-dimensional dataset $\Delta A(\lambda, t)$ that contains probe wavelength, pump-probe delay and signal amplitude. This hyperspectral cube is usually displayed as a color-coded heat map, often called a “2D spectrum”, or explored via kinetic or spectral traces extracted at selected probe wavelengths or delay times.³⁴

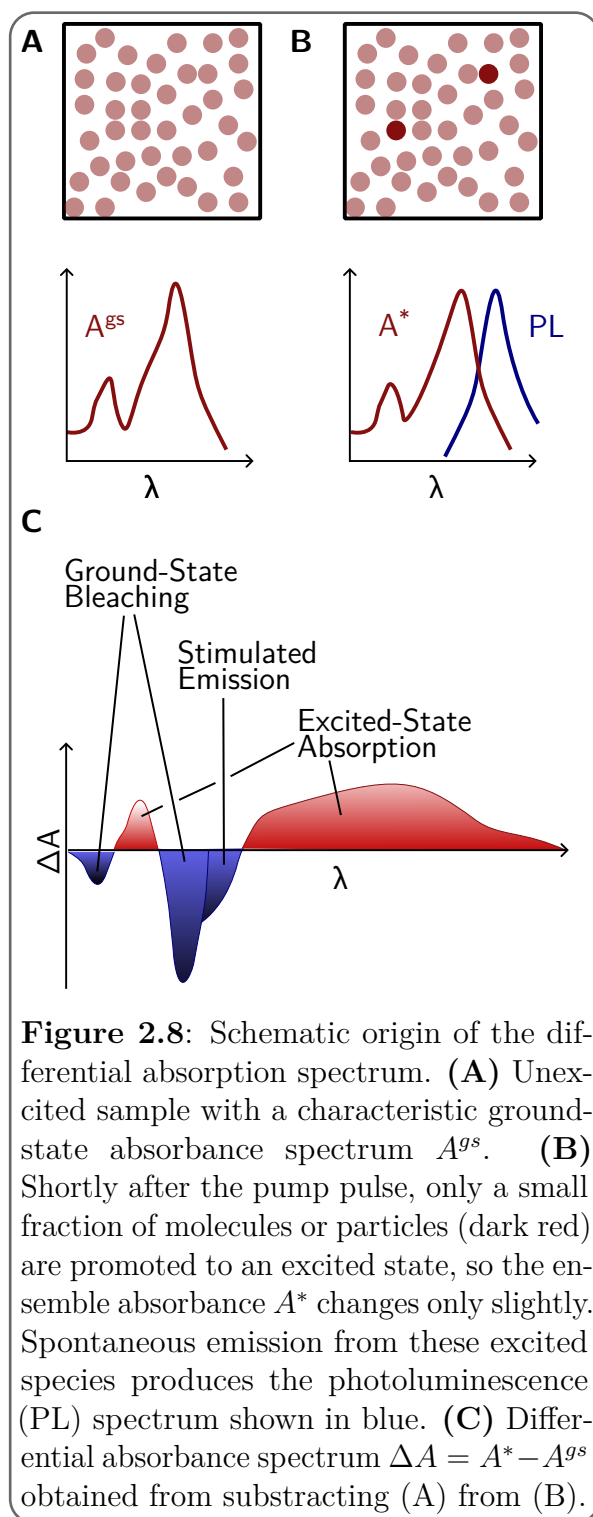


Figure 2.8: Schematic origin of the differential absorption spectrum. (A) Unexcited sample with a characteristic ground-state absorbance spectrum A^{gs} . (B) Shortly after the pump pulse, only a small fraction of molecules or particles (dark red) are promoted to an excited state, so the ensemble absorbance A^* changes only slightly. Spontaneous emission from these excited species produces the photoluminescence (PL) spectrum shown in blue. (C) Differential absorption spectrum $\Delta A = A^* - A^{gs}$ obtained from subtracting (A) from (B).

Spectral Contributions In these data, signals from several transient species and processes are superimposed. The main contributions, particularly in dilute molecular systems, are illustrated in **Figure 2.8 C**. Because the pump removes a fraction of molecules from S_0 , transitions from $S_0 \rightarrow S_n$

are weakened, producing a negative ΔA feature known as the ground-state bleaching (GSB). If the sample is emissive, stimulated emission from the excited state adds a second negative feature whose shape mirrors the steady-state photoluminescence. In contrast to spontaneous emission, stimulated emission occurs when an excited state interacts with an incoming photon of the appropriate energy, prompting the state to decay and emit a second photon identical to the incident one. Owing to the small Stokes shift, stimulated emission often overlaps the GSB. Positive ΔA signals occur whenever the excited ensemble absorbs more light than the ground state. This happens when molecules are promoted from an excited state to an even higher state (excited-state absorption (ESA)) or when transient photoproducts such as triplet states, exciplexes or radical-ion pairs possess their own absorption bands. In the latter cases the collective term photo-induced absorption (PIA) is commonly used.^{31,33} The spectral signatures discussed above are collected in **Figure 2.9 A - C**.

In semiconductors and other solids, where large numbers of charge carriers interact, additional derivative-like features appear.¹⁶¹ Photo-generated electrons and holes screen their mutual Coulomb interactions, which can lower the band gap and produces an overall red shift of the absorption edge (**Figure 2.9 D**) which is known as band-gap renormalization (BGR).^{162–164} The same screening also reduces the exciton-binding energy, shifting the excitonic resonance to higher energy (a blue shift). Beyond the GSB, associated with depletion of the valence band (VB) edge, Pauli blocking of the lowest conduction band (CB) states forces photons to span a larger energy to create an electron-hole pair. The apparent band gap therefore increases, giving a blue-shifted feature attributed to Burstein-Moss filling (**Figure 2.9 E**).^{162,165} Finally, processes such as exciton coherence, hot-carrier scattering, transient electric fields and carrier cooling

can modify the homogeneous or inhomogeneous linewidth, leading to a transient broadening or narrowing of the bands and the characteristic second-derivative line shapes shown in (**Figure 2.9 F, G**).^{163,166,167}

Kinetic Contributions The spectral features discussed above can be exploited not only to identify transient species and estimate reorganization energies, but also to extract their lifetimes and rate constants. These kinetics can be fitted locally at a single probe energy or globally over the entire spectral range, yielding a comprehensive view of the relaxation pathway. Unlike time-resolved emission spectroscopy, whose kinetics are usually described by a parallel scheme of independent first-order decays ($A \rightarrow C, B \rightarrow C$), TA data often involve more elaborate scenarios, including sequential processes ($A \rightarrow B \rightarrow C$) and branching pathways ($A \rightarrow B, A \rightarrow C$). Modeling such schemes with their many degrees of freedom (d.o.f) provides meaningful insight only when supported by complementary experiments, theoretical calculations or prior knowledge that can constrain the parameter space. This strategy, known as target analysis, tests specific kinetic models against the data.^{31,34} Further details are given in **Section 2.5.3**.

Time Resolution As noted for time-resolved emission spectroscopy, the IRF determines the ultimate temporal resolution. In TA measurements, the IRF is the convolution of the pump pulse with the detector response i.e. the probe pulse. In practice, this resolution can be degraded by group-velocity dispersion in the probe continuum and by nonlinear artifacts such as multiphoton absorption, stimulated Raman scattering and cross-phase modulation when pump and probe overlap.^{31,34,168} These issues are discussed in detail in **Section 2.5.2**.

2.3.5 Variable-Parameter Spectroscopy

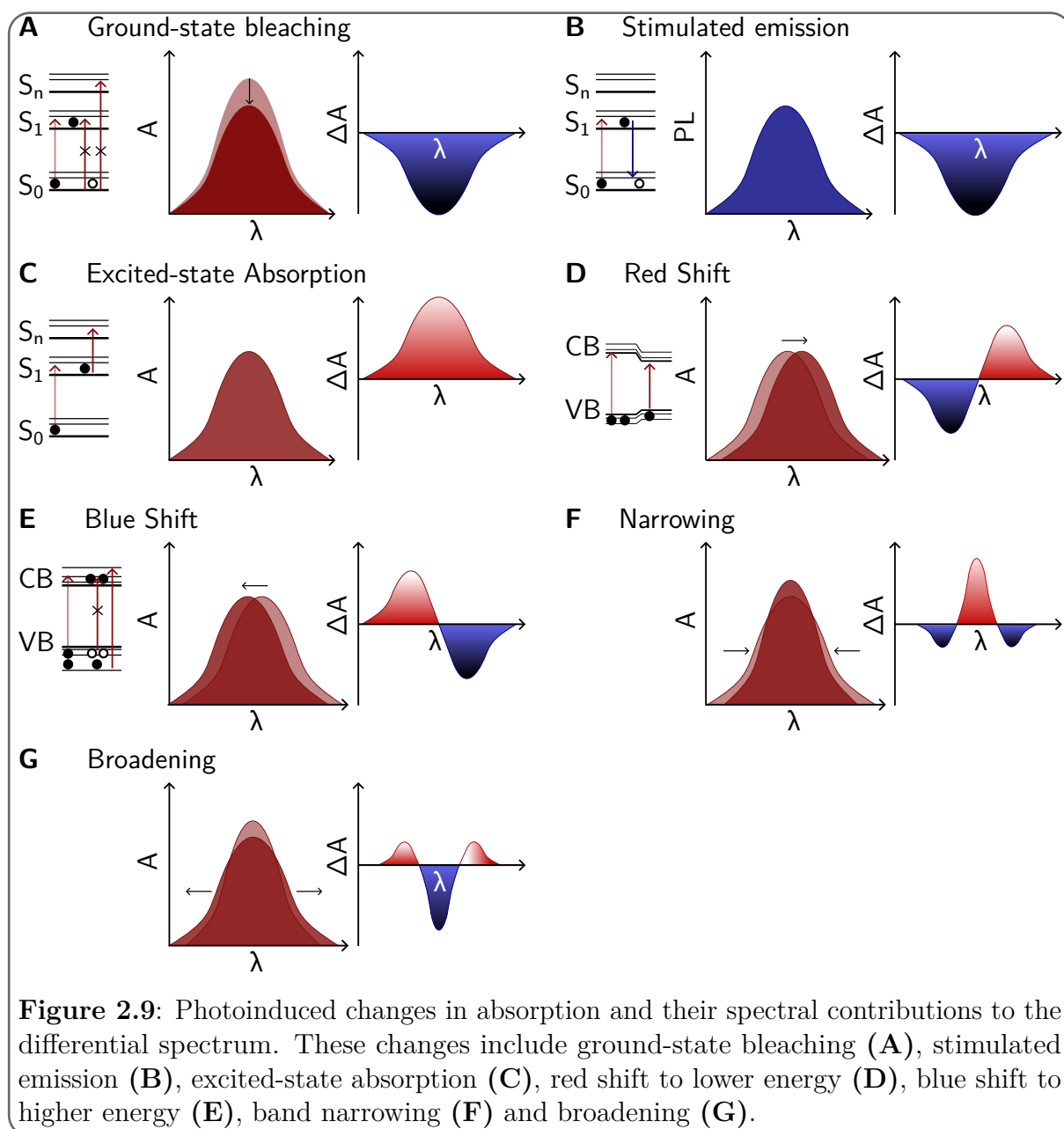
This section shows how the spectroscopic methods described above can be coupled with controlled changes of external parameters to reveal mechanistic details of photophysical processes. For instance, recording steady-state infrared absorbance as a function of pH can track conformational changes, while emission spectroscopy can report on different redox states or on pH-dependent relaxation pathways of chromophores.^{169–171}

Concentration Other studies focus on the bimolecular relaxation pathways discussed in **Section 2.2.5**. Varying the analyte concentration, together with emission or TA spectroscopy, has clarified the roles of excimer and aggregate formation in the SF dynamics of acene derivatives.¹⁷² In investigations of triplet-state quenching and singlet-oxygen generation, the emission lifetime or the corresponding TA signal and the emission intensity are measured as functions of the dissolved-oxygen concentration $[O_2]$. These data allow to extract the bimolecular quenching rate k_q and to distinguish static from dynamic quenching via the Stern-Volmer relation in **Equation 2.22**.^{114,173}

$$\frac{1}{I_{PL}} \propto k_q [O_2] \quad (2.22)$$

In dynamic quenching the quencher collides with the excited species, reducing the emission lifetime in the same reciprocal manner as the intensity I_{PL} . In static quenching, where a non-emissive ground-state complex is formed, only the emission intensity follows this linear relationship.

Temperature Triplet emitters often display pronounced temperature-dependent emission spectra and lifetimes, because the three spin-sublevels are populated to different extents as the thermal energy varies. Recording the emission lifetime over a range of temperatures therefore allows one to extract both the decay rates and the en-



ergy splitting of these sublevels by fitting a Boltzmann-type expression for thermally activated rates:

$$k_{tot} = \frac{k_1 + k_2 e^{\frac{-\Delta E_{1,2}}{k_B T}} + k_3 e^{\frac{-\Delta E_{1,3}}{k_B T}}}{1 + e^{\frac{-\Delta E_{1,2}}{k_B T}} + e^{\frac{-\Delta E_{1,3}}{k_B T}}} \quad (2.23)$$

In **Equation 2.23** k_B is the Boltzmann constant, k_1 , k_2 and k_3 are the decay rates of the three triplet sublevels and

$\Delta E_{1,2}$ and $\Delta E_{1,3}$ are their respective energy gaps. Using this approach, the zero-field splitting (ZFS) of complexes such as Ru(II), Pt(II) and Mo(II) has been quantified from temperature-dependent emission-lifetime measurements.^{106,174,175}

Environment Solvent-dependent absorption, emission and TA studies can be used to estimate ground- and excited state dipole moments. Methods such as the Lippert-Mataga relation and the Ravi approach correlate the observed Stokes shift with the molecular dipole moment

and specific solvent parameters.^{176–180} The effect of solvent polarity on excited-state dynamics can likewise be tracked by TA spectroscopy, revealing how different environments stabilize or modify the excited state.^{101,181}

In summary, this section introduced the basic principles of the measurement techniques employed in this work and explains how they reveal specific excited-state transitions and mechanisms. The next section details the structure of a TA setup, along with its operating principles and experimental conditions.

2.4 Transient Absorption Instrumentation

This section describes the TA setup and the methods used to perform broadband TA experiments over timescales spanning femto- to microseconds. A simplified schematic of the apparatus employed in this work is presented in **Figure 2.10**.

A one-box titanium-sapphire (Ti:Sapphire) amplifier is used to create the fundamental beam with 90 fs pulses centered at 800 nm with a repetition rate of 1 kHz. Details of the laser system and the production of such high-intensity, ultrashort pulses are given in **Section 2.4.1**. A beamsplitter directs 90 % of the light (≈ 2 mJ) to the excitation arm and 10 % (≈ 0.2 mJ) to the probe arm. To avoid restricting the experiment to the laser wavelength, the pump beam is wavelength-tuned in an optical parametric amplifier (OPA), producing excitation pulses from the UV to the NIR. The underlying principles are summarized in **Section 2.4.2**. To obtain the reference spectrum required for the differential signal (see **Equation 2.21**), a mechanical chopper blocks every second

pump pulse, so 500 A^{gs}/A^* pairs can be acquired and averaged each second at the 1 kHz repetition rate.

Depending on the timescale of interest, the pump-probe delay t is set either electronically for ns-TA (< 1 ns time resolution up to 450 μ s) or mechanically with a delay line for fs-TA measurements (200 fs time resolution up to 8 ns). This synchronization is discussed in **Section 2.4.3**. A broadband WLC is created either in specific crystals pumped by the 800 nm fundamental beam (femtosecond regime) or in a photonic-crystal fiber (nanosecond regime, see **Section 2.4.2**). A small fraction of the probe is diverted before the sample to serve as a reference, compensating for pump-to-pump fluctuations.

Finally, the white-light probe traverses the excited or unexcited sample volume, and the transmitted intensity is recorded by a spectrometer at each delay time. Iterating over delays builds the three-dimensional TA data cube.

2.4.1 Femtosecond Light Sources

The properties of the excitation and probe beams are the main factor that limit pump-probe experiments, determining both the temporal resolution (pulse duration) and the signal-to-noise ratio (stability).³¹ Ideally, one would like a pulse whose width, shape, energy and repetition rate can all be tuned independently, which is something no single light source can provide.¹⁸² Since the first working laser was demonstrated in 1960, lasers have advanced to the point where they can deliver ultrashort pulses of only a few femtoseconds.^{183,184} Combined with amplification, frequency-conversion and post-compression techniques, they now satisfy the stringent demands of ultrafast spectroscopy.^{37,182,185} At the start of the 21st century, these advances made attosecond spectroscopy possible, allowing researchers to probe even faster electronic processes that are invisible to conventional

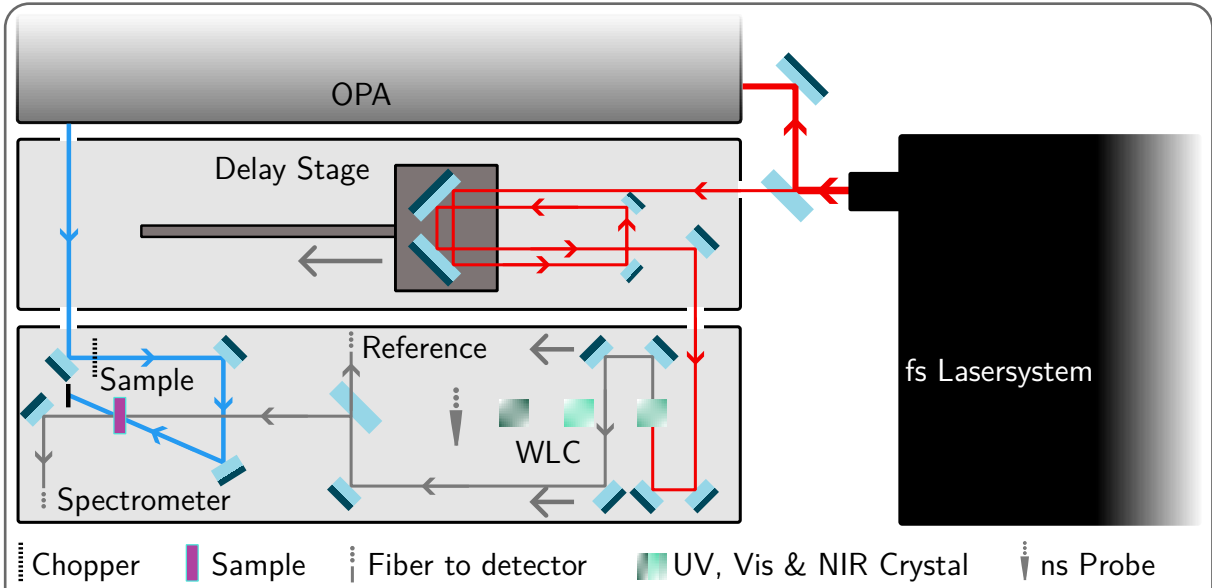


Figure 2.10: Simplified schematic of the TA apparatus used in this work. A femtosecond laser system delivers 90 fs, 800 nm pulses that are split into pump and probe arms. The pump wavelength is tuned with an optical parametric amplifier (OPA) and a mechanical chopper blocks every other pump pulse before it reaches the sample. The probe delay relative to the pump is set by a mechanical delay line with a movable mirror assembly. A WLC probe is generated in nonlinear crystals selected for the desired spectral window. For ns-TA experiments, the WLC is generated externally and the delay time is set electronically. Immediately after WLC generation, a fraction of the probe is diverted as a reference, while the remainder propagates with the pump through the sample.

fs-TA spectrometers.^{186,187} The basic operating principles of the laser system used in this work are outlined below. For more details, the reader is referred to the specialized literature.^{37,184,188}

Basic Principle Laser is an acronym for light amplification by stimulated emission of radiation. A gain medium is excited (pumped) by an external energy source inside an optical resonator until a population inversion is reached. Photons circulating in the resonator stimulate further emission from the excited atoms or ions, producing coherent amplification.³⁷ Although the longitudinal modes are individually monochromatic, their relative phases are normally random, so the output is continuous-wave.

Pulsed Lasers Pulsed operation is obtained by forcing the modes to share a common phase (mode-locking). This can be done

passively by Kerr-lens mode-locking.¹⁸⁹ The optical Kerr effect describes the intensity-dependent refractive index changes of a material and causes intense, time-localized spikes to self-focus through the cavity's soft aperture, while lower-intensity background light is defocused and clipped, acting as an ultrafast amplitude filter.^{37,39,188}

Because of the time-bandwidth (uncertainty) relation, the pulse duration Δt_P and the spectral bandwidth $\Delta \nu_P$ are not independent. For Gaussian pulses this can be expressed with **Equation 2.24**

$$\Delta t_P \Delta \nu_P \geq 0.44 \quad (2.24)$$

resulting in a 10 fs pulse centered at 800 nm requiring a FWHM bandwidth of roughly 100 nm.³³ Ti:Sapphire is an ideal gain medium for such pulses.³⁷ Pumped by green light, it offers a very broad emission

band and a strong Kerr effect, allowing its many longitudinal modes to lock passively and generate femtosecond pulses.¹⁹⁰

Laser Amplification The oscillator used in this work (Vitara-S, Verdi-G, Coherent) delivers ≈ 20 fs pulses at 800 nm and a repetition rate of 80 MHz.^{191,192} However, these "seed" pulses are too weak to perform TA experiments. Direct amplification would raise their peak power to destructive levels, so they are first stretched in a grating stretcher, which delays the high-frequency components and therefore lengthens each pulse to ≈ 200 ps. The seed then enters a regenerative amplifier containing a second, diode-pumped Ti:Sapphire crystal operated at 1 kHz (Revolution, Coherent).^{33,193} On each round-trip the stretched seed extracts energy from the inverted crystal, a scheme known as chirped-pulse amplification.^{194,195} After 10 to 20 passes the amplified pulse is ejected by a pair of Pockels cells, whose electro-optic effect rotates the polarization when a voltage is applied. Finally, a grating compressor reverses the stretcher's dispersion, yielding 90 fs pulses centered at 800 nm with an energy of about 7.5 mJ (7.5 W average power) at 1 kHz.⁴⁰

2.4.2 Nonlinear Frequency Conversion

There are multiple nonlinear methods to extend or convert the spectral range of lasers which is crucial when they serve as the excitation or probe source in TA spectroscopy. The most relevant methods are summarized below. More details of the underlying processes can be found in the literature.^{196–199}

Nonlinear Optics At low light intensities, the induced electrical polarization P is proportional to the electric field E_F which can be expressed with **Equation 2.25**

$$P(t) = \epsilon_e \chi_1 E_F(t), \quad (2.25)$$

where ϵ_e is the vacuum permittivity and

χ_1 the linear susceptibility. For high values of E_F , the material response saturates and can be modeled by a nonlinear susceptibility given by a power-series expansion in **Equation 2.26**.

$$P(t) = \epsilon_e \chi_1 E_F(t) + \epsilon_e \chi_2 E_F(t)^2 + \epsilon_e \chi_3 E_F(t)^3 + \dots \quad (2.26)$$

χ_2 and χ_3 are the second- and third-order nonlinear susceptibilities.^{37,197} Second order χ_2 nonlinear processes such as second-harmonic generation (frequency doubling), sum- or difference-frequency generation and optical parametric generation occur only in non-centrosymmetric materials like β -barium borate (BBO).^{200,201} Third order χ_3 effects include the optical Kerr effect already introduced in the previous section through the self-focusing effect in the Kerr lens, and self-phase modulation, which can spectrally broaden ultrashort pulses and produce smooth white-light continua.^{202,203}

Sum-Frequency Generation As a χ_2 process, sum-frequency generation requires the interaction of high intensity light in a non-centrosymmetric medium. It describes the mixing of two input photons with frequency v_1 and v_2 generating a third photon with frequency v_3 , satisfying the energy conservation (**Equation 2.27**).^{204,205} Constructive interference additionally requires phase matching (phase-matching condition) expressed in **Equation 2.28** where $\vec{k}_i$ are the respective wave vectors.^{37,206}

$$v_3 = v_1 + v_2 \quad (2.27)$$

$$\vec{k}_3 \approx \vec{k}_1 + \vec{k}_2 \quad (2.28)$$

Phase matching is typically achieved in a birefringent crystal by adjusting the beam polarizations and the angle of incidence (angle tuning). BBO is particularly well suited, being inexpensive, transparent over a wide spectral range, non-centrosymmetric crystal, damage resistant and birefringent.^{37,200,201,207}

Second harmonic generation is a special case of sum-frequency generation where $v_1 = v_2$, resulting in frequency doubling.²⁰⁸ Higher-order harmonic generation involving three photons (third-harmonic generation, four-wave mixing) or four photons (fourth-harmonic generation) is usually less efficient, so sequential χ_2 frequency mixing or doubling steps are often preferred.

Parametric Amplification Parametric amplification is a second-order χ_2 process based on difference-frequency mixing. Inside a nonlinear crystal, a strong pump wave of frequency v_p interacts with a weaker signal wave of frequency v_s generating an idler at v_i such that $v_i = v_p - v_s$ (see **Figure 2.11**).^{37,209} The coupled interaction simultaneously depletes the pump and amplifies both the signal and idler.^{198,210}

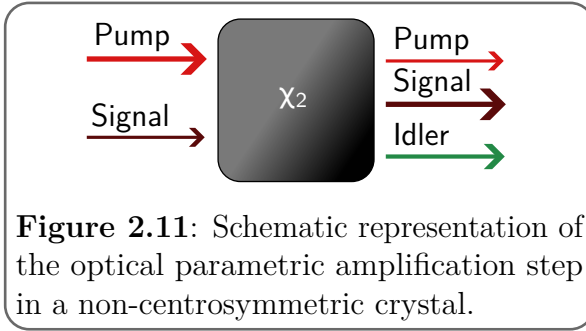


Figure 2.11: Schematic representation of the optical parametric amplification step in a non-centrosymmetric crystal.

White-Light Generation When an intense light pulse traverses a medium, the χ_3 optical Kerr effect modulates the refractive index adding a time-dependent phase-shift (self-phase modulation) that continuously changes the frequency across the pulse. Focusing such a light pulse into suitable crystals like sapphire or yttrium aluminum garnet (YAG) therefore generates a WLC.^{37,211} Typical crystals and their material-dependent wavelength coverage which were used in this work are listed in **Table 2.4**.^{43,44}

A photonic crystal fiber, whose microstructured core guides light, can extend the continuum even further. A high-intensity pulse coupled into such a fiber triggers a cascade

Table 2.4: Spectral ranges of white-light continua generated by self-phase modulation in different materials.

Material	Wavelength Range (nm)
CaF ₂	320 - 650
Sapphire	420 - 820
YAG	820 - 1600
Photonic Crystal Fiber	350 - 2200

of χ_3 effects including self-phase modulation, four-wave mixing and stimulated Raman scattering, which broaden the original pulse.^{38,212,213} Such a photonic crystal fiber was used for the WLC generation for the ns-TA experiments.

Optical Parametric Amplifier An OPA exploits the different nonlinear processes discussed above to convert the fundamental beam to a wide range of wavelengths.^{198,199} In this work, a two-stage OPA provides tunable excitation wavelengths from 300 to 2600 nm (Apollo-T, Ultrafast Systems).⁴¹ The incident pump beam is split into three arms: A small proportion is routed through a crystal producing a WLC seed, while the other two portions sequentially amplify the desired wavelength in birefringent crystals whose phase matching is adjusted by crystal rotation. The amplified signal (1150 to 1600 nm) or idler (1600 to 2600 nm) can be frequency doubled once or twice, or frequency mixed with the initial 800 nm beam. The resulting wavelength widows are summarized in **Table 2.5**.⁴¹

2.4.3 Pump-Probe Synchronization

Similar to time-resolved emission spectroscopy, the TA setup is adjusted to match the timescale of interest. For nanosecond and slower dynamics (ns-TA), the pump-probe delay t is set electronically by synchronizing the trigger signals of pump and probe.

Table 2.5: Wavelength coverage of the different nonlinear processes inside an optical parametric amplifier (Apollo-T, Ultrafast Systems)

Mode	Wavelength Range (nm)
Fourth Harmonic Signal	300 - 400
Fourth Harmonic Idler	400 - 480
Sum-Frequency Signal	480 - 540
Sum-Frequency Idler	540 - 600
Second Harmonic Signal	600 - 800
Second Harmonic Idler	800 - 1150
Signal	1150 - 1600
Idler	1600 - 2600

Therefore, different light sources can be used for excitation and probing. For femtosecond dynamics (fs-TA), the delay is generated mechanically with an optical delay line that exploits the finite speed of light. Both the excitation pulse and the probing pulse originate from the same fundamental beam. To obtain a delay of 8 ns between both arms, one pulse must travel 2.4 m farther than the other. By using a multi-pass retro-reflector that sends the beam through the delay stage four times (see **Figure 2.10**), the physical length of the delay line needs to be 60 cm. Although the minimum step size can be only a few fs, the practical resolution of a delay line is generally limited by the bi-directional repeatability. The delay line employed in this work (Ultrafast Systems) offers a repeatability of 14 fs and is well below the resolution limit imposed by ≥ 90 fs pulse duration.²¹⁴

For both time regimes, the detector integrates the photoelectronic signal at each delay and then steps to the next delay value. Because all sub-picosecond timing is encoded optically, no ultrafast electronics are required unlike in the emission techniques discussed in **Section 2.3.3**.^{33,168,215}

2.4.4 Experimental Conditions

In TA experiments, multiple parameters must be optimized including the pump intensity and energy, concentration and environment, measurement time, delay step size and the accessible spectral and temporal windows. Steady-state data and prior knowledge of the material provide useful starting points, but the conditions usually require iterative refinement, particularly when the transient signal is weak or the sample is vulnerable to photodegradation, as is often the case for triplet emitters that generate singlet oxygen.

Several strategies can boost the signal-to-noise ratio, each with inherent trade-offs:

- Higher concentration increases the signal but can promote aggregation or other unwanted intermolecular effects.
- Higher pump fluence likewise increases the signal yet risks photobleaching and nonlinear processes.
- Longer acquisition time averages down noise but makes the data susceptible to baseline drifts, optical instabilities and cumulative photochemical reactions.

Balancing these factors is therefore a central part of experimental design in TA spectroscopy.

After each TA experiment, the raw data cube must be examined carefully for artifacts, unwanted nonlinear signals, sample degradation and instrumental instabilities. In doubt, the measurement should be repeated under altered conditions. Once suitable parameters have been identified and the results are reproducible, additional runs can be carried out in different spectral or temporal windows and then combined, yielding a complete picture of the photophysical relaxation pathways of the system under study.

This section illustrated the basic TA setup principle and the underlying fundamental

nonlinear processes used to generate ultra-short and tunable laser pulses as well as broadband probes. The next section outlines common artifacts and preprocessing steps, before turning to data-cube modeling strategies for extracting quantitative rates and resolving transient species.

2.5 Modeling Transient-Absorption Data

After a TA experiment has been completed and the raw data cube has been screened for unwanted nonlinear processes, intermolecular interactions or sample degradation, the data must be preprocessed and corrected for intrinsic artifacts. The main steps and underlying concepts used in this work are covered in **Sections 2.5.1 and 2.5.2**.

The processed data can then be fitted with a kinetic model, either at a single probe energy (local fit) or globally across the entire spectral range. A theoretical background of the kinetic schemes is presented in **Section 2.5.3**. Although multidimensional fits often converge, it is essential to verify that the results are physically meaningful. A good starting estimate for parameters and time constants, together with a sound statistical treatment of uncertainties, is therefore indispensable. These aspects are addressed in **Sections 2.5.4 and 2.5.5**. Finally, the algorithmic implementation developed in this work are outlined in **Section 2.5.6**.

2.5.1 Raw Data and Preprocessing

An uncorrected TA hyperspectrum of a tungsten iodide cluster in acetonitrile is shown as an example in **Figure 2.12**. In **A**, the 2D hyperspectrum is plotted with probe wavelength versus delay time. The differential absorbance is color-coded, with blue indicating a loss in excited-state absorbance (negative ΔA), red a gain (positive ΔA), and grey no

change. Above the plot, the steady-state absorbance (red) and emission (blue) spectra are shown. I will use this color scheme throughout the thesis. Several issues are evident in the raw data:

First, the WLC generated for this experiment is meaningful only between 320 nm and 650 nm. Data outside this window are noisy or dominated by artifacts and should be trimmed.

Second, near 350 nm there is a strong time-independent bleach at the pump wavelength, and from ≈ 600 nm onwards another time-independent bleach obscures the underlying signals. Signals that persist across the entire delay axis or appear before time zero, often arise from scattered pump light or photoluminescence. Because the detector integrates over a long temporal gate (typically 20 μ s), such photons are recorded independently of the probe, yielding negative ΔA across the time window. While baseline subtraction can mitigate these contributions, strong scatter may still distort the true dynamics. In practice it is preferable to suppress scatter optically (e.g. with filters or adjusted excitation conditions).

Third, the dataset shows a pronounced wavelength-dependent rise time: near the blue edge the signal onset is close to "time zero", but it shifts to ≈ 2 ps toward the red. This behavior is also visible in the kinetic traces in **Figure 2.12 B** (vertical guide lines indicate the selected wavelengths). The origin and correction of this artifact are discussed in the next section.

Finally, short-lived features are superimposed on the rising edge, most prominently around 400 nm. Those signals arise from so-called coherent artifacts (CAs) and will also be addressed below.

Other, more situational preprocessing steps include subtracting a background surface (e.g. to account for solvent effects), re-sampling the data cube or applying filters. Such procedures can introduce new artifacts and should therefore be used sparingly. A fully corrected TA spectrum is

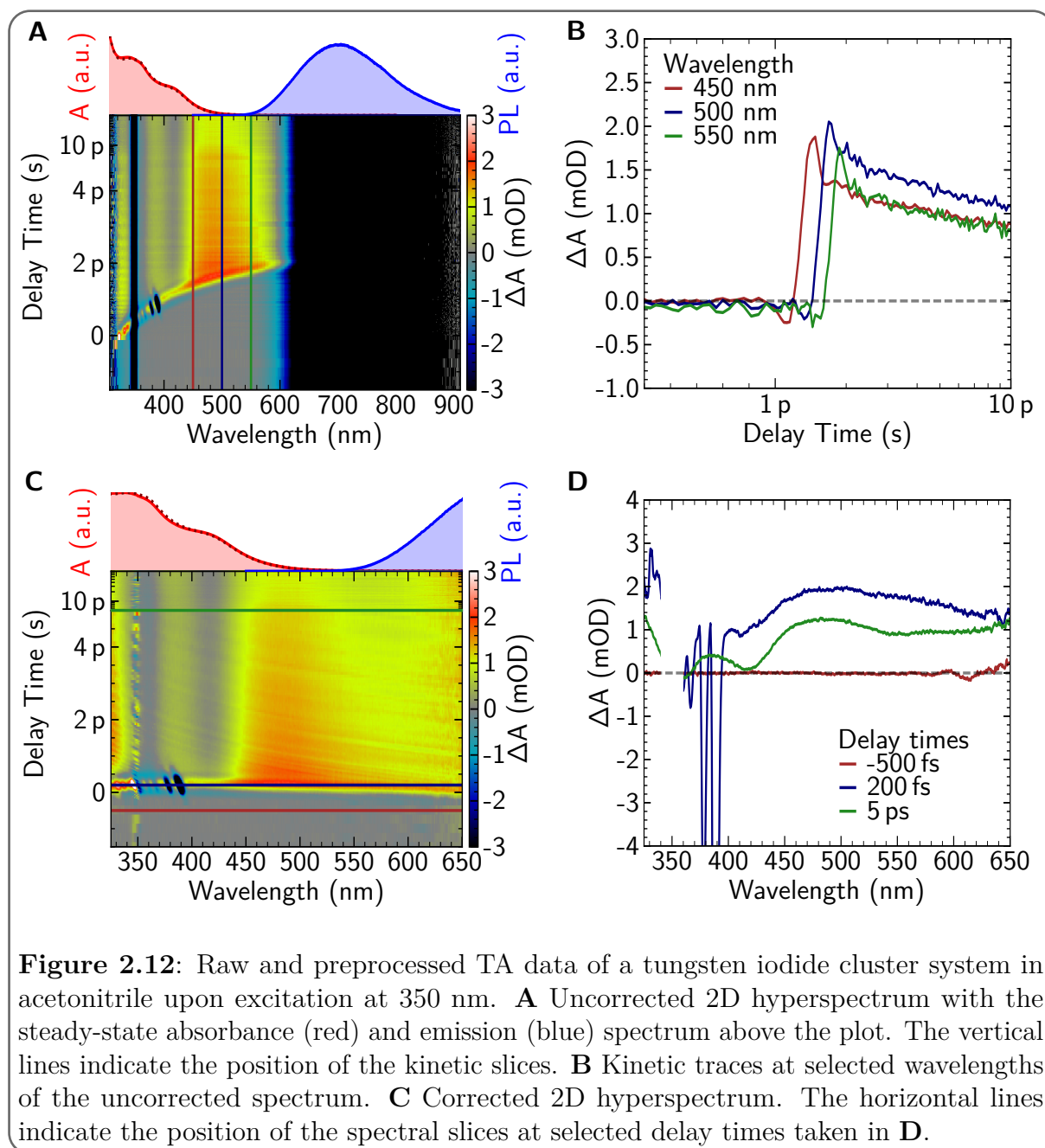


Figure 2.12: Raw and preprocessed TA data of a tungsten iodide cluster system in acetonitrile upon excitation at 350 nm. **A** Uncorrected 2D hyperspectrum with the steady-state absorbance (red) and emission (blue) spectrum above the plot. The vertical lines indicate the position of the kinetic slices. **B** Kinetic traces at selected wavelengths of the uncorrected spectrum. **C** Corrected 2D hyperspectrum. The horizontal lines indicate the position of the spectral slices at selected delay times taken in **D**.

shown in **Figure 2.12 C**, with spectral slices at selected delays in **Figure 2.12 D**. After removal of unusable spectral regions, background light and the wavelength-dependent time-zero shift, the pre-zero traces exhibit only minimal residual structure (see the red trace). Clear GSB features appear at 410 nm and 360 nm, matching the steady-state absorbance bands, together with a broad, unstructured ESA across the entire range. At 200 fs (blue trace), a short-lived CA contribution is still visible.

2.5.2 Dispersion and Artifacts

Group Velocity Dispersion The WLC generation discussed in **Section 2.4.2** inherently produces a temporal "chirp", meaning that longer "red" wavelengths are generated earlier in time than the shorter "blue" ones.^{31,33,216} Filters, lenses and the cuvette add further intrinsic group velocity dispersion to the probe, leading to a noticeable wavelength dependency of the "time-zero" delay points, as seen in **Figure 2.12**. Time

zero denotes the moment of zero delay between pump and probe within the sample volume. Because each optics slightly change the arrival time of both pulses, time zero must be recalibrated for any change in filters or in the excitation or probing wavelength.³³ Practically, time zero is often set visually to the moment before the ΔA signal starts to rise. For data modeling, the temporal mean of the pump-probe cross-correlation is frequently adopted as time zero.

To correct for the group velocity dispersion, a polynomial or a Sellmeier-based function is fitted to the time-zero values versus wavelength.^{217,218} These values can be estimated directly from the experiment or from an IRF reference and the resulting dispersion function is then used to align the time-zero positions across the spectrum typically by interpolation.^{31,34,216,219}

Coherent Artifacts On very fast time scales within a few hundred femtoseconds, signals that do not origin from population dynamics can overlay the TA response. These nonlinear χ_3 effects include, among others, cross-phase modulation, stimulated Raman amplification and two-photon absorption, driven by the intrinsic high pump power densities of fs-TA pulses and are therefore difficult to avoid.^{31,33,168,220}

Recording a solvent/cuvette reference often allows subtraction of these contributions, though small drifts can already undermine this correction.³³ Because such signals arise from pump-probe interactions, their temporal profile follows the pump-probe cross-correlation (the IRF; see Time Resolution in **Section 2.3.4**). They can therefore be modeled as a sum of derivatives of the IRF.^{34,219,221}

Modeling strategies for the IRF, CA terms and kinetic components are discussed in detail in the next section.

2.5.3 Kinetic Models

As noted above, the goal of TA spectroscopy is often to extract the relaxation pathways

that follow photoexcitation and to assign lifetimes (rate constants) and spectra to the underlying transient species. The temporal and spectral evolution of ΔA reflects the relaxation of these species. Because multiple states typically coexist, owing to competing processes or sequential transformations, the observed ΔA is usually a superposition of several contributions and must be interpreted with a kinetic model to disentangle the associated rates and spectra.^{31,33} This separability can be written in **Equation 2.29** as

$$\Delta A(t, \lambda) = \sum_i^{n_{\text{comp}}} [i](t) \varepsilon_i(\lambda), \quad (2.29)$$

where each component i contributes a time-dependent relative concentration profile $[i](t)$ and a wavelength-dependent spectrum $\varepsilon_i(\lambda)$.^{34,45,221–223} By modeling the concentration profiles with an appropriate kinetic scheme, the relative concentrations, and thus the relative amplitudes, can be estimated. The scheme can be extended to include the IRF, CAs and other processes. The following sections present the principal kinetic and artifact models used in this work.

First-Order Processes Temporal changes in component concentrations are usually described by ordinary differential equations (ODEs).⁴⁵ In the simplest case, an excited state A decays to the ground state GS with rate constant k :



The corresponding time-dependent change of concentration of A obeys

$$\frac{\partial[A]}{\partial t} = -k[A], \quad (2.31)$$

where $[A]$ is the concentration of the excited state A and k (in s^{-1}) is the rate constant. Since the rate depends on the concentration of only one species and under the assumption of a single-step process, the overall

kinetics are first-order.^{52,224} Solving **Equation 2.31** yields the familiar exponential decay (see also **Equation 2.6**):

$$[A](t) = [A_0] e^{-kt} \quad (2.32)$$

with lifetime $\tau = 1/k$.

Importantly, an observed monoexponential, first-order decay does not necessarily imply a single microscopic process. As noted in **Section 2.3.3**, the measured rate or lifetime reflects the sum of all first-order relaxation pathways from that state. For example, two competing channels,



lead to an ODE with a single effective rate constant

$$\begin{aligned} \frac{\partial[A]}{\partial t} &= -k_1[A] - k_2[A] \\ &= -k_{eff}[A] \end{aligned} \quad (2.34)$$

which is indistinguishable from **Equation 2.31**.

Parallel Scheme If the pump simultaneously populates independent initial species that each relax to the ground state on their own, a parallel kinetic model applies:



The corresponding ODEs are

$$\begin{aligned} \frac{\partial[A]}{\partial t} &= -k_1[A] \\ \frac{\partial[B]}{\partial t} &= -k_2[B] \\ \dots \end{aligned} \quad (2.36)$$

with the usual monoexponential solutions. This model is particularly important in

time-resolved emission spectroscopy and is also often used to estimate lifetimes in TA data and to extract decay-associated spectra (DAS).^{31,225,226}

In the following, I use a typical TA kinetic trace as an example and illustrate how different kinetic schemes can model the data. In **Figure 2.13**, the “experimental” trace is shown in dark blue. It exhibits a small dip around time zero (CAs), an IRF-limited rise within ≈ 200 fs, and two distinct steps, one within ≈ 1 ps and another around 10 ps, with no further decay within the measurement window. Fitting a three-component parallel model yields the red curve. The individual component contributions, weighted by their spectral amplitudes ε_i , are shown as shaded areas.

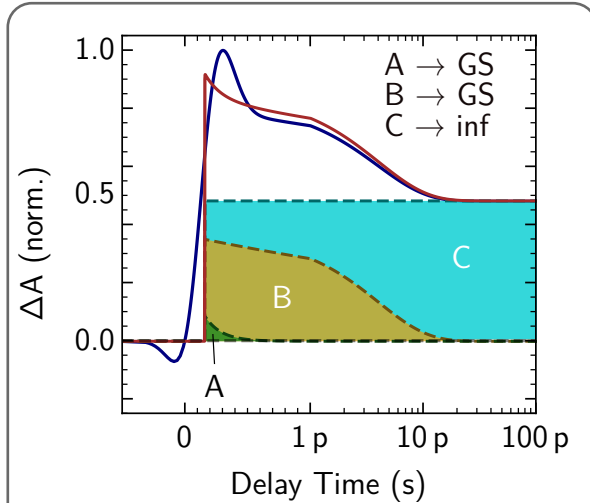
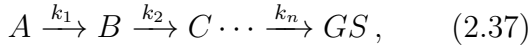


Figure 2.13: Kinetic trace of a TA experiment (dark blue) and parallel model (red). Component A (green) and B (yellow) decay to the ground state (GS) within 130 fs and 4 ps, respectively, while component C (blue) does not decay within the measurement window. Note that the x-axis changes from a linear to a logarithmic scale after 1 ps.

Sequential Scheme An unbranched, unidirectional sequential model is often a useful starting point for describing relaxation

pathways:



where each arrow indicates a monoexponential step with its own characteristic lifetime and evolution-associated spectrum (EAS).^{31,33,34} Although the corresponding ODEs are straightforward to write down (**Equation 2.38**), the closed-form solutions quickly become cumbersome (**Equation 2.39**) and are impractical beyond three components. Algorithmic strategies used in modern analysis software to handle larger schemes are discussed in **Section 2.5.6**.

$$\begin{aligned} \frac{\partial[A]}{\partial t} &= -k_1[A] \\ \frac{\partial[B]}{\partial t} &= k_1[A] - k_2[B] \end{aligned} \quad (2.38)$$

$$[B](t) = [A_0] \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (2.39)$$

In **Figure 2.14**, the sequential scheme of the example data is shown, providing a model quality comparable to the parallel scheme discussed above.

Throughout this work, the sequential scheme is frequently applied to efficient triplet emitters to extract ISC and phosphorescence lifetimes as it directly represents the transitions $S_1 \rightarrow T_1 \rightarrow S_0$.

Instrument Response Function So far, the modeled decays assume an instantaneous population of excited states upon excitation resulting in a step-like onset at time zero. In practice, the finite time resolution, set primarily by the pump and probe pulse widths, causes the signal to rise over a finite interval. This temporal blurring is described by the IRF, which is commonly approximated by a Gaussian pulse in **Equation 2.40**.^{34,45,221}

$$\text{IRF} = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right), \quad (2.40)$$

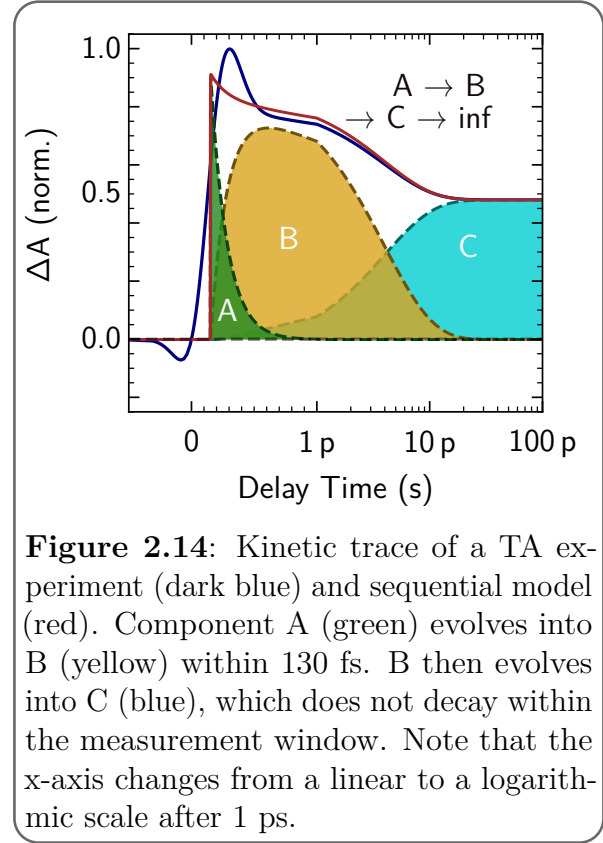


Figure 2.14: Kinetic trace of a TA experiment (dark blue) and sequential model (red). Component A (green) evolves into B (yellow) within 130 fs. B then evolves into C (blue), which does not decay within the measurement window. Note that the x-axis changes from a linear to a logarithmic scale after 1 ps.

where σ is the standard deviation and relates to the FWHM via **Equation 2.41**:

$$\sigma = \frac{\text{FWHM}}{2\sqrt{2 \ln 2}} \quad (2.41)$$

The measured signal $s(t)$ is the convolution of the IRF and the excited-state population $c(t)$.^{34,45,221,226}

$$s(t) = (\text{IRF} \otimes c)(t) \quad (2.42)$$

Equation 2.42 can be evaluated numerically or analytically. A common approximation uses the Gaussian cumulative distribution function (CDF)^{45,101}

$$s_{\text{CDF}}(t) = \frac{1}{2} \exp\left(-\frac{t-t_0}{\tau}\right) \cdot \left[1 + \text{erf}\left(\frac{t-t_0}{\sqrt{2}\sigma}\right)\right], \quad (2.43)$$

while the exact analytical result for a monoexponential convolved with a Gaussian is

the exponentially-modified Gaussian (EMG) function^{34,227}

$$s_{\text{EMG}}(t) = \frac{k}{2} \exp\left(\frac{1}{2}(k\sigma)^2 - k(t - t_0)\right) \cdot \left[1 - \operatorname{erf}\left(\frac{k\sigma^2 - (t - t_0)}{\sqrt{2}\sigma}\right)\right]. \quad (2.44)$$

Because exact numerical or EMG evaluations are more computationally demanding, **Equation 2.43** is often used, provided the lifetimes significantly exceed the IRF width. In **Chapter 3**, a fast and accurate algorithmic implementation of the EMG function for IRF modeling is introduced.

Fitting the rise (i.e. the IRF) and extracting σ or the FWHM is a standard way to determine the overall temporal resolution of the setup, from pulse generation to detection.^{33,34}

Convolving the parallel and sequential schemes above with the IRF markedly improves the agreement with the data, as shown in **Figure 2.15**: the model (red) closely follows the experimental trace (dark blue). The remaining deviation near time zero arises from CAs, which is addressed in the next section.

Coherent Artifacts As discussed in **Section 2.5.2**, CAs are difficult to avoid and simple background subtraction is often not feasible. Because their temporal profile follows the IRF, they can be modeled by constraining them to derivatives of the IRF, leaving only an amplitude (for a single kinetic trace) or a spectral shape (for a 2D hyperspectrum) as the remaining d.o.f.^{34,219,221} In the example in **Figure 2.16**, using the zeroth-order (CA_0) and first-order (CA_1) derivatives of the Gaussian IRF suffices to reproduce the data. Here, the initial fast first component A in the previous models can be fully explained as a CA within the time resolution of ≈ 200 fs. In some reports, CA modeling employs higher-order derivatives or a superposition of damped oscillations.^{168,221,228}

This example also illustrates that the

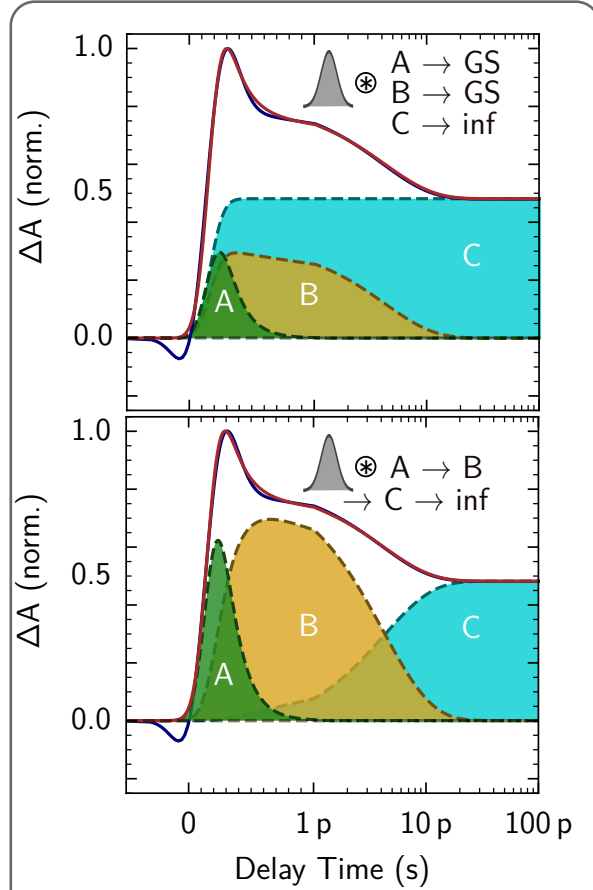


Figure 2.15: Kinetic trace of a TA experiment (dark blue) and a parallel (top) and sequential (bottom) model (red) convolved with the Gaussian IRF.

slower kinetics are not significantly affected by the CA or by IRF modeling. For this reason, many studies simply exclude data near time zero rather than explicitly modeling CAs, especially when the processes of interest are slow relative to the time resolution.

Branched, Multistep & Higher-Order Processes More complex kinetic schemes can include branching, distributed rates, back reactions and higher-order processes, in which the rate depends on more than one species, e.g.^{45,224,229,230}

$$\frac{\partial[A]}{\partial t} = -k[A][B]. \quad (2.45)$$

In general, if the kinetics can be written as a system of ODEs, the data can be fitted

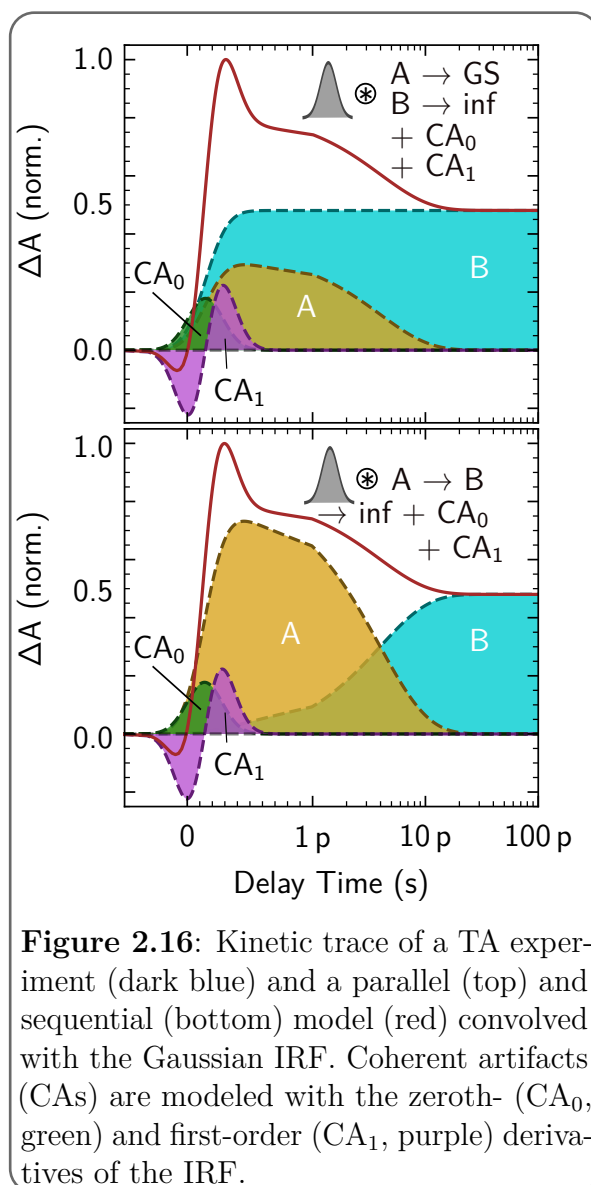


Figure 2.16: Kinetic trace of a TA experiment (dark blue) and a parallel (top) and sequential (bottom) model (red) convolved with the Gaussian IRF. Coherent artifacts (CAs) are modeled with the zeroth- (CA_0 , green) and first-order (CA_1 , purple) derivatives of the IRF.

with that model.⁴⁵ However, such models often introduce many parameters and d.o.f which can destabilize the fit and yield multiple statistically equivalent solutions. It is therefore essential to choose physically reasonable models and to constrain parameters whenever possible using a priori knowledge or complementary experiments.^{31,34} Modeling of such specific schemes is often referred to as target analysis in contrast to global analysis and the resulting spectra are called species-associated spectra (SAS) to emphasize the characteristics of the "pure" excited- or product state.^{33,34,231} If a system would be fully explainable with a sequential scheme, the resulting EAS would be similar to the

SAS.

The next section outlines strategies for robust model and parameter selection.

2.5.4 Model and Parameter Selection

Fitting the models above to TA data yields lifetimes and relative amplitudes of the components. However, multi-exponential decays are often ill-posed, especially when lifetimes have similar magnitudes. This makes parameter estimates unstable in the presence of noise, drift or artifacts and leads to many parameter sets with statistically indistinguishable fit quality.^{232–235} It is therefore important to use sensible initial values and constraints to guide the optimization toward a physically meaningful solution and to avoid local minima in this ill-conditioned problem. Here, "physically meaningful" denotes a solution that is consistent with experimental reality and physical laws, and that is also unique and stable under small perturbations of the data.²³⁶ The principal strategies employed in this work are outlined below.

Number of Components Assuming the data have been preprocessed and analyzed for CAs, the first step is to determine a reasonable number of components. Data exploration and prior knowledge of the material class already provide useful guidance.^{33,34} For example, a semilogarithmic plot of a local kinetic trace can help estimate how many components are present. If the system under study is a triplet emitter with a triplet quantum yield near unity, the expected number of components (excluding artifacts) can range from one (T_1) when the time resolution is slower than the ISC, up to four if IC processes are resolved ($S_n \rightarrow S_1 \xrightarrow{ISC} T_n \rightarrow T_1 \rightarrow S_0$).

Singular value decomposition (SVD) provides another way to estimate an upper bound for the number of components.^{31,34} The key idea is to factorize the data matrix D as

$$D = U\Sigma V^*, \quad (2.46)$$

where U and V are unitary matrices and Σ a diagonal matrix. The diagonal entries of Σ are the singular values, while the columns of U and V are the left- and right-singular vectors of D , respectively, carrying the spectral and temporal information (depending on how D is arranged). The data can then be approximated by its leading terms so that the remaining singular values are at the noise floor:

$$D \approx \sum_{i=1}^{n_{\text{comp}}} \sigma_i u_i v_i^* \quad (2.47)$$

with the singular values σ_i and the corresponding orthonormal singular vectors u_i and v_i taken from the matrix U and V , respectively. The number of leading terms needed to rebuild the data provides an estimate of the upper bound on the required components. SVD analysis can also be used to denoise the data by truncating small singular values.^{237,238}

Starting Values & Constraints After defining the number of components, it is crucial to provide good initial starting parameters, since multiexponential fits are highly sensitive to starting values.^{31,222,232} Initial guesses can sometimes be obtained visually by inspecting kinetic traces or from the temporal shapes of the singular vectors in an SVD analysis. Complementary measurements, such as time-resolved emission experiments or an accurate determination of the IRF, are also valuable, since extracted lifetimes (or the IRF width/time zero) can be fixed or tightly bounded in the fitting analysis.^{31,34}

Light, physically motivated constraints can stabilize the fit and break symmetries without being too restrictive. For example, in a sequential scheme one may constrain lifetimes to increase monotonically. Spectra associated with expected ESA features can be constrained to be non-negative

and GSB or stimulated-emission components can be constrained to follow the steady-state absorbance or emission shape, respectively.^{34,45,221,232}

Starting with a local (single-wavelength) fit can simplify the estimation of initial values, albeit at the cost of greater instability. Robustness is typically improved by extending the fit to a global analysis over the full dataset.²³⁹

2.5.5 Uncertainty Quantification

Given the strong sensitivity of the initial parameters on the final result, estimates of rate constants should be accompanied by rigorous uncertainty quantification and by comparisons across alternative models. Nevertheless, TA publications often report only goodness-of-fit metrics (if any) without addressing the robustness or uniqueness of the solution, in part because popular software lacks such tools. In this work, methods to transparently assess the stability and mutual correlations of the fitted parameter sets are developed and tested (see **Chapter 3**). Below, I summarize the key ideas behind the fitting metrics used in this work and in the literature.

Fit Adequacy To quantify how well a model reproduces the data, the first step is to inspect the residuals, defined as the difference between observed and calculated values. For a 2D data grid with N delay points ranging from $i = 1, 2 \dots N$ and L wavelength channels ranging from $j = 1, 2 \dots L$, the residuals res are defined as

$$\text{res}_{ij} = \Delta A_{ij} - \Delta A_{ij}^{\text{calc}}, \quad (2.48)$$

where ΔA_{ij} and $\Delta A_{ij}^{\text{calc}}$ are the measured and modeled values, respectively. Ideally, the residuals are small and show no discernible structure or correlation. From the residuals one can compute standard goodness-of-fit metrics, including the sum of squared residuals (SSR), the sum of squares

total (SST), the coefficient of determination (r^2), the root-mean-square error (RMSE), mean absolute error (MAE) and residual standard deviation $\hat{\sigma}$. If the measurement-noise standard deviation σ is known or externally estimated, the (reduced) χ^2 values can be derived as well.^{240,241}

$$\text{SSR} = \sum_{i=1}^N \sum_{j=1}^L \text{res}_{ij}^2 \quad (2.49)$$

$$\overline{\Delta A} = \frac{1}{NL} \sum_{i=1}^N \sum_{j=1}^L \Delta A_{ij} \quad (2.50)$$

$$\text{SST} = \sum_{i=1}^N \sum_{j=1}^L (\Delta A_{ij} - \overline{\Delta A})^2 \quad (2.51)$$

$$r^2 = 1 - \frac{\text{SSR}}{\text{SST}} \quad (2.52)$$

$$\text{RMSE} = \sqrt{\frac{\text{SSR}}{NL}} \quad (2.53)$$

$$\text{MAE} = \frac{1}{NL} \sum_{i=1}^N \sum_{j=1}^L |\text{res}_{ij}| \quad (2.54)$$

$$\chi^2 = \sum_{i=1}^N \sum_{j=1}^L \left(\frac{\text{res}_{ij}}{\sigma_{ij}} \right)^2 \quad (2.55)$$

$$\chi_{\text{red}}^2 = \frac{\chi^2}{\text{d.o.f.}} \quad (2.56)$$

$$\hat{\sigma} = \sqrt{\frac{\text{SSR}}{\text{d.o.f.}}} \quad (2.57)$$

While the RMSE penalizes large residuals more strongly, the MAE weights all residuals equally and is therefore always $\leq$ RMSE.²⁴⁰ The coefficient of determination is a measure on how well the model replicates the data with a $r^2 = 1$ being a perfect match. A reduced chi-square $\chi_{\text{red}}^2 \approx 1$ suggests an adequate model given the stated noise, $\chi_{\text{red}}^2 < 1$ can indicate overfitting or overestimated uncertainties, whereas $\chi_{\text{red}}^2 > 1$ points to underfitting or underestimated noise.²⁴² Here, d.o.f denotes the degrees of freedom (i.e. the number of data points (NL) subtracted by the number of free parameters).

Local Identifiability If the Jacobian matrix Jac of the residuals is computed alongside the parameter estimates, the co-

variance Cov of the parameter vector θ can be estimated by

$$\text{Cov}(\theta) \approx \hat{\sigma}^2 (\text{Jac}^T \text{Jac})^{-1}, \quad (2.58)$$

which yields the standard error SE of parameter l and parameter-parameter correlation $\text{Corr}(\theta_l, \theta_m)$ between parameter l and m .^{243–245}

$$\text{SE}(\theta_l) = \sqrt{\text{Cov}(\theta_{l,l})} \quad (2.59)$$

$$\text{Corr}(\theta_l, \theta_m) = \frac{\text{Cov}(\theta_{l,m})}{\text{SE}(\theta_l) \text{SE}(\theta_m)}. \quad (2.60)$$

Large standard errors or strong parameter-parameter correlations (values near ± 1) are useful indicators of weak identifiability or potential over-parameterization. However, when the residual Jacobian is ill-conditioned, **Equation 2.58** may be inaccurate or even intractable. In such cases, uncertainties should be assessed by alternative approaches (e.g. bootstrap resampling or profile-likelihood methods), as discussed below.

Global Identifiability A practical, prior-free approach is to use an F-test on the profile of each optimized parameter. Perturbing one parameter away from its optimum and re-optimizing all others will slightly increase the SSR. This stepping is repeated until a predefined F-threshold is reached so that the resulting SSR cannot be explained statistically anymore yielding confidence intervals (CIs) of the analyzed parameter. This procedure is then repeated for all the other parameters.⁴⁵

To obtain data-driven CIs and parameter correlations, bootstrap resampling can be applied. Synthetic datasets are generated either from a noise model (parametric bootstrap) or by resampling residuals (non-parametric bootstrap). Refitting each synthetic dataset yields an empirical distribution of the parameters from which CIs and correlations are derived.^{246–248}

Whereas bootstrapping perturbs the data and re-estimates parameters, Markov chain Monte Carlo (MCMC) perturbs the parameters directly and explores the posterior distribution. The result is a full joint uncertainty description including correlations and credible intervals (CrIs) for each parameter.^{249–251}

Model Comparison When comparing alternative models for the same experiment, multiple criteria should be considered. Beyond fit adequacy and parameter identifiability, the inferred lifetimes and spectra should be stable with respect to initial guesses, insensitive to modest preprocessing changes, physically plausible, and consistent with independent theoretical or spectroscopic evidence.^{34,45}

As relative measures of fit quality that penalize model complexity, the Akaike information criterion (AIC) and Bayesian information criterion (BIC) are useful:

$$\text{AIC} = n \ln \left(\frac{\chi^2}{n} \right) + 2n_{\text{params}} \quad (2.61)$$

$$\text{BIC} = n \ln \left(\frac{\chi^2}{n} \right) + n_{\text{params}} \ln(n) \quad (2.62)$$

with the number of data points n and the number of free parameters n_{params} . While both compare competing models on the same data, the BIC favors simpler models more strongly, whereas the AIC penalizes complexity more lightly. The preferred model is the one with the smaller criterion value.^{252–254}

2.5.6 Algorithmic Implementation for Global Kinetics

This section briefly outlines the computational methods commonly used to model TA data. For detailed discussions, see the following reviews^{31,34,231} and implementation papers.^{45,221–223}

Variable Projection Algorithm Starting from the superposition principle introduced in **Equation 2.29** which separates

temporal and spectral factors, a concentration model (**Section 2.5.3**) with parameters θ is defined. The experimental data can be written as

$$\Delta A(\lambda, t) = \sum_i^{n_{\text{comp}}} c_{i,\lambda}(t, \theta) \varepsilon_i(\lambda), \quad (2.63)$$

with the concentration $c_{i,\lambda}(t, \theta)$ as a function of delay time t and parameter vector θ of component i and the spectral contribution $\varepsilon(\lambda)$ as a function of wavelength λ .

Equation 2.63 naturally separates the linear parameters ε from the nonlinear kinetic parameters θ . Solving first for the linear parameters, which is an efficient step, reduces the overall problem to a purely nonlinear least-squares optimization. Concretely, at each iteration one forms the concentration matrix $C(\theta)$ and solves the inner linear least-squares problem

$$\min_{\varepsilon} \|\Delta A - C(\theta)\varepsilon\|_2 \quad (2.64)$$

to obtain the wavelength-dependent amplitudes ε . These are then fed to the outer nonlinear solver that updates θ . This two-level procedure is known as the Variable Projection algorithm.^{255–257}

Computing Concentration Profiles

To construct the concentration matrix from the ODEs, two common approaches are used. The first converts the ODEs into a rate matrix K with $c' = Kc$ and solves^{31,34}

$$c(t) = e^{Kt}c(0) \quad (2.65)$$

For a two-component model with rates k_1 and k_2 , the rate matrices for a parallel K_{par} and sequential K_{seq} are, for example,

$$K_{\text{par}} = \begin{bmatrix} -k_1 & 0 \\ 0 & -k_2 \end{bmatrix}, \quad K_{\text{seq}} = \begin{bmatrix} -k_1 & 0 \\ k_1 & -k_2 \end{bmatrix}. \quad (2.66)$$

This method is exact for linear first-order systems and can also accommodate branching and other target models. The software

Glutaran (based on the package TIMP) and its successor `pyglutaran` implement this approach.^{221–223}

A more flexible alternative, at the cost of speed and potential stability issues, is to integrate the ODEs stepwise on a chosen time grid, which allows time-dependent rates and nonlinear terms. This strategy is used by `KiMoPack`.⁴⁵

In the early stages of this work (e.g. **Chapter 4**), the free software Glutaran was used for global fitting of TA data. In later studies, the software TAPAS, developed throughout this work (see **Chapter 3**) and based on stepwise ODE integration, was employed.

Optimization Algorithms Several optimization algorithms for nonlinear least-squares problems can be used for the outer step of the Variable Projection scheme. Gradient-based methods such as Levenberg-Marquardt²⁴⁴ and BFGS^{258,259} typically converge quickly when the residuals are smooth and differentiable. Direct-search (derivative-free) methods such as Powell²⁶⁰ or Nelder-Mead^{261,262} are often more robust to irregularities but are usually slower than gradient-based methods.

All of the above are local optimizers, meaning they can converge to different minima depending on the starting values. By contrast, global search strategies, such as differential-evolution^{263,264} or Adaptive Memory Programming for Global Optimization (AMPGO),²⁶⁵ do not rely on precise initial guesses and explore the parameter space more broadly at the cost of speed.

In summary, modeling of TA data requires preprocessing and chirp compensation before selecting a specific kinetic model, the number of components and starting estimates. Since the results are often highly sensitive to priors, model and parameter quality/identifiability should be assessed in multiple layers. The next section introduces the reference system and investigated materials.

2.6 Investigated Material Systems

Throughout this work, a variety of material classes were investigated with an emphasis on triplet generation and behavior. Materials exhibiting appreciable ISC rates and phosphorescence are of significant interest for applications in oxygen sensing and singlet-oxygen production, PDT, bioimaging, LEDs and photovoltaic devices.^{113,266,267} However, the mechanisms governing triplet formation, migration and decay are often not fully understood, which hampers rational materials design.^{7,268–270} Because triplet characteristics are not only system-specific (see **Section 2.2.3**) but also highly sensitive to the local environment (see **Section 2.2.5**), TA spectroscopy is particularly well suited to disentangle these processes. Conversely, since these dynamics are typically multistep and feature-rich over broad spectral and temporal ranges, such materials also provide stringent testbeds for benchmarking TA setups and analysis software.

In the following, the three material classes studied in this work are introduced with a focus on their optical and excited-state properties.

2.6.1 Reference System: Xanthene Dyes

Xanthenes The xanthene dye family comprises synthetic organic chromophores with outstanding photophysical properties, including high fluorescence quantum yields, large extinction coefficients and good photostability. The xanthene core (**Figure 2.17 A**) is readily modified and substituted, enabling systematic tuning of the π -electron system and, consequently, the optical properties. This versatility makes xanthenes valuable for applications ranging from biological staining to PDT, as well as for use as model systems.^{271–274} They are commonly grouped into fluoresceins, rhodamines and rhodols. While most xanthenes are engi-

neered for bright fluorescence with minimal triplet formation, heavy-atom substitution markedly enhances SOC and ISC. As discussed in **Section 2.2.3**, the halogenated fluoresceins eosin Y (Br_4 -fluorescein) and erythrosin B (I_4 -fluorescein) exhibit strongly increased ISC rates (see **Table 2.2**).^{91–93}

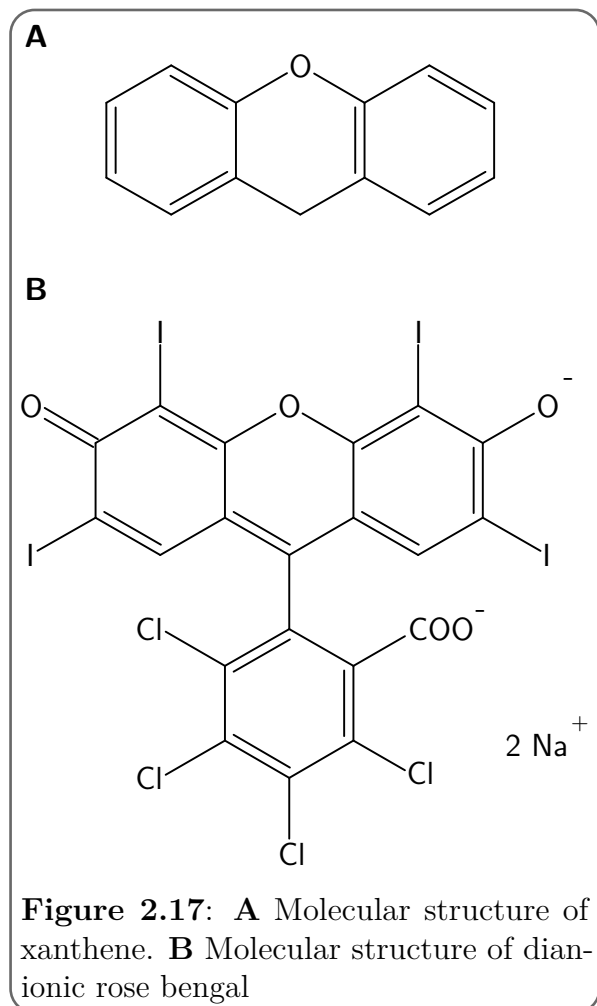


Figure 2.17: **A** Molecular structure of xanthene. **B** Molecular structure of dianionic rose bengal

Optical Properties of Rose Bengal

Rose bengal (RB), another xanthene dye derived from fluorescein, can exist in multiple anionic forms depending on solvent and pH. **Figure 2.17 B** shows the dianionic species. Owing to the heavy-atom effect, RB exhibits an ISC quantum yield of up to 0.98 in aqueous solution.^{275,276}

Although the environmental dependence and origins of these photophysical properties have been investigated for decades, they remain under active debate. In 1975, Martin and coworkers showed that intermolecular

hydrogen bonding between solvent and fluorescein not only red-shifts the absorbance and emission features, but also increases the ISC rate at the expense of the fluorescence quantum yield.²⁷⁷ Building on this, Fleming and colleagues reported for fluorescein derivatives that changing the solvent from isopropanol to ethanol, methanol and finally H_2O decreases the $S_1 - T_1$ energy gap and increases the ISC rate.²⁷⁶ Recently, we used TA spectroscopy to extract ISC rates of RB in water/methanol mixtures and found a quasi-linear tunability of ISC lifetimes from ≈ 70 ps in pure water to ≈ 500 ps in pure methanol.¹⁰¹

Beyond solvent interactions, the ISC rate also depends on dye concentration and aggregation. Joshi and Pant showed that increasing the concentration can reduce the ISC rate by up to two orders of magnitude.²⁷⁸ In 2022, Kappes and coworkers combined time-resolved photoelectron spectroscopy with TA to study anionic and dianionic RB in the gas phase, finding that the two charge states exhibit different ISC rates.²⁷⁹ They also observed rapid structural relaxation within 4 ps, giving rise to an oscillatory decay of the S_1 state.

Furthermore, RB has a rich photochemistry including singlet oxygen production, bimolecular self-quenching, electron transfer reactions and TTA, whose rate constants in degassed aqueous or acetonitrile solution have been determined using pulse radiolysis, time-resolved emission spectroscopy and nanosecond TA spectroscopy.^{122,276,280}

Rose Bengal as a Model System RB remains an active research subject because of its multiple excited-state relaxation pathways and complex self- and solvent interactions. Owing to extensive prior work, many properties such as emission quantum yields and ISC rates are available from different groups under a variety of conditions. Combined with its strong visible absorption and rich transient features over broad spectral and temporal ranges, RB is an excellent reference system for TA spectroscopy across

diverse windows. Moreover, assembling multiple TA datasets into a single global analysis, while incorporating complementary results from the literature, can provide both an instructive and more comprehensive picture of RB's complex kinetics, as well as a clear demonstration of global and target analyses (and their statistics) for broadband TA. Such integrated case studies remain relatively rare in literature.

2.6.2 Octahedral Metal Halide Clusters

Octahedral transition-metal halide clusters are a material class known for bright and long-lived red to NIR phosphorescence, high emission quantum yields, and efficient oxygen quenching with singlet-oxygen formation.¹¹³ They comprise an octahedral metal core of molybdenum(II) or tungsten(II), capped by eight tightly bound inner halides across the octahedral faces and six exchangeable outer ligands along the edges, as illustrated in **Figure 2.18**. Their general formula is $A_2[(M_6X_8)L_6]^{2-}$, where A is the counter-ion, M the metal (red), X the inner halogen (grey) and L an outer apical ligand (yellow). The apical ligands are natively halides but they can be exchanged for carboxylates, tosylates (OTss), or other donor groups.^{19,112,114}

First reports on halides of Mo(II) and W(II) date to the mid-19th century, but the first crystallographic characterization of the (M_6X_8) cluster core appeared in 1945.^{112,281} The bright red phosphorescence of the $[(Mo_6Cl_8)Cl_6]^{2-}$ cluster with a lifetime of 120 μ s in the solid state, was first analyzed in 1981 by Gray and Maverick, followed in 1982 by photophysical studies on $[(Mo_6Br_8)Br_6]^{2-}$ and $[(W_6Cl_8)Cl_6]^{2-}$ by the same group.^{112,282} Their ability to generate singlet oxygen via excited-state quenching by molecular oxygen was first described in 1990.¹⁸ Over the subsequent decades, numerous ligand-substituted Mo(II) clusters and Re(III) chalcogenide clusters were synthe-

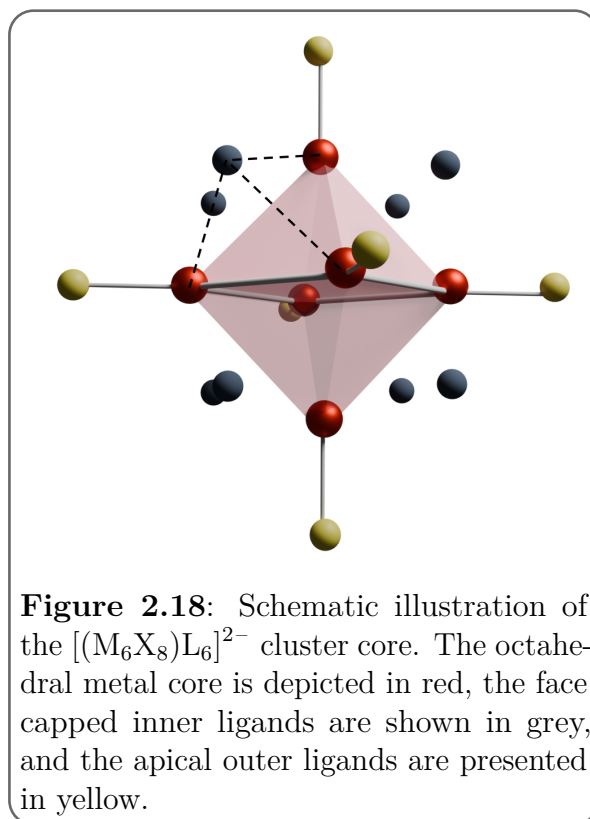


Figure 2.18: Schematic illustration of the $[(M_6X_8)L_6]^{2-}$ cluster core. The octahedral metal core is depicted in red, the face capped inner ligands are shown in grey, and the apical outer ligands are presented in yellow.

sized and characterized, some of which exhibiting emission or singlet-oxygen quantum yields near unity, underscoring their potential in oxygen sensing, PDT, bioimaging and catalysis^{15–17,114,283–294}

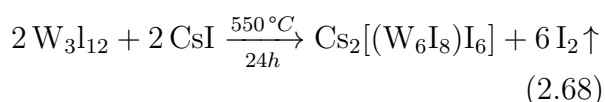
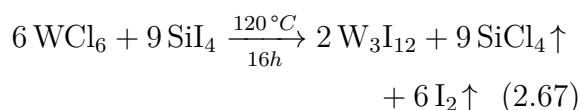
Thanks to an improved synthesis route, binary tungsten iodide clusters have been readily accessible since 2016, catalyzing various ligand-substituted tungsten iodide derivatives.^{19,114,295,296} Their synthesis and ligand-exchange strategies are outlined in the following paragraph.

Octahedral Tungsten Iodide Clusters

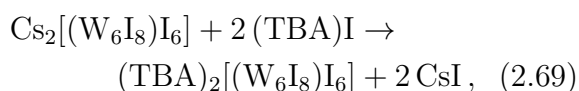
In contrast to tungsten chloride and tungsten bromide systems, where compounds with tungsten oxidation states higher than +2 are common (e.g. in WCl_4 , WCl_5 or WCl_6),^{297–299} binary tungsten iodides with oxidation states of +3 and above are not known. Nevertheless, numerous tungsten iodide clusters have been reported with trigonal (e.g. W_3I_8),³⁰⁰ tetrahedral (e.g. W_4I_{10}),³⁰¹ square pyramidal (e.g. W_5I_{11})³⁰² and octahedral (e.g. W_6I_{14})³⁰³ cores, stabilized in part by iodine's ability to form I_2 or

I_3^- bridges.^{304,305}

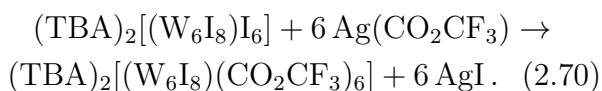
Binary tungsten iodides can be synthesized in several ways. One route reacts tungsten metal with iodine at 600 - 800 °C, but requires long reaction times and typically affords low yields.²⁹⁵ Alternative approaches use $\text{W}(\text{CO})_6$ and iodine, evolving CO and posing a significant detonation risk,^{306,307} or perform halide exchange starting from W_6Cl_{12} .³⁰⁸ In 2016, the Meyer group reported a safe and rapid synthesis of W_3I_{12} (**Equation 2.67**), which serves as a versatile precursor for numerous tungsten iodide species, including the octahedral prototype $[(\text{W}_6\text{I}_8)\text{I}_6]^{2-}$ (**Equation 2.68**).^{295,309}



The ternary tungsten iodide cluster $\text{A}_x[(\text{W}_6\text{I}_8)\text{I}_6]$ can be further modified in solution via cation exchange reactions e.g. replacing A^+ with tetra-*n*-butylammonium (TBA)⁺



or by exchanging the apical iodide via salt metathesis using the according silver salts, e.g.^{19,296}



Cationic Tungsten Iodide Clusters

Neutral or cationic cluster species, where the six apical ligands are partially or fully replaced by ligands like pyridine, dimethylformamide (DMF), dimethyl sulfoxide (DMSO) or water, have been

investigated to a lesser extent, particularly regarding their optical properties. Most reported examples are Mo-based systems like $[(\text{Mo}_6\text{I}_8)(\text{DMSO})_6](\text{NO}_3)_4$, $[(\text{Mo}_6\text{I}_8)(\text{OH}_2)_4(\text{OH})_2](\text{OTs})_2$ or $[(\text{Mo}_6\text{I}_8)(\text{OH}_2)_2(\text{OH})_4]$.^{107,310} More recently, neutral tungsten iodide $\text{W}_6\text{I}_{12}(\text{NCC}_6\text{H}_5)_2$ and the cationic species $[(\text{W}_6\text{I}_8)(\text{DMSO})_6]^{4+}$ and $[(\text{W}_6\text{I}_8)\text{I}_3(\text{CH}_3\text{CN})_3]^+$ have been reported.^{310–312}

However, their excited-state and temperature-dependent properties remain sparsely characterized. Combined with the limited number of known species, this leaves open questions about how neutral ligands influence the optical behavior of these cluster systems.

Optical Properties & Singlet Oxygen Production

Octahedral transition-metal halide clusters typically appear orange to red, absorbing in the blue to UV.²⁸² Upon photoexcitation into S_n they undergo rapid ISC to T_n followed by deactivation either via phosphorescence or quenching by molecular oxygen.^{18,99,114}

Their ability to generate singlet oxygen is commonly quantified with the Stern–Volmer method by measuring the emission lifetime at different oxygen concentrations (see **Section 2.3.5**).^{19,114} Reported quantum yields for singlet-oxygen generation often reach $\geq 70\%$, depending on the ligand set. This efficiency is rationalized by a favorable triplet-state energy, a sufficiently long triplet lifetime, and a triplet that is geometrically accessible to $^3\text{O}_2$, enabling efficient energy transfer.¹⁹ However, a detailed mechanism that predicts how specific ligands modulate oxygen sensitivity is still lacking.

Reported emission lifetimes are on the order of several tens of microseconds for W-based clusters, and up to a few hundred microseconds for Mo-based clusters under inert conditions, although values can vary across ostensibly similar compounds.²⁹⁶ As a general trend for Mo- and W-based systems, replacing apical ligands with electron-withdrawing groups of low pK_a (e.g. tri-

fluoroacetate (TFA) or OTs) increases the emission lifetime and quantum yield and blue-shifts the emission maximum.^{114,313,314} Mikhaylov and co-workers rationalize this using the energy-gap law (see **Equation 2.11**): lower pK_a ligands reduce the nonradiative rate k_{nr} by blue-shifting the triplet energy and altering vibronic coupling.^{296,315} Nonetheless, there are counterexamples where the simple correlations between emission maximum and k_{nr} , or between pK_a and k_{nr} , do not hold.¹⁰⁶ In addition, ligand substitution can modify the triplet-state ZFS, further affecting the photophysics and, in particular, the temperature dependence of the emission.²² This aspect is discussed in more detail in the following section.

Temperature-Dependent Emission

Octahedral transition-metal halide clusters not only exhibit long-lived emission, but also unusually broad emission spectra whose FWHM can exceed several hundred meV and whose lifetimes, FWHM and peak positions show a strong and often nonlinear temperature dependence.²²

Several models have been proposed to explain these photophysical properties, particularly the broad, temperature-dependent emission, yet the nature of the underlying triplet states remains incompletely understood. Non-relativistic calculations from 1988 suggest that the lowest triplet state, $^3T_{1u}$ splits via first-order SOC within the O_h symmetry into three spin sublevels ($T_{2u} + E_u$ (degenerate), T_{1u} and A_{1u}).³¹⁶ Second-order SOC then lifts the degeneracy of $T_{2u} + E_u$ yielding four distinct emissive sublevels, each with its inherent emission energy and rate. The splitting is illustrated in **Figure 2.19**. Among these, the T_{1u} state is expected to undergo an electronically allowed dipole transition, producing an intense, short-lived emission that dominates over the higher-lying A_{1u} state (grey). Experimentally, this often leads to the observation of three emissive sublevels (the so-called three-spin-sublevel model).²²

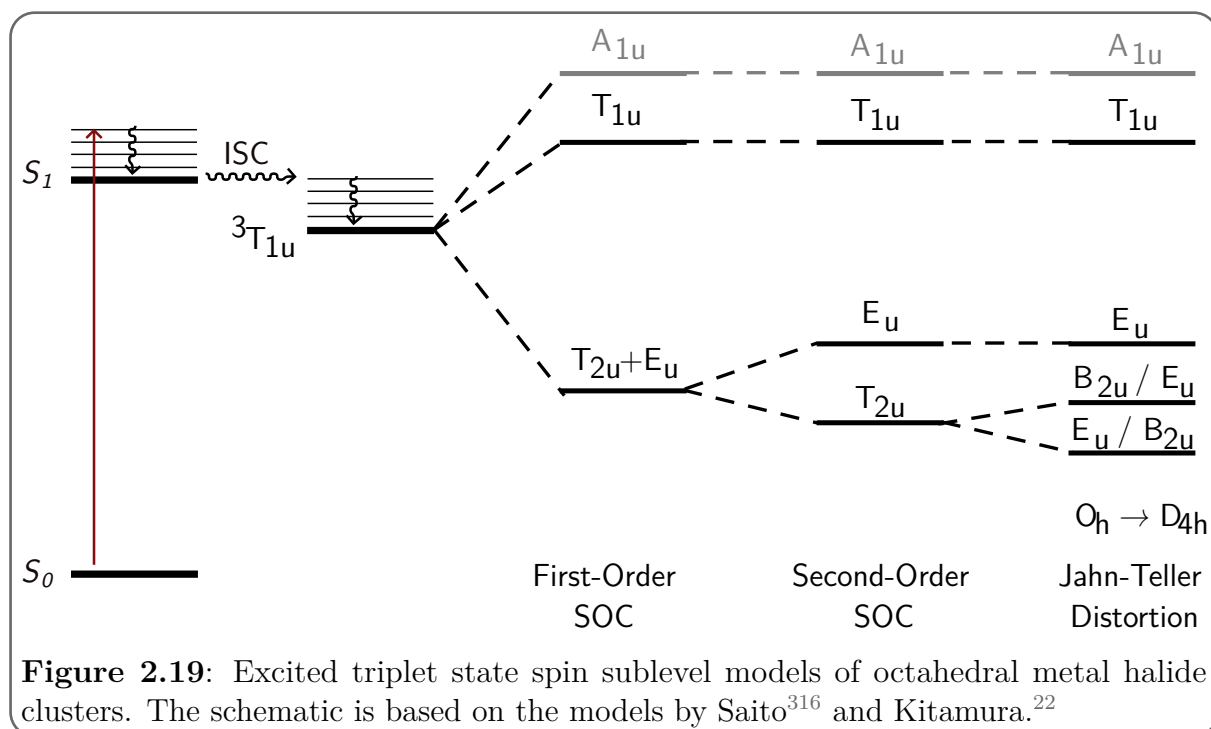
Because the population of each sublevel is

temperature-dependent and can be described by a Boltzmann distribution, this framework explains both the broad, temperature-dependent emission and enables extraction of the energy gaps between sublevels via **Equation 2.23** from **Section 2.3.5**. This approach has been applied to complexes of Mo(II),³¹⁷ Pt(II),³¹⁸ Ir(II)³¹⁹ and Ru(II).³²⁰

Relativistic density functional theory (DFT) calculations, however, predict a noticeable distortion of the excited triplet state which would lead to a symmetry lowering and loss of degeneracy from the O_h symmetry, lowering the symmetry and removing degeneracies assumed in the three-spin-sublevel model.^{20,21,321,322} Building on this, Kitamura and coworkers proposed a four-spin-sublevel model in which a Jahn-Teller-type distortion lowers the symmetry from O_h to D_{4h} resulting in a splitting of T_{2u} into B_{2u} and E_u (see **Figure 2.19**).²² With four emissive components, they successfully modeled a range of $[(Mo_6X_8)L_6]^{2-}$ clusters over 4 to 300 K, which was not achievable with only three states. They further identified correlations between the strength of ZFS (i.e. the energy separations among sublevels) and the nature of both, the inner and outer ligand.^{106,323,324}

However, a fourth emissive component was not observed for $[(Re_6S_8)Cl_6]^{4-}$ or $[(W_6Cl_8)Cl_6]^{2-}$, even though DFT calculations also predict symmetry lowering for these systems.²² In fact, the calculated distortions of the excited triplet states of Mo(II), W(II) and Re(III) clusters can reduce the symmetry to D_{2h} , C_{2v} or even C_s , implying a complete lifting of degeneracy across the nine sublevels.^{20,21,321,322} This raises doubts about whether a simple group-theoretical picture can adequately describe the triplet configuration in these clusters.

Costuas and coworkers combined time-resolved emission with DFT for $[(Mo_6Br_8)Br_6]^{2-}$ and showed that the photophysics can depend on the excitation route and wavelength.²⁰ They attributed this to at least two emissive triplet states arising from distinct geometric relaxations,



underlining that SOC and vibronic coupling alone are insufficient to explain the behavior of Mo-based clusters.

Most experimental and theoretical studies of temperature-dependent emission and excited-state structure have focused on Mo-based systems. Extending these investigations to W-based clusters and testing the competing models under debate would help clarify the complex nature of the emissive triplet states and, in turn, support applications of W-based clusters in medicine, sensing and imaging.

Excited-State Dynamics Although the emissive properties of transition-metal halide clusters have been studied extensively, little is known about their excited singlet states or ISC rates. Time-resolved emission measurements have suggested singlet-state emission in $(\text{TBA})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$ occurring between 600 and 1200 ps.³²⁵ By contrast, fs-TA studies on Mo-based clusters in solution report ISC within ≈ 2 ps, followed by a hot triplet cooling on a 5 ps timescale.⁹⁹

While ns-TA is occasionally used in conjunction with time-resolved emission to track the emissive T_1 state in Mo-based

systems,^{16,291} there appear to be no corresponding TA studies on W-based clusters that probe ISC rates and the nature of the excited singlet and triplet states. As a result, fundamental questions about ISC kinetics and the electronic character of the excited states in W-based clusters remain open.

2.6.3 Acenes

Acenes are polycyclic aromatic hydrocarbons composed of linearly fused benzene rings (**Figure 2.20**).^{326,327} They possess a single aromatic π -sextett, delocalized over the whole π -system, making them ideal model systems for quantifying aromaticity and useful building blocks for graphene and carbon nanotubes.^{328–330}

Their characteristic π -electron framework leads to a decrease in the $S_0 \rightarrow S_1$ and $S_1 \rightarrow T_1$ transition energies with increasing ring number, shifting absorption and emission to lower energies.^{326,331} Consequently, acenes evolve from insulators to semiconductors, with an extrapolated optical band gap of 1.23 eV for an infinitely long "polyacene".^{27,332} The names of the smaller acenes are listed in **Table 2.6**.

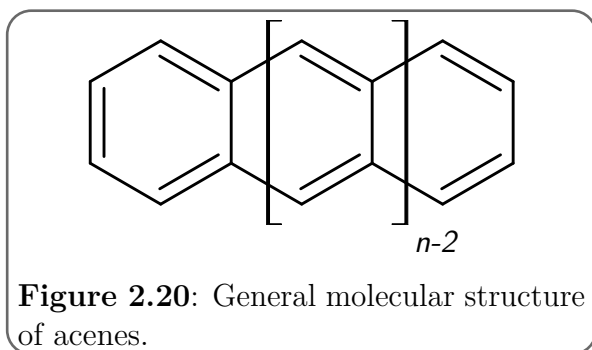


Table 2.6: Names of the first smaller acenes and their number of rings.

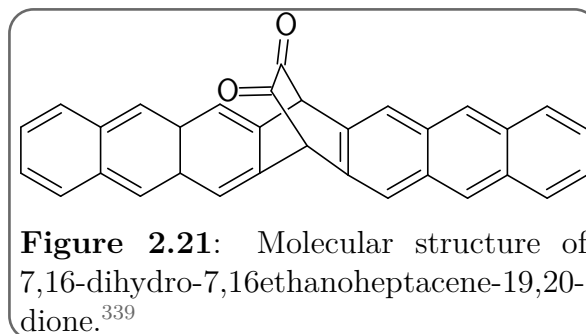
Name	Number of Rings
Anthracene	3
Tetracene	4
Pentacene	5
Hexacene	6
Heptacene	7
Octacene	8

Because of their bandwidth and high charge-carrier mobilities, tetracene and higher acenes are promising candidates for organic electronic applications such as organic LEDs and organic field-effect transistors.^{25,333,334}

However, the decreasing gap also increases the diradicaloid character and chemical reactivity (photooxidation, dimerization) of the higher members.^{27,331,335,336} For example, hexacene already shows decomposition in solution.²⁶ As a result, extensive experimental studies on higher acenes such as heptacene remain limited by low stability and synthetic challenges.³³⁰ A brief overview of synthesis strategies and analytical approaches for these higher acenes is provided in the following section.

Synthesis & Stability Due to their pronounced tendencies toward dimerization, photooxidation and poor solubility, higher acenes are often synthesized with stabilizing silyl-ethynyl substituents (e.g. triisopropylsilyl (TIPS)) to enable experimental

probing of their optoelectronic properties in solution.^{335–338} Heptacene is the highest unsubstituted acene that has been synthesized and characterized in solution from various precursors. A synthetic route published in 2006 employs photodecarbonylation of a diketone precursor (**Figure 2.21**) in a polymer matrix, yielding heptacene that remains stable for only a few hours.^{339,340} In solution, however, this approach does not produce heptacene. Using a covalent dimer as a precursor, heptacene could be generated and studied in solution and in the solid state by nuclear magnetic resonance (NMR) and absorption spectroscopy.³⁴¹ Nevertheless, for extensive optical measurements, including TA spectroscopy, the intrinsic stability and solubility of pristine heptacene remain insufficient.



Over the past decade, several kinetically stabilized heptacene derivatives have been synthesized and characterized. However, most studies focus on the structure or basic optical properties.^{342–345} Comprehensive steady-state and excited-state analyses in solution, as performed for anthracene and pentacene derivatives, are still scarce.^{118,120} Such studies are essential not only for understanding heptacene's intrinsic optoelectronic behavior, but also for placing it within the broader acene series and benchmarking computational models and predictions. Notably, theory suggests that heptacene marks a turning point at which the electronic configuration and thus the optical properties change.³⁴⁶ This point will be developed in more detail below.

Photophysical Properties Absorption spectra of acenes feature three principal bands, each with pronounced vibrational fine structure. The p-band according to Clar³⁴⁷ or the 1L_a band according to Platt³⁴⁸ correspond to the lowest-energy $\pi \rightarrow \pi^*$ or $S_1 \rightarrow S_0$ transition. Its vibrational progression typically has a dominant 0-0 transition from the lowest vibrational level of S_0 to that of S_1 .³⁴¹ The α or 1L_b band ($S_0 \rightarrow S_2$) is usually weak in acenes, whereas the β or 1B_b band exhibits strong transitions (e.g. $S_0 \rightarrow S_6$ for anthracene) in the UV.³⁴⁹

Computational and theoretical descriptions of the electrical and optical properties of acenes are challenging and often controversial, because the large system size typically demands semi-empirical methods that are less accurate but computationally affordable.^{346,350} DFT, while widely used to describe electronic structures, fails to reproduce the correct 1A_g ground state.³⁵¹ From anthracene to hexacene, the $^1A_g \rightarrow ^1B_{2u}$ transition is generally taken as the lowest excited-singlet to ground-state transition.³³⁰ For higher acenes beginning with heptacene, calculations predict that the lowest excited state switches to 1A_g symmetry, rendering it Laporte-forbidden.^{341,346}

Owing to the stability constraints and associated synthetic challenges, experimental confirmation of the nature of the lowest excited state in heptacene and related compounds is still lacking.

Triplet State Population As discussed in **Section 2.2.5**, SF is a spin-allowed process, in which one high-energy S_1 excited state (exciton) splits into two triplet excitons ($T_1 + T_1$).¹⁴ Interest in SF has grown rapidly because, in principle, a SF sensitizer could raise the power-conversion efficiency of an ideal single-junction photovoltaic cell from ≈ 33 to ≈ 44 % over the solar spectrum beyond the Shockley-Queisser limit).^{12,13} Acenes are among the few molecular classes known to undergo SF, owing to their tendency to aggregate and their favorable energy alignment ($E(S_1) \approx 2E(T_1)$).¹⁴ Anthracene and pen-

tacene have been studied extensively in this context, and pentacene-based photovoltaics with external quantum efficiencies exceeding 100 % have already been reported.^{23,24} Nevertheless, the nature of the multiexciton state and the detailed mechanism of triplet generation remain unclear, due to the complex interplay of concentration-dependent SF, ISC, TTA, and the intrinsic delicacy of the acene framework.^{28,29}

As an example, in highly concentrated TIPS-pentacene solutions, Walker and co-workers argued that excimer formation occurs as part of the SF process without aggregate formation.¹²⁰ In contrast, Grieco and colleagues used TA spectroscopy on the same system and concluded that aggregation does occur in solution, mediated by the TIPS groups, and that it is important for SF efficiency.³⁵² More recently, however, a separate study reported no evidence of excimer formation in concentrated TIPS-pentacene and argued that, although aggregation is present, SF proceeds primarily via diffusive encounters and does not rely on aggregation.¹⁷²

For higher acenes such as heptacene and its derivatives, SF and triplet-state population have not yet been explored in detail experimentally. Photodecarbonylation of the α -diketone precursor of heptacene enabled detection of a triplet state by TA spectroscopy, with a lifetime of 11 μ s, however, the relaxation pathway from the excited singlet to the triplet state could not be resolved.³³⁹ Because SF becomes more exothermic with increasing ring size, and because heptacene exhibits enhanced biradical character, the efficiency of SF may be reduced, making ISC a more competitive relaxation channel.^{353–355}

This section introduced the investigated materials beginning with rose bengal as a literature-known reference system for benchmarking the developed processing, modeling and uncertainty analysis of TA data. Further, the octahedral metal halide cluster family and the acene family were outlined highlighting recent findings and open questions in their photophysics. The following chapters present the results of the main studies.

TAPAS: Transient Absorption Processing and Analysis Software

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3.1 Abstract

We present TAPAS (Transient Absorption Processing and Analysis Software), an open-source, Python-based graphical platform that covers the entire transient absorption (TA) workflow, from raw data import and preprocessing to visualization, global and target fitting, and statistical evaluation. Users operate TAPAS through an intuitive, seven-tab GUI, yet all underlying modules remain accessible for inspection and extension, merging GUI convenience with script-level flexibility. The fitting engine employs just-in-time compilation via an open-source machine learning compiler ecosystem, delivering 2-20-fold speed gains over established packages. Automatic differentiation and residual-based effective-sample-size calculations yield reliable confidence intervals and correlation matrices, while an integrated sampling routine provides full Bayesian posterior exploration - diagnostics which are rarely available in other TA tools. All raw, processed, and fitted data are written to standardized HDF5 containers and automatically annotated with rich metadata, ensuring complete provenance. An extended case study on rose bengal shows how TAPAS first reveals hidden lifetime correlations, then employs broadband global and target analysis to merge TA traces with complementary steady-state and literature data, yielding a single, self-consistent kinetic model. By uniting advanced uncertainty quantification and transparent data management within a user-friendly interface, TAPAS closes the gap between accessibility and rigorous statistical treatment in transient absorption spectroscopy.

3.2 Introduction

Transient absorption spectroscopy (TAS) is a powerful technique for probing the excited-state dynamics of photoactive

molecules, nanocrystals and solids. Upon excitation with a pulsed laser, the temporal and spectral evolution of the excited states can be followed by monitoring changes in absorption. Since this technique is not limited by the emission of photons, dark states and non-emissive relaxation paths can be traced as well, resulting in a multivariant time-resolved spectral map with often complex kinetic and spectral traces. In practice, processes such as internal conversion,³⁵⁸⁻³⁶⁰ band-gap renormalization,^{162,361,362} refractive index changes,¹⁶² conformational changes,³⁶³⁻³⁶⁵ fluorescence,³⁶⁶ intersystem crossing (ISC),^{101,279,366,367} phosphorescence^{291,368} and charge separation^{122,369,370} are superimposed. In addition to these material-specific contributions, instrument and solvent effects can complicate the dynamics in the sub-picosecond regime even further. These effects encompass group-velocity dispersion ("chirp"), instrument-response broadening ("IRF"), scattered light, solvent reorganization and pump-probe photon interactions such as two-photon absorption, cross-phase modulation and stimulated Raman amplification, collectively termed "coherent artifacts" (CAs).^{31,216,220,370}

To fully disentangle these contributions, prior theoretical knowledge of the specific material, multiple TA experiments with varying spectral windows, delay ranges, solvents, or complementary techniques (steady-state absorption/emission, time-resolved fluorescence) are typically combined. The two-dimensional TA raw data is then preprocessed including background subtraction, chirp compensation, filtering, trimming and resampling. After the general inspection and visualization of the preprocessed data, exploratory analyses like singular value decomposition (SVD)^{237,238} guide the selection of well-founded estimates of the number of components and expected spectral shapes and rates, which is critical for the success of the subsequent model fit. Initial parameters are attempted by an educated guess,

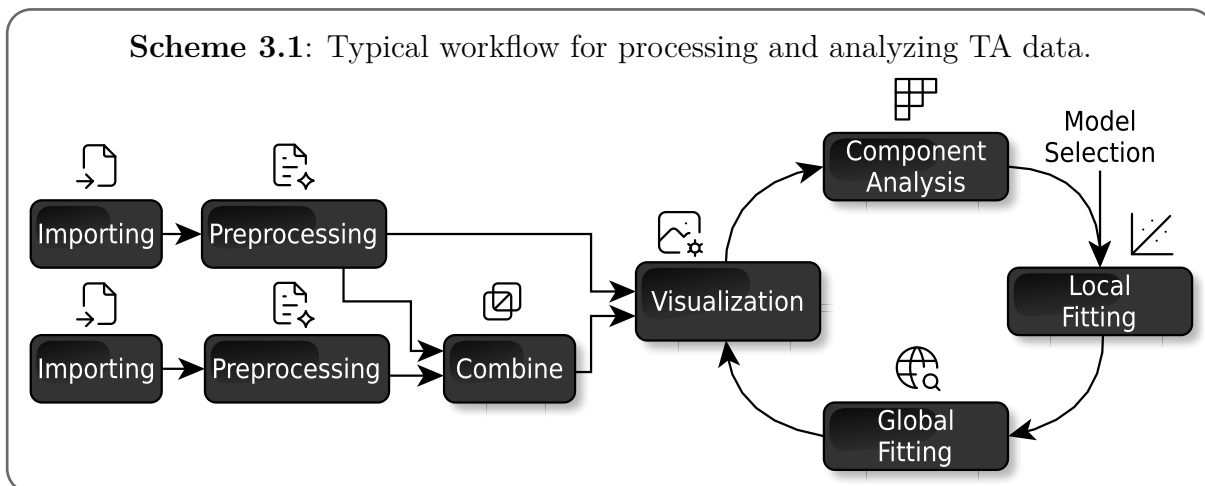
which must be verified by modeling the data locally at a given wavelength. To optimize these parameters with stable and physically relevant results, global fitting is applied, using a parallel scheme of independently decaying exponentials or an unbranched unidirectional sequential model, followed by a fitting algorithm. The outcome is a set of spectra and population dynamics for each kinetic component, obtained with confidence intervals (CIs) derived via error analysis. Further, more complex kinetic models can be evaluated through target fits, revealing the underlying species.^{34,369} Ultimately, the fitting results and accompanying statistics must be presented and visualized comprehensively. The general workflow is summarized in **Scheme 3.1**.

An ideal TAS software should be open-source and transparent, GUI-driven and easy to use, modular for custom extensions, equipped with robust fitting and uncertainty analysis, and able to automate metadata to guarantee reproducibility. Examples of exemplary TAS software projects aiming to fulfill the aforementioned properties are the script-based packages KiMoPack⁴⁵ and pyglotaran²²¹ both offering a large functionality and a modular, customizable design. However, they both require users to install and configure a Python environment and to have basic coding skills. Additionally, their batch-oriented workflows offer limited real-time responsiveness: dynamic data ex-

ploration and immediate visual feedback are generally limited, which can impede an intuitive, interactive analysis experience. Few GUI tools truly lower the barrier to entry for TA analysis. The legacy version of Glotaran (2015)^{222,223} which is from the same lab as pyglotaran, for example, delivers responsive performance but its installation process and fitting workflow is perceived cumbersome by some users.³⁷¹ Furthermore, it offers limited flexibility and customizability in visualization, model construction, fitting routines, and related tasks.⁴⁵

In this paper, we introduce the TAS software TAPAS as a fully integrated, open-source GUI built on Python 3.11 and PyQt6³⁷² that unites an intuitive workflow with state-of-the-art fitting algorithms and rich error analysis, including Bayesian inference via Markov-chain Monte-Carlo (MCMC)-based posterior parameter exploration.^{250,251,373} By leveraging accelerated linear algebra and just-in-time compilation,³⁷⁴ TAPAS completes global fits 2 to 20 times faster than established software while returning realistic CIs and parameter correlations within seconds (see **Appendix A.6**). Distributed as a portable executable for Windows, macOS, and Linux, it requires no prior environment setup, yet all source code and configuration files remain fully exposed for inspection and modification. In practice, a user can open the accompanying Python module, adjust or ex-

Scheme 3.1: Typical workflow for processing and analyzing TA data.



tend a kinetic-model function, and see those changes reflected immediately within the interface. Raw data, processed arrays, and fit results are consolidated into efficient and open Hierarchical Data Format 5 (HDF5)³⁷⁵ containers and automatically annotated with rich metadata, greatly simplifying reproducibility and FAIR data management.⁴⁶ In this way, TAPAS bridges the gap between a novice-friendly GUI and the extensibility of script-based frameworks, delivering both accessibility and deep customizability.

Both, the source code and prebuilt binaries, are available on GitHub (<https://github.com/pytapas/tapas>), and comprehensive user documentation is provided (<https://tapas-docs.readthedocs.io/en/latest/>). In addition to the portable executables, TAPAS can be installed directly from PyPI (<https://pypi.org/project/pytapas>) for users who prefer a standard Python environment.

The paper is organized as follows. We begin with an overview of TAPAS, outlining the graphical interface, the underlying modular architecture, and their interplay. The next part summarizes the theoretical background and numerical algorithms that underpin the fitting and error-analysis routines. The complete workflow is showcased by analyzing the transient absorption spectrum of the organic dye rose bengal, thereby highlighting practical aspects of data import, preprocessing, global fitting, and interpretation. We conclude with positioning TAPAS within the landscape of existing TAS software, comparing functionality, extensibility, and performance.

3.3 Design and Implementation of TAPAS

3.3.1 User Interface

A persistent menu bar and toolbar at the top of the interface provide access to project-wide operations such as linking to licenses, documentation, and source code, loading and saving HDF5 projects, and configuring GUI or plot settings. A status bar at the bottom displays real-time progress updates and error messages when inputs or algorithms fail. To maximize flexibility and ease of use, TAPAS accepts a variety of input formats (e.g., “450,4 nm,” “450.4 nm,” “4.504e-9 m,” or “0.4505 μm ”), while explanatory tooltips and sensible default values further streamline user interaction. TAPAS uses the same seven sequential tabs outlined in **Scheme 3.1** and their key tasks and principal outputs are summarized in **Table 3.1**. Detailed algorithmic notes and extended descriptions for every tab are collected in the **Appendix A.1**.

While the preceding section described the graphical interface and its workflow, advanced users may wish to extend TAPAS by inserting new kinetic schemes, altering optimization routines, or interfacing with external libraries. Doing so requires familiarity with the internal module layout and the principles that govern the code base. The next section therefore examines the backend architecture, outlining layers, package hierarchy, and extension points that enable such customization.

3.3.2 Background Architecture

TAPAS adopts a lightweight, Model-View-Controller (MVC)-inspired layout that keeps user-interface code, workflow logic, and numerical routines in separate namespaces while avoiding the overhead of a strict, multilayer framework. This loose separation lets users locate and modify the relevant code

Table 3.1: Overview of the TAPAS workflow tabs.

Tab	Task	Key Output
Import	• Parse raw 2-D TA, solvent and steady-state files, convert units, average • Attach optional metadata	• Standardized HDF5 project
Preprocessing	• Interactive inspection • Trimming, resampling, filtering, chirp / background / solvent / time-zero corrections	• New dataset object linked to the raw file • Metadata of every operation
Combine Projects	• Fuse datasets covering different spectral / temporal regions	• Merged project with unified ΔA grid and links to all parent datasets.
Visualization	• Generate 2-D contour maps, kinetic / spectral slices, and fit-result plots • Customizable via interactive controls & <code>matplotlib.rcParams</code>³⁷⁶	• Vector (PDF, SVG) & raster (PNG, JPG, TIFF) files • CSV of plotted data
Component Analysis	• Apply SVD	• Eigenvalues & Eigenvectors of leading components
Local Fit / Global Fit	• Single-trace fit (chosen wavelength or averaged window) • Optimize full ΔA matrix with shared kinetics • Select components, parameters, model, algorithm, coherent artifact model, ground-state recovery model, wavelength-dependent weighting • Bayesian MCMC posterior sampling	• Parameters estimates, metrics, posterior space • Fitted curve, EAS/DAS/SAS, residuals, concentration, reconstructed surface • Dataset-linked metadata

quickly, while preserving a clear mapping between the conceptual architecture and the folder structure. The basic structure is illustrated in **Scheme 3.2** and **Table 3.2**.

The next part examines the mathematical models and numerical algorithms that drive data convolution, optimization, and error estimation.

3.4 Algorithms and Theoretical Background

3.4.1 Global Analysis Algorithm

Following the superposition principle, the experimental data (ΔA) as a function of delay time t and wavelength λ can be expressed by a linear superposition of the contribution of n components given by

$$\Delta A(\lambda, t) = \sum_i^n c_i(t) \varepsilon_i(\lambda) \quad (3.1)$$

with c_i and ε_i denote the unknown concentration and spectrum of component i .^{34,221,223} After defining a concentration model with parameters θ , **Equation 3.1** can be expressed as

$$\Delta A(\lambda, t) = \sum_i^n c_{i,\lambda}(t, \theta) \varepsilon_i(\lambda). \quad (3.2)$$

TAPAS uses the Variable Projection algorithm^{255,256} by implicitly solving for the conditionally linear parameters $\varepsilon_i(\lambda)$ in **Equation 3.2** which is a standard procedure in global analysis.^{31,34,45,221,223} At every evaluation of the nonlinear parameter vector θ , TAPAS constructs the kinetics-design matrix $C(\theta)$ depending on the chosen model and solves the linear least-squares subproblem

$$\min_{\varepsilon} \|\Delta A - C(\theta)\varepsilon\|_2 \quad (3.3)$$

for the wavelength-dependent amplitudes ε . This is fully implemented with the python library **JAX**,³⁷⁴ whose computation graph is passed to the open-source machine learning ecosystem Open Accelerated Linear Algebra (**OpenXLA**)³⁷⁷ for just-in-time (JIT) compilation which translates the graph into machine code moments before execution. During this JIT step, XLA fuses the convolution, design-matrix assembly, and linear least-squares fits into a single, highly optimized kernel, removing Python overhead, preserving automatic differentiation and delivering a substantial speed-up. The resulting residuals vector $r(\theta) = \Delta A - C(\theta)\varepsilon'(\theta)$ feeds the outer optimization process performed by the python package **LMFIT**,³⁷⁸ yielding a clean separation between the fast, compiled inner solve and the flexible, high-level parameter search.

TAPAS natively implements several optimization algorithms, each with distinct performance characteristics which are summarized in **Table 3.3**.

The next section describes the kinetic schemes built into TAPAS and explains how each one is translated into its corresponding concentration matrix $C(\theta)$.

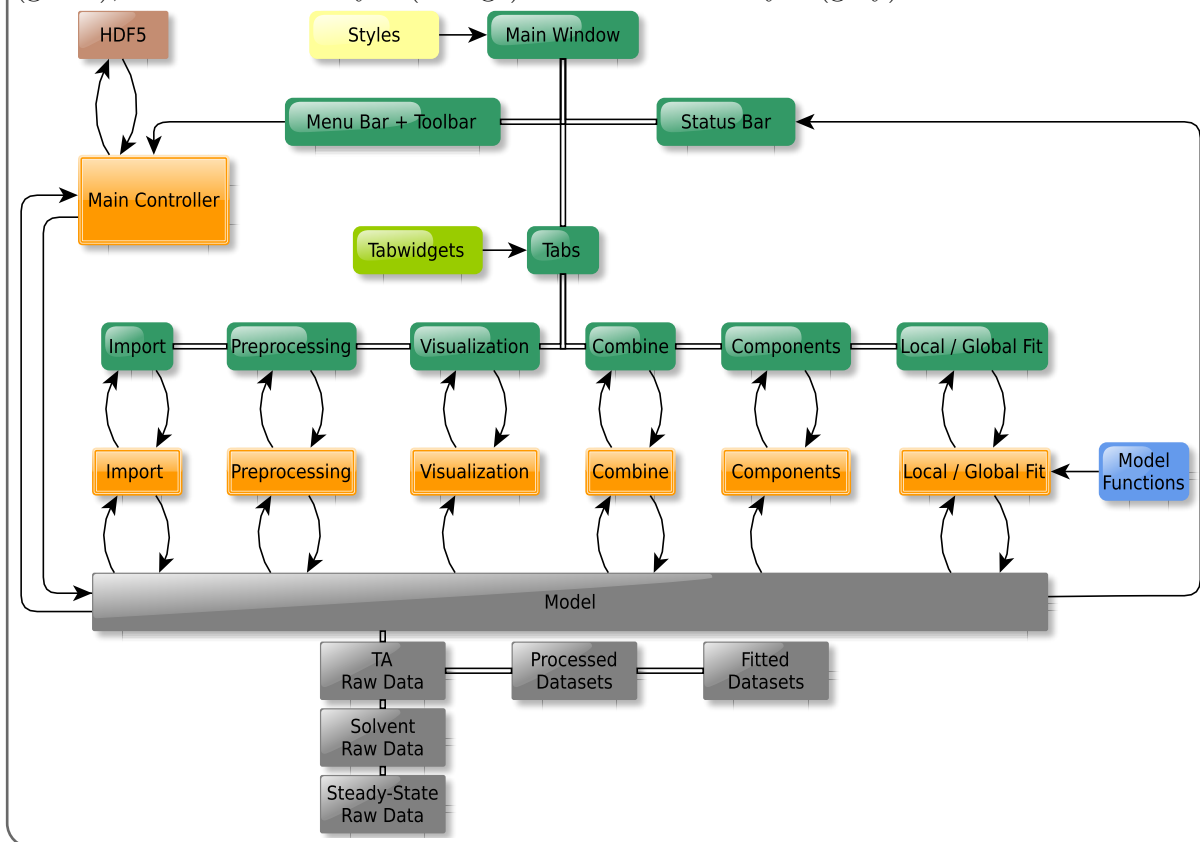
3.4.2 Kinetic Models

TAPAS offers two complementary routes for assembling the concentration (design) matrix $C(\theta)$. In the parallel scheme of independently decaying exponentials, each excited pool decays in isolation with a characteristic lifetime τ . The experimentally observed population profile is the Exponentially-Modified Gaussian (EMG)

$$c_i(t, \tau, \sigma) = \frac{1}{2\tau} \exp\left(\frac{\sigma^2}{2\tau^2} - \frac{t}{\tau}\right) \cdot \left[1 - \operatorname{erf}\left(\frac{\sigma^2 - \tau t}{\sqrt{2}\sigma\tau}\right)\right], \quad (3.4)$$

which is the analytical convolution of an exponential decay with the Gaussian IRF of

Scheme 3.2: An overview of TAPAS MVC-Architecture consisting of a View layer (green), the Controller layer (orange) and the Model layer (grey).



standard deviation σ .²²⁷ The fit parameter reported in TAPAS as "IRF" is the FWHM of the Gaussian IRF which is related to σ by the $\sigma = \text{IRF}/2\sqrt{2\ln 2}$.³⁴ An optional non-decaying component is represented by the Gaussian Cumulative Distribution Function (CDF), which accumulates the fraction that never decays within the time window. The CDF form is a common and fast approximation to the IRF convolution and is adequate when lifetimes are much longer than the IRF width but becomes biased at lifetimes near the IRF. The analytic EMG avoids this bias at comparable runtime in our JIT implementation. More information about the difference in using the CDF or EMG for analytical convolving the IRF with the experimental decay is available in **Appendix A.1**.

If an unbranched unidirectional sequential model or a custom kinetic scheme is used, the dynamics are described by a set of coupled ordinary differential equations

(ODEs) $dc = f(c, \text{PDF}(t))$ with the Gaussian Probability Density function (PDF) injecting the population according to the laser pulse. The equations are propagated over successive experimental time intervals with a fourth-order Runge–Kutta (RK4) scheme.³⁷⁹ This modular architecture allows additional kinetic schemes to be incorporated straightforwardly: once the relevant differential rate equations are specified, the framework integrates them and inserts the resulting concentration profiles directly into the global analysis (**Appendix A.5.4**).

Further, CA signals that appear while pump and probe pulse overlap can be represented by one or two additional components whose temporal shapes are the Gaussian IRF and its time-derivative.²²¹ Because these columns are concatenated ahead of the kinetic basis, the least-squares step determines their wavelength-dependent amplitudes in the same linear least-squares fit,

Table 3.2: Modules and responsibilities in the TAPAS framework.

Layer / Module	Responsibility	Structure
Controller (orange)	Orchestrates the workflow: imports data, launches pre-processing tasks, calls fitting engines, updates application state	One controller per major tab & main controller for project-wide tasks
View (green)	Renders the tab-based GUI, handles all user interaction and basic input validation	One view module per major tab and main window. Child widgets are defined in Tabwidget modules (light green)
Model (grey)	Maintains the hierarchical state of the application and emits change-signals to the GUI	One model class per datatype
Fitting Models (blue)	Implements the kinetic models and optimization routines used by the Local- and Global Fit tabs	Collection of kinetic-, IRF- and CA functions in a separate module, JAX-based
GUI / Plot Config (yellow)	Supplies style sheets, default parameters, plot styles, labels and messages that customize the View	External configuration files loaded at start-up

Table 3.3: Optimization algorithms and their key characteristics used by TAPAS.

Algorithm	Method Class	Characteristics	Typical Speed
Nelder-Mead ²⁶¹	Direct-search, derivative-free	Robust on noisy surfaces, no gradients required	moderate
Levenberg-Marquardt ²⁴⁴	Gradient-based least-squares	may diverge on ill-conditioned problems	fast
Differential Evolution ^{263,264}	Population-based global optimizer	Explores parameter space broadly, less prone to local minima	slow

without altering the rate equation block. bleach.

Likewise, an explicit ground-state (GS) component defined as the sum of all excited-state populations can be introduced to describe GS recovery. Optionally, this vector can be scaled by a slightly wavelength-shifted, FFT-broadened copy of the steady-state absorption spectrum to represent the broadband

Having established the global-analysis framework and its kinetic models, we now turn to the estimation of parameter uncertainties, detailing how standard errors and CIs are derived for the fitted parameters.

3.4.3 Fit Metrics

After the optimizer has converged, TAPAS automatically compiles a suite of fit-quality statistics and uncertainty estimates that address three complementary questions: *How well does the model reproduce the data? Are the noise assumptions credible? How precisely are the parameters determined?* All underlying equations are listed in **Appendix A.4**.

Goodness-of-fit indicators like the coefficient of determination (r^2), sum of squared residuals (SSR), root mean square error (RMSE) and mean absolute error (MAE) are extracted from the (weighted) residuals.²⁴⁰ Values of r^2 approaching 1 and low RMSE/MAE indicate a close correspondence between model and measurement, but they should be read in conjunction with the diagnostics below since high r^2 values can mask systematic mis-fits when the data are highly structured or oversampled.

Noise and correlation diagnostics are important since the sampling density of ultrafast data often renders adjacent points strongly correlated. Assuming they were independent would exaggerate the nominal number of degrees of freedom (d.o.f.) and underestimate the variance $\sigma^2 = \text{SSR}/\text{d.o.f.}$. TAPAS therefore examines the residual sequence and computes the lag-1 autocorrelation and integrated autocorrelation time (IAC) along both dimensions, reducing the effective sample size and therefore the effective d.o.f. Large IAC and lag-1 autocorrelation values close to 1 signal residual structure either due to heteroscedastic noise or an incomplete kinetic model and alerts the user that further refinement may be required.

Because every step of the fit is differentiable, TAPAS obtains the Jacobian J by automatic differentiation and calculates the condition number. If the Jacobian is not ill-conditioned, the first order covariance matrix $\text{Cov}(\theta) = \sigma^2(J^T J)^{-1}$ yields standard errors, parameter-parameter correlations, and the corresponding approximate 68 % CIs.^{31,34}

When non-Gaussian posteriors are sus-

pected or for problems that remain ambiguous, the user can launch an affine-invariant ensemble MCMC sampler, provided by the Python package `emcee`,³⁷³ to draw representative samples from the full posterior distribution. The sampled posterior highlights skewness, multimodality, or compensating parameter drifts that the Jacobian-based errors cannot capture.

Finally, the numerical metrics should always be complemented by a direct, critical look at what remains unexplained. TAPAS therefore plots and performs an SVD of the residual matrix so that any systematic time- or wavelength-dependent structure including periodicity, sign reversals, or delayed features stands out immediately. If such structure is visible, if component spectra appear as mirror images of one another, or if the solution drifts with different initial guesses, the safest conclusion is that the kinetic model is incomplete or physically implausible. In practice, the best fits are those that pass the statistical tests and satisfy common-sense criteria: non-mirrored spectra, robustness to starting values, and full consistency with independent spectroscopic or theoretical evidence.

3.5 Results: Case Study Rose Bengal

The xanthene dye Rose Bengal (RB) has a prominent absorption maximum near 550 nm and an ISC quantum yield close to unity in aqueous solution.^{275,276} Its triplet state is efficiently quenched by dissolved oxygen, which underlies applications that range from biological staining to oxygen sensing and photodynamic therapy.³⁸⁰ Because the dye exhibits rich, solvent-dependent excited-state dynamics and generates transient absorption signals across a broad spectral and temporal window, it serves as an excellent benchmark for TAS software.¹⁰¹ In the following, we will outline the principal stages

of the analysis. A step-by-step protocol is included in **Appendix A.5** and the accompanying raw datasets plus HDF5 project files are provided, allowing readers to reproduce the complete workflow in TAPAS.

The measurements were carried out on a 20 μM aqueous solution of RB in 0.01 M NaOH to ensure its primary dianionic configuration (RB^{2-}) using 520 nm pump pulses to target a vibrational mode of the $S_0 \rightarrow S_1$ transition.^{101,279} The experimental series comprises fs-TA scans in both, the visible and near-infrared (NIR) regions, nanosecond TA experiments in the visible, TA on neat solvent, and complementary steady-state spectra. More information on the experimental conditions as well as the laser and spectrometer setup can be found in **Appendix A.5.1**.

3.5.1 NIR Exploration and Sequential Kinetic Modeling

A preliminary survey of the fs-TA data reveals more intricate kinetics in the visible range than in the NIR driven by a stronger solvent response, CAs, and overlapping processes in the ground-state bleach region (vibrational relaxation, stimulated emission). Consequently, initial parameter exploration was focused on the NIR dataset from 830 nm to 1400 nm.

A local sequential fit at 1200 nm with three unbranched exponentials (including one infinite) and a zero-order coherent artifact term converged rapidly, yielding excellent agreement between model and data and residuals devoid of significant structure (**Figure 3.1 A**). This kinetic scheme was chosen on the basis of an SVD performed after standard preprocessing (trimming, chirp correction, background subtraction), which indicated at least three kinetic components, coherent artifacts, and a long-lived species beyond the experimental window, as detailed in **Appendix A.5.2** and **Figure A.16**. The fit metrics calculated

by TAPAS (see **Figure A.18** for full output) also seem good with parameter estimates of $\tau_1 = 76 \text{ ps} \pm 6 \text{ ps}$ (8.5 %) and $\tau_2 = 186 \text{ ps} \pm 25 \text{ ps}$ (13.5 %) with $r^2 = 0.998$, $\text{RMSE}(\Delta A) = 3.2 \times 10^{-5}$, $\text{MAE}(\Delta A) = 2.5 \times 10^{-5}$ and the effective residual $\sigma(\Delta A) = 8 \times 10^{-5}$. However, TAPAS also finds a strong correlation between τ_1 and τ_2 of -0.9. This can be further examined by performing a posterior parameter exploration of the fit confirming this behavior and returning uncertainties (68 % credible intervals) and correlations which are in excellent agreement to the quick first-order error estimates. It should be noted that, although we did not bind the parameters in the initial fit, the local posterior analysis needed the constraint that τ_1 cannot exceed and τ_2 cannot fall below 100 ps. Omitting this constraint can result in τ_1 and τ_2 switching places (**Figure A.23**) and different overall results.

Building on these local results, a global sequential fit was performed using the same initial parameters and incorporating both zero- and first-order Gaussian IRF derivatives for the CAs. **Figure 3.2 A** shows the 2D fit with residuals ($\pm 1 \times 10^{-4}$ threshold), yielding $\text{RMSE}(\Delta A) = 6 \times 10^{-5}$ and $\text{MAE}(\Delta A) = 4 \times 10^{-5}$. The residual signal is confined mainly to the early-time coherent-artifact region, the spectral window edges, and thin wavelength-aligned stripes originating from pump-intensity fluctuations. The sequential concentration profiles (**Figure 3.2 B**) and spectral/kinetic cuts (**Figure 3.2 C–D**) demonstrate excellent model fidelity. MCMC-derived uncertainties are tighter than in the local fit and do not drift anymore, giving $\tau_1 = 64 \text{ ps} \pm 0.7 \text{ ps}$ (1.1 %) and $\tau_2 = 241 \text{ ps} \pm 5 \text{ ps}$ (2.1 %), though their strong anticorrelation (-0.85) persists. The evolution-associated spectra (EAS) and results of the MCMC parameter analysis are presented in **Figure A.25**.

In the following section, we construct a comprehensive target model and fit it globally. This unified approach not only refines the kinetic parameters obtained from the

sequential fit but also links each spectral signature to its underlying photophysical or photochemical species.

3.5.2 Comprehensive Target Analysis

Building on the sequential description established in the NIR, we now extend our analysis to encompass the full spectral and temporal span of the dataset, incorporating both visible and nanosecond TA measurements. By integrating these additional datasets with prior theoretical knowledge and literature benchmarks, we can more confidently assign species-associated spectra (SAS) and resolve slower processes that lie beyond the femtosecond-picosecond window.

The visible-range TA data (410-750 nm) were preprocessed analogously to the NIR

measurements, with the additional subtraction of the solvent response surface to suppress early-time solvent contributions (compare **Table A.2**). Afterwards, the Combine Project functionality of TAPAS was used to unify both experimental datasets. Unlike in the NIR, accurate modeling of the $S_0 \rightarrow S_1$ bleach region requires an extra ultrafast component ($\tau \approx 1$ ps). To mitigate artifacts from scattered pump light near 520 nm and the interpolation gap between 750 nm and 830 nm, we applied a custom weighting vector during optimization. We also incorporated the steady-state absorbance spectrum into TAPAS's ground-state model to facilitate interpretation of the ensuing EAS. Using the NIR-derived parameter estimates augmented by the new fast component, the broadband sequential fit (410-1400 nm) converged rapidly. **Fig-**

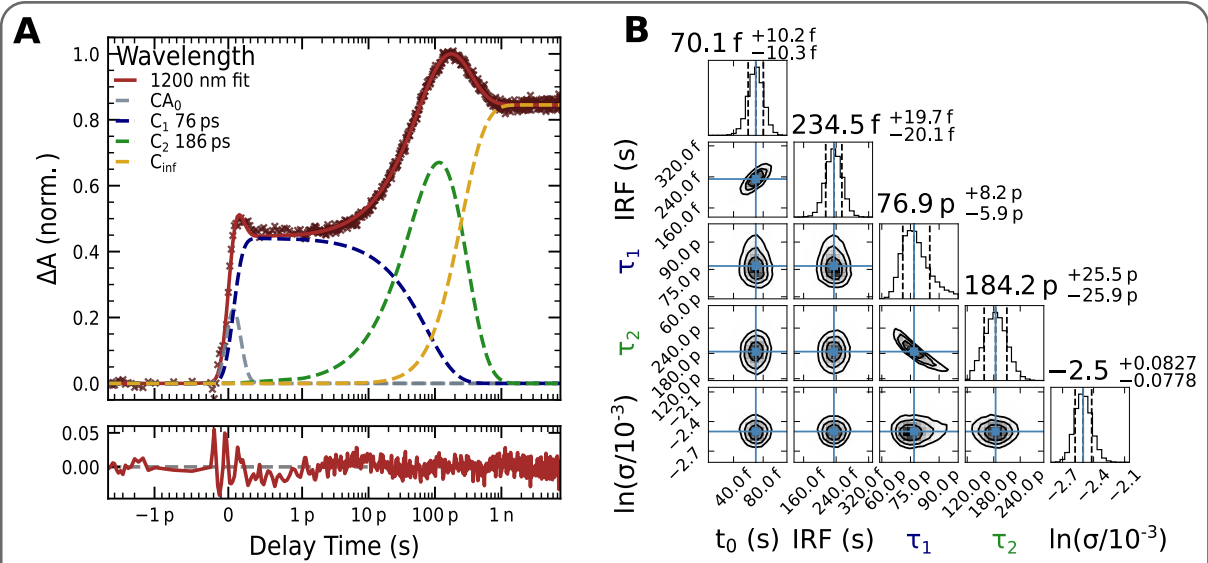


Figure 3.1: Sequential fit and posterior analysis of the 1200 nm kinetic trace for Rose Bengal. **(A)** Experimental $\Delta A(t)$ trace (brown crosses) with the best-fit sequential model (solid brown). Individual contributions are shown as: zero-order coherent artifact (CA , grey), component 1 ($\tau_1 = 76$ ps, blue), component 2 ($\tau_2 = 186$ ps, green), and a long-lived species beyond the measurement window ($\tau_3 \gg 8$ ns window, yellow). The lower subpanel displays the fit residuals. **(B)** Corner plot of the MCMC posterior distributions for the fitted parameters and sigma. Along the diagonal are the one-dimensional marginal histograms with median values (solid blue lines) and 68 % credible intervals (dashed lines); off-diagonal panels present the two-dimensional joint distributions. The pronounced tilt in the $\tau_1 - \tau_2$ joint distribution highlights their strong negative correlation.

Figure 3.3 A presents the combined 2D contour map with the steady-state spectrum overlaid. The resulting EAS and ground-state model are shown in **Figure 3.3 B**, and temporal slices in **Figure 3.3 C** demonstrate good agreement between experiment and model ($r^2 = 0.999$, $\text{RMSE}(\Delta A) = 2.5 \times 10^{-4}$, $\text{MAE}(\Delta A) = 7 \times 10^{-5}$). Finally, MCMC analysis (**Figure 3.3 D**) yields tight credible intervals and no longer exhibits the strong anticorrelation between the ≈ 60 ps and ≈ 200 ps components observed in the NIR only global fit.

The ns-TA experiment conducted over the 1 ns - 450 μs window revealed a mono-exponential decay with a lifetime of 40 μs for the long-lived species. Based on these kinetics and on the known photophysics of xanthene dyes, we attribute this oxygen-sensitive component to the triplet excited state, whereas the ≈ 70 ps feature is assigned to ISC from S_1 to T_1 , consistent with literature values.^{101,123,279} The earliest sub-70 ps component displays a spectrum (EAS_1) that closely resembles that of the singlet state (EAS_2) but is slightly blue-shifted, in-

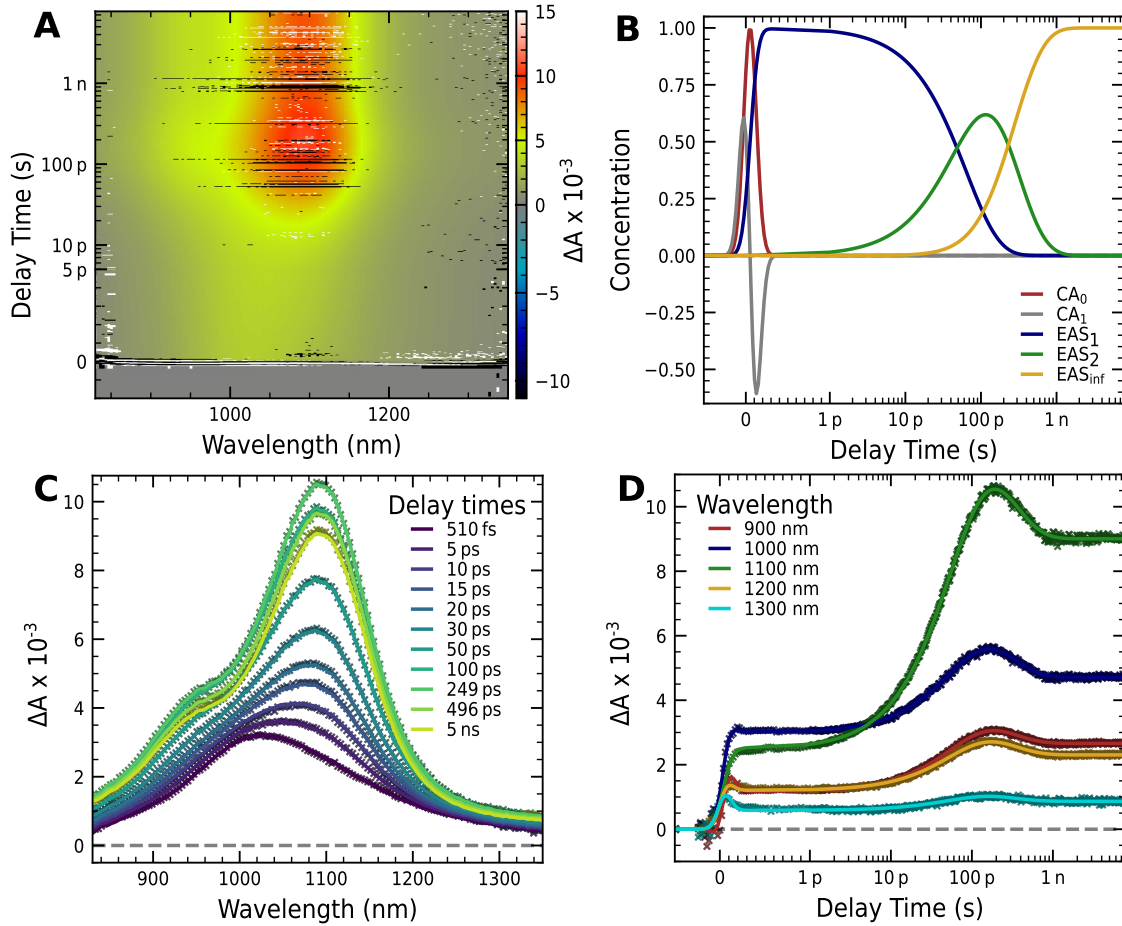
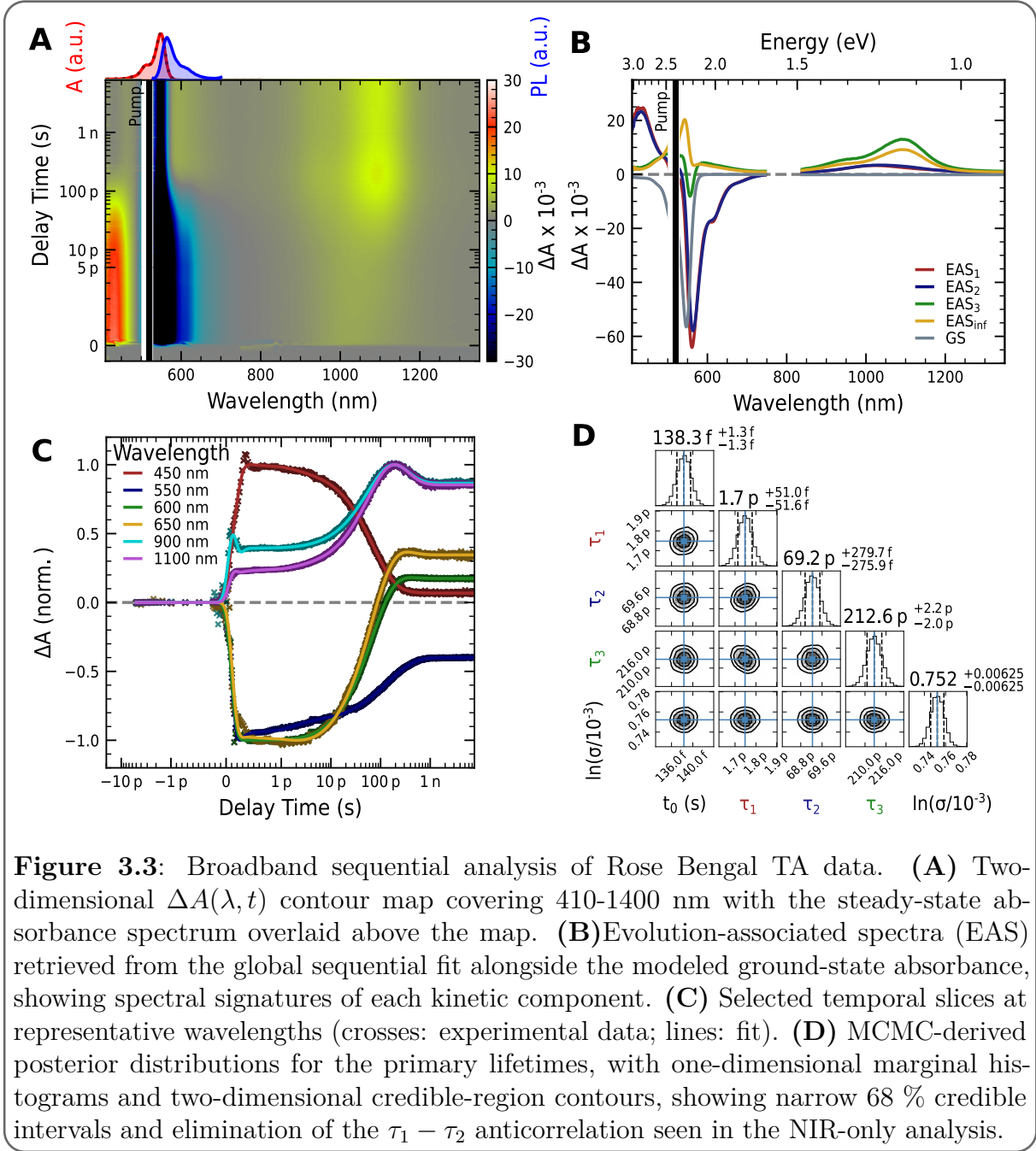


Figure 3.2: Global sequential fit of the Rose Bengal TA NIR dataset. **(A)** Two-dimensional contour of the modeled $\Delta A(\lambda, t)$ data (color-coded) overlaid with the global fit residuals: positive deviations in white and negative in black ($\pm 1 \times 10^{-4}$ threshold). **(B)** Extracted concentration (population) profiles $c_i(t)$ for the sequential kinetic components with zero- and first-order IRF contributions. **(C)** Spectral slices at selected delay times (crosses: experiment; solid lines: model). **(D)** Kinetic traces at representative wavelengths (crosses: experiment; solid lines: model).



dicative of vibrational cooling to the relaxed S_1 minimum.¹⁰¹ A 200 ps process appears only in aqueous solution and is absent in less polar media.¹⁰¹ We therefore ascribe it to the slow dielectric or structural reorganization of the water cage around the nascent triplet. A similar solvent-controlled relaxation has been observed for xanthonic acid, whose triplet transformation slows from 50 ps in ethanol to 300 ps in water.³⁸¹

For the subsequent target analysis, we

fixed two rate constants obtained independently: (i) the radiative decay constant determined by Fleming and co-workers²⁷⁶ ($k_r = 1.89 \cdot 10^8 \text{ s}^{-1}$, $\tau = 5.29 \text{ ns}$) and (ii) the bimolecular redox-pair formation (${}^3\text{RB}^{2- *} + \text{RB}^{2-} \rightarrow \text{RB}^{\bullet -} + \text{RB}^{\bullet 3-}$) with a bimolecular rate constant $k_{\text{redox}} = 5.39 \cdot 10^7 \text{ s}^{-1} \text{ M}^{-1}$.¹²² At the initial dye concentration of 20 μM , this second-order rate translates to a pseudo-first-order rate constant of $1.08 \cdot 10^3 \text{ s}^{-1}$, corresponding to a lifetime of

0.93 ms.

The kinetic scheme is as follows. Photoexcitation promotes RB to a vibronically hot singlet S_1^* (red). This state relaxes to the lowest-vibrational singlet S_1 (blue) with lifetime τ_1 . Population in S_1 partitions either to the triplet manifold by intersystem crossing with lifetime τ_2 (green) or to the ground state (GS, grey) by fluorescence with lifetime τ_6 . The nascent triplet T_1^* and the solvent cage then reorganize over lifetime τ_3 to produce the solvent-relaxed triplet T_1 (yellow). From T_1 the system returns to the GS with lifetime τ_4 or reacts with GS RB to form the redox pair C_{redox} (cyan) through lifetime τ_5 which remains essentially static during our observation window. The steps needed to implement such a target model in TAPAS are summarized in **Appendix A.5.4**.

Figure 3.4 B-D display the optimized concentration profiles, the SAS, and representative spectral slices at selected delay times, respectively. With τ_5 (redox formation) and τ_6 (fluorescence) fixed to literature values, the global fit converged reliably and produced excellent statistical metrics with no significant residual structure left (**Figures A.29 and A.30**). MCMC sampling confirmed well-behaved parameter distributions, narrow credible intervals, and only minor correlations (**Figure A.31**).

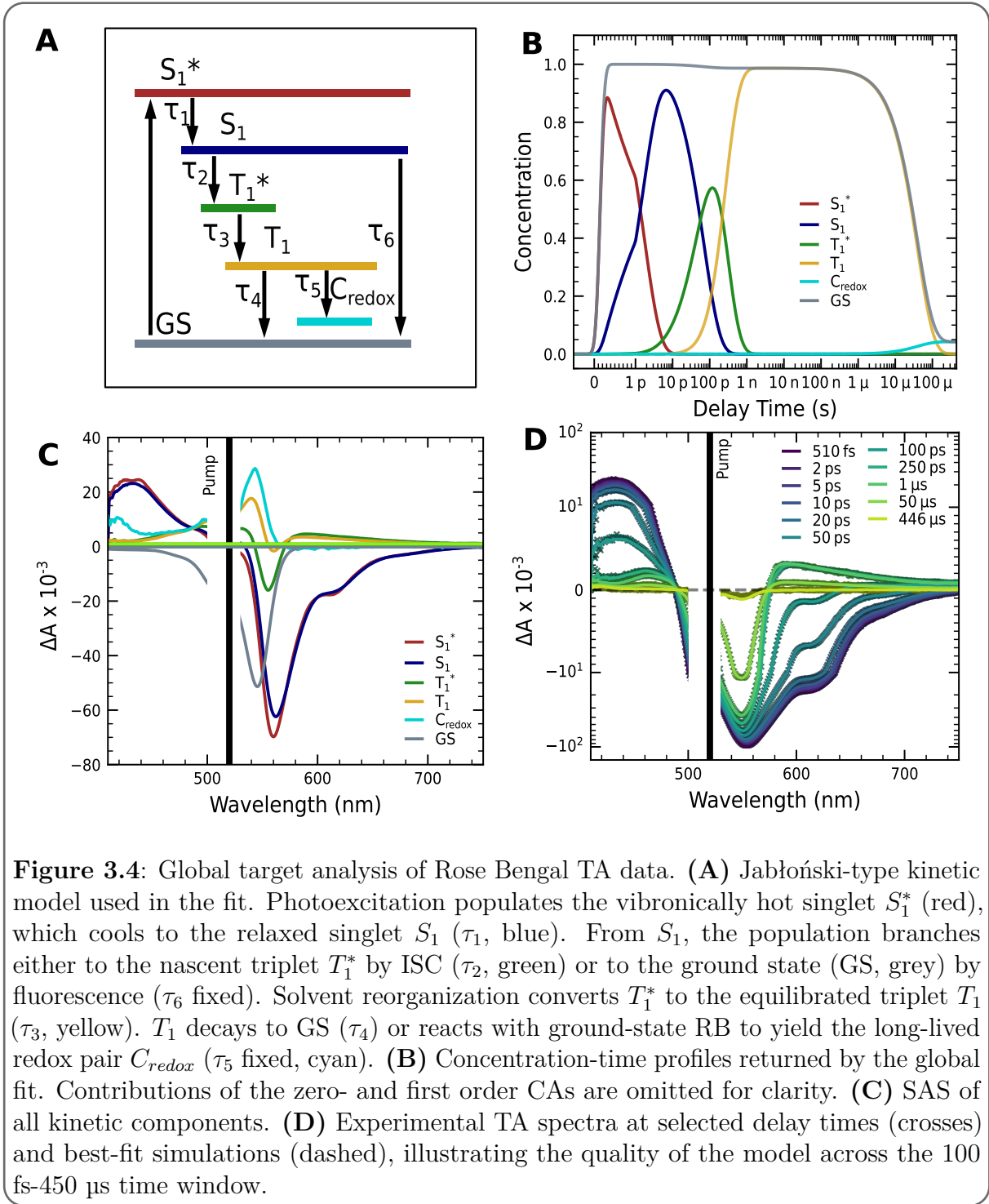
The fitted SAS for S_1^* is broader and blue-shifted relative to the relaxed S_1 , as expected for vibrational cooling that completes within about two picoseconds. Using the fixed radiative rate, the model requires that approximately 98 % of the S_1 population undergoes ISC, consistent with published quantum yields.¹⁰¹ Finally, the bifurcation of the T_1 decay and the appearance of the C_{redox} signature at 420 nm reproduce earlier reports of rose bengal’s photoredox chemistry.¹²²

3.6 Discussion

The RB case study demonstrates that routine inspection of parameter correlations is essential for judging fit stability. TAPAS computes the correlation matrix and visualizes it automatically after every optimization. For the NIR-only data set (**Figure 3.2**) the fast (≈ 64 ps) and slow (≈ 241 ps) decay components display a strong negative correlation (≈ -0.9). Such anti-correlation indicates that the two lifetimes are not independently constrained, so very different lifetime pairs (e.g. 64 ps and 241 ps versus 80 ps and 163 ps) yield fits of virtually identical quality (r^2 : 0.999, RMSE(ΔA) $8.5\text{--}8.9 \times 10^{-5}$). However, without this information, the tight standard errors or CIs provided by TAPAS, Glotaran or KiMoPack give a misleading impression of uniqueness (see **Appendix A.6.1**). We therefore regard instantaneous correlation estimates as an important requirement for reliable global fitting, and their inclusion represents a key advantage of TAPAS.

Because pronounced correlations often generate multimodal or elongated χ^2 valleys, we extended the analysis with the built-in MCMC engine (**Section 3.4.3**). Posterior density plots (**Figure 3.1 A**, **Figure A.25 B**) confirm the elongation along the lifetime-lifetime axis and reveal secondary modes that conventional optimization cannot resolve. The ability to launch MCMC directly from the GUI, without external scripting, lowers the barrier for Bayesian diagnostics and makes posterior exploration a routine, rather than exceptional, step. To our knowledge, no other public TA package currently provides correlation estimates or an integrated Bayesian workflow.

TAPAS derives approximate 68 % CIs from the covariance matrix scaled by the effective sample size, obtained via the integrated autocorrelation time of residuals (**Section 3.4.3** and **Appendix A.4**). For the RB data, the resulting standard errors are in the same range as those obtained with the computationally expensive F-test implemented in



KiMoPack which can take around 500 times as long as the first order approximation by TAPAS (**Appendix A.6**). The agreement validates the rapid, yet rigorous alternative and demonstrates that TAPAS delivers statistically sound uncertainties without resorting to repeated refits.

The target model tested in TAPAS unifies

our TA data with steady-state spectra and literature datasets from independent laboratories. The model reproduces all transient and static observables, and the extracted lifetimes match the consensus values reported in the literature. This agreement highlights two practical strengths of TAPAS. First, the flexible model editor and cross-experiment

linking let users merge data from different sources into a single kinetic scheme. Second, fitting the full spectral range across multiple data sets separates overlapping processes, weakens parameter correlations, and makes the extracted parameters more reliable.

TAPAS is optimized for interactive exploration and diagnostics. For large-scale batch automation, where identical preprocessing and fits are applied across many datasets, a script-based workflow can be more convenient and integrates more easily with pipelines. For very large datasets, continuous plotting and GUI updates can be more computationally demanding than lighter script tools. Although we did not observe a practical loss of responsiveness in our tests, this may become disadvantageous when computational resources are limited or when downsampling is not feasible. The modular design of TAPAS and exposed source let users reuse the same components in scripts.

relation provide rapid, statistically sound CIs and correlation matrices, while an optional MCMC engine maps the full Bayesian posterior, capabilities seldomly available in other TA software. All raw, processed, and fitted data are written to standardized HDF5 containers and automatically annotated with rich metadata, ensuring complete provenance and easy reuse. By uniting high-performance computation, advanced uncertainty quantification, and transparent data management within an intuitive GUI, TAPAS closes the gap between ease of use and rigorous statistical treatment in transient absorption analysis.

3.7 Conclusion

In this work, we have introduced TAPAS, an open-source, fully integrated graphical environment that spans the entire transient absorption workflow from raw-data import and preprocessing through visualization, global and target fitting, and statistical diagnostics. Although the program can be operated entirely through its GUI, every Python module remains accessible for inspection or extension, combining the convenience of a classical point-and-click interface with the flexibility of script-based tools.

The kinetic-fitting core is accelerated with XLA-optimized, just-in-time compilation, delivering order-of-magnitude speed-ups over established packages which are mainly relevant for repeated-fit workloads such as bootstrap resampling, MCMC and F-tests. Automatic differentiation and effective-sample-size estimates based on residual autocor-

Preparation, Photoluminescence and Excited State Properties of the Homoleptic Cluster Cation $[(\text{W}_6\text{I}_8)(\text{CH}_3\text{CN})_6]^{4+}$

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4.1 Abstract

Solvated tungsten iodide cluster compounds are presented with the homoleptic cluster cation [(W₆I₈)(CH₃CN)₆]⁴⁺ and the heteroleptic [(W₆I₈)I(CH₃CN)₅]³⁺, synthesized from W₆I₂₂ in acetonitrile. Crystal structures were solved and refined on deep red single-crystals of [(W₆I₈)(CH₃CN)₆](I₃)(BF₄)₃·H₂O, [(W₆I₈)I(CH₃CN)₅](I₃)₂(BF₄), and on a yellow single-crystal of [W₆I₈(CH₃CN)₆](BF₄)₄·2(CH₃CN) on the basis of X-ray diffraction data. The structure of the homoleptic [(W₆I₈)(CH₃CN)₆]⁴⁺ cluster is based on the octahedral [W₆I₈]⁴⁺ tungsten iodide cluster core, coordinated by six apical acetonitrile ligands. The electron localisation function of [(W₆I₈)(CH₃CN)₆]⁴⁺ is calculated and solid-state photoluminescence and its temperature dependence are reported. Additionally, photoluminescence and transient absorption measurements in acetonitrile are shown. Results of the obtained data are compared to compounds containing [(M₆I₈)I₆]²⁻ and [(M₆I₈)L₆]²⁻ (M = Mo or W; L = ligand) clusters.

4.2 Introduction

Octahedral metal halide clusters [M₆X₁₄]²⁻ with M = Mo, W and X = Cl, Br, I are known for their photophysical properties, in particular their bright red luminescence, high quantum yields, long life times, and oxygen quenching.^{112,382} The luminescence is based on ground state photoexcitation (*S*₀) leading to excited states (*S*_{*n*}) and inter-system crossing into triplet states (*T*_{*n*}).³⁸³ Luminescence from these triplet states may be quenched in the presence of molecular oxygen to form singlet oxygen O₂(a¹Δ_g).¹⁸

Some cluster compounds derived from [M₆X₁₄]²⁻ have been optimized to obtain remarkable properties with regard to oxygen sensing,³⁸⁴ photoreduction of CO₂,³⁸⁵

photocatalysis³⁸⁶ and medical applications (as photodynamic therapeutic agents,¹⁵ X-ray contrast agents,³⁸⁷ and bactericide²⁹⁰).

The clusters of interest are based on an octahedral metal core, surrounded by eight inner (i) and six outer (a) ligands as [M₆X₈^{*i*}X₆^{*a*}]²⁻.³⁸⁸ Apical halide ligands are bound more weakly to the cluster and can be exchanged by organic ligands, usually starting from the soluble cluster species (TBA)₂[M₆X₈^{*i*}X₆^{*a*}] (TBA = tetrabutylammonium) to react with inorganic/organic silver salts.^{19,283,389}

Ligand substituted compounds of the type (TBA)₂[M₆X₈^{*i*}L₆^{*a*}] with L being an apical ligand have shown remarkably enhanced photophysical properties depending on the nature of L, when compared to the all-halide cluster counterpart. Ligands with strong electron withdrawing effects have shown to provide the highest luminescence (phosphorescence) quantum yields and the strongest luminescence quenching in the presence of molecular oxygen.^{19,283,296,314,315,390} One of the most remarkable compounds, (TBA)₂[Mo₆I₈(CO₂CF₃)₆] is reported with a luminescence quantum yield of 1 in (oxygen-free) acetonitrile solution.²⁸³ The solid state phosphorescence of (TBA)₂[Mo₆I₈(CO₂CF₃)₆] is expectedly, lower. However, with a remarkable luminescence quenching of 95 % under pure oxygen.¹⁹

To simulate the cluster luminescence, a model with four different emitting triplet sublevels has been developed describing the observations very accurately.²² The energetically highest one of these emitting triplet sublevels possesses an allowed transition to the ground state. Recently, it has been shown that a high d-electron density on the metal atoms leads to a low energy difference between the different triplet states, while a low density leads to a large difference.³²⁴ Thus, the lower the d-electron density, the bigger the energetic splitting and the lower the thermal population of the highest triplet state. This results in long triplet lifetimes

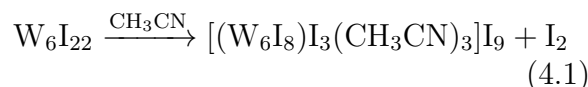
in the solid state even at room temperature, especially for iodide clusters bearing strong electron withdrawing ligands. An example is (TBA)₂[Mo₆I₈(CO₂C₃F₇)₆] with lifetimes of around 235 μs at room temperature.³²³ The long decay time is a result of low thermal population of the highest triplet sub-level. For the analogous species with tungsten (TBA)₂[W₆I₈(CO₂C₃F₇)₆] a similar reason for its long triplet lifetime of up to 55 μs²⁹⁶ can be assumed.

In general, the aforementioned investigations of the photophysical properties of tungsten and molybdenum halide clusters have been carried out on anionic species ([M₆X₈L₆]²⁻). While neutral and cationic clusters are reported to exist with various different solvents as ligands,^{308,391–393} only a few crystal structures^{310,311,394,395} are reported, and for only three compounds, namely [M₆I₈(DMSO)₆](NO₃)₄ (M = Mo, W) and [Mo₆I₈(pyridine)₂]I₄ have the luminescence properties been studied.^{310,395} Therefore, our aim was to synthesize new cationic tungsten halide clusters and characterize their photoluminescence properties. Recently we discovered the cationic tungsten iodide cluster species [(W₆I₈)I₃(CH₃CN)₃]I₉, which features a black body color due to the high iodine content.³¹¹

On the basis of aforementioned research, we report on the synthesis of the novel cationic tungsten halide cluster species [(W₆I₈)I(CH₃CN)₅](I₃)₂(BF₄) (**I**), [(W₆I₈)(CH₃CN)₆](I₃)(BF₄)₃ · (H₂O) (**II**) and [(W₆I₈)(CH₃CN)₆](BF₄)₄ · (CH₃CN)₂ (**III**) and their crystal structures. Additionally, we investigated the photoluminescence properties and the electron localization function of (**III**) and compare it to previously reported results for different anionic tungsten halide cluster species.

4.3 Results and Discussion

The recently reported compound [(W₆I₈)I₃(CH₃CN)₃]I₉ is formed by reaction of W₆I₂₂ in acetonitrile (**Equation 4.1**).³¹¹



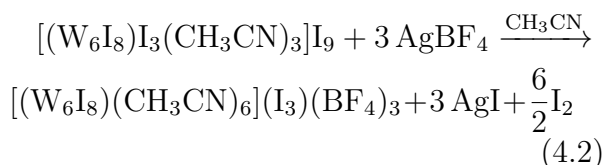
W₆I₂₂ on the other hand, is obtained from the reaction of W₆I₁₂ with iodine,³⁰³ whereby the connectivity between adjacent clusters softens up due to the incorporation of iodine molecules into the structure, leading to an overall increase of the solubility.

General attempts to synthesize isolated or dissolved clusters can depart from common methods used in cluster synthesis and may involve a significant number of reaction steps.^{19,310,389,396,397}

Moreover, individual attempts may be required for different metal halide systems, as Köckerling has shown for a vast number of cluster compounds.^{398–405} A general attempt includes the extraction in an appropriate solvent in the presence of a Lewis acid (ZnCl₂, AlCl₃, or SbCl₅) as exemplified with MCl₃ for the conversion of K₂[(Zr₆B)Cl₁₅] into [Zr₆BCl₁₂(CH₃CN)₆]MCl₄ (M = Al, Ga, In).⁴⁰⁶ Another general attempt, which was adopted on the reactions presented here, is the employment of silver salts (AgBF₄) and subsequent precipitation of silver halide.⁴⁰⁷

After the discovery of the mixed ligand cluster [(W₆I₈)I₃(CH₃CN)₃]⁻, a whole series of cluster species can be regarded to exist as [(W₆I₈)I_{6-n}(CH₃CN)_n]⁽ⁿ⁻²⁾⁺, where *n* may range between zero and six.

Acetonitrile-rich members with *n* = 5 and 6 are obtained in reactions departing from [(W₆I₈)I₃(CH₃CN)₃]I₉ (*n* = 3) with acetonitrile and Ag(BF₄) exemplified in **Equation 4.2**.



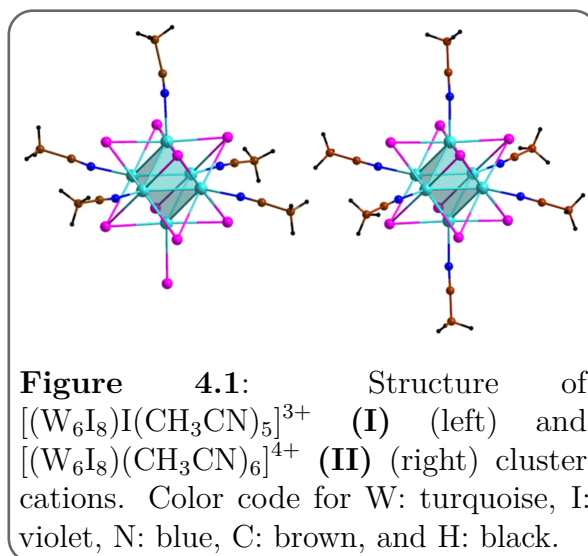
The heteroleptic cluster [(W₆I₈)I(CH₃CN)₅](I₃)₂(BF₄) **I** (*n* = 5) and the homoleptic acetonitrile cluster [(W₆I₈)(CH₃CN)₆](I₃)(BF₄)₃·(H₂O) **II** (*n* = 6) are obtained in similar reactions crystallizing as deep-red crystals. Dark reddish or brown body colors are typical for polyiodides including (I₃)[−] in given structures and (I₇)[−] contained in the structure of [(W₆I₈)I₃(CH₃CN)₃](I₇)·I₂ making these compounds rather unattractive for optical studies. Nevertheless, yellow crystals of [(W₆I₈)(CH₃CN)₆](BF₄)₄·2(CH₃CN) **III** showing orange luminescence were obtained following a similar synthesis (see Experimental).

Crystal structures of all three compounds were solved and refined on the basis of single-crystal X-ray diffraction data with monoclinic or triclinic space groups (**Table 4.1**).

The most interesting result of this work is the presence of the homoleptic [(W₆I₈)(CH₃CN)₆]⁴⁺ cluster cation, shown in **Figure 4.1**. This complements the also-obtained heteroleptic [(W₆I₈)I(CH₃CN)₅]³⁺, and the recently reported [(W₆I₈)I₃(CH₃CN)₃]⁺ cluster cations, whereas the neutral species [(W₆I₈)I₄(CH₃CN)₂] remains missing. With 24 electrons per cluster, all these clusters possess the same electron count as binary W₆I₁₂.

Structures of compounds **I** and **II** reveal layered arrangements with clusters and I₃[−] units alternating with layers of BF₄[−] ions and H₂O, as shown for **II** in **Figure 4.2**. The structure of **III** is also dominated by a layered arrangement of nearly spherical clusters (**Figure 4.1**) surrounded by anions and free acetonitrile filling the voids of this arrangement as shown in **Figure 4.3**.

The [(W₆I₈)(CH₃CN)₆]⁴⁺ cluster is based



on an octahedral tungsten cluster, bearing eight (*i* = inner) iodide ligands forming the [W₆I₈]⁴⁺ cluster core, plus six (*a* = outer) acetonitrile ligands. W–W distances of the octahedral cluster cores are in the range at 265.16(5)–267.81(8) pm and appear similar to other compounds with the [(W₆I₈)I₆]^{2−} cluster. The averaged W–I^{*i*} distances (278.2(1) pm) of the reported compounds (**I–III**) are similar to corresponding distances in [(W₆I₈^{*i*})I₆]^{2−} (278.3(2) pm).³⁰⁹

This similarity is not unexpected since there is no change of the oxidation state of the tungsten atoms. Two of the three (I₃)[−] ions in the structure of **I** are symmetric with bond lengths at 291.3(1) and 291.6(1) pm while one is nearly symmetric with 290.2(1) (I–I) and 293.4(1) pm (I···I–I). Compound **II** also shows a symmetric (I₃)[−] anion with a bond length of 292.2(1). For octahedral tungsten iodide clusters symmetric (I₃)[−] ions are unusual³⁰⁴ but, in the literature, there are quite a few examples that adopt symmetrical I₃[−] units with bond lengths around 290 pm.^{408–416}

Coordination W–N bonds range from 214.4(9) to 217.3(9) pm for the homoleptic[(W₆I₈)(CH₃CN)₆]⁴⁺ cluster. Corresponding W–N distances with (NCO)[−] ligands in (TBA)₂[W₆I₈(NCO)₆] were reported quite similar, with 217(1) pm (**Table 4.2**).⁴¹⁷

Table 4.1: Crystal data for $[(W_6I_8)I(CH_3CN)_5](I_3)_2(BF_4)$ **I**, $[(W_6I_8)(CH_3CN)_6](I_3)(BF_4)_3 \cdot H_2O$ **II**, and $[(W_6I_8)(CH_3CN)_6](BF_4)_4 \cdot (CH_3CN)_2$ **III**.

Compound	$[(W_6I_8)I(CH_3CN)_5](I_3)_2(BF_4)$	$[(W_6I_8)(CH_3CN)_6](I_3)(BF_4)_3 \cdot H_2O$	$[(W_6I_8)(CH_3CN)_6](BF_4)_4 \cdot (CH_3CN)_2$
CCDC code	2064394 ^b	2115682	2152223
Formula weight (g mol ⁻¹)	3298.68	3023.77	2793.97
Temperature (K)	100.0(1)	100.0(1)	150.0(1)
Wavelength (pm)	71.073	71.073	71.073
Space group	P2 ₁ /c	C2/c	P2 ₁ /n
Lattice parameters (<i>a</i> , <i>b</i> , <i>c</i> in pm; β in degree)	1226.89(3); 1834.07(1); 1366.22(3); 109.093(3)	1226.89(3); 2205.46(2); 2189.26(4); 109.543(1)	1857.87(5); 1234.68(1); 1633.92(4); 94.424(2)
Volume (nm ³)	4.6236(2)	4.70653(7)	4.8725(2)
Z	4	4	4
Density (calculated)	4.739 g cm ⁻³	4.267 g cm ⁻³	3.809 g cm ⁻³
Absorption coefficient	24.914 mm ⁻¹	21.890 mm ⁻¹	19.263 mm ⁻¹
Goodness-of-fit on F^2	1.023	1.171	1.153
R_1^a ($I > 2\sigma(I)$)	0.0512	0.0198	0.0371
wR_2 ($I > 2\sigma(I)$)	0.1065	0.0442	0.0973
R_1 (all data)	0.0826	0.0207	0.0435
wR_2 (all data)	0.1174	0.0445	0.0998

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; \quad wR_2 = (\sum w[(F_o)^2 - (F_c)^2]^2 / \sum w(F_o)^4)^{1/2}.$$

^bFlorian Pachel, Markus Ströbele, H.-Jürgen Meyer, CCDC 2064394, *CSD Commun.*, 2022, DOI: 10.5517/ccdc.csd.cc2795c3.

Table 4.2: Interatomic W–W and W–N distances (pm) for compounds **III**.

Compound	W–W	W–N
$[(W_6I_8)I(CH_3CN)_5]^{3+}$ (I)	265.66(8)–267.81(8)	213.8(13)–225.5(1)
$[(W_6I_8)(CH_3CN)_6]^{4+}$ (II)	265.84(2)–267.14(2)	215.5(4)–216.3(4)
$[(W_6I_8)(CH_3CN)_6]^{4+}$ (III)	265.16(5)–267.63(5)	214.4(9)–217.3(9)

Our research interest was first of all focused on the homoleptic compound **III**. The absence of additional I_3^- units, like in **I** or **II**, is responsible for the desirable transparency with bright yellow color of crystalline **III** and allows for the observation of a bright orange-red luminescence that is clearly visible to

the naked eye (**Figure B.1**). Luminescence studies of **III** should give first insights into the photophysical behavior of cationic cluster species.

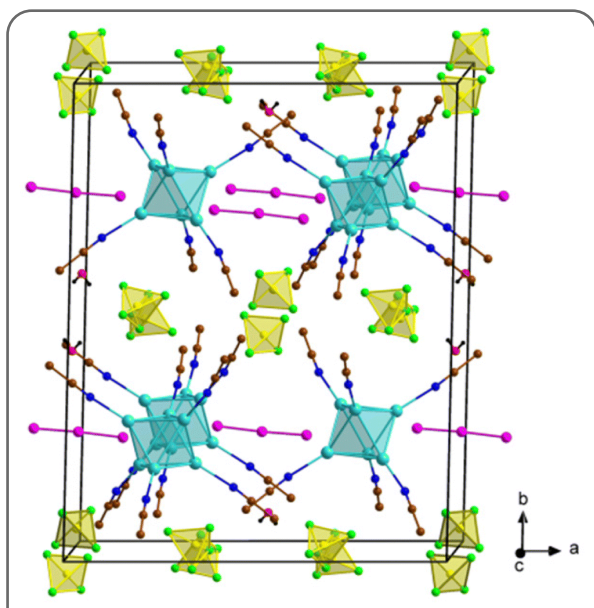


Figure 4.2: Projection of the crystal structure of **II** in the *ab* plane. The iodide ligands and hydrogen atoms of acetonitrile are omitted for clarity. Color code for W: turquoise, I: violet, N: blue, C: brown, B: yellow, F: green, O: red and H: black.

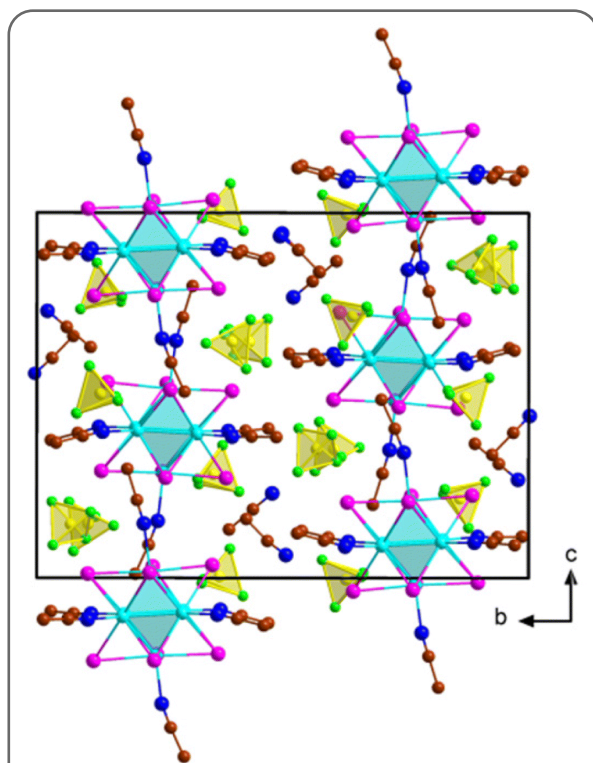


Figure 4.3: Projection of the crystal structure of **III**. The $[W_6I_8(CH_3CN)_6]^{4+}$ units are showing a layered arrangement along the *b* axis with BF_4^- and free acetonitrile filling the voids. Hydrogen of clusters are omitted for clarity. Color code for W: turquoise, N: blue, C: brown, F: green, and B: yellow.

4.3.1 Electron Localization Function

To investigate the nature of the W–N bond, the electron localization function (ELF) of **III** was calculated (**Figure 4.4** left). For comparison, we have also calculated the ELF of $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$ as a representative anionic tungsten iodide cluster bearing strong electron withdrawing ligands (**Figure 4.4**).

Comparison of the ELF of **III** and $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$ shows that **III** has a higher density of localized electrons at the W site, indicating reduced ionicity.⁴¹⁸ Four local maxima can be found along the W–N bond of **III**, while only two are present along the W–O bond of $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$, which can be attributed to a higher covalency of **III**.

However, as a nodal plane is present at the centre of both W–N/O bonds, the bond for both compounds is primarily ionic. The ELFs around the I atoms are similar for both

compounds.

4.3.2 Photoluminescence Studies

The characteristic photophysical properties of $[(W_6I_8)I_6]^{2-}$ and $[(W_6I_8)L_6]^{2-}$ clusters have been recently reported. Crystalline powders of these compounds typically appear with yellow to orange colors. Upon UV radiation or visible light photoexcitation, they emit red luminescence (phosphorescence) from excited triplet states.^{19,114,290,296,314,390,396,419–421}

The bonding of six apical iodide ligands in $[(W_6I_8)I_6]^{2-}$ cluster compounds is represented by covalent W–I interactions. However, it has been shown that the presence of

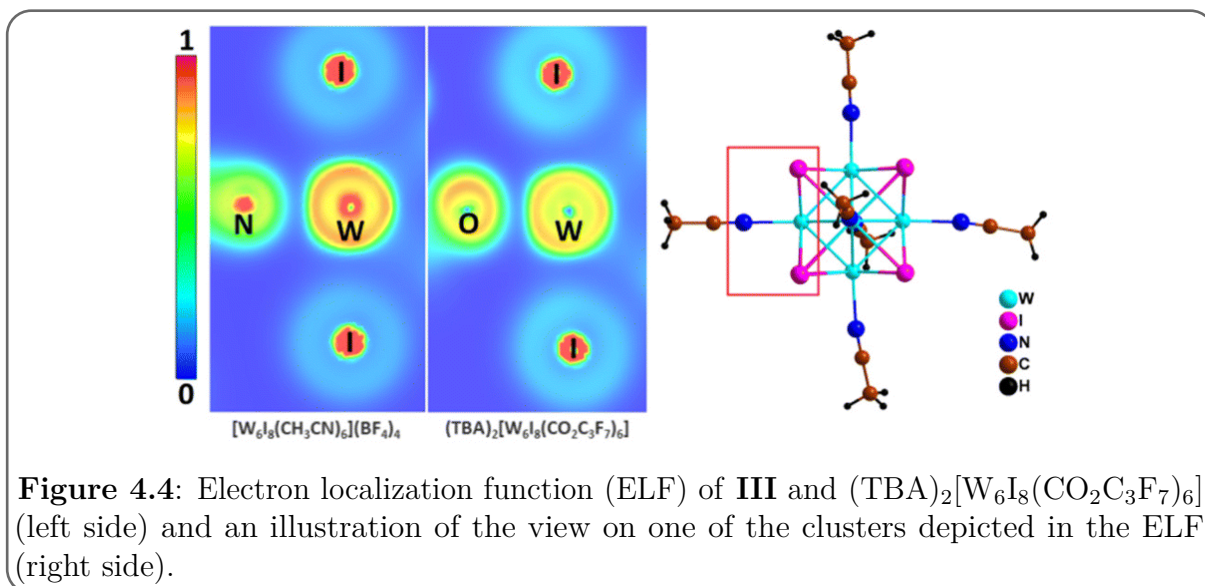


Figure 4.4: Electron localization function (ELF) of **III** and $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$ (left side) and an illustration of the view on one of the clusters depicted in the ELF (right side).

strongly electron withdrawing ligands (L) in $[(W_6I_8)L_6]^{2-}$ clusters can lead to a blue shift of the emission maximum, which is often related to significantly increased luminescence lifetimes or quantum yields.^{19,283,296,315}

To explain some of these observations, a model for the emitting excited triplet states developed for molybdenum and tungsten halide clusters can be employed. Kitamura *et al.* used a model with four different emitting excited triplet state sublevels to explain the cluster emission.²² They further noted that the highest lying sublevel can couple with the ground state by an electronically allowed dipole transition, giving rise to an intense and short-lived emission. Emission from the other spin sublevels is forbidden. Studies on molybdenum halide clusters having different d-electron densities revealed splittings between these spin-triplet sublevels, whereas a low density led to a high splitting and *vice versa*.³²⁴ Additional investigations on the temperature dependence of the emission of $(TBA)_2[Mo_6X_8(CO_2C_3F_7)_6]$ (X = Cl, Br, I) revealed smaller full width at half maximum (FWHM) values and changes in the emission lifetime between 3 K and 300 K by switching inner ligands from Cl to I. This is attributed to a growing splitting between spin sublevels. Furthermore, increasing the temperature from 3 K to 300

K leads to a red shift of the emission for $(TBA)_2[Mo_6I_8(CO_2C_3F_7)_6]$ instead of the observed blue shift for the species bearing Cl and Br ligands.³²³ The different thermal behavior of the emission is observed for clusters with different inner halide ligands as well as for different organic outer ligands.¹⁰⁶

The herein monitored excitation and emission spectra of $[(W_6I_8)(CH_3CN)_6](BF_4)_4 \cdot 2(CH_3CN)$ powder show a broad excitation feature between 275 and 500 nm ($\lambda_{em} = 630$ nm) and a broad emission band between 500 and 800 nm ($\lambda_{exc} = 390$ nm), presented in **Figure 4.5**. Interestingly, this emission of **III** is not very different from that of $[(W_6I_8)(CO_2C_3F_7)_6]^{2-}$ ($\lambda_{em,max} \approx 630$ nm) carrying a strongly electron withdrawing ligand. However, a comparison of the emission lifetimes reveals a significantly shorter lifetime of **III** ($\tau = 11$ μ s, **Figure B.2**) compared to $(TBA)_2[(W_6I_8)(CO_2C_3F_7)_6]$.²⁹⁶ Specifically, the original work reported a biexponential decay with $\tau = 27$ and 55 μ s, and our own lifetime measurements of $(TBA)_2[(W_6I_8)(CO_2C_3F_7)_6]$ yield a monoexponential decay with $\tau = 36$ μ s (**Figure B.3**). Likewise, the behavior in the presence of molecular oxygen is also very different (**Figures B.4 and 4.5**), with **III** showing nearly no quenching of the

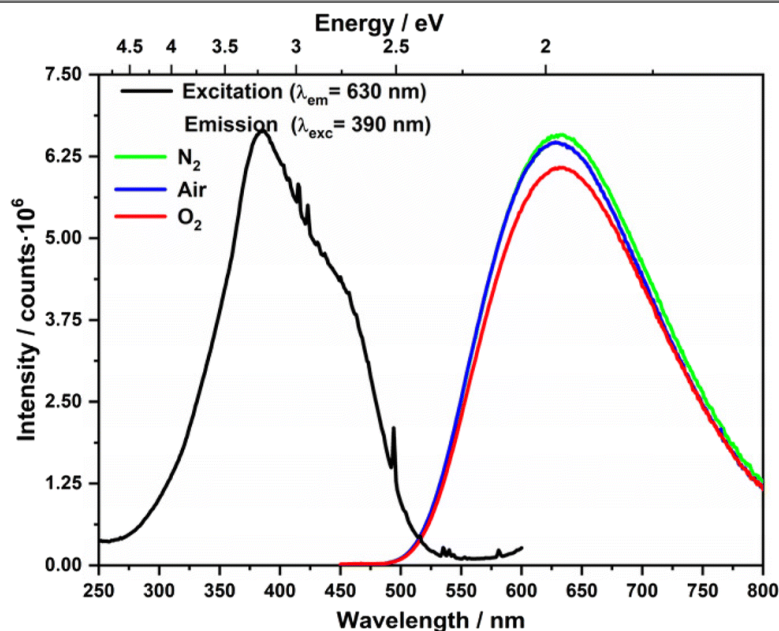


Figure 4.5: Excitation (black) and emission (red, blue, green) spectra of crystalline $[(W_6I_8)(CH_3CN)_6](BF_4)_4 \cdot 2 (CH_3CN)$ (**III**) powder.

emission, while $(TBA)_2[(W_6I_8)(CO_2C_3F_7)_6]$ quenches strongly. In general, tungsten iodide compounds featuring strong oxygen quenching of the emission usually exhibit long emission lifetimes. This supports the fact that the quenching is related to the lifetime of the emission process in tungsten iodide clusters.

A comparison of the d-electron density in **III** (Figure 4.4) and $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$ shows a higher density for **III** and a less ionic bonding between tungsten and the ligand atom. The consideration of our observations and those of Kitamura *et al.*^{323,324} lead to the conclusion that the very short emission lifetime of **III** could stem from a low energetic splitting of the spin sublevels and therefore strong thermal population of the highest level responsible for a short emission lifetime. For $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$, a high energetic splitting can be expected, leading to a long lifetime.

Temperature-dependent photoluminescence studies of **III** (Figure 4.6) show a blue shift of the emission with increasing temperature from 100 K to

300 K. This is in contrast to the red shift reported for $(TBA)_2[Mo_6I_8(CO_2C_3F_7)_6]$ ³²³ and the steady emission of $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$ (Figure B.5). The same applies for the FWHM values observed, which are $\sim 3100\text{ cm}^{-1}$ at 100 K and $\sim 4100\text{ cm}^{-1}$ at 300 K for **III** and $\sim 2800\text{ cm}^{-1}$ at 100 K and $\sim 3600\text{ cm}^{-1}$ at 300 K for $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$. In the case of $(TBA)_2[Mo_6I_8(CO_2C_3F_7)_6]$, $\sim 1500\text{ cm}^{-1}$ at 3 K and $\sim 2400\text{ cm}^{-1}$ at 300 K are reported. Both, the blue shift and the large FWHM value for **III** compared to $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$ or the molybdenum species could stem from strong contribution of the energetically highest emissive triplet sublevel to the photoluminescence.

4.3.3 Excited-State Studies

We investigated the excited state properties of **III** in acetonitrile solution by femtosecond and nanosecond transient absorption measurements. To observe the fast dynamics, we excited the sample with 90 fs laser pulses at a wavelength of 300 nm (1 μJ per pulse).

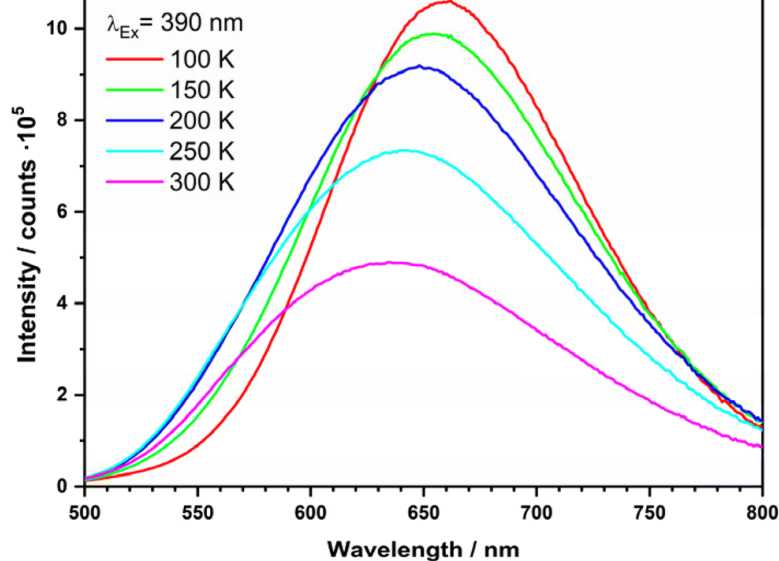


Figure 4.6: Temperature-dependent photoluminescence spectra of **III** in the temperature range of 100 K to 300 K.

Sequential global fitting analysis found three different components, with decay times of 2.2 ps, 87 ps and a decay significantly longer than the measurement window of 7.5 ns (**Figures B.7 and 4.7**). These observations are in good agreement with previously reported data obtained for $(TBA)_2[Mo_6X_8Y_6]$ ($X = Cl, Br, I$; $Y = Cl, Br, I, CO_2CF_3$).⁹⁹ We attribute component 2 and 3 to the excited triplet states of the cluster since the obtained spectra are in accordance with spectra obtained on the microsecond timescale (**Figure B.8**). As described for molybdenum compounds, the second component is probably related to a hot triplet state, while component 1 has a different shape and is likely due to an excited singlet state which decays *via* intersystem crossing into the hot triplet state (component 2).

The observed lifetime of 2.2 ps for the singlet state deviates slightly from the reported lifetimes for molybdenum iodide clusters, which are typically between 0.5 ps and 1.7 ps.⁹⁹ Moreover, the 87 ps lifetime of the hot triplet is about one order of magnitude larger than the reported lifetimes for molybdenum iodide clusters. We conclude that the decay of the various excited states of

III is generally slower than that of the corresponding excited states in molybdenum iodide clusters. A definitive attribution of this finding to the effect of the metal atom or the different apical ligands would require additional transient absorption data, e.g. of the molybdenum analogues with the same apical ligands, which is currently not available. To study the slower dynamics beyond 7.5 ns, e.g. the broad excited-state absorption feature (ESA) between 350 and 530 nm, we conduct nanosecond transient absorption spectroscopy at an excitation wavelength of 390 nm (2 μ J per pulse) (**Figure 4.8**). We find a mono-exponential decay with a lifetime of 28 μ s under nitrogen (red) and 12 μ s (component 3) under ambient conditions (black) over the whole spectral range. This is in excellent agreement with time-resolved photoluminescence decay studies in acetonitrile solution (12 μ s, blue curve), indicating that the long-lived ESA signal corresponds to the excited triplet state responsible for the emission.

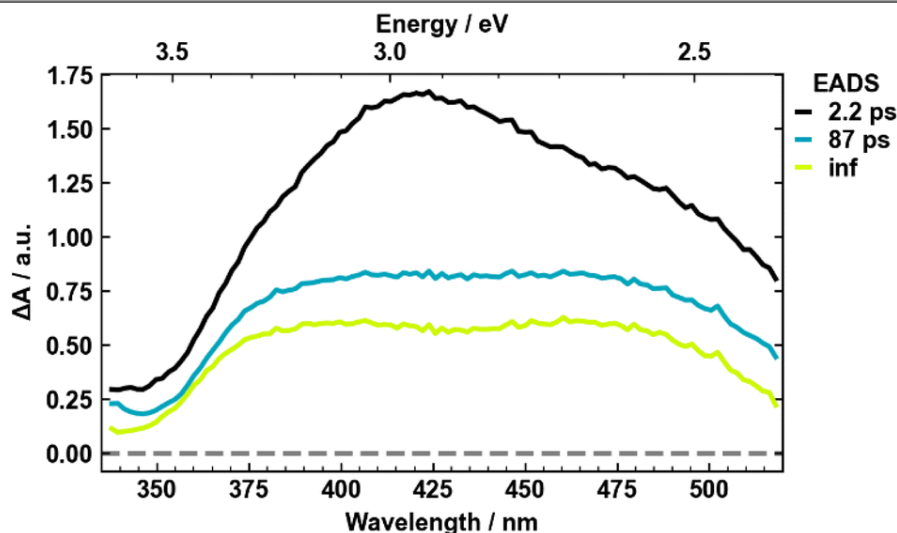


Figure 4.7: Evolution-associated difference spectra (EADS) resulting from the global analysis of **III** in acetonitrile after excitation at 300 nm. The black spectrum forms instantaneously at time zero and evolves in 2.2 ps into the blue component which decays in 87 ps into the yellow component with a lifetime longer than the measurement window.

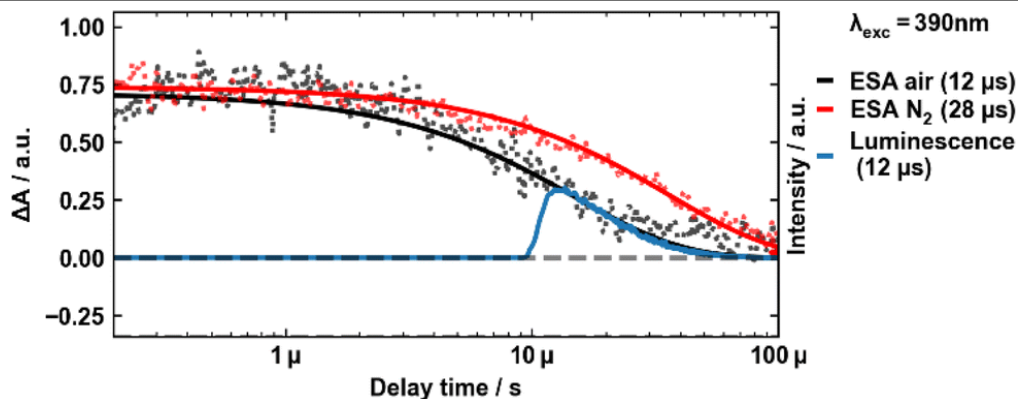


Figure 4.8: Kinetic trace of **III**, measured at the excited-state absorption (ESA) feature at 470 nm after excitation at 390 nm in acetonitrile, revealing a mono exponential decay with a lifetime of 28 μ s under N_2 (red) and 12 μ s under ambient conditions (black). The photoluminescence decay spectrum is shown in blue ($\lambda_{exc} = 390$ nm, $\lambda_{em} = 630$ nm).

4.4 Experimental Section

4.4.1 Synthetic Procedures

Synthesis of $[(W_6I_8)I(CH_3CN)_5](I_3)_2(BF_4)$ (I) The preparation of the starting material $[W_6I_{11}(CH_3CN)_3](I_7) \cdot I_2$ was previously reported.³¹¹

A 4 ml screwcap vial was filled with 25.0

mg (6.6 mmol) $[W_6I_{11}(CH_3CN)_3](I_7) \cdot I_2$ and 1.3 mg (6.6 mmol) $AgBF_4$ and 3 ml acetonitrile. The vial was placed in a furnace at 85 $^{\circ}C$ for 2 weeks. Afterwards it was removed from the furnace for cooling to room temperature. Clear dark red plate-shaped crystals had formed on the wall of the vial (estimated yield of single crystals: 5 %).

Synthesis of $[(W_6I_8)(CH_3CN)_6](I_3)(BF_4)_3 \cdot (H_2O)$ (II) Similar to **I**, a 4

ml screwcap vial was filled with 25.0 mg (6.6 mmol) $[W_6I_{11}(CH_3CN)_3](I_7) \cdot I_2$ and 3.9 mg (19.9 mmol) $AgBF_4$ and 3 ml acetonitrile. The vial was placed in a furnace at 85 °C for 2 weeks. Afterwards it was removed from the furnace for cooling to room temperature. Clear red plate-shaped crystals had formed on the wall of the vial (estimated yield of single crystals: 5 %).

Synthesis of $[(W_6I_8)(CH_3CN)_6](BF_4)_4 \cdot (CH_3CN)_2$ (III) A thimble was filled with 150 mg (39.9 mmol) $[W_6I_{11}(CH_3CN)_3](I_7) \cdot 4 I_2$ and 33 mg (159.4 mmol) $AgBF_4$ and placed in a Soxhlet extractor. A round flask with 120 ml of acetonitrile was connected to the extractor. The flask with acetonitrile was heated under reflux for 16 h and then cooled to room temperature. After the extraction the solvent showed a yellow color, white and small amounts of yellow precipitate were at the bottom of the flask. The yellow solution was collected and the acetonitrile evaporated to give a yellow crystalline powder and small plate-shaped crystals (yield: 74 mg; 34.0 μ mol; 67 %). Both the powder and the crystals showed orange luminescence when irradiated with UV light. $[(W_6I_8)(CH_3CN)_6](BF_4)_4 \cdot 2 (CH_3CN)$ could be handled in air but showed a slight color change after remaining in air for two weeks. 1H -NMR ($[W_6I_8(CH_3CN)_6]^{4+}$, 400 MHz, CD_3CN) δ 2.77 (3H, s, CH_3). Elemental analysis for **III**: 0.69 H, 3.18 N, 5.39 C; calculated with co-crystallized solvent 0.86 H, 4.01 N, 6.87 C without solvent 0.67 H, 3.10 N, 5.32 C. IR: 2999 (C–H), 2937 (C–H); 2312 ($C \equiv N$), 2281 ($C \equiv N$); 1660 ($C \equiv N$), 1564 ($C \equiv N$); 1410 (C–H), 1367 (C–H), 1284 (C–H); 1055 (C–H); 519 (W–N).^{422–425}

4.4.2 Single-Crystal X-ray Diffraction

The single-crystal X-ray diffraction (XRD) studies on the obtained compounds $[(W_6I_8)I(CH_3CN)_5](I_3)_2(BF_4)_4$, $[(W_6I_8)(CH_3CN)_6](I_3)(BF_4)_3 \cdot H_2O$,

$[(W_6I_8)(CH_3CN)_6](BF_4)_4 \cdot (CH_3CN)_2$ were performed using a Rigaku XtaLab Synergy-S diffractometer with Mo- K_α radiation ($\lambda = 0.71073$ Å) and a mirror monochromator. Yellow or red plate-shaped single-crystals were used for the measurement under N_2 cooling at 100 K. Corrections for absorption effects were applied with CrysAlisPro 1.171.41.65a (Rigaku Oxford Diffraction, 2020). The structure was solved by direct methods (SHELXT),⁴²⁶ and full-matrix least-squares structure refinements were performed with SHELXL-2014⁴²⁷ implemented in Olex2 1.3-ac4.

4.4.3 Luminescence Studies

Excitation and emission spectra of powder samples of $[(W_6I_8)(CH_3CN)_6](BF_4)_4 \cdot (CH_3CN)_2$ were collected by using a fluorescence spectrometer FLS920 (*Edinburgh Instruments*) equipped with a 450 W xenon discharge lamp (*OSRAM*) and a cryostat "*MicrostatN*" from *Oxford Instruments* as the sample chamber for adjusting the atmosphere during the measurements and to adjust the temperature. Additionally, a mirror optic for powder samples was applied. For detection, a *R2658P* single-photon-counting photomultiplier tube (*Hamamatsu*) was used. All photoluminescence spectra were recorded with a spectral resolution of 1 nm, a dwell time of 0.5 s in 1 nm steps and 2 repeats.

4.4.4 Density Functional Theory

Density functional theory (DFT) was used to calculate the ELF of **III** and $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$ within the Abinit software package.⁴²⁸ Calculations were performed using a 36 Ha planewave basis set energy cutoff and $2 \times 1 \times 2$ (**III**) and $2 \times 2 \times 2$ ($(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$) Monkhorst–Pack grids⁴²⁹ of k points. Norm-conserving pseudopotentials were used as received from the Abinit library. Example

input files are available as part of the Electronic Supplementary Material.³⁶⁷

4.4.5 Transient Absorption Spectroscopy

Pump probe spectroscopy was conducted using a femtosecond transient absorption spectrometer (HELIOS Fire) and a nanosecond transient absorption spectrometer (EOS Fire) from Ultrafast Systems. 90 fs excitation laser pulses at 1 kHz repetition rate and 800 nm wavelength were generated with an Astrella-F ultrafast Ti:sapphire amplifier from Coherent and split into a pump and probe beam. The pump beam wavelength was varied by nonlinear frequency mixing and second harmonic generation in an Apollo-T optical parametric amplifier from Ultrafast Systems, from which monochromatic 300 nm or 390 nm pulses with approximately 1 μ J per pulse or 2 μ J per pulse were obtained. For the femtosecond experiments, a broadband probe spectrum from 320 to 640 nm was generated by focusing the 800 nm probe beam onto a CaF₂ crystal by nonlinear processes, while a mechanical delay stage controlled the pump-probe delay. For the nanosecond experiments, a photonic crystal fiber-based white-light probe continuum from 380 to 800 nm was generated and the pump-probe delay was controlled electronically.

All samples were prepared in dry acetonitrile under inert conditions in a quartz glass microcuvette with an optical path length of 2 mm and an optical density of 0.2 and 0.4 at 300 nm.

Global analysis was performed using the free software program Glotaran.²²³

4.4.6 NMR studies

The ¹H-NMR spectrum was recorded from acetonitrile-d₃ solution at room temperature on a Bruker AVII+ 400 spectrometer.

4.4.7 IR Studies

FTIR spectra of **III** and acetonitrile were recorded on a Bruker vertex 70 spectrometer. For solid **III** a KBr disk and for liquid acetonitrile a drop between two KBr disks was measured.

4.4.8 Elemental Analyses

Elemental Analyses was obtained using a UNICUBE apparatus from ELEMENTAR.

4.5 Conclusion

Solvated [W₆I₈]⁴⁺ clusters were synthesised in three different compounds. Among them is the homoleptic [(W₆I₈)(CH₃CN)₆]⁴⁺ cluster cation, having the same electron cluster count as [(W₆I₈)I₆]²⁺. The excited state properties were investigated by photoluminescence and transient absorption measurements. The emission maximum of solid [(W₆I₈)(CH₃CN)₆](BF₄)₄·2(CH₃CN) is observed at $\lambda_{\text{em,max}} = 630$ nm and therefore in a quite similar range as [W₆I₈L₆]²⁺ clusters bearing electron withdrawing ligands. Results of the transient absorption measurements revealed excited state absorption with three different components. Two of them featuring short decay times on the picosecond scale, while the short one is attributed to an excited singlet state and the longer one to a hot triplet state. This is in good agreement with a previous report on octahedral molybdenum halide clusters.⁹⁹

Observations of longer time scales reveal a single component absorption with a lifetime of 12 μ s, which we attribute to the excited triplet state of **III** which are supporting the results of the decay measurements for solid **III** (11 μ s) and in acetonitrile solution (12 μ s). Compared to other clusters like (TBA)₂[W₆I₈(CO₂C₃F₇)₆] with reported lifetimes being up to 55 μ s, these photoluminescence lifetimes appear short. In contrast to the behavior of (TBA)₂[W₆I₈(CO₂C₃F₇)₆]

the quenching of the luminescence in presence of molecular oxygen is low.

Additionally, the photoluminescence studies on **III** showed a higher FWHM of the emission compared to $(\text{TBA})_2[\text{W}_6\text{I}_8(\text{CO}_2\text{C}_3\text{F}_7)_6]$ and a blue shift of the emission going to higher temperatures, indicating stronger participation of higher lying triplet sublevels. A comparison of the ELF of **III** and $(\text{TBA})_2[\text{W}_6\text{I}_8(\text{CO}_2\text{C}_3\text{F}_7)_6]$ revealed higher electron density on the tungsten atoms and a less ionic bonding in **III**.

This observation suggests a strong influence of the metal-to-L bond polarity on the photoluminescence properties of octahedral molybdenum or tungsten halide clusters. High bond polarity is achieved using strong electron withdrawing ligands such as fluorinated ligands, leading to tungsten or molybdenum halide clusters with long lasting luminescence and strong oxygen quenching.

Time- and Temperature-Resolved Triplet Dynamics in Tungsten Iodide Clusters

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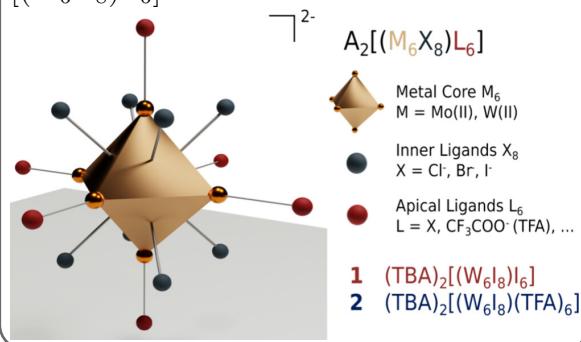
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5.1 Abstract

This study comprehensively investigates the excited-state dynamics of two tungsten iodide prototype clusters, $[(W_6I_8)I_6]^{2-}$ and $[(W_6I_8)(TFA)_6]^{2-}$ (TFA = trifluoroacetate), utilizing a combination of ultrafast transient absorption spectroscopy from 200 fs up to 400 μ s and temperature-dependent emission spectroscopy from 4 to 340 K. Both clusters exhibit rapid intersystem crossing occurring within 6 ps, populating triplet states that subsequently deactivate through emission or dynamical bimolecular quenching involving molecular oxygen. The temperature-dependent emission behavior aligns well with a group-theoretical spin-sublevel model, indicating three distinct emissive sublevels. However, contrary to previous findings in molybdenum-based clusters, no additional splitting of the lowest triplet states was observed experimentally. Time-dependent density functional theory calculations highlight substantial excited-state geometrical distortions, suggesting limitations in sole group-theoretical descriptions. Instead, we propose a relativistic model with three thermally accessible excited-state geometries, each presenting three triplet sublevels.

was demonstrated to yield a bright and long-lived luminescence in the far-red to NIR.²⁸² Upon exposure to oxygen, the excited state can be efficiently quenched through the generation of singlet oxygen, which was first described in 1990.¹⁸ In the following years, various ligand-substituted molybdenum and rhenium-based clusters have been synthesized and optimized toward higher luminescence quantum yields, enhancing their potential for oxygen sensing, bioimaging, and cancer therapy.^{15,16,284–289,291,292,294,431} Since 2016, corresponding tungsten iodide clusters have been reported with photoluminescence and singlet oxygen generation quantum yields compared to molybdenum-based counterparts.^{17,19,114,290,296}

Chart 5.1: Structure of Octahedral Hexanuclear M(II) Clusters of the Type $[(M_6X_8)L_6]^{2-}$.



5.2 Introduction

Octahedral transition metal halide clusters have long been of interest due to their intriguing structural diversity and remarkable optical properties. As illustrated in **Chart 5.1**, they are characterized by a central metal octahedron ($M = Mo(II), W(II), Re(III)$) surrounded by eight tightly bound face-capping inner ligands ($X =$ halogenide for $M(II)$ or chalcogenide for $M(III)$) and six exchangeable apical outer ligands ($L = X, RCOO^-, tosyl^-, \dots$) as $[(M_6X_8)L_6]^{2-}$.^{20,112,294} In 1981, the excitation of $(TBA)_2[(Mo_6Cl_8)Cl_6]$ (TBA = tetra-n-butylammonium) with blue to UV light

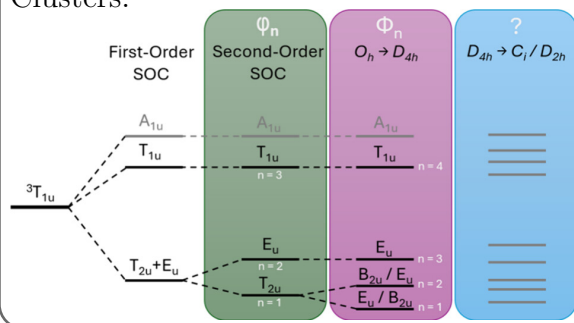
The origin of the unusual broad emission and high sensitivity to temperature and ligand has been discussed by several research groups. There is evidence that these clusters undergo intersystem crossing (ISC) into emissive triplet states, which can transfer their energy to molecular oxygen under the formation of singlet oxygen.^{18,19,99,114,316,383} However, studies regarding the excited singlet state are limited. Time-resolved photoluminescence spectroscopy on crystalline $(TBA)_2[(Mo_6Cl_8)Cl_6]$ indicates singlet-state emission between 600 and 1100 ps.³²⁵ Contrarily, transient absorption spectroscopy (TAS) of molybdenum clusters in solution implied an ISC within 2 ps, followed by a hot triplet cooling within 5 ps.⁹⁹ For the clus-

ter cation $[(W_6I_8)(CH_3CN)_6]^{4+}$, we recently reported ISC times of 2 ps, followed by an additional relaxation within 90 ps.³⁶⁷

Most importantly, the nature of the emissive triplet states has been debated controversially, with input from several theoretical and experimental investigations. Azumi and Saito discussed the splitting of several low-energy states due to electron repulsion and spin-orbit coupling (SOC).³¹⁶ In their nonrelativistic calculations, they identified the $^3T_{1u}$ state as the emissive state, splitting into four sublevels T_{2u} , E_u , T_{1u} , and A_{1u} in O_h geometry (compare **Chart 5.2**, green patch). Due to an allowed dipole transition, T_{1u} is predicted to have the strongest emission, outcompeting the higher lying forbidden A_{1u} state. This model, using three emissive states, was able to model the temperature-dependent emission, e.g., for Mo(II),³¹⁷ Ru(II),³²⁰ Pt(II),³¹⁸ and Ir(II) complexes.³¹⁹ However, the need for a fourth emissive component at temperatures below 10 K emerged recently for Mo(II)-based clusters.²² Kitamura and co-workers studied a comprehensive $[(Mo_6X_8)L_6]^{2-}$ cluster series and found that four emissive sublevels not only modeled the data better but also revealed strong correlations between the ligand nature and the strength of the cluster sublevel splitting.^{106,323,324} They rationalized this fourth component by symmetry lowering due to Jahn-Teller distortion from O_h to D_{4h} , resulting in a splitting of the T_{2u} state into B_{2u} and E_u (compare **Chart 5.2**, purple patch). Following their notation, the model using three emissive sublevels due to SOC will be named the φ_n model, while the ϕ_n model uses four emissive sublevels due to a combination of SOC and symmetry lowering. However, for $[(Re_6S_8)Cl_6]^{4-}$ and $[(W_6Cl_8)Cl_6]^{2-}$, the authors could not identify a statistical justification of the ϕ_n model over the φ_n model.²² Relativistic quantum chemical density functional theory (DFT) calculations support symmetry lowering of the excited triplet states, leading to a loss of degeneracy from the O_h symmetry ini-

tially assumed by the φ_n model. Besides the symmetry reduction to D_{4h} , further distortions to D_{2h} , C_{2v} , or C_s are also observed for Mo(II), W(II), and Re(III) clusters, which are not accounted for by the ϕ_n model (compare blue patch in **Chart 5.2**).^{20,21,321,322} Complementary experimental evidence for such symmetry-breaking relaxations comes from the combined time-resolved photoluminescence and quantum-chemical study of Costuas et al. on $[(Mo_6Br_8)Br_6]^{2-}$, revealing at least two distinct emissive triplet states arising from sizable geometrical relaxations in the triplet state.^{20,432} Furthermore, they revealed that the emission properties can depend on the excitation wavelength and the irradiation type, further emphasizing that vibronic coupling and SOC alone cannot explain the observed emission properties.

Chart 5.2: Lowest-Lying Excited Triplet State Spin Sublevel Models of M(II) Clusters.^{22,316}



Resolving the nature and splitting of the emissive triplet sublevels is essential as it directly impacts oxygen sensing accuracy, photodynamic therapy efficiency, and the reliability of bioimaging techniques. Clarifying this photophysical model will enable a more precise tuning of cluster properties, significantly enhancing their practical applicability in biomedical contexts.

Although the emission properties of $[W_6X_8)L_6]^{2-}$ have been extensively studied in the past decade, low-temperature or excited-state studies remain limited. Aside from the mentioned study on crystalline $(TBA)_2[(W_6Cl_8)Cl_6]$,²² we are not aware of any other experimental research addressing

this fundamental question about the nature of the emissive triplet states in W(II) cluster complexes.

Here, we approach this long-standing question by analyzing the prototype $(\text{TBA})_2[(\text{W}_6\text{I}_8)\text{I}_6]$ cluster **1** (red) and $(\text{TBA})_2[(\text{W}_6\text{I}_8)(\text{TFA})_6]$ (TFA = trifluoroacetate) cluster **2** (blue) in solution and dispersed in poly(methyl methacrylate) (PMMA). We combine ultrafast TAS, nanosecond TAS, and temperature-dependent emission (PL) spectroscopy with scalar relativistic time-dependent DFT (TDDFT) calculations to draw a clearer picture of the excited-state properties of W_6I_8 cluster complexes. As a result, we report ISC times, oxygen quenching rates, and triplet splitting characteristics based on the tested models. We find that three sublevels are sufficient to describe the experimental observations of tungsten iodide clusters. However, calculated excited-state geometries indicate a complete loss of degeneracy, resulting in three thermally accessible triplet sets. Each of these nine states contributes to the ensemble emission, albeit through slightly different excited-state geometries. To our knowledge, this is the first spectroscopic quantification of ISC rates and the triplet sublevel splitting in anionic $[(\text{W}_6\text{I}_8)\text{L}_6]^{2-}$ clusters and its mechanistic correspondence to distinct relaxed excited-state geometries.

5.3 Experimental Section

5.3.1 Sample Preparation and Containers

1 and **2** were synthesized following published protocols.^{19,295} Briefly, WCl_6 and SiI_4 react at 120 °C, forming W_3I_{12} , which can be converted with CsI at 550 °C to $\text{Cs}_2[(\text{W}_6\text{I}_8)\text{I}_6]$. The cation can be exchanged in solution with tetra-*n*-butylammonium iodide ((TBA)I), forming **1**, and the *apical* ligand can be ex-

changed via salt metathesis with $\text{Ag}(\text{TFA})$, forming **2**.

All spectroscopic measurements (steady-state absorption and emission, emission lifetime, and TA) were conducted on samples prepared either in acetonitrile solution or embedded in PMMA thin films, as described below.

For the spectroscopic measurements in solution, HPLC-grade acetonitrile was distilled over molecular sieves and subsequently purified by neutral Al_2O_3 (Brockmann activity I) chromatography in a glovebox. The cluster concentrations for the TA and steady-state absorbance experiments were set to 60 μM (optical density at 350 nm (OD_{350}) $\cong$ 0.1) and 30 μM for the PL experiments, respectively.

For the spectroscopic measurements in a PMMA thin film, the microcrystalline cluster and PMMA were dissolved in absolute acetone and mixed to achieve a cluster concentration of 0.33 mg/mL or 100 μM and a PMMA concentration of 8 wt %. The solution was spin-coated at 20 rpm on a glass substrate and dried under vacuum for 12 h (see **Figure C.1**).

Steady-state absorption and emission experiments at room temperature were performed in acetonitrile solution and in a PMMA thin film.

The TA experiments were performed in 2 mm quartz glass cuvettes from Helma Analytics, with a home-built opening featuring a stopcock with a polytetrafluoroethylene key and a septum (see **Figure C.2**). This way, the oxygen levels can be adjusted by gently bubbling a premixed N_2/O_2 stream from Westfalen Gas (5.0 purity) through a needle for 30 min.

Regular borosilicate glass NMR tubes with a screw cap and septum were used for the room-temperature and 77 K PL experiments. The oxygen level was adjusted in the same way as that for the TA experiments.

For the variable-temperature PL measurements in acetonitrile, the cluster solution was transferred into a borosilicate glass NMR

tube with J. Young valve, and gases were removed through five freeze-pump-thaw cycles. While the solution was frozen in liquid nitrogen, the upper section of the tube was melted off by using a gas burner.

5.3.2 Spectroscopic Measurements

Steady-state absorption measurements were performed on a UV-vis-NIR Cary 5000 spectrometer from Agilent Technologies.

5.3.3 Emission Spectroscopy

Steady-state spectra were measured on a Horiba Fluorolog-3 spectrofluorimeter equipped with a 450 W xenon lamp for steady-state measurements. For fluorescence lifetime measurements, a pulsed laser (PicoQuant LDH-P-C-375, $\lambda_{\text{exc}} = 371 \pm 2$ nm, pulse width ca. 50 ps FWHM, $P_{\text{max,avg}} \approx 5$ mW) was used. For phosphorescence lifetime measurements, excitation was performed with a pulsed xenon lamp (pulse width ca. 2 μ s FWHM) using the excitation monochromator pathway or using adapted burst pulse sequences (PicoQuant PDL820) with the given laser setup. Emitted light was detected by a Hamamatsu R13456 PMT (UV/vis/NIR, $200 \text{ nm} < \lambda_{\text{em}} < 950 \text{ nm}$). A double grating monochromator 320DFX (1200 grooves/nm, blazed at 330 nm or 600 grooves/nm, blazed at 750 nm) was used for spectral selection in the excitation path, while in the visible emission path, the single grating monochromators iHR550 (1200 grooves/mm, blazed at 500 nm; 950 grooves/mm, blazed at 900 nm; 1800 grooves/mm, blazed at 500 nm) and iHR320 (600 grooves/mm, blazed at 1000 nm) were used. To avoid higher-order excitation light, long-pass filter glass plates (Schott, 3 mm thickness) were used in the emission beam path when needed. To avoid longerwavelength emission of LDH-P-C-375, we used a 475 nm Techspec (Edmund optics) short-pass filter (OD > 4.0) in front of the laser diode.

To obtain more stable lifetime results for the variable-temperature experiments, the determination of the PL lifetimes was realized as a TRES (time-resolved emission spectra) measurement. This involved the determination of the luminescence decays at 5–6 wavelengths of the emission band and the global fitting of these decays.

5.3.4 Cryogenic Emission Spectroscopy

For 77 K PL spectra, solvents forming a glass upon rapid cooling were preferred but were not compulsively used. For cooling and spectrum detection, the sample tube within a quartz dewar (Horiba/PTI) filled with liquid nitrogen was placed into the light path.

Temperature-dependent PL measurements in the range of 4–340 K were carried out using a Horiba Fluorolog-3 with the same general instrument configuration as described above but equipped with a closed-cycle helium cryostat CS204-X1.AI operated with a helium compressor module ARS-4HW (Advanced Research Systems) and a temperature controller LS-335 (Lake Shore Cryotronics). The cryostat was configured with high-purity quartz windows (W-X1HPQ) and with a custom-made copper sample holder for borosilicate glass tubes (outer diameter 5 mm, length ca. 2.5 cm). The cryostat volume was evacuated with a regular oil pump, reaching at least 10^{-2} hPa during the operation. The temperature was measured by using the standard silicon diode sensors of the cryostat attached to the base of the sample holder. The sample tubes containing the samples were about 5 cm below the temperature sensor.

5.3.5 Transient Absorption Measurements

TAS was conducted with a fs TA spectrometer HELIOS Fire and the ns-TA spectrometer EOS Fire, both from Ultrafast Systems. 90 fs laser pulses at a repetition rate of 1 kHz

and 800 nm central wavelength were generated with an Astrella-F ultrafast Ti/sapphire amplifier from Coherent. The fundamental beam was split into a pump and probe beam, and the wavelength of the pump was adjusted to 350 nm by using the fourth harmonic of the signal in the optical parametric amplifier Apollo-T from Ultrafast Systems. The pump intensity was set between 0.5 and 1 $\mu\text{J}/\text{pulse}$ to exclude nonlinear dynamics (photons per molecule $< 2\%$). Impure excitation light and scattered light were purged with appropriate filters. For the fs experiments, a white-light continuum (WLC) from 320 to 650 nm was generated with a CaF_2 crystal, while for the ns experiments, the WLC was generated with a photonic crystal fiber. The delay between the pump and probe was altered by a mechanical delay stage for the ultrafast experiments up to 2 ns, while for the ns pump-probe measurements, the delay up to 450 μs was controlled electronically. To account for energy fluctuations, a reference channel for the probe was used, and multiple scans were acquired and averaged. The samples were stirred, and the integrity of the samples was confirmed with absorption measurements before and after the experiments.

5.3.6 TDDFT Calculations

DFT and TDDFT calculations were performed in ORCA 6.⁴³³ For the calculations, the hybrid functional PBE0 was employed alongside Grimme’s D4 dispersion correction, and scalar relativistic effects were accounted for using the eXact Two-Component (X2C) Hamiltonian.^{434–446} Specifically, excited-state geometry optimizations used the diagonal local approximation to the unitary transformation matrix (DLU approximation) within the X2C calculation.⁴⁴⁷ A triple- ζ basis set optimized for X2C (X2C-TZVPPALL) and its corresponding auxiliary set (X2C/J) were used to ensure accurate representation of the electronic structure.^{448,449} Spin-orbit effects were handled with the RI-SOMF(1X) approach,

and a Gaussian finite nucleus model was applied.⁴⁵⁰ The strict self-consistent field (SCF) convergence criterion, TightSCF, was used alongside TightOPT for geometry optimization.

As initial input geometry, a structure from single-crystal X-ray diffraction was used. The preoptimized structure DFT (PBE0|X2C-TZVPPALL) was used for the TDDFT geometry optimizations of the structures of ground and excited states, including spin-orbit coupling. For TDDFT calculations of the spectra, typically, the 50 lowest singlet and triplet excited states/transitions (50 roots) were requested, corresponding to 200 transitions in the spin-orbit-coupled TDDFT calculation.

5.3.7 Model Fitting and Software

Emission data were acquired using FluorEssence and DataStation, both from HORIBA Scientific. PL lifetime data analysis (deconvolution, statistical parameters, etc.) was performed using the DAS6 software package from Horiba. The decay data were analyzed by tail-fitting (exclusion of the lamp-pulse region). The emission lifetime was calculated by globally fitting the emission kinetics at least at five different wavelengths using DAS6 from HORIBA Scientific.

TA data were acquired with the software Surface Xplorer 4.5, while the data were processed and fitted in Python 3.11 using the packages NumPy, SciPy, Matplotlib, and lmfit.³⁷⁸

Sublevel-model fitting of the temperature-dependent emission data was performed in Python using lmfit, and the posterior distribution of parameters was evaluated using emcee.³⁷³

5.4 Results and Discussion

5.4.1 Steady-State Properties

Before analyzing the excited-state properties in acetonitrile and PMMA, **1** and **2** were examined by UV/vis absorption and photoluminescence spectroscopy to manifest a possible influence of the solvent and PMMA. This comparison is depicted in **Figure 5.1 A**. At room temperature, we observe the first broad absorption shoulder at around 417 nm and a second band at 355 nm for both clusters, independent of the matrix. For **1**, the asymmetric emission is centered around 700 nm in acetonitrile and 695 nm in PMMA matrix, respectively, while for **2**, the emission maximum is blue-shifted at 675 nm for acetonitrile and PMMA. The values in solution at room temperature are consistent with other reports.^{19,114} The comparable spectra regardless of the medium lead us to the conclusion that the clusters are well dispersed in the PMMA matrix and that cluster-cluster or cluster-polymer interactions are negligible for the concentrations used in this study. The emission lifetimes at 298 K in solution are in line with the lifetimes in PMMA for both compounds, which further support this claim. The photophysical properties of **1** and **2** are summarized in **Table 5.1**.

Figure 5.1 B, C compares the excitation and emission spectra of **1** and **2** at 4 K and room temperature. We note that the excitation spectra at room temperature in PMMA match well the absorbance spectra from **Figure 5.1 A**. At 4 K, the peaks get narrower, revealing maxima at 470, 408, and 363 nm for **1** and 450, 400, and 353 nm for **2**.

Likewise, the emission bands get narrower and more symmetrical at 4 K, accompanied by a hypsochromic shift of 13 nm for **2**. The temperature dependence is consistent with published emission data on related compounds^{22,106,323,324,367} and will be analyzed in detail below.

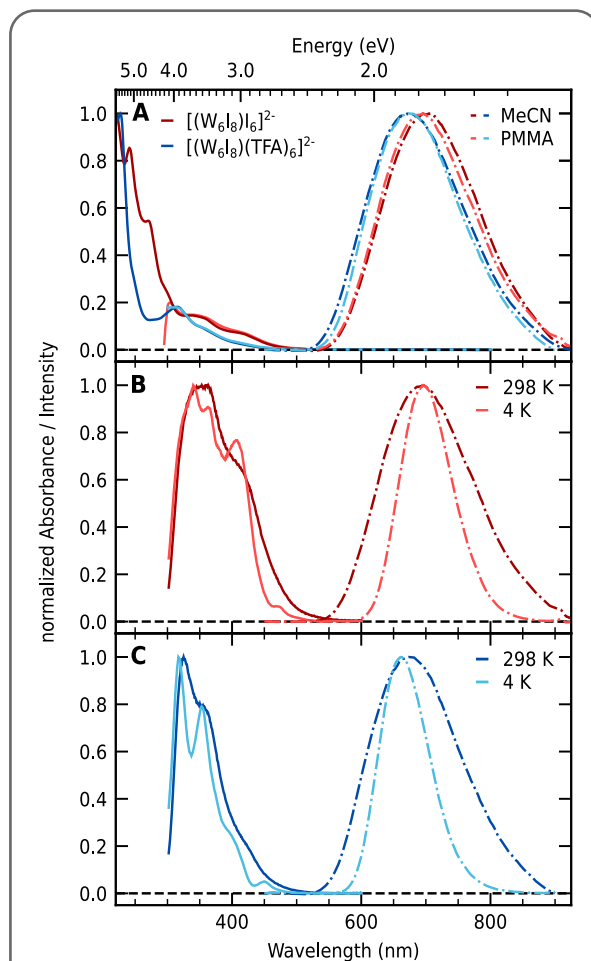


Figure 5.1: Optical properties of **1** (red) and **2** (blue). **(A)** Absorbance (straight) and emission (dashed) at 298 K in an acetonitrile (dark) and PMMA matrix (bright). The excitation wavelength was 370 nm for all of the emission measurements. Note that the glass substrate used for the PMMA films has a wavelength cut-off of 310 nm. **(B, C)** Excitation (straight) and emission (dashed) spectra of **1** and **2** in PMMA at room temperature (dark) and at 4 K (bright).

5.4.2 Ultrafast Spectroscopy of Excited States

We sought to identify the correct sublevel model for **1** and **2**, respectively, by a variety of complementary time-resolved spectroscopy experiments. We begin our investigation with femtosecond TAS, where we

Table 5.1: Photophysical properties of **1** and **2** at 297 K in acetonitrile and PMMA.

Compound	$\lambda_{\max}$ / nm	FWHM / meV	τ_T (PL) / μs	τ_T (TAS) / μs	k_q (PL) / $10^8 \text{ M}^{-1}\text{s}^{-1}$	k_q (TAS) / $10^8 \text{ M}^{-1}\text{s}^{-1}$	ISC / ps
1 (TBA) ₂ [(W ₆ I ₈)I ₆]	700, 695 ^a	438, 434 ^a	27, 24 ^a	22	9.9	9.2	4
2 (TBA) ₂ [(W ₆ I ₈)(TFA) ₆]	675, 675 ^a	481, 447 ^a	38, 34 ^a	33	3.5	3.7	6

^aCorresponding data in PMMA.

follow the excited-state properties and relaxation pathways for both clusters from 100 fs up to 2 ns (**Figure 5.2**). **Figure 5.2 A** shows a background-corrected femtosecond 2D transient absorption spectrum of **1** in acetonitrile. The analysis of the femtosecond TAS experiments of **2** can be found in **Appendix C.2**. The differential absorbance is color-coded, where blue means a loss in absorbance of the excited sample compared to the unexcited sample and red represents a gain in absorbance. Upon excitation with 90 fs laser pulses at 350 nm, we find broad excited-state absorption (ESA) over the whole spectral range superimposed with ground-state bleaching at the steady-state absorbance maxima due to Pauli blocking and ground-state depletion (compare the absorbance spectrum in red above the 2D plot). Analysis of the kinetics at 500 nm (**Figure 5.2 B**) reveals three distinct components, which can be fitted by a sequential exponential model with lifetimes of 130 fs, 4 ps, and a lifetime larger than the measurement window (coefficient of determination $r^2 = 0.99$). More details on the selected sequential model and the variability in the fitting results can be found in **Appendix C.2**. Global fitting over the whole spectral range with the same model gives comparable lifetimes ($r^2 = 0.98$), with the corresponding evolution-associated difference spectra (EADS) shown in **Figure 5.2 C**. We note that the second and third components have a similar spectral evolution, while the first differs more. The ultrafast first component has a lifetime close to the instrument response function (IRF) of our system of 200

fs and is overlaid by the solvent response and so-called coherent artifacts, which are very prominent within the first 500 fs. The TA spectrum of the pure solvent under the same experimental conditions is analyzed in **Appendix C.2**. Since the first component mainly originates from the solvent response and coherent artifacts, we will not include it in the following analysis.

5.4.3 Excited Triplet State Properties and Oxygen Quenching

In continuation of our time-resolved analysis, we now use nanosecond TAS to specifically study the long-lived component in further detail. We find that under inert conditions, the third component decays monoexponentially with lifetimes of 22 μs for **1** and 33 μs for **2**. This component can be quenched reversibly by oxygen down to 90 ns for **1** and 250 ns for **2** with an oxygen-saturated atmosphere. In **Figure 5.3 A**, the kinetic traces at 500 nm of **1** (red) and **2** (blue) at different oxygen concentrations are depicted together with their monoexponential fits (compare with **Table C.2**). The covariance matrix was used to estimate the uncertainties of the fit, yielding errors around 10 %. For the first two components, we do not observe any oxygen dependence on the kinetics.

We hypothesize that the third component corresponds to an emissive triplet state, which should exhibit similar kinetics in TAS and PL lifetime measurements. To test this, we conduct time-resolved photoluminescence as a third technique using the same oxygen

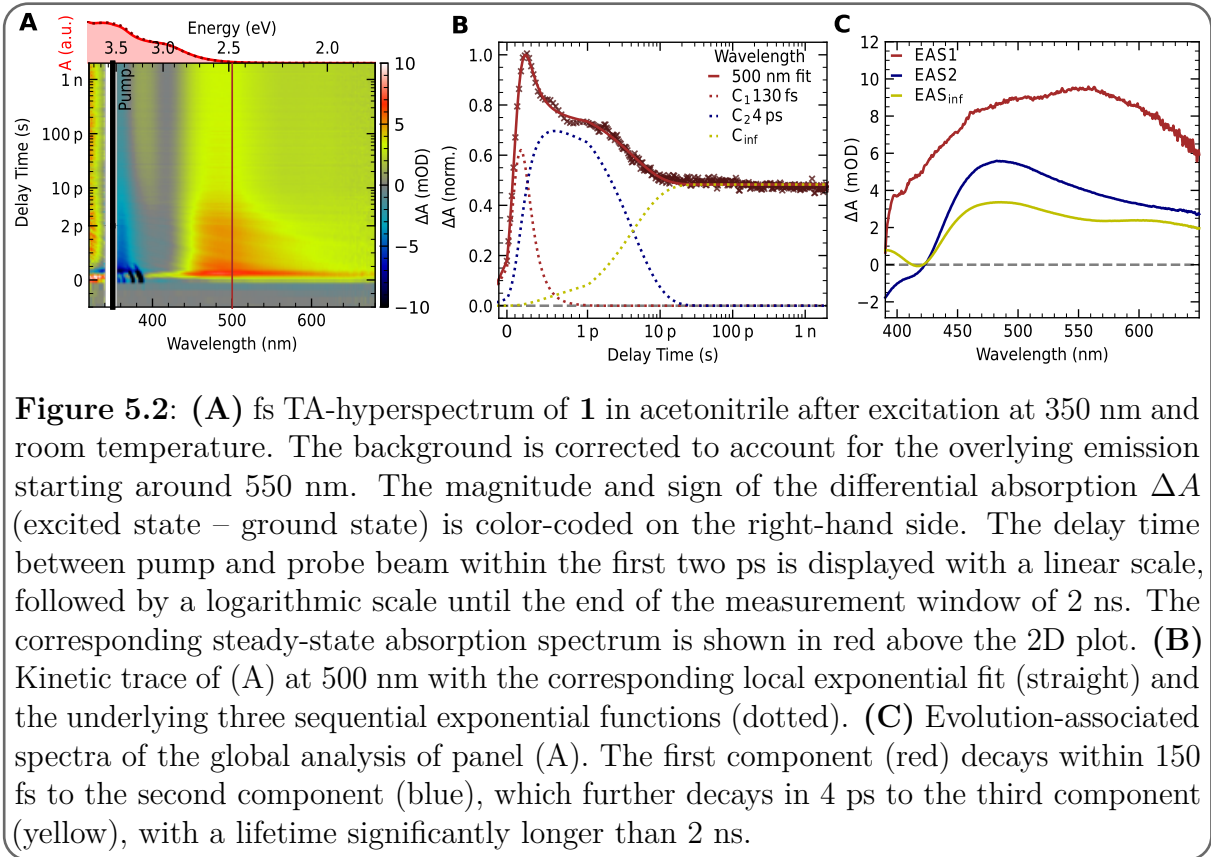


Figure 5.2: (A) fs TA-hyperspectrum of **1** in acetonitrile after excitation at 350 nm and room temperature. The background is corrected to account for the overlying emission starting around 550 nm. The magnitude and sign of the differential absorption ΔA (excited state – ground state) is color-coded on the right-hand side. The delay time between pump and probe beam within the first two ps is displayed with a linear scale, followed by a logarithmic scale until the end of the measurement window of 2 ns. The corresponding steady-state absorption spectrum is shown in red above the 2D plot. (B) Kinetic trace of (A) at 500 nm with the corresponding local exponential fit (straight) and the underlying three sequential exponential functions (dotted). (C) Evolution-associated spectra of the global analysis of panel (A). The first component (red) decays within 150 fs to the second component (blue), which further decays in 4 ps to the third component (yellow), with a lifetime significantly longer than 2 ns.

concentrations as for the ns TA experiments (compare **Appendix C.3**). As detailed in **Figure 5.3 B**, the inverse lifetimes as a function of the oxygen concentration in both experiments are in good agreement, which supports our hypothesis. The linear relation between $1/\tau$ and the oxygen concentration hints to a dynamic collisional quenching, whose bimolecular quenching constant k_q can be determined using **Equation 5.1**:

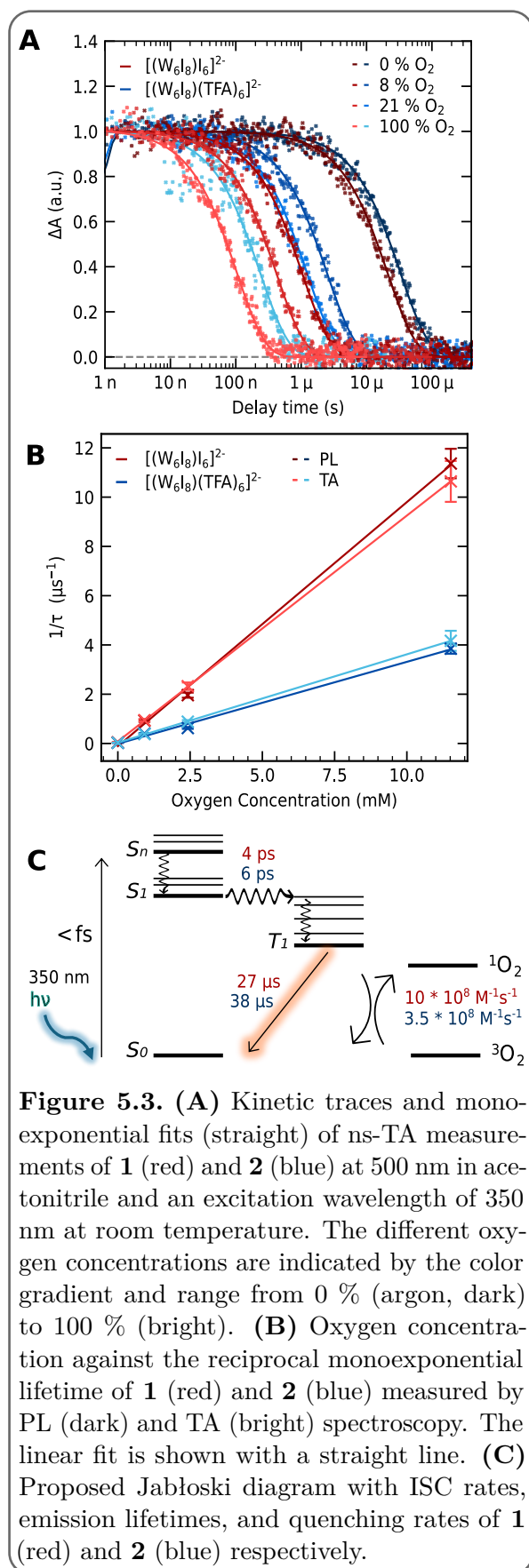
$$\frac{1}{\tau} \propto k_q \times [\text{O}_2] \quad (5.1)$$

where τ is the triplet lifetime at a given triplet oxygen concentration $[\text{O}_2]$ and k_q is the dynamic quenching constant. An oxygen concentration of 2.42 mM in acetonitrile exposed to synthetic air was used.⁴⁵¹ The values are summarized in **Table 5.1** and are in accordance with published work using emission spectroscopy to derive the quenching rates.^{19,114} The deviations of the lifetimes and subsequently the bimolecular quenching constants are within the error estimates of

10 % for the TA experiments and 5 % for the PL measurements, respectively. We assume that most of the deviation originates from uncertainties in setting and maintaining the oxygen concentration for and during the experiment, especially since TA experiments take significantly longer than corresponding PL experiments (h vs min).

The findings of the TA and PL verify the previous assumption that the third component observed in the TA experiments is the emissive triplet state and lead us to the conclusion that the second component is an excited singlet state. Following this reasoning, both clusters would undergo an ultrafast ISC into a long-lived triplet state within 6 ps. This is in accordance with our recent work on a related cationic tungsten iodide cluster, where we found an ISC occurring within 2.2 ps.³⁶⁷ In that study, we found an additional excited state decaying within 90 ps, which we could not observe in the current study.

The electronic transitions and lifetimes are summarized in a Jabłoski diagram in **Fig-**



ure 5.3 C. The observation that the clusters relax to their final excited state (third component) within picoseconds with no significant deactivation occurring over 6 orders of magnitude is remarkable. This behavior accounts for their high phosphorescence quantum yields and pronounced sensitivity to oxygen. Note that these systems experience strong spin-orbit coupling, making singlet and triplet states lose their strict identity. It would therefore be more precise to describe these as mixed states with, e.g., a dominant singlet or triplet character.

Kirakci et al. investigated, with similar experimental conditions, molybdenum clusters and also found three components with comparable lifetimes and spectral shapes.⁹⁹ They assigned the first component to an excited singlet state and the second component to a hot triplet state, relaxing to the third emissive component. This contrasts with our observations that the first component mainly originates from the solvent response and coherent artifacts close to the resolution limit. However, to this point, we cannot exclude the possibility that these features overshadow additional components close to our IRF.

Within experimental uncertainty, the temporal and spectral evolution of the ultrafast TA signals is comparable for both clusters studied and closely matches that reported for the cationic tungsten iodide cluster and molybdenum-based analogues.^{99,367} In all cases, the spectrum is dominated by a broad and unstructured ESA, revealing a multitude of contributing electronic states superimposed with ground-state bleaching, in line with steady-state absorbance data. The only significant difference is a modest variation in oscillator strength imposed by the axial ligands, highlighting that the ultrafast photophysical properties are mainly driven by the M_6X_8 core.

5.4.4 T-Dependent Emission Characteristics in Solution

To further investigate the excited-state properties of the emissive triplets, we performed a series of temperature-dependent measurements from 4 to 340 K. At every temperature step, besides an emission spectrum, lifetimes were measured at least at 5 different emission wavelengths and globally fitted to increase the stability of the fit (see **Section 5.3** for more details). Although measurements in solution involve a more elaborate sample preparation, more scattered light in frozen solvents, and a phase transition, they should reflect the fundamental photophysics better than polymer matrices or microcrystalline samples due to their well-defined and uniform properties. In acetonitrile, we found that below the melting point, the kinetics for **1** consistently changed from a mono- to a biexponential decay with lower overall lifetimes (see **Figure C.7**). In preliminary experiments, we identified that the addition of (TBA)I reversed this and led to a longer and monoexponential decay in the solid state. This hints to a dynamic exchange reaction in solution and a disturbed and eventually frozen equilibrium while falling below the melting point, which is beyond the scope of this study (see **Appendix C.4** for a more detailed discussion). In the following study in PMMA, we did not observe this behavior.

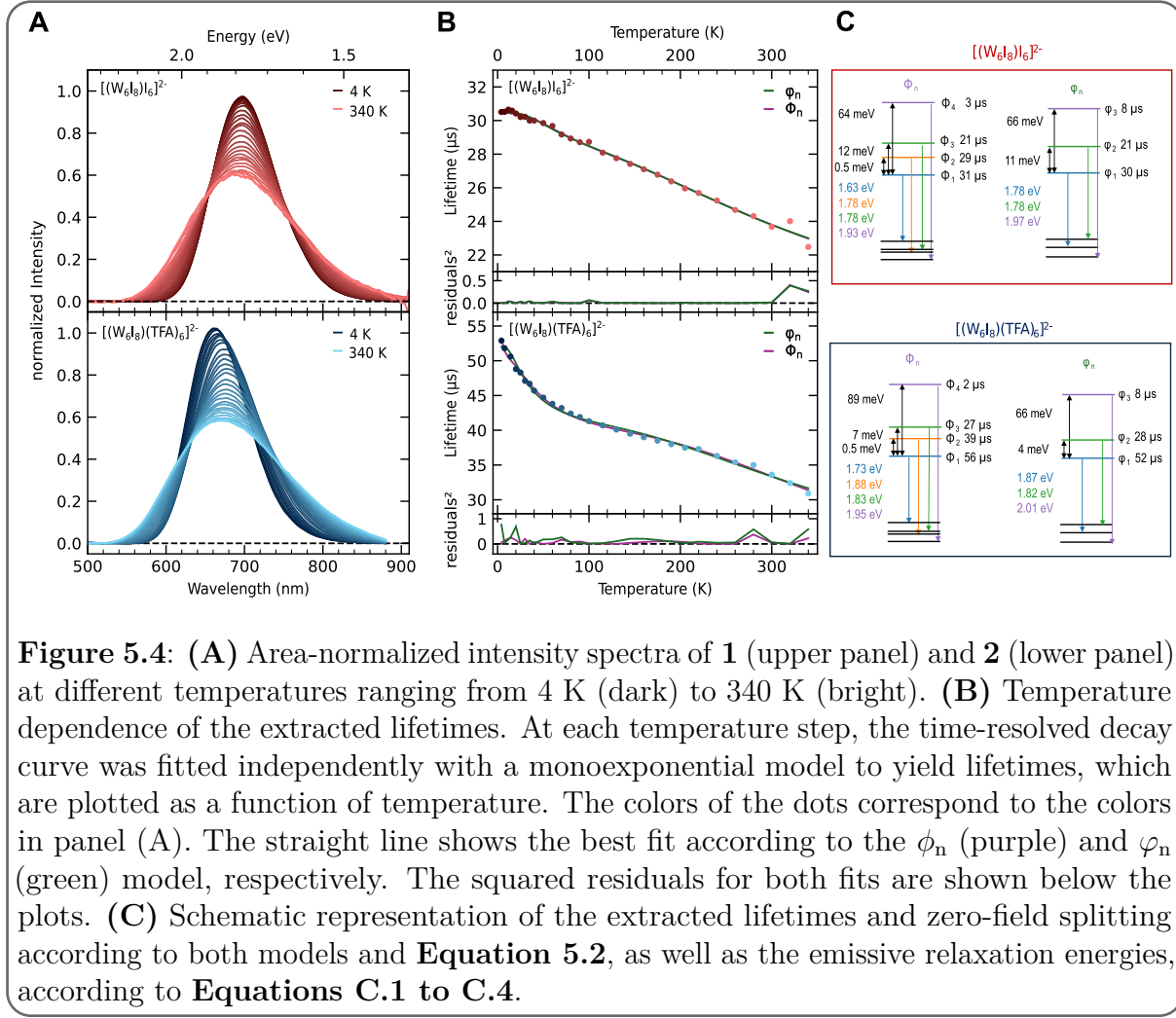
5.4.5 T-Dependent Emission Properties in PMMA

The temperature-dependent emission spectra and lifetimes for both clusters in PMMA are shown in **Figure 5.4**, with color-coded temperature steps ranging from 4 K (dark) to 340 K (bright). At each step, an emission spectrum and multiple lifetimes were measured. In the emission spectra in **Figure 5.4 A**, an asymmetrical broadening can be observed for both clusters upon increasing the temperature (compare FWHM values in

Table 5.2 and **Figure C.9**). However, a significant shift of the emission maximum can only be determined for **2**. Here, the maximum shifts from 4 and 662 to 675 nm toward 60 K and subsequently remains constant up to 340 K. In **Figure C.9**, the emission maxima and FWHM are displayed against the temperature.

The resulting lifetimes are shown in **Figure 5.4 B**. For **1**, we find a monotonous, quasilinear decrease in the lifetime. In contrast, **2** features a sharp decrease in lifetime within the first 60 K, followed by an inflection point at around 150 K and subsequently a more gradual decrease (**Table 5.2**). It is noticeable that the dynamics found in the emission spectra are also reflected in the lifetime changes. While the spectral and kinetic evolution of **1** shows a more continuous course, the prominent emission shift upon increasing the temperature from 4 to 60 K for **2** correlates with a sharp decrease in the lifetime.

Especially for **1**, the emission and lifetime changes as a function of temperature appear to be small. From 4 K to room temperature, the relative lifetime change $\Delta_{\tau_{4-300\text{ K}}}$ is 20 % for **1** and 38 % for **2**. Kitamura and co-workers found lifetime changes in a crystalline $(\text{TBA})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_8]$ sample from 42 μs at 3 K to 8 μs at 300 K, which results in a $\Delta_{\tau_{4-300\text{ K}}}$ of 81 %.²² Although high-resolution, temperature-dependent emission and lifetime measurements of tungsten clusters are scarce, related molybdenum clusters have been studied in more detail.^{22,106,323,324} Temperature-dependent emission measurements of $[(\text{Mo}_6\text{I}_8)(\text{n-C}_3\text{F}_7\text{COO})_6]^{2-}$ revealed a comparable temperature sensitivity with a $\Delta_{\tau_{4-300\text{ K}}}$ of 31 %.³²³ In a follow-up study,³²⁴ the influence of the inner and apical ligands of $[(\text{Mo}_6\text{X}_8)\text{L}_6]^{2-}$ has been investigated further. In the series of $[(\text{Mo}_6\text{X}_8)\text{I}_6]^{2-}$, the temperature sensitivity of the lifetime decreased gradually from $\Delta_{\tau_{4-300\text{ K}}} = 78\%$ for $\text{X} = \text{Cl}$, over 70 % for $\text{X} = \text{Br}$, to 55 % for $\text{X} = \text{I}$. In contrast, for $(\text{Mo}_6\text{X}_8)\text{Br}_6$ or a variation of the *apical* ligands, a trend could not be

**Table 5.2:** Temperature-dependent parameters for **1** and **2** (4–300 K).

Compound	$\Delta\lambda_{\max}$, 4–300 K / meV	FWHM _{4K}	Δ FWHM 4–300K	τ_{4K} / K	$\Delta\tau$ 4–300K	φ_n model		ϕ_n model	
						ΔE_{1n} / meV		ΔE_{1n} / meV	
1 (TBA) ₂ [(W ₆ I ₈)I ₆]	< 1%	243	44%	30	20%	$n = 2 : 11$	$n = 3 : 66$	$n = 2 : 0.5$ (fixed)	$n = 3 : 12$ $n = 4 : 64$
2 (TBA) ₂ [(W ₆ I ₈)(TFA) ₆]	2%	254	43%	53	38%	$n = 2 : 4$	$n = 3 : 66$	$n = 2 : 0.5$ (fixed)	$n = 3 : 7$ $n = 4 : 89$

found. Although the authors identified a correlation between the properties of the ligands and the strength of the energy splitting of the triplet spin sublevels, no systematic change in the intrinsic emission lifetimes of these sublevels could be discerned. Given that the observed thermally equilibrated monoexponential lifetime is dependent on both

the population and intrinsic emission lifetimes of the contributing spin sublevels, a prediction of the measured equilibrated lifetimes is not trivial.

5.4.6 T-Dependent Emission Lifetime Model in PMMA

As detailed in **Section 5.2**, the symmetry-based spin-sublevel model was successfully applied for various molybdenum cluster complexes and explained systematic changes of the zero-magnetic-field splitting as a consequence of a change in electron density at the metal center.^{106,324} In the following, we fit and simulate our data with the proposed φ_n model using three triplet sublevels due to SOC and the ϕ_n model using four nondegenerate sublevels due to a combination of SOC and symmetry lowering due to Jahn-Teller distortion. For the lifetime fit, we assume that every emitting level is in a Boltzmann equilibrium at any temperature. Hence, the overall lifetime as a function of temperature can be described as a sum of thermally activated individual rates as expressed in **Equation 5.2**:

$$\tau(T) = \frac{\sum_n g_n e^{-\frac{\Delta E_{1n}}{k_B T}}}{\sum_n \frac{g_n}{\tau_n} e^{-\frac{\Delta E_{1n}}{k_B T}}} \quad (5.2)$$

where g_n and τ_n are the degrees of degeneracy (see **Table C.8**) and emission lifetimes of the sublevel φ_n or ϕ_n , respectively, and ΔE_{1n} is the energy difference between $\varphi_1 \rightarrow \varphi_n$ or $\phi_1 \rightarrow \phi_n$ ($\Delta E_{11} = 0$). Furthermore, the ϕ_n model predicts a constant energy difference ΔE_{12} of 4 cm⁻¹ or 0.5 meV due to Jahn-Teller distortion.³²⁴

In **Figure 5.4 B**, the results of the fitting of the φ_n (green) and ϕ_n models (purple) are shown. We were not able to fit the data with only two components. Statistically, both models describe the temperature dependence of **1** equally well with a coefficient of determination (r^2) of 0.994 for the φ_n model and $r_{\phi_n}^2 = 0.995$. This is also found in the square of the residuals below the plot, showing no significant improvement of the ϕ_n model over

φ_n . The additional degree of freedom of the ϕ_n model is compensated by the small difference in lifetime of ϕ_1 and ϕ_2 of only 6 %. For **2**, we find a minimal improvement of the fit noticeable in the residuals below 20 K with coefficients of determination of $r_{\varphi_n}^2 = 0.995$ and $r_{\phi_n}^2 = 0.998$. In the literature on molybdenum clusters, $r_{\phi_n}^2$ values between 0.982 and 0.999 are calculated.^{323,324} This indicates that our data and fit quality are comparable, although the lifetimes of tungsten clusters are normally about 1 order of magnitude faster than equivalent molybdenum clusters. Just based on the $\tau(T)$ data, a statistical justification of four sublevels instead of three is questionable, especially for **1**. Based on the Bayesian information criterion (BIC), the φ_n model is slightly preferred for **1**, and the ϕ_n model is preferred for **2**. However, potential systematic errors in temperature measurements, which are hard to model, may become particularly significant at lower temperatures. Based on a more elaborate analysis of the posterior probability distribution of the parameter space (see **Appendix C.5**), the absolute values of the energy splitting and lifetimes should be considered as rough estimates due to correlations between sublevel splitting and the corresponding lifetime.

The extracted lifetimes and energy differences of the sublevels for both clusters and models are summarized in **Figure 5.4 C** and **Table 5.2**. The variability of the fits can be found in **Table C.4**. Note that the provided relaxation energies from the excited states to the relaxed ground states are based on the evaluation of the temperature-dependent emission spectra in **Figure 5.5**. The sublevel splitting therein is consistent with published work on $[(\text{Mo}_6\text{I}_8)\text{l}_6]^{2-}$ ($\Delta E_{13} = 8.7$ meV, $\Delta E_{14} = 91$ meV) and $[(\text{W}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ ($\Delta E_{13} = 5$ meV, $\Delta E_{14} = 77$ meV).^{22,324} By introducing an electron-withdrawing ligand with trifluoroacetate, the ϕ_n model predicts an increase in the zero-magnetic-field splitting, which we could observe for ΔE_{14} , but not for ΔE_{13} .

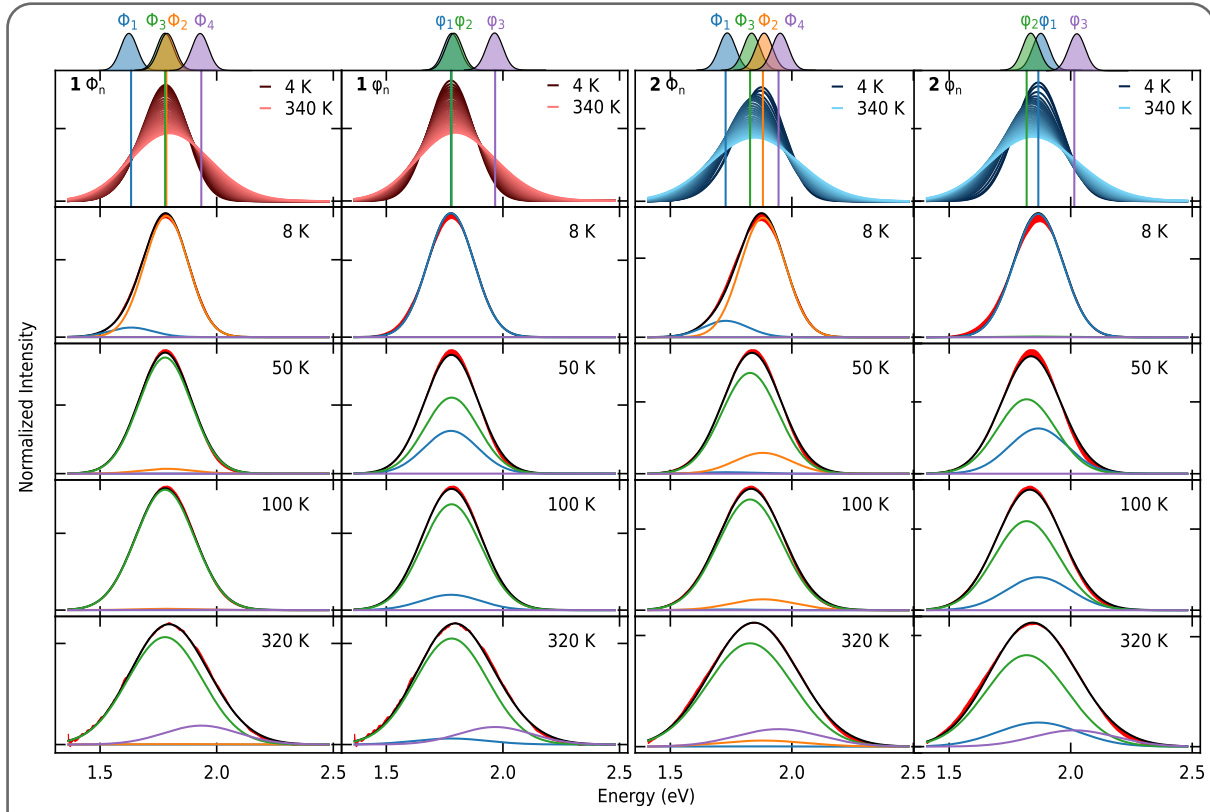


Figure 5.5: Simulated and observed temperature-dependent emission spectra of **1** (first two panels) and **2** (third and fourth panel) based on ϕ_n (left) and the φ_n model (right). The energy positions of the states are shown in the first row. The spectral contribution of each sublevel to the overall fit (straight black line) is shown at selected temperatures. The residuals between the experimental data and the fit are highlighted in red.

5.4.7 T-Dependent Emission Spectrum Model in PMMA

Based on the applied model, each sublevel contributes to the overall emission with an intrinsic emissive rate, emission maximum, and FWHM. At low temperatures, only the lowest sublevels should be populated, while with increasing temperature, the higher lying states become thermally accessible. Additional information is given in **Appendix C.6**. We tested this model on the emission spectra of **Figure 5.4 A** by applying the calculated zero-magnetic-field splitting of the sublevels from the lifetime measurements. The FWHM for every sublevel is kept constant at a given temperature, and a homogeneous Doppler broadening ($\propto \sqrt{T}$) is assumed.

Figure 5.5 shows the results of the intensity simulations according to **Equations C.1 to C.4**. The first two columns show the fits of **1** using the ϕ_n model with four sublevels and the φ_n model using three sublevels, respectively. The same is displayed for **2** in the third and fourth column. The emission maximum of each sublevel E_n is depicted in the first row, and their corresponding spectra, as well as the envelope (straight black line), are displayed. When comparing the residuals between experimental and modeled data (highlighted in red), we find that both models can describe the emission data of **1** and **2** very well ($r^2 < 0.996$). At temperatures below 50 K, the additional splitting in the ϕ_n model leads to a small improvement, which is most noticeable for **2**. Note that the lowest-lying sublevel ϕ_1 only leads to a small correction at temperatures below 8 K (first

column and third column, blue component), which compensates the additional parameter in the ϕ_n - over the φ_n model. This observation is consistent with the lifetime fits in **Figure 5.4**, where we found no or only a slight improvement with the ϕ_n model.

The fitting results are depicted in **Figure 5.4 C** and **Table C.5**. A detailed statistical analysis of the fitted models can be found in **Appendix C.5**.

Based on these results, we find no clear experimental evidence that more than three energetically nondegenerate states are present for **1** and **2**, which is in line with the low-temperature investigations of crystalline $(\text{TBA})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]$.²² We conclude that the additional spitting of the lowest-lying state (e.g., $\text{T}_{2u}\{\text{O}_h\} \rightarrow \text{E}_u + \text{B}_{2u}\{\text{D}_{4h}\}$) predicted by the ϕ_n model is not required to describe the temperature-dependent emission data of octahedral W(II) clusters. To further interpret these findings, we performed TDDFT calculations of **1**, which will be discussed in the following section.

5.4.8 TDDFT Computations

Although the φ_n/ϕ_n models include SOC and possible deformations, they are based only on group-theoretical symmetry considerations, resulting in a fine-structure splitting of the triplet states.

We performed TDDFT geometry optimizations, including scalar relativistic effects and SOC of the ground state (“SOC0”) and the three lowest-lying excited states (“SOC1-3”) based on a hybrid density functional that mixes PBE with Hartree-Fock exchange (see **Section 5.3** for more details). In **Figure 5.6**, the calculated absorbance spectrum with the underlying transitions of **1** from the geometry-optimized SOC ground state SOC0 is shown, as well as the steady-state absorbance spectrum from **Figure 5.1**. We determine good agreement between our theoretical calculations, including relativistic SOC, and the experimental data.

As a result of the geometry optimization of the lowest excited SOC states, we found

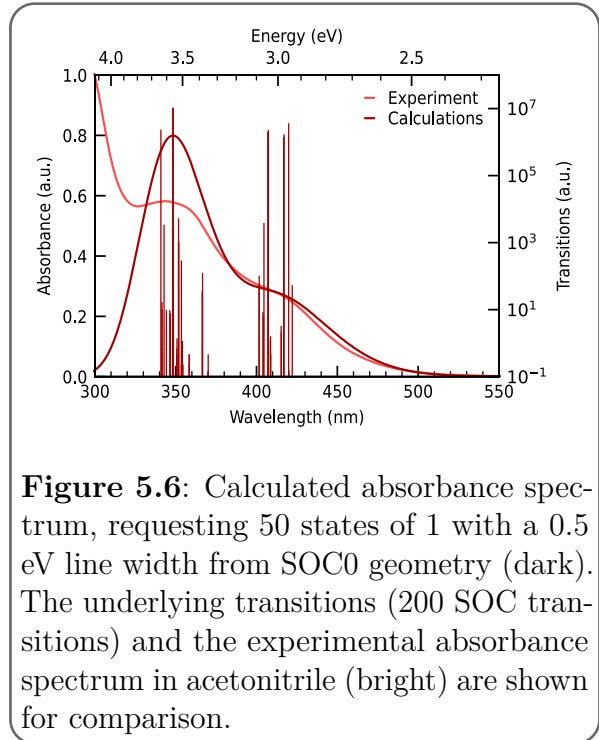


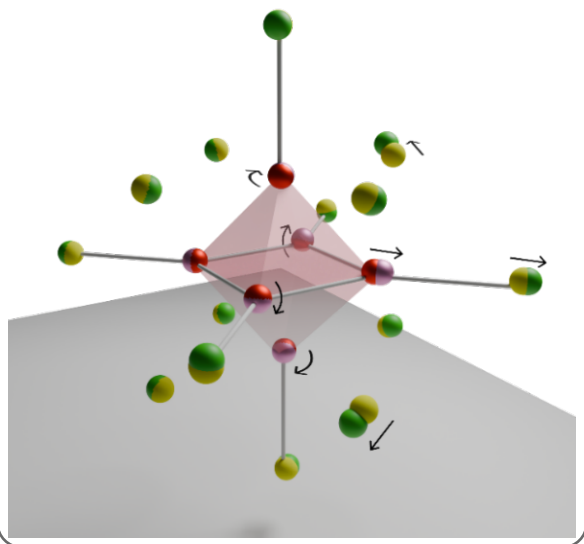
Figure 5.6: Calculated absorbance spectrum, requesting 50 states of **1** with a 0.5 eV line width from SOC0 geometry (dark). The underlying transitions (200 SOC transitions) and the experimental absorbance spectrum in acetonitrile (bright) are shown for comparison.

significant distortions in the geometry relaxations, which are presented in **Chart 5.3** and **Table C.17**. Here, the SOC0 (W = red, I = yellow) and SOC1 (W = purple, I = green) geometries of **1** are depicted. We found that the symmetry of the O_h breaks by an outstretching of one W-I axis, accompanied by a movement of two adjacent inner iodide ions and a subtle twisting of the whole metal core. This is in line with TDDFT calculations on $[\text{Mo}_6\text{Br}_{14}]^{2-}$ by Cordier and colleagues,²⁰ who found a deformation of the metal core in the lowest triplet states, resulting in a similar symmetry reduction (C_{2v} , C_s , C_1). The optimized SOC2 and SOC3 geometries can be found in **Chart C.1**. Note that this reduction in symmetry to C_{2v} or even C_s for SOC2 would already mean a complete loss of degeneracy of the initially well-defined triplet states involved in the φ_n/ϕ_n models.

We report the sublevel energies of the SOC ground state and SOC1-3 geometries, as well as their corresponding mixture of the non-relativistic basis states in **Chart 5.4** and **Tables C.9 to C.12**.

We find that the three lowest excited states of each SOC geometry have mainly triplet

Chart 5.3: Distortions Found in the SOC1 Geometry (W = Purple, I = Green) Compared to SOC0 Geometry (W = Red, I = Yellow).



character, while from the fourth level onward, significantly more states mix in. The theoretical calculations reveal that the energy barrier for the fourth substate (350 meV) is too high to allow a significant thermal population even at room temperature ($E_{rt} \cong 26$ meV). These results support the luminescence data of both clusters, where only three distinct states were observed. The calculated relaxation energies from the respective excited-state geometry to the ground

state and energy splitting within a single excited-state geometry are consistent with experimental data and fitted results, showing values of approximately 2 eV compared to 1.8 eV, and 4 and 16 meV compared to 12 and 66 meV.

We note that all three SOC geometries are close in energy, composition, and sublevel splitting, which is in accordance with TDDFT calculations on $[\text{Mo}_6\text{Br}_{14}]^{2-}$.²⁰ Therefore, they can all contribute to the emission of the cluster, leading to a total of nine emissive states. Although these nine states are theoretically distinct and not required to be degenerate by symmetry, their energy difference can be too small to be probed individually even at 4 K, leading to a pseudo-degeneracy.

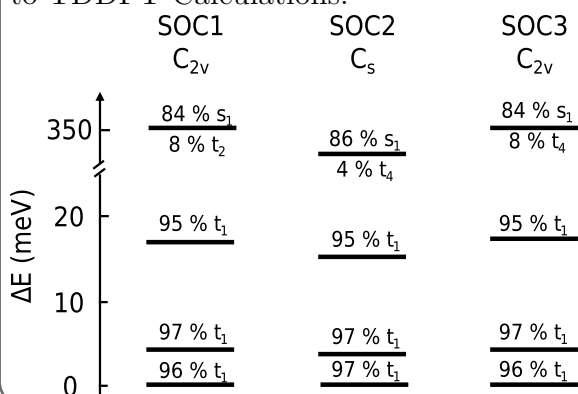
Preliminary nonrelativistic calculations for **2** indicate a comparable symmetry reduction to that observed for **1** (see **Chart C.2** and **Table C.20**).

5.5 Conclusion

In this comprehensive study, we analyzed two tungsten iodide prototype clusters $(\text{TBA})_2[(\text{W}_6\text{I}_8)\text{I}_6]$ (**1**) and $(\text{TBA})_2[(\text{W}_6\text{I}_8)(\text{TFA})_6]$ (**2**) using various time- and temperature-dependent experimental techniques. Ultrafast TAS reveals that both clusters undergo ISC within 6 ps, rapidly populating their relaxed triplet states. Subsequently, excited-state deactivation occurs via emission or dynamical bimolecular quenching through $^3\text{O}_2$, which was traced by transient absorption and emission spectroscopy.

The temperature-dependent emission characteristics of both clusters in PMMA from 4 to 340 K can be satisfactorily modeled by three emissive sublevels, as predicted by the group-theoretical φ_n model. Unlike observations in molybdenum-based clusters, no evidence for an additional splitting of the lowest triplet sublevels was detected. In

Chart 5.4: Sublevel Splitting of the Three Lowest-Lying SOC Geometries According to TDDFT Calculations.



fact, TDDFT calculations suggest significant excited-state geometry distortion, questioning whether purely group-theoretical descriptions adequately capture the emission behavior in tungsten iodide clusters. According to the model presented here, emission from the initial 9-fold degenerate triplet manifold arises from three distinct excited-state geometries, each providing three accessible triplet states. These excited-state geometries are energetically close and thermally accessible, probably leading to pseudo-degeneracy and the experimentally resolvable states. Consequently, subtle variations in ligand environment or cluster packing may influence the excited-state landscape, potentially lifting pseudo-degeneracies and uncovering additional spin-orbit-coupled sublevels.

This picture extends the Mo-based framework of Costuas et al., where at least two relaxed geometries contribute to the NIR luminescence, to tungsten iodide clusters in the methodological context of this study.²⁰

However, direct quantitative comparison across models is limited due to different experimental and computational methods and the strong influence of the different metal centers and ligands. Alternative explanations based on diffusion-controlled kinetics, solvation, or vibrational cooling can be ruled out due to the rigid PMMA matrix used and the strictly monoexponential decay trace at each temperature.

Resolving these subtleties in the emissive triplet-state manifold is critical, not only for a deeper photophysical understanding but also for advancing the practical utility of tungsten iodide clusters in biomedical imaging and oxygen-sensitive therapeutic applications. Future investigations should thus correlate subtle structural variations directly with emission properties and TDDFT calculations to enhance the predictive design of cluster-based functional materials.

The Lowest Excited State of Heptacenes Is Dark

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6.1 Abstract

Understanding the electronic structure of polycyclic aromatic compounds is of fundamental importance for their potential applications. The optoelectronic properties of shorter acenes such as tetracene and pentacene have been extensively studied with regard to excitation, emission, and nonlinear effects such as singlet fission. The longer homologues present a unique challenge due to their low stability both in the solid state and in solution. In this work, we synthesized persistent 6,8,15,17-tetrakis((triisopropylsilyl)ethynyl)heptacene and investigated its photophysical properties as well as those of the parent heptacene. Our steady-state electronic absorption and emission experiments combined with transient absorption spectroscopy show that the Franck–Condon electric-dipole-forbidden (“dark”) transition to the 2^1A_g singlet state is the lowest-energy excited state of heptacene. This contrasts with the optical properties of the well-known shorter acenes. Transient absorption data further suggest singlet fission or intersystem crossing as potential pathways to rapid population of the triplet state facilitated by the dark singlet state.

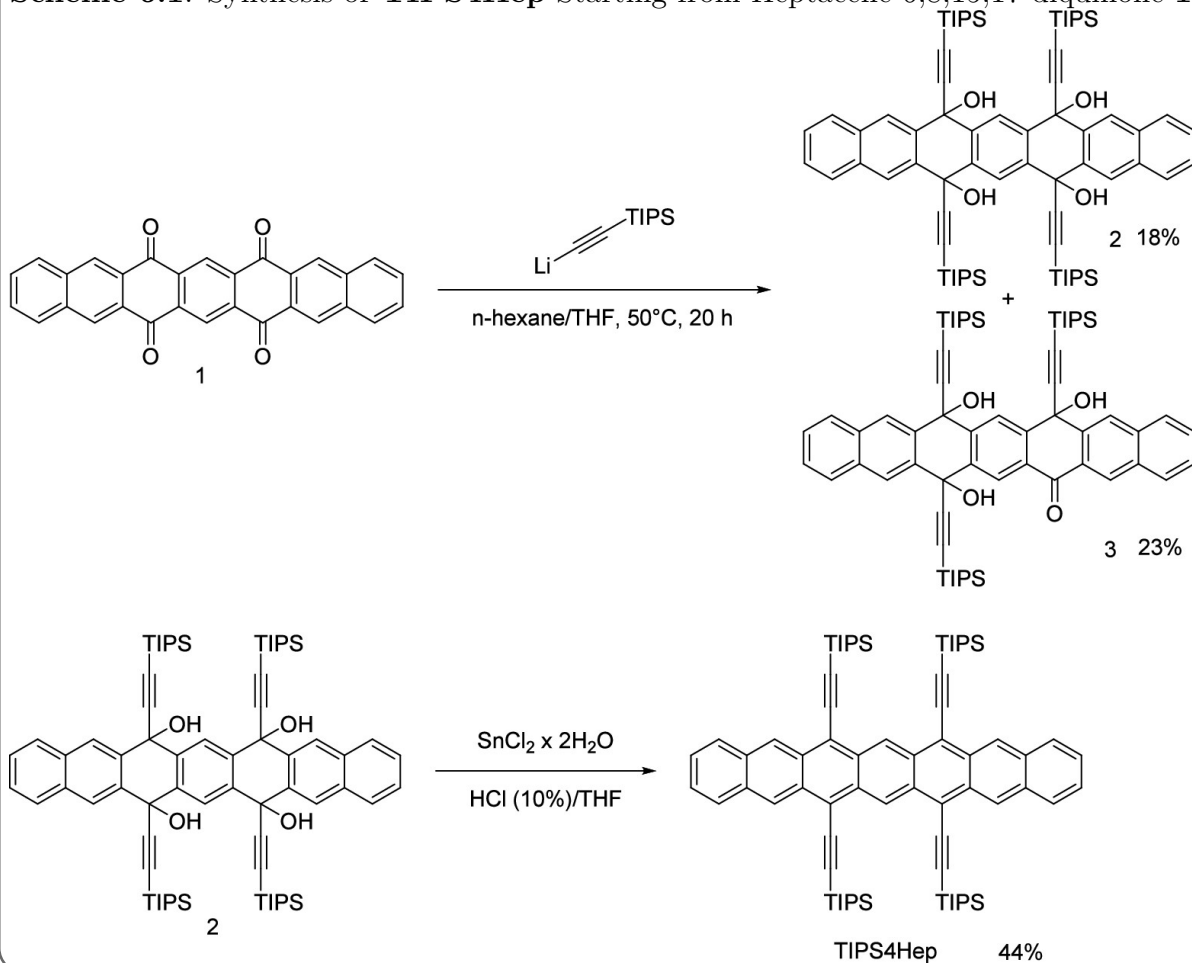
6.2 Introduction

The electronic structure of polycyclic aromatic compounds is the key to their application as organic optoelectronic materials. A particularly important class of condensed polyaromatics are oligoacenes, as their study has driven development in singlet fission research over the past decade.^{14,453,454} The energies of the lowest-energy singlet and triplet states, S_1 and T_1 , of the most important representatives, tetracene and pentacene, fulfill the energy requirement $E(S_1) \approx 2E(T_1)$ for singlet fission.^{349,453,455,456} Electronic excitation from the ground state to the S_1

state ($1^1A_g \rightarrow 1^1B_{2u}$ transition) gives rise to a prominent band (p band according to Clar,³⁴⁷ 1^1L_a according to Platt³⁴⁸) in the absorption spectra of tetracene and pentacene.³³⁰

Increasing the conjugation length results in a bathochromic shift of the 1^1L_a band due to a decrease of the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).^{332,349} A decreasing HOMO–LUMO gap can result in a change of the character of the S_1 state. For example, from octatetraene onward, polyenes have a lowest excited state that has the same symmetry as the ground state (1^1A_g).^{457–460} According to computations using the particle–particle random phase approximation in combination with density functional theory (pp-RPA-B3LYP)³⁴⁶ and the multiconfiguration coupled-electron pair approximation (MC-CEPA),³⁴¹ heptacene is the first acene in which, within the Franck–Condon approximation, the electric-dipole-forbidden $1^1A_g \rightarrow 2^1A_g$ (“dark”) transition is lower in energy than the electric-dipole-allowed (“bright”) $1^1A_g \rightarrow 1^1B_{2u}$ transition.^{341,346} The electronic absorption spectra of heptacene in solution, in a cryogenic argon matrix, and in organic glasses and polymers show a weak feature at lower energy than the 1^1L_a band that is absent in the shorter homologues.^{330,340–342,461–463} This feature, a shoulder in most cases and only in argon an individual new band,^{330,341,461} was tentatively associated with a forbidden transition in a previous study based on comparison with the computational data.³⁴¹

We reasoned that the high kinetic stability of a heptacene derivative would be beneficial for the detailed optical spectroscopic investigations and opted for the synthesis of the persistent derivative 6,8,15,17-tetrakis((triisopropylsilyl)ethynyl)heptacene (**TIPS4Hep**) (**Scheme 6.1**). During the course of our work, this compound was obtained by Bunz et al. using a different synthetic route.^{345,463} Here, by combining

Scheme 6.1: Synthesis of **TIPS4Hep** Starting from Heptacene-6,8,15,17-diquinone **1**.

steady-state and transient absorption spectroscopy of **TIPS4Hep** and the parent heptacene (**Hep**), we show that the dark state 2^1A_g becomes the lowest singlet excited state in the acene series. Unlike the conventional S_1 state (1^1L_a , 1^1B_{2u}), this dark state has a different leading electronic configuration (H^0L^2 ; $\text{H} = \text{HOMO}$, $\text{L} = \text{LUMO}$) compared to the T_1 state (H^1L^1). This change in state order facilitates energy transfer from the dark state to an excited triplet state via intersystem crossing or singlet fission because of El-Sayed’s rule.

6.3 Results and Discussion

The synthesis of **TIPS4Hep** was performed using heptacene diquinone **1** (Scheme 6.1). The latter was synthesized following the route of Baxter et al.⁴⁶⁴ In addition to the analytical data given previously (IR, UV/vis, and EA),⁴⁶⁴ we achieved characterization by HR-APCI-MS as well as ^1H NMR in D_2SO_4 (see the **Appendix D**). Treatment of the diquinone with lithium triisopropylsilylacetylide at 50°C not only gives the fourfold addition product tetrol **2** (18 %) but also the threefold addition product triol **3** (23 %). When this reaction is performed at room temperature, only threefold addition occurs. Tetrol **2** was further reduced with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ to the fully aro-

matic **TIPS4Hep** (Scheme 6.1). This reaction was performed in the absence of light in degassed solvents and gave the product in 44 % isolated yield. **TIPS4Hep** is stable enough for chromatography to be performed over a short column in the dark, thus achieving the purity needed for detailed photophysical measurements.

TIPS4Hep was fully characterized by NMR, HRMS, and single-crystal X-ray crystallography. Bunz et al. recorded the ^1H NMR spectrum in CDCl_3 and justified the broad signals with the diradicaloid character of heptacene.⁴⁶⁵ We measured the ^1H NMR spectrum in C_6D_6 and obtained sharp signals (see the Appendix D). The broadening in CDCl_3 likely stems from aggregation at the concentration required for NMR spectroscopy. We were able to measure a ^{13}C NMR spectrum in C_6D_6 (see Appendix D), while Bunz et al.⁴⁶⁵ stated that this was impossible due to the instability of **TIPS4Hep**. Unlike Bunz et al.,⁴⁶⁵ we could not detect an EPR signal in DCM, C_6F_6 , or *n*-hexane. We could grow single crystals of **TIPS4Hep** suitable for single-crystal X-ray analysis (Figure D.1, CCDC 2272243, $R = 1.9\%$) by slow evaporation of a solution in DCM/*n*-hexane. The compound crystallized in space group $P2_1/c$. Bunz et al. reported two crystal structures of this compound, one in space group $P\bar{1}$ (CCDC 2254466, C_6H_6 , $R = 5.7\%$)⁴⁶⁵ and the other one also in $P2_1/c$ (CCDC 2254465, $\text{CHCl}_3/\text{MeOH}$, $R = 5.5\%$).³⁴⁵

The absorption spectrum of **TIPS4Hep** shows unusual features in the low-energy range compared to shorter acenes besides the known p band at 851 nm (A1), namely the shoulder at 887 nm (A2) and the weak band at 1010 nm (A3) (Figure 6.1). C_6F_6 proved to be suitable for our measurements, as it does not possess any absorption bands below 2000 nm, unlike other solvents with C–H bonds (Figures D.8 and D.9). Similar features were observed for **TIPS4Hep** by Bunz et al.⁴⁶⁵ as well as for other substituted heptacenes by Anthony et al.⁴⁶² and Wudl

et al.³⁴² (Figures D.4 and D.5). Their origin was, however, not discussed in previous studies. TD-DFT calculations of the electronic absorption spectrum and the vibrational coupling for the parent heptacene cannot explain these peaks, as previously discussed (Figure D.4).³⁴¹

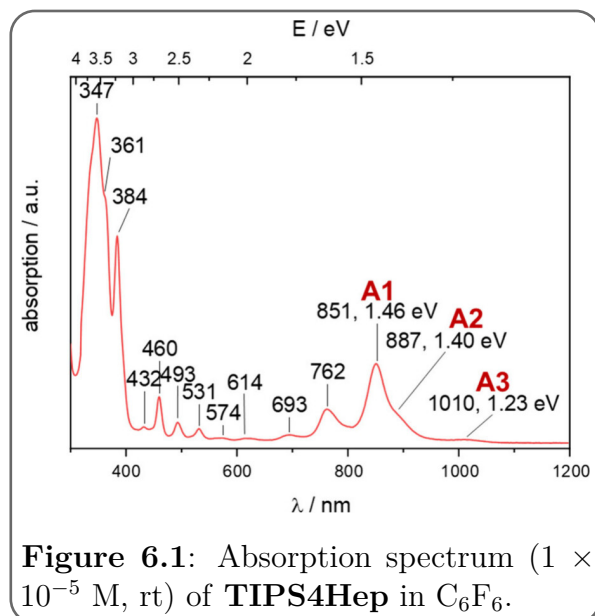


Figure 6.1: Absorption spectrum (1×10^{-5} M, rt) of **TIPS4Hep** in C_6F_6 .

We performed a series of absorption spectroscopy experiments to confirm that the shoulder (887 nm, A2) as well as the 1010 nm band (A3) are due to **TIPS4Hep**. Measurements in solvents of different polarities revealed that A2 and A3 become more prominent with increasing polarity (Figure 6.2 a). In *n*-hexane A3 was barely visible, whereas in 1:3 DCM/ CH_2I_2 shoulder A2 and A3 are most prominent. The concentration-dependent measurements (Figure 6.2 b) in the range 5×10^{-6} to 2×10^{-4} mol/L verified that neither transition is due to aggregation phenomena. Temperature-dependent measurements (Figure 6.2 c) in toluene from $+80\text{ }^\circ\text{C}$ to $-80\text{ }^\circ\text{C}$ showed that with decreasing temperature both A3 and A2 become more prominent, ruling out a possible hot band. At lower temperature another shoulder of the second vibrational progression at 800 nm appears. Oxidation of **TIPS4Hep** with $\text{Ag}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ ⁴⁶⁶ (Figure 6.2 d) resulted in a completely dif-

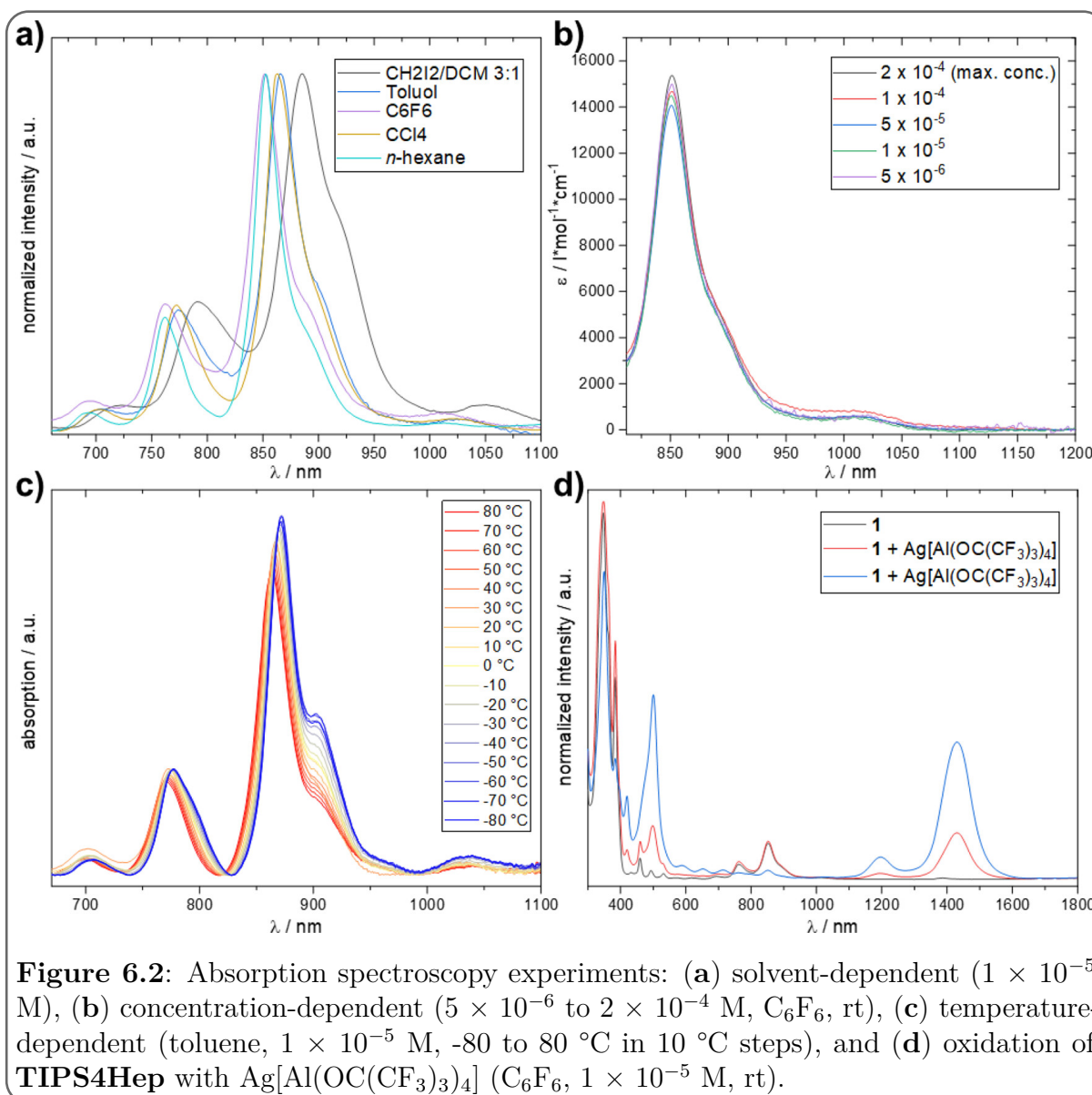


Figure 6.2: Absorption spectroscopy experiments: (a) solvent-dependent (1×10^{-5} M), (b) concentration-dependent (5×10^{-6} to 2×10^{-4} M, C₆F₆, rt), (c) temperature-dependent (toluene, 1×10^{-5} M, -80 to 80 °C in 10 °C steps), and (d) oxidation of **TIPS4Hep** with Ag[Al(OC(CF₃)₃)₄] (C₆F₆, 1×10^{-5} M, rt).

ferent spectrum, which fits into the series of monocationic acenes reported by Krossing et al.⁴⁶⁷ and is quite similar to that of the heptacene radical cation reported earlier under matrix isolation and gas-phase conditions.^{461,468} Hence, the latter experiment proves that the additional peaks are not due to traces of the radical cation. An EPR spectrum of this radical cation could be recorded (**Figure D.15**) and is comparable to the EPR signals of a radical cation of sixfold-substituted heptacene reported by Bunz et al.⁴⁶³

The shoulder A2 in the absorption spectrum of **TIPS4Hep** resembles features ob-

served previously for **Hep** under cryogenic (Ar, 10 K) and room-temperature (PMMA) matrix isolation conditions and in solution (1-methylnaphthalene, 230 °C).^{330,341,461} In the solid argon spectrum of **Hep**, a distinct band with a maximum shifted by 730 cm⁻¹ from the ¹L_a maximum is observed, while in solution there is a shoulder shifted by about 650 cm⁻¹ from the maximum to lower energies (see **Figure D.6**).³⁴¹ The shoulder in **TIPS4Hep** is similarly shifted in C₆F₆ by about 590 cm⁻¹ from the maximum. This suggests that the carrier of A2 is related in **Hep** and **TIPS4Hep**. The weak maximum of **TIPS4Hep** at 1010 nm (A3,

bathochromic shift of $\sim 1850\text{ cm}^{-1}$ with respect to the maximum), on the other hand, is not related to any known transition of **Hep**.

To investigate the possible origin of the A3 band of **TIPS4Hep** further, we employed fluorescence spectroscopy in different solvents. Characteristic for the fluorescence spectra of acenes are the small Stokes shift and the vibrational fine structure of the emission band that mirrors the absorption spectrum.³⁴⁹ The longest acene for which fluorescence spectra are known is hexacene.³⁴⁹ Fluorescence spectra of larger acenes are not available, to the best of our knowledge. We could obtain fluorescence spectra of **TIPS4Hep** in C_6F_6 , toluene, and *n*-hexane (**Figure 6.3 a**). CCl_4 and C_2Cl_4 turned out to be unsuitable, as it appears that photoexcited heptacene can react with these solvents. This was shown by a red coloration of the initially almost colorless solution (**Figure D.10**) and no detectable fluorescence. In all cases the strongest maxima of the fluorescence spectra were at very long wavelengths (C_6F_6 , 1040 nm; toluene, 1064 nm; *n*-hexane, 1031 nm). The measured spectra looked very similar, showing consistency across the measurements in different solvents. In *n*-hexane (red), more features of the spectrum are resolved, as the shoulder at 1162 nm became more prominent compared to the other solvents and another shoulder at 1220 nm could be detected. Measurements in frozen solutions at 77 K (**Figure 6.3 b**) revealed more features in toluene (1028, 1176 nm) and particularly in *n*-hexane (1019, 1064, 1158, and 1239 nm), as this solvent can form a Shpol’skii matrix,^{469–471} which surrounds the molecule with a well-defined frozen solvent structure. The features of the corresponding excitation spectra largely follow the absorption spectra (**Figure 6.3 c,d**). At higher energies, all main features are visible, but at longer wavelengths, the agreement is not as strong. Especially the band at 850 nm does not contribute to the emission as much as the less

intense absorbing peak at approximately 760 nm. This possibly stems from effects of the gratings, which do not perform very well in these wavelength regions.

To further support these measurements, we decided to take a closer look at parent **Hep**. Studying the photophysics of this molecule is quite challenging, as it can dimerize or polymerize in solution,⁴⁷² although measurement in 1-methylnaphthalene at 230 °C allowed an absorption spectrum in solution to be recorded.³⁴¹ A convenient alternative is to use a photoprecursor of **Hep** and a solid matrix, as has been shown by Neckers, Bettinger, and co-workers.^{330,340,461} In the present work, we used the monocarbonyl precursor **COHep**⁴⁷³ (**Figure 6.4**), which is known to give **Hep** upon thermolysis in the solid state, as shown by Chow et al.⁴⁷⁴ The absorption spectrum of **Hep** in an argon matrix generated from **COHep** (**Figure D.14**) is very similar to that obtained from the α -diketone precursor reported previously.^{340,473} Irradiation of the precursor **COHep** in a 2-methyltetrahydrofuran (MeTHF) glass at 77 K using a medium-pressure mercury vapor lamp and a dichroic mirror (350–450 nm) resulted in **Hep** (**Figure 6.4 a,b**), as confirmed by characteristic signals of the heptacene π system in the 700–800 nm range.^{330,340,341,461}

The fluorescence spectrum was measured under argon inside a J. Young tube in MeTHF at 77 K (for the absorption spectrum in a J. Young tube, see **Figure D.2**), and a signal at approximately 1030 nm was the only signal that we could detect (**Figure 6.4 c**). Comparison of the fluorescence excitation and absorption spectra (**Figure 6.4 d**) shows some resemblance at short wavelengths, while at longer wavelengths discrepancies are apparent. This is consistent with the fluorescence excitation and absorption spectra of **TIPS4Hep** (**Figure 6.3**) discussed above. Emission at around 1030 nm would imply a very large Stokes shift if the longest-wavelength absorption at around 800 nm were considered as the

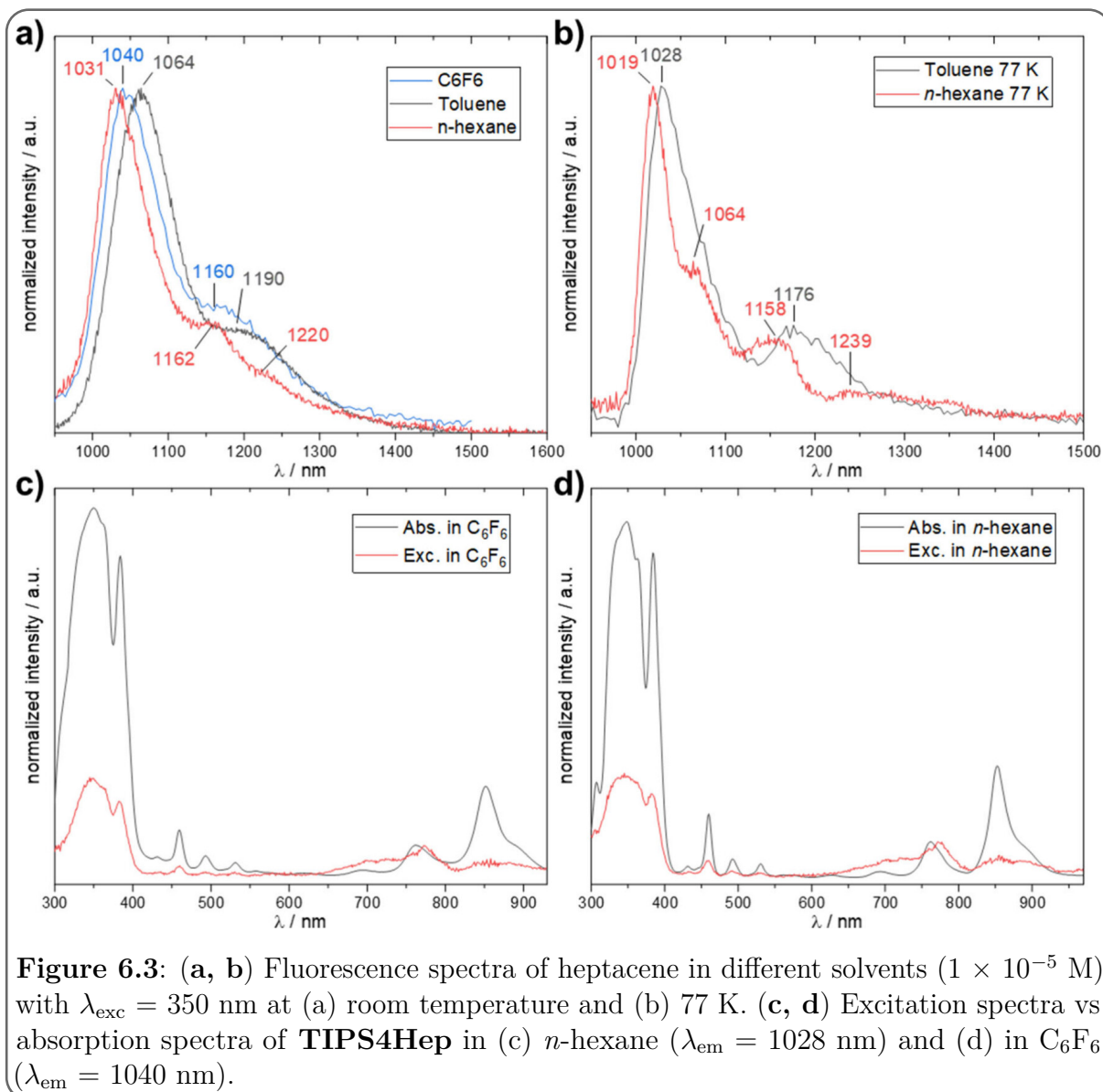
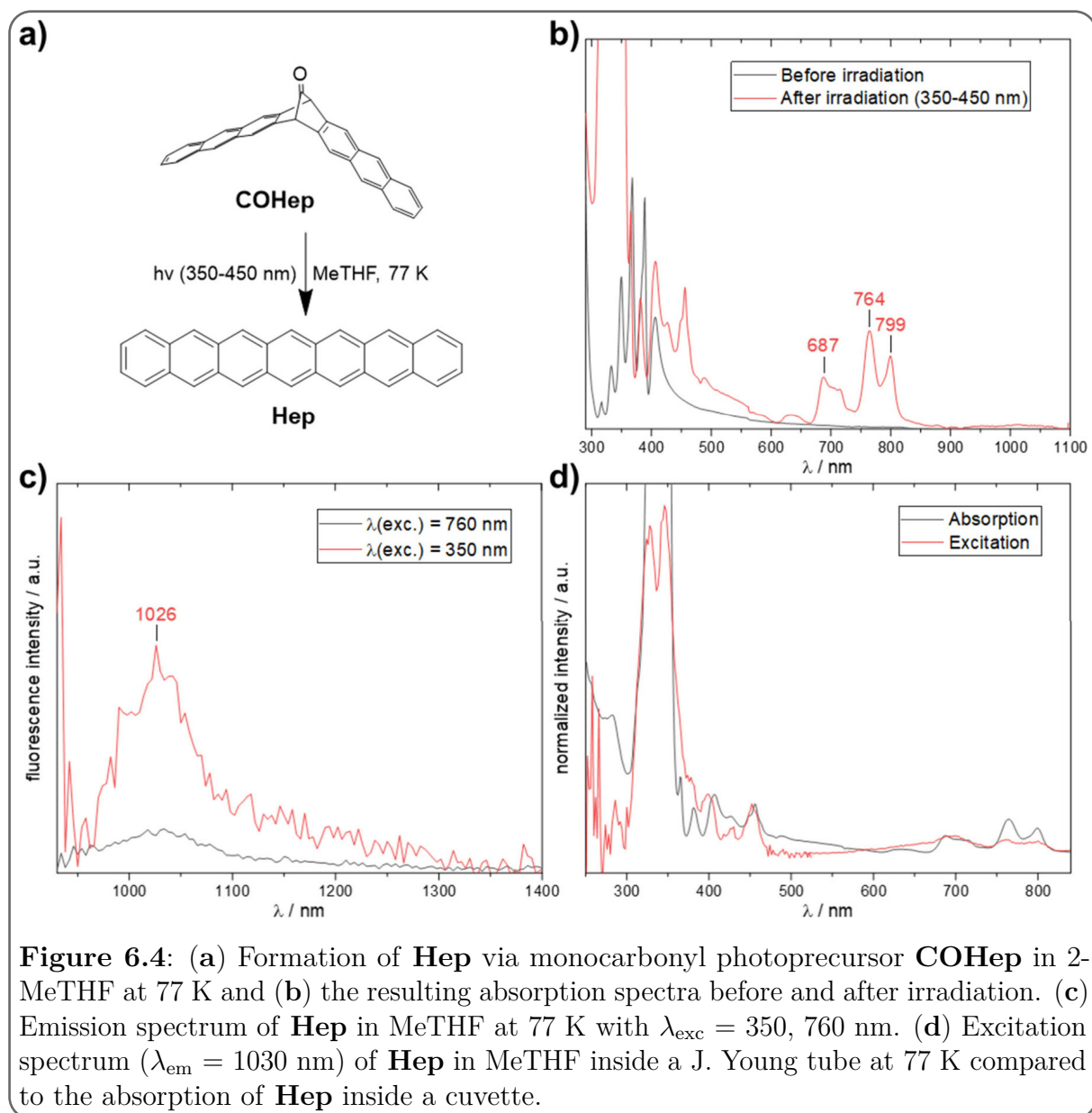


Figure 6.3: (a, b) Fluorescence spectra of heptacene in different solvents (1×10^{-5} M) with $\lambda_{\text{exc}} = 350$ nm at (a) room temperature and (b) 77 K. (c, d) Excitation spectra vs absorption spectra of **TIPS4Hep** in (c) *n*-hexane ($\lambda_{\text{em}} = 1028$ nm) and (d) in C_6F_6 ($\lambda_{\text{em}} = 1040$ nm).

emitting state, which seems highly unlikely in view of the typically very small Stokes shifts exhibited by shorter acenes.³⁴⁹

A plausible interpretation of the absorption and emission spectra of **Hep** and **TIPS4Hep** involves the 2^1A_g state as the lowest-energy excited singlet state S_1 of the heptacene framework. The lowest-energy excitation, $1^1\text{A}_g \rightarrow 2^1\text{A}_g$ ($S_0 \rightarrow S_1$), is electric-dipole-forbidden within the Franck–Condon approximation in this case and not detectable for **Hep** but appears as a low-intensity band (A3) at 1010 nm for the lower-symmetry **TIPS4Hep**. The energy difference between the p band maximum

A1 ($1^1\text{A}_g \rightarrow 1^1\text{B}_{2u}$) at 852 nm and A3 in *n*-hexane is 0.23 eV (0.23 eV in C_6F_6 , 0.22 eV in toluene, and 0.22 eV in 1:3 DCM/ CH_2I_2), which is in reasonable agreement with the energy gap computed previously for these states (0.17 eV).³⁴¹ Assuming a similar energy gap between 1^1B_{2u} and 2^1A_g for **Hep** as for **TIPS4Hep**, we would expect the $1^1\text{A}_g \rightarrow 2^1\text{A}_g$ absorption to be located at around 932 nm for **Hep**. Emission spectroscopy can reveal the $2^1\text{A}_g \rightarrow 1^1\text{A}_g$ transition due to its sensitivity for both **Hep** and **TIPS4Hep**. The Stokes shift of 0.02 eV (181 cm^{-1}) for **TIPS4Hep** in *n*-hexane is reasonably small, as typically observed for



acenes. The predicted $1^1A_g \rightarrow 2^1A_g$ absorption of **Hep** at 932 nm could correspond to a Stokes shift of 0.13 eV (1021 cm^{-1}), which appears to be too large. Adding the Stokes shift of **TIPS4Hep** to the fluorescence signal of **Hep** would lead to a predicted $1^1A_g \rightarrow 2^1A_g$ absorption at 1016 nm. Thus, we would expect the missing transition of **Hep** to be between 932 and 1016 nm. The vibrational fine structure of the fluorescence spectrum of **TIPS4Hep** indicates that the $2^1A_g \rightarrow 2^1A_g$ transition goes along with vibrational excitation, and the same must be expected for the $1^1A_g \rightarrow 2^1A_g$ absorption. The first

vibrational band in the fluorescence spectrum of **TIPS4Hep** in *n*-hexane at room temperature at 1162 nm is shifted by 1094 cm^{-1} (C_6F_6 , 995 cm^{-1} ; *n*-hexane (77 K), 1178 cm^{-1} ; toluene, 1022 cm^{-1} ; toluene (77 K), 1225 cm^{-1}) from the fluorescence origin (**Figure 6.3 a**), and assuming a similar shift in the $1^1A_g \rightarrow 2^1A_g$ absorption, the shoulder (A2) at 890 nm (C_6F_6 , 887 nm; toluene, 898 nm) is due to the vibrational feature of this transition (expected at 911 nm with these numbers; C_6F_6 , 919 nm; toluene, 930 nm; **Figure D.3**). This gains intensity from the nearby $1^1A_g \rightarrow 1^1B_{2u}$ transition. The low-

temperature absorption spectrum in toluene in **Figure 6.3 c** shows another shoulder at the first p vibrational band. Between this shoulder, the main shoulder A2 and the 1010 nm band A3, an energy gap of 0.18 eV (1450 cm^{-1}) can be determined, which is a further indication of a vibrational progression. Likewise, the weak band at 768 nm in the matrix spectra of **Hep** is due to a vibrational progression of the $1^1A_g \rightarrow 2^1A_{1g}$ transition.^{330,341}

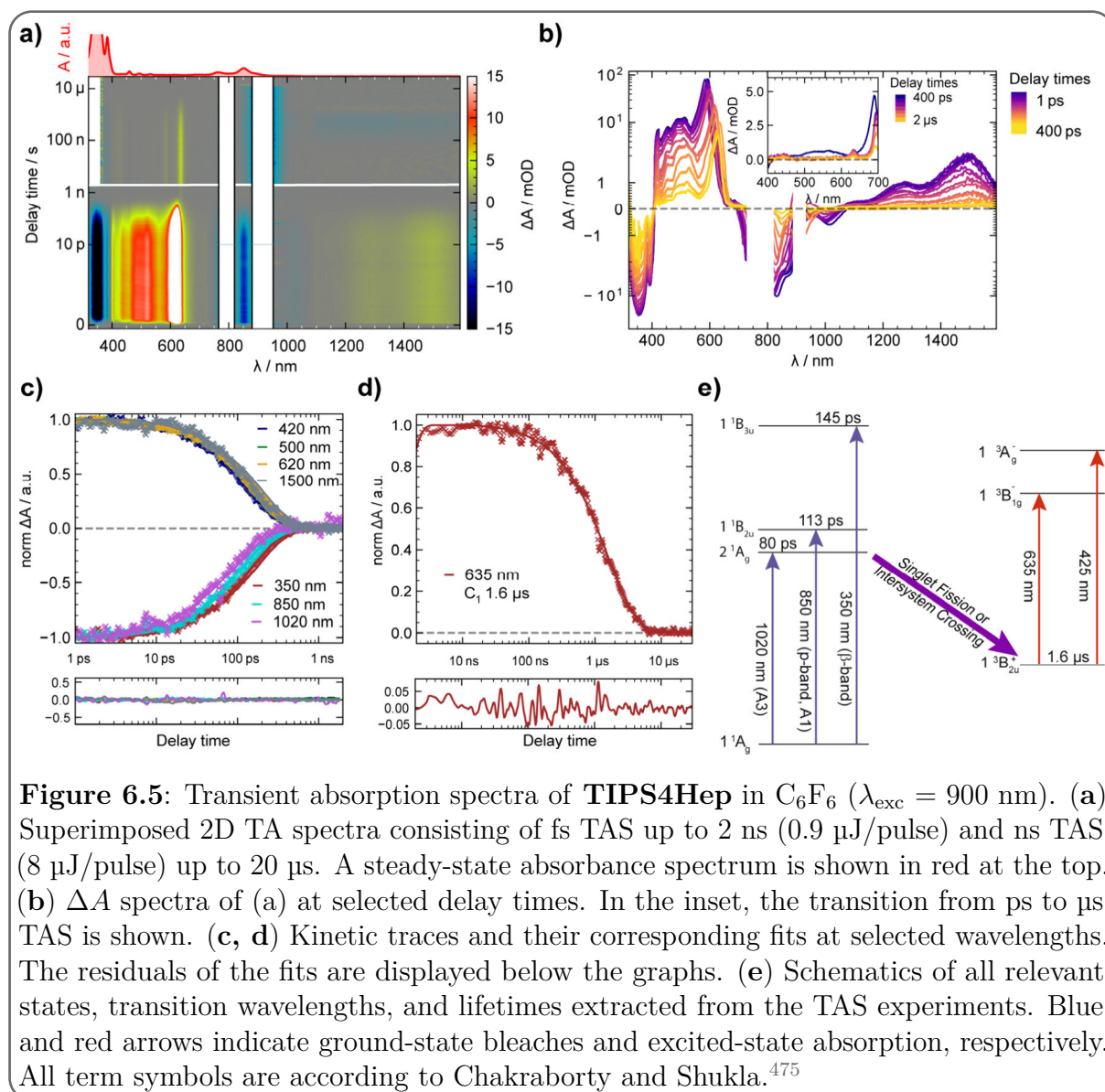
We performed transient absorption spectroscopy (TAS) of a 50 μM **TIPS4Hep** solution in C_6F_6 under argon to further corroborate our hypothesis of a 2^1A_g singlet excited state. TAS probes the temporal evolution of the excited state by determining the differential absorbance ΔA , which is the difference in absorbance between the excited and ground states. We pumped **TIPS4Hep** with 90 fs laser pulses at 900 nm to selectively target the A3 transition and monitor the excited-state absorption within a time window of 200 fs to 20 μs . Experiments at short time scales ($<2\text{ ns}$) were carried out with 0.9 $\mu\text{J}/\text{pulse}$. To enhance the visibility of the weaker signals at long delay times, we display here the spectra obtained with 8 $\mu\text{J}/\text{pulse}$ but note that similar results (with less favorable signal-to-noise ratio) were observed with 0.9 $\mu\text{J}/\text{pulse}$ (see the **Appendix D** for more details).

Figure 6.5 a depicts a superimposed 2D hyperspectrum as a function of the pump-probe delay time and ΔA , which is color-coded on the right. The white patches indicate spectral regions that cannot be probed due to scattered pump or weak probe light. Detailed ΔA spectra at selected delay times below 400 ps are shown in **Figure 6.5 b** and **Figure D.11**. We find bands with negative ΔA centered at 350, 383, 850, and 1020 nm, which are consistent with the steady-state absorbance shown in red above the 2D spectrum in **Figure 6.5 a** and **Figure 6.1**. Negative ΔA values indicate ground-state bleaching (GSB) due to a partial depopulation of the ground state as

well as Pauli blocking ($S_0 \rightarrow S_n$, $n \neq 0$) due to partial filling of an excited state. The fact that the β band at 350 nm and the p band at 850 nm (A1) both exhibit GSB under 900 nm excitation is a strong indication that the band at 1020 nm (A3) involves the 1^1A_g ground state. In addition, we observe bands with positive ΔA , indicating excited-state absorbance (ESA) ($S_n \rightarrow S_n + x$, $n, x \neq 0$), which is most prominent at 620 nm and some features around 500 nm. In the NIR, weak ESA around 1120, 1290, and 1500 nm emerges, showing a possible vibrational progression (compare **Figure D.11**).

We fitted the kinetics of all prominent GSB and ESA features in **Figure 6.5 c** and found that most of the transient signals decay monoexponentially within 130 to 160 ps. Across the full probe spectrum, we observe no significant kinetics within the first picosecond other than the $\sim 400\text{ fs}$ population rise imposed by the instrument response and very weak residual coherent artifacts. The lifetimes of the three prominent GSB signals are 145 ps at 350 nm (red, β -band), 113 ps for the p band (cyan, A1), and 80 ps for A3 (purple). These overall comparable magnitudes are supporting evidence that the A3 transition belongs to **TIPS4Hep**. The small but significant differences in the lifetimes of the three transitions can be rationalized in terms of a shared ground state but different excited states. This is consistent with our attribution of the A3 band to a $1^1A_g \rightarrow 2^1A_g$ transition. With respect to the ESA kinetics, the most notable finding is that the band at 635 nm exhibits complex kinetics with a near-monoexponential decay to 3 % of the peak ΔA value, where it remains as a residual, constant ESA for $>8\text{ ns}$ (see **Figure D.12**).

In **Figure 6.5 d**, we display the further monoexponential decay of this residual ESA and determine a lifetime of 1.6 μs . We note additional ESA signals with such long lifetimes in **Figure 6.5 a** at 425, 585, and 635 nm, which are plotted in more detail in the inset of **Figure 6.5 b**. We argue that these features are evidence for a populated triplet



state and assign the ESA at 635 and 425 nm to the $1^3B_{2u}^+ \rightarrow 1^3B_{1g}^-$ and $1^3B_{2u}^+ \rightarrow 1^3A_g^-$ transitions, respectively. We rationalize this with two previous findings: heptacene prepared in situ by the photodecarbonylation of α -diketones revealed a triplet with a lifetime of 11 μs featuring a sharp ESA centered at 580 nm (2.14 eV) and a broad band between 400 and 500 nm.³³⁹ ESA from the 1^3B_{2u} triplet in heptacene has been calculated with a prominent transition at 580 nm ($1^3B_{2u}^+ \rightarrow 1^3B_{1g}^-$) and a weaker transition at 393 nm ($1^3B_{2u}^+ \rightarrow 1^3A_g^-$).⁴⁷⁵ These values are in reasonable agreement with our experimental results for **TIPS4Hep**,

accepting a shift of ~ 0.2 eV to lower energies for both transitions, which may be the effect of the TIPS-ethynyl substituents. In line with this, our computed absorption spectrum (**Figure D.13**) of T_1 -**TIPS4Hep** obtained using TD-UDFT (UB3LYP/6-311+G**//M06-2X/def2-SVP) shows two main transitions with high oscillator strengths at 703 nm ($f = 0.85$) and 457 nm ($f = 0.14$), that is, at lower energies than the computational results for heptacene at the same level (see the **Appendix D** for more details). The unassigned third transition at 585 nm can be regarded as a vibrational progression of the transition at 635 nm.

We conclude by discussing the population mechanism of the T_1 state in **TIPS4Hep** based on our TAS data. We argue that the most likely pathway is via singlet fission (SF) or intersystem crossing (ISC) of the 2^1A_g singlet. This would also explain why the GSB of the $1^1A_g \rightarrow 2^1A_g$ transition has the shortest lifetime, as it would decay due to relaxation to S_0 and T_1 simultaneously. An involvement of the 1^1B_{2u} state is unlikely for three reasons: (1) for this state to be populated with a 900 nm pump pulse, two-photon absorption would be required, which is unlikely with the 0.9 $\mu\text{J}/\text{pulse}$ utilized by us; (2) the ISC from this state is expected to be slow due to El-Sayed’s rule, which is incompatible with the competition with the rather fast decay of the 1^1B_{2u} state (113 ps); (3) SF of the 1^1B_{2u} state occurs on short enough time scales for TIPS-ethynyl-pentacene derivatives, where the ideal scenario of $E(S_1) = E(^1(TT))$ is met almost perfectly.^{28,172} For higher acenes, however, SF is increasingly exothermic, which greatly decreases its efficiency and favors triplet pair recombination before the free T_1 state is formed.³⁵³

Assuming a similar energy for the 1^3B_{2u} state in **TIPS4Hep** as the 0.5–0.6 eV calculated for **Hep**,^{341,346} SF should be much more favorable from the 2^1A_g state (1.2 eV). We note that SF typically requires concentrations larger than 4×10^{-4} M,¹⁷² which is slightly more than the 5×10^{-5} M used by us. A possible explanation could be the temporal formation of small aggregates in solution.

Alternatively, the T_1 state may be populated from the 2^1A_g state via fast ISC, since it is favored by El-Sayed’s rule. Moreover, organic π radicals have shown ISC lifetimes on the order of picoseconds due to radical enhanced intersystem crossing (REISC).^{354,355,476} Heptacene is known for its biradical character,³⁴⁶ and this property could render ISC competitive to the S_0 relaxation with $\tau = 80$ ps.

We summarize our TAS results concerning

the nature of all observed transitions, their lifetimes, the two coexisting spin systems, and the pathway of transition between them in **Figure 6.5 e**.

6.4 Conclusion

In conclusion, we have developed an alternative synthesis for **TIPS4Hep** and conducted a comprehensive photophysical study using steady-state and transient absorption spectroscopy. Comparing these results with complementary spectroscopic data on the less stable parent **Hep** suggests that **TIPS4Hep** is a suitable proxy to understand the electronic structure and excited-state dynamics of **Hep**. Its absorption spectrum reveals a weak band at 1010 nm, assigned to a forbidden $1^1A_g \rightarrow 2^1A_g$ transition that is partially allowed due to vibronic coupling and proximity to allowed transitions. Similar spectral features are observed for **Hep**, although its higher symmetry renders the $1^1A_g \rightarrow 2^1A_g$ origin unobservable. In accordance with computational spectroscopy, we assign this dark excited state to the S_1 state of heptacene. We show that the dark state relaxes within 80 ps to a long-lived triplet state, and we discuss singlet fission and intersystem crossing as the most likely mechanisms for this action.

Conclusion & Outlook

This section summarizes the main findings of this thesis and provides an outlook for further studies and developments. In **Section 7.1**, the software framework TAPAS (**Chapter 3**), which was constantly developed and extended throughout the course of this work, is discussed in the broader context of existing TA software and common practices in TA modeling and uncertainty handling. Forthcoming features and developments of TAPAS are outlined. **Section 7.2** summarizes the findings of the two cluster studies (see **Chapter 4** and **Chapter 5**) and shows how TAPAS, together with a more elaborated posterior-based uncertainty analysis separates models that are truly supported by the data from those that merely accommodate it. New study designs to address remaining research questions are also proposed. Finally, **Section 7.3** discusses the outcomes of the TA analysis of the heptacene derivative and suggests further investigations to more tightly constrain the triplet-state population mechanism in heptacene systems.

7.1 TAPAS in Practice

One main issue identified at the beginning of this work was the absence of a versatile, powerful yet easy-to-use and transparent TA analysis and processing software with rigorous error handling. The commercial TA setup in our laboratory shipped with the closed-source processing software SURFACE XPLOERER from Ultrafast Systems with only rudimentary fitting capabilities.⁴⁷⁷ While its GUI makes basic preprocessing straightforward and integrates smoothly with the proprietary raw format, it lacks flexibility for target analysis and provides little transparency regarding the fitting and uncertainty-estimation algorithms. As proprietary software with a closed data format, it also impedes communication, data exchange, and interoperability with groups not using Ultrafast Systems' hardware.

A free and open-source alternative with an intuitive GUI that is also capable of performing target analyses is Glotaran. However, the legacy 2015 release is increasingly dated resulting in cumbersome installation and fitting workflows, and limited flexibility in model construction, visualization, and uncertainty evaluation.²²³

During the development of TAPAS,

two script-based alternative TA packages were released, namely **KiMoPack** and **pyglotaran**.^{45,221} Both offer great functionality and modularity, but they require at least basic coding skills and a configured programming environment. Their sequential, script-driven workflows can feel less intuitive and provide reduced real-time responsiveness. While this is advantageous for batch and automated processing, the GUI-driven, tab-based workflow of TAPAS enables more fluid, exploratory interaction with the data. All processing and fitting steps automatically generate metadata, and complementary or additional experiments can be merged into a single project using the open Hierarchical Data Format (HDF) format, facilitating FAIR data management.

Generally, GUIs tend to be slower than script-based solutions because rendering interfaces and translating user input introduce latency. Nevertheless, TAPAS integrates modern, high-performance array computing common in machine-learning workflows into its fitting models. This implementation allows TAPAS to outperform packages that rely on more conventional algorithms, despite the inherent GUI overhead.

Further, the algorithmic implementation enables virtually instant first-order uncertainty and correlation estimates as well as slower yet manageable Bayesian posterior analyses of the parameter space, capabilities not available in other public TA software. On the rose bengal benchmark, TAPAS produced uncertainty estimates comparable to the much slower F-test in **KiMoPack**.

Crucially, the parameter correlation analysis whether via the rapid first-order approach or the fuller posterior exploration, exposed fit instabilities, especially for local fits, that conventional error analyses in other packages failed to reveal. Thus, we could demonstrate that correlation estimates are essential for judging model quality and parameter identifiability. Even when models visually reproduce the data and CIs appear tight, one cannot generally conclude that parameters

are robust and unique. Because correlation and parameter-space analyses are built natively into TAPAS, these features support the extraction of trustworthy and reliable parameters which is vital for reproducibility and sound scientific inference.

Details are provided in **Chapter 3** and have been accepted for publication in *ChemPhotoChem*.

Outlook Although TAPAS already covers the full TA workflow including preprocessing, visualization and custom fitting, it is under active development. This section outlines several forthcoming and useful features.

TAPAS currently consolidates metadata, complementary experiments such as steady-state absorption/emission, solvent references or additional TA windows into a single self-contained file. However, related TA experiments from a larger study such as series varying pump fluence, concentration or solvent cannot yet be grouped within a single, hierarchically structured HDF project and interpreted jointly. Users must instead manage subprojects via file/folder naming, a cumbersome and non-standardized approach with limited query capability. This can be circumvented by integrating an Structured Query Language (SQL) database engine into TAPAS. By doing so, the user could organize and query projects by TA-specific metadata like solvent, analyte, pump fluence, etc. and in a following step, perform simultaneous analyses across multiple TA project files. Standardized databases would also streamline data exchange and collaboration between groups and pave the way for a large TA repository suitable for both human and machine learning.

A deep learning neural network trained on synthetic TA data was demonstrated in 2020 by Buckup and colleagues, helping to identify kinetic models and artifacts in an unbiased, data-driven manner.⁴⁷⁸ Providing easy access to such functionality within TAPAS could help users propose plausible target models more reliably and would be a valu-

able addition.

Finally, as TAPAS is applied to increasingly specific research questions, its library of pre-shipped target models will expand. Planned extensions include support for vibrational oscillations on ultrafast timescales, distributed-rate models, and explicit back-reaction pathways.

7.2 Tungsten Iodide Clusters: From ISC to Sublevels

Initially, we analyzed the optoelectronic properties of a new cationic tungsten iodide cluster species $[(W_6I_8)(CH_3CN)_6]^{4+}$ in **Chapter 4**. Beyond structural and electronic characterization, absorption and photoluminescence measurements revealed blue-shifted optical features relative to the general $[(W_6I_8)L_6]^{2-}$ family, behavior otherwise seen only with strongly electron-withdrawing ligands such as $(CO_2C_3F_7)^-$. A comparatively short emission lifetime with pronounced temperature dependence was also observed. Within the framework of Kitamura’s sublevel splitting model,²² this points to a relatively small energetic separation between triplet sublevels and, consequently, substantial population of a higher-lying sublevel with a short radiative lifetime. Using TA spectroscopy over 200 fs to 100 μ s, we tracked triplet formation and relaxation in tungsten iodide clusters for the first time, extracting an ultrafast ISC happening within 2 ps followed by triplet reorganization or cooling within 90 ps. Further, we correlated a long-lived TA signal to the emissive triplet which could be quenched by molecular oxygen. For this study, an early TAPAS prototype was employed for preprocessing and visualization, while global analysis was conducted with Glotaran.

Details on these results are given in **Chapter 4** and have been published in *Dalton*

Transactions.

With this study, we could confirm that TA spectroscopy can yield ISC rates as well as emission lifetimes and oxygen quenching rates complementing time-resolved emission measurements. Due to the relatively low ΔA signals and cluster decomposition at higher pump fluences, long acquisition times were required making the setup especially susceptible to oxygen inflow and instrumental drift, both of which can alter excited-state properties and promote singlet-oxygen-induced degradation. We therefore optimized experimental parameters and sample cells carefully to ensure reproducible results.

Building on this experience, we turned from the novel cationic tungsten iodide cluster to the literature-known and more conventional anionic cluster systems $[(W_6I_8)I_6]^{2-}$ and $[(W_6I_8)(TFA)_6]^{2-}$ and analyzed their triplet manifolds using TA together with high-resolution, temperature-dependent, time-resolved emission spectroscopy. For both clusters, we extracted triplet-state population within around 5 ps and found no significant deactivation beyond phosphorescence or oxygen quenching, consistent with their long emission lifetimes and intrinsically high triplet yields. These analyses were performed in TAPAS, which indicated good identifiability of the ISC parameters and revealed an additional component near the time resolution that we assign to coherent artefacts.

By measuring temperature-dependent emission spectra and lifetimes in a cluster-poly(methyl methacrylate) (PMMA) matrix from 4 to 340 K, we tested the three and four triplet state models established for molybdenum-based clusters, extracted sublevel splittings and lifetimes and found no statistical evidence for more than three emissive components contrasting recent studies on Mo-based systems. More importantly, posterior parameter-space analyses (as implemented for TA fits in TAPAS) revealed poor identifiability of the inferred triplet sublevel splittings and corresponding lifetimes,

especially when fitting four sublevels. This not only challenges the justification for a four-spin-sublevel model but also calls into question the reliability of the derived parameters regardless of the number of states, owing to the inherently strong correlations in multi-exponential models.

Relativistic TDDFT geometry optimizations of the lowest excited states, including SOC, further indicated substantial excited-state distortions, lowering the symmetry and completely lifting the triplet degeneracy assumed by those models. Based on these results, we propose a relativistic framework with three thermally accessible excited-state geometries, each possessing three triplet sublevels, to explain the triplet nature of tungsten iodide clusters.

These findings were published in *Inorganic Chemistry*, further details are given in **Chapter 5**.

Outlook For Mo-based systems, systematic correlations have been reported between triplet sublevel splittings and the nature of the inner and apical ligands. Although tungsten analogues often show similar trends in emission maxima and lifetimes, correlations with ZFS remain speculative due to limited experimental evidence. The same holds for ISC rates as a function of ligand set. Future work should therefore systematically vary inner and outer ligands in $[(W_6X_8)L_6]^n$ system and determine ISC rates and sublevel splitting via time- and temperature-dependent TA and emission spectroscopy.

While temperature-dependent TA measurements or single molecule emission experiments are challenging for these weak-signal clusters, tracking the temperature-dependent triplet-state population dynamics and spectral shapes by TA or the emission of individual molecules, could help disentangle underlying excited-state geometric relaxations and clarify the structure of the triplet manifold.

Finally, preliminary temperature-dependent emission and lifetime data in solution indicate a dynamic exchange

between apical ligands of the cluster system and solvent molecules that can be shifted in line with Le Chatelier’s principle by adding excess ligand (see **Appendix C.4**). Such exchange could by itself account for solvent-dependent optical changes when nominally altering the apical ligand, because the relative populations of partially solvent-exchanged species would also change due to a different binding situation. Although many studies on those clusters are performed in solid-state or a polymer matrix, the binding situation and cluster composition in solution must therefore be understood before correlating ligand electronics with the ensemble optical properties. Doing so will not only clarify differences between solution and solid-state behavior but also illuminate degradation pathways, suggest new synthesis routes, and reveal how solvents and ligands stabilize the clusters.

7.3 Heptacene: Between Singlet Fission & ISC

Due to the low photochemical stability of heptacene, its photophysics are not accessible by TA at room temperature. However, the successful synthesis of the heptacene derivative 6,8,15,17-tetrakis((triisopropylsilyl)ethynyl)heptacene (TIPS4Hep) enabled a comprehensive study combining steady-state absorption and emission with broadband TA. By doing so, we showed that the electric-dipole-forbidden transition to 2^1A_g is the lowest excited state, in accordance with theoretical considerations. Additionally, TA spectroscopy monitored triplet state formation within 80 ps and decay after 2 μ s in oxygen-free conditions, presumably mediated by the lowest-lying dark 2^1A_g state. We identified that both ISC and SF

are, in principle, viable pathways for triplet generation, and we provide the specific electronic configuration, experimental conditions and kinetics.

These results were published in *The Journal of Physical Chemistry Letters*, further details are given in **Chapter 6**.

Outlook The mechanism of triplet formation in heptacene and its derivatives remains an open question. As a bimolecular process, SF should display a concentration-dependent triplet formation rate (approximately linear in concentration). A systematic concentration series probing triplet population and relaxation would therefore help discriminate between SF and ISC, and could also reveal higher-concentration phenomena such as static dimers, aggregates, or exciplexes.

Additionally, the introduction of heavy atoms into solution (e.g. iodobenzene, CH_2I_2 etc.) or embedding the analyte in an acryl halide matrix could invoke an external heavy-atom effect and enhance ISC, directly testing whether triplets arise via ISC.^{268,479} If synthetically feasible, heavy-atom substitution on the heptacene derivative itself could further clarify the dominant triplet-formation pathway in longer acenes.

To conclude, this work uses TA spectroscopy to address fundamental questions about triplet-state formation and relaxation in tungsten iodide clusters and acenes, demonstrating its versatility for monitoring and disentangling processes across broad spectral and temporal ranges. Beyond the experimental nuances of handling delicate systems under controlled environments and intense, long-duration excitation, this thesis also delivers an open-source, end-to-end framework for preprocessing, visualizing and modeling TA data in a FAIR and statistically rigorous manner. This framework, which is not limited to triplet analysis, further establishes TA spectroscopy as a powerful, general tool for determining complex photophysical and photochemical processes across various materials.

Supplementary Information for Chapter 3

TAPAS: Transient Absorption Processing and Analysis Software

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A.1 Detailed Information on the Workflow Tabs

In the **Import Tab**, data files including raw TA data, solvent TA data, and steady-state data can be imported by selecting file(s) in a file dialog, pasting file path(s) or by dragging and dropping. Behind the scenes, TAPAS parses each input according to the chosen delimiter, constructs wavelength and delay-time vectors and a differential absorbance matrix, extracts any trailing metadata, and converts all values to SI units. This way TAPAS can accept a variety of formats, resulting in a standardized, machine-readable HDF5 dataset with metadata stored separately. Multiple TA scans can be averaged automatically, and steady-state measurements recorded before and after the TA experiment are evaluated to flag potential sample degradation. Users may also supply additional contextual metadata such as experiment name, sample identifier, or excitation wavelength, which TAPAS then uses to generate descriptive plot titles, organize output directories, and highlight features like scattered pump light.

The **Preprocessing Tab** provides an interactive view of the imported 2-D transient absorption surface. A movable cross-hair simultaneously displays the corresponding kinetic trace (ΔA vs time) and spectral slice (ΔA vs wavelength), allowing rapid inspection of raw features before any manipulation. Preprocessing steps may include trimming, resampling, chirp correction, background correction, solvent correction, time-zero correction and filtering. Wavelength-dependent group-velocity dispersion shifts the apparent time-zero across the probe spectrum, often referred to as “chirp”. TAPAS can locate the arrival time at each wavelength with a user-defined heuristic (e.g. the delay at which the signal first exceeds 10 % of its maximum or crosses a threshold of 2×10^{-4}). The resulting arrival-time trace is then smoothed with a fourth-order polynomial, which is evaluated on the full spectral grid and subtracted from the delay axis to produce a chirp-corrected data set. Alternatively, the user may pick arrival-time markers directly in the canvas which replace the automatic heuristic and are fitted by the same quartic polynomial, giving full manual control while retaining the smooth correction profile. All preprocessing steps can be previewed in the canvas and then applied to a copy of the raw measurement, referred to within TAPAS as a dataset. Every subsequent visualization or fit refers to a specific dataset, retaining an immutable link to its parent raw file. This hierarchy is preserved on export/import via the associated HDF5 container. Each preprocessing action automatically generates structured metadata and attaches it to the affected dataset. This built-in provenance tracking ensures that all transformations are recorded, which enhances reproducibility, and makes it straightforward to audit or replicate an analysis pipeline at any stage.

The **Combine Projects Tab** allows datasets that probe different spectral or temporal windows of otherwise similar experimental conditions to be fused onto a single, unified grid. After selecting the source datasets, the user specifies how to handle overlapping regions and an extrapolation rule for filling gaps. TAPAS then constructs the merged matrix, writes it as a new root dataset in a separate project, and stores links to the two parent projects. The resulting project therefore presents a coherent data surface for further analysis while retaining full provenance of all contributing measurements.

In the **Visualization Tab**, publication-quality graphics are generated ranging from 2D contour maps to ΔA spectral and kinetic slices, as well as specialized plots for the results of local and global analysis. Many graphical attributes like colors, axis limits, scales, legends, normalizations, figure sizes and fonts can be tuned interactively or supplied as `matplotlib.rcParams`. Complete `matplotlibrc` files can be loaded to match specific

journal styles. Output is available as scalable-vector formats (PDF, SVG) or raster graphics (JPG, PNG, TIFF), and the plotted data can be exported as CSV for further manipulation in external graphics software.

The **Component Analysis Tab** applies an SVD to the transient absorption matrix, extracts the leading principal components, and presents the normalized singular-value spectrum, the corresponding spectral and temporal eigenvectors, and the residual surface remaining after reconstruction with a user-selected number of components.

The **Local Fit Tab** fits an individual kinetic trace either at a user-selected wavelength or over an averaged spectral window, whereas the **Global Fit Tab** optimizes the entire time-wavelength matrix. In both views, the analyst first chooses the number of kinetic components (with an optional non-decaying offset), the kinetic scheme, the optimization algorithm and the coherent artifact (CA) model (no modeling, zero order Gaussian, combined zero and first-order Gaussian). A parameter table then lists the lifetimes, the time-zero t_0 and the IRF (Gaussian FWHM). Each entry accepts initial guesses, upper and lower bounds, and a flag indicating whether the parameter is fixed and not included in the optimization.

Time-zero can be handled in two ways. The experimentally convenient definition takes t_0 as the onset of the signal, determined by TAPAS by the delay at which the transient first reaches 5 % of its rising edge. However, such a choice couples t_0 tightly to the IRF width and can destabilize the optimization when both parameters are allowed to vary (see **Appendix A.3**). TAPAS therefore offers a second option that sets t_0 to the center of the Gaussian IRF, corresponding to the point of maximum temporal overlap between pump and probe. This analytically precise definition is common in pump-probe spectroscopy and removes the undesired correlation.

The **Global Fit Tab** adds further options: inclusion of an explicit ground-state recovery component and fixing that component to an external steady-state absorption spectrum, wavelength-dependent weighting, and a preview panel that renders the selected kinetic scheme with its compartments and lifetimes which is particularly useful in target analyses.

Before the actual optimization, a preliminary “initial-guess” run can be executed. This step is invaluable for exposing inconsistencies in the chosen model, parameter bounds or starting values and should not be skipped because multiexponential fits are particularly sensitive to poorly chosen initial conditions. After a local fit, TAPAS displays the experimental trace alongside the simulated curve, the individual kinetic components, and the residuals. A global fit produces the complete suite of decay-associated spectra (DAS) and evolution-associated spectra (EAS), or species-associated spectra (SAS) when a target model is used, together with the corresponding concentration profiles, a residual map, and the SVD of those residuals. The optimized parameters are reported with both absolute and relative standard errors, and a comprehensive table summarizes goodness-of-fit measures, parameter and residual correlations, and stability diagnostics (full definitions of these metrics are given in Sections “Fit Metrics” of the main manuscript and in **Appendix A.4**). Additionally, Bayesian posterior exploration is available through an optional Markov-chain Monte-Carlo routine, analyzing the resulting sample cloud reveals parameter asymmetries, drifts, or compensating correlations that are not captured by the first-order error estimates.

The fit results can be saved to the selected dataset, further investigated in the Visualization Tab or remodeled closing the workflow cycle.

A.2 CDF or EMG for Analytical Convolving the IRF

The instrument-response function (IRF) of TA experiments is normally described by a Gaussian pulse

$$g(t) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right), \quad (\text{A.1})$$

and the excited population c is a mono-exponential that switches on at $t = t_0$,

$$c(t) = H(t-t_0) \exp\left(-\frac{t-t_0}{\tau}\right), \quad (\text{A.2})$$

where H is the Heaviside step, $\sigma = \text{FWHM}/(2\sqrt{2\ln 2})$, and τ is the lifetime. The measured signal s is therefore the convolution

$$s(t) = (g \otimes c)(t). \quad (\text{A.3})$$

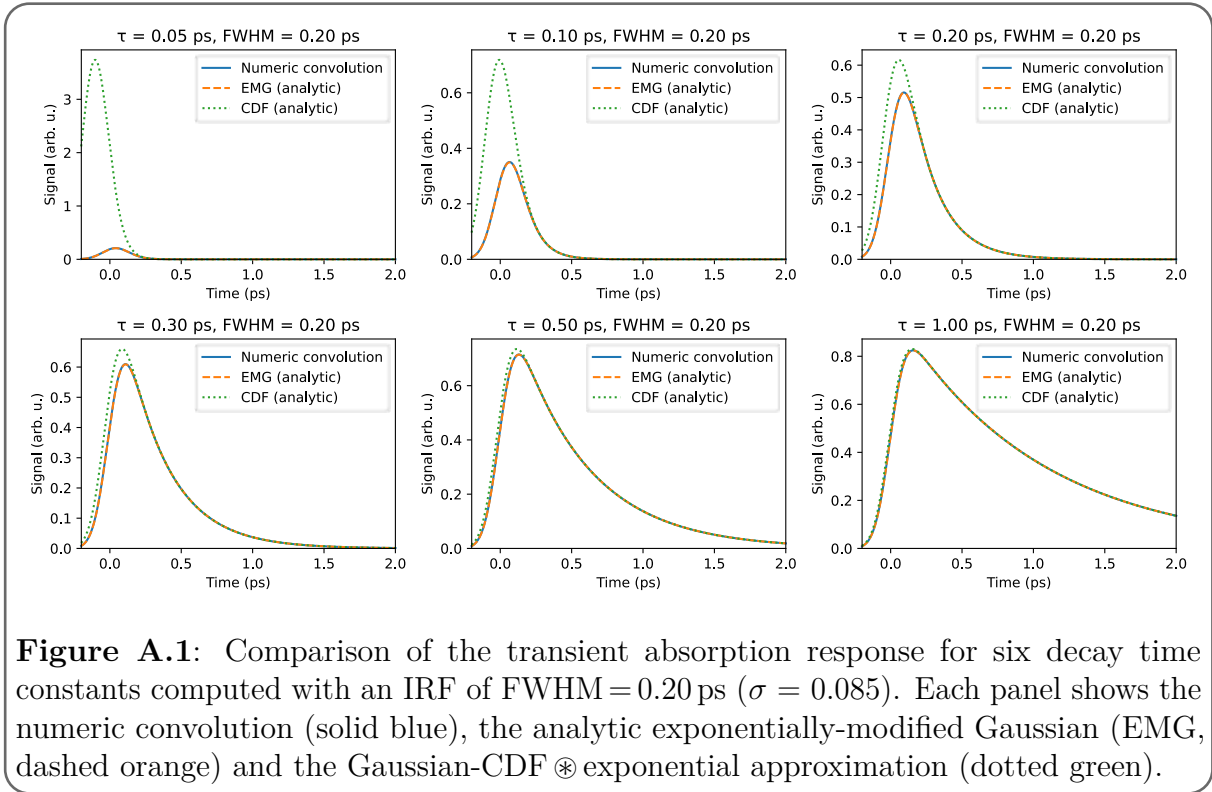
Evaluating this integral numerically at every optimization step is slow, so most fitting codes substitute the Gaussian cumulative distribution function (CDF) approximation

$$s_{\text{CDF}}(t) = \frac{1}{2} \left[1 + \text{erf}\left(\frac{t-t_0}{\sqrt{2}\sigma}\right) \right] \exp\left(-\frac{t-t_0}{\tau}\right), \quad (\text{A.4})$$

which is the leading-order term of the true exponentially modified Gaussian (EMG)

$$s_{\text{EMG}}(t) = \frac{1}{2\tau} \exp\left(\frac{\sigma^2}{2\tau^2} - \frac{t-t_0}{\tau}\right) \left[1 - \text{erf}\left(\frac{\sigma^2 - \tau(t-t_0)}{\sqrt{2}\sigma\tau}\right) \right]. \quad (\text{A.5})$$

Equation **Equation A.4** is unbiased only when $\tau \gg \sigma$. As τ approaches the IRF width, it underestimates the initial rise and returns lifetimes that are systematically too long (see **Figure A.1**). Because the EMG of **Equation A.5** is analytic and, under JAX just-in-time compilation, no more expensive to evaluate than **Equation A.4**, we adopt the full EMG in all fits. This removes the lifetime-dependent bias and, together with a precisely characterized IRF, allows extracting kinetics slightly below the nominal time-resolution limit of the instrument. When the fastest observed lifetime is roughly two to five times the IRF FWHM, the CDF is an adequate approximation and can be noticeably faster than the EMG in conventional implementations without just in time compilation.



The corresponding Python code producing the plots in **Figure A.1** is:

```

1 import numpy as np
2 import matplotlib.pyplot as plt
3 from math import erf
4
5
6 # Helper functions
7 -----
8 def sigma(fwhm):
9     return fwhm / (2*np.sqrt(2*np.log(2)))
10
11 v_erf = np.vectorize(erf)
12
13
14 def emg(t, tau, t0, fwhm):
15     sig = sigma(fwhm)
16     r = 1 / tau
17     dt = t - t0
18     arg = (sig**2 * r - dt) / (np.sqrt(2) * sig)
19     return 0.5 * np.exp(0.5 * (sig * r) ** 2 - r * dt) * (1 -
20         v_erf(arg))
21
22 def erf_exp_approx(t, tau, t0, fwhm, A=1.0):
23     sig = sigma(fwhm)
24     dt = t - t0

```

```

25     return 0.5 * (1 + v_erf(dt / (np.sqrt(2) * sig))) * A *
26         np.exp(-dt / tau)
27
28 def numeric_conv(t, tau, t0, fwhm):
29     dt = t[1] - t[0]
30     sig = sigma(fwhm)
31
32     g = np.exp(-0.5*((t - t0)/sig)**2) / (sig*np.sqrt(2*np.pi))
33     e = np.where(t >= t0, np.exp(-(t - t0)/tau), 0)
34
35     full = np.convolve(g, e, mode='full') * dt
36     start = int(round((t0 - t[0]) / dt))
37     return full[start:start + len(t)]
38
39
40 # Simulation parameters
41 -----
42 t = np.linspace(-0.5, 4.0, 4500)
43 fwhm = 0.2
44 t0 = 0
45 sig = sigma(fwhm)
46
47 taus = [0.05, 0.1, 0.2, 0.3, 0.5, 1] # ps
48 plt.close()
49 fig, axes = plt.subplots(2, 3, figsize=(12, 6))
50 axes_flat = axes.flatten()
51
52 for ax, tau in zip(axes_flat, taus):
53     A = np.exp(0.5 * (sig / tau) ** 2)
54
55     y_num = numeric_conv(t, tau, t0, fwhm)
56     y_emg = emg(t, tau, t0, fwhm)
57     y_approx = erf_exp_approx(t, tau, t0, fwhm, A=A)
58
59     ax.plot(t, y_num, label="Numeric convolution")
60     ax.plot(t, y_emg, linestyle="--", label="EMG (analytic)")
61     ax.plot(t, y_approx, linestyle=":", label="erf x exp approx")
62     ax.set_xlim(-0.2, 2.0)
63     ax.set_ylim(bottom=0)
64     ax.set_xlabel("Time (ps)")
65     ax.set_ylabel("Signal (arb. u.)")
66     ax.set_title(f"$\tau$ = {tau:.2f} ps, FWHM = {fwhm:.2f} ps")
67     ax.legend()
68
69 plt.tight_layout()
70 plt.show()
71 fig.savefig("comparizon.svg", format="svg")

```

A.3 Time-Zero Definition

In modeling of ultrafast pump-probe experiments, the choice of "time zero" (t_0) determines how the finite IRF couples into every kinetic parameter that is subsequently extracted. Experimentally, t_0 is often set to the onset of the macroscopic signal rise, e.g. the point where the transient first departs from the pre-pump baseline. This definition is convenient: it provides an easily recognizable reference on the spectrometer, allows quick alignment between scans recorded under different conditions and lets the experimentalist tune the optimal amount of data points at every delay time.

From a modeling standpoint, however, the physically consistent choice is the center of the Gaussian IRF (the temporal mean of the pump-probe cross-correlation) because the analytic convolution kernels (Gaussian $\otimes$ exponential, Gaussian CDF, EMG) are written with that center as the natural origin. Besides the Gaussian center as t_0 , TAPAS implements the experimental definition by using the 5 % rise point of the IRF as an empirical threshold to calculate t_0 . This naturally leads to a pronounced correlation between the fitted t_0 and the IRF width (FWHM) because a broader Gaussian delays the same fractional rise. That correlation can inflate confidence intervals on both parameters and destabilize fits. The t_0 -FWHM correlation can be eliminated by fixing the IRF width to a value determined independently (e.g. from solvent-only scans), leaving only a single, well-defined temporal offset to refine in the model.

This is illustrated in the following by analyzing a local fit of Rose Bengal at 1100 nm (see main text or **Appendix A.5** for more information). For both t_0 representations, the algorithm converges quickly and finds similar parameter results and confidence intervals (**Table A.1** and **Figure A.2 A**). However, quick first-order error estimates already hint to a strong correlation between t_0 and the IRF parameter with "5 %-threshold" definition, which is confirmed by a posterior parameter exploration using MCMC (**Figure A.2 B,C**).

Table A.1: Comparison of parameter estimates and correlations for the two settings.

"5%-threshold"				Gaussian Center			
Parameter estimates				Parameter estimates			
t_0: $-106.4 \text{ fs} \pm 19 \text{ fs}$ (18.26%) - IRF: $205.1 \text{ fs} \pm 26 \text{ fs}$ (12.88%) τ_1: 10% $63.0 \text{ ps} \pm 2 \text{ ps}$ (3.21%) τ_2: 52% $247.5 \text{ ps} \pm 20 \text{ ps}$ (7.90%) A_{inf}: 38%				t_0: $-106.4 \text{ fs} \pm 19 \text{ fs}$ (18.26%) - IRF: $205.1 \text{ fs} \pm 26 \text{ fs}$ (12.88%) τ_1: 10% $63.0 \text{ ps} \pm 2 \text{ ps}$ (3.21%) τ_2: 52% $247.5 \text{ ps} \pm 20 \text{ ps}$ (7.90%) A_{inf}: 38%			
Correlations				Correlations			
	t_0	IRF	τ_1		t_0	IRF	τ_1
IRF	-0.91			IRF	0.01		
τ_1	-0.03	0.07		τ_1	0.09	0.07	
τ_2	0.01	-0.04	-0.85	τ_2	-0.05	-0.04	-0.85

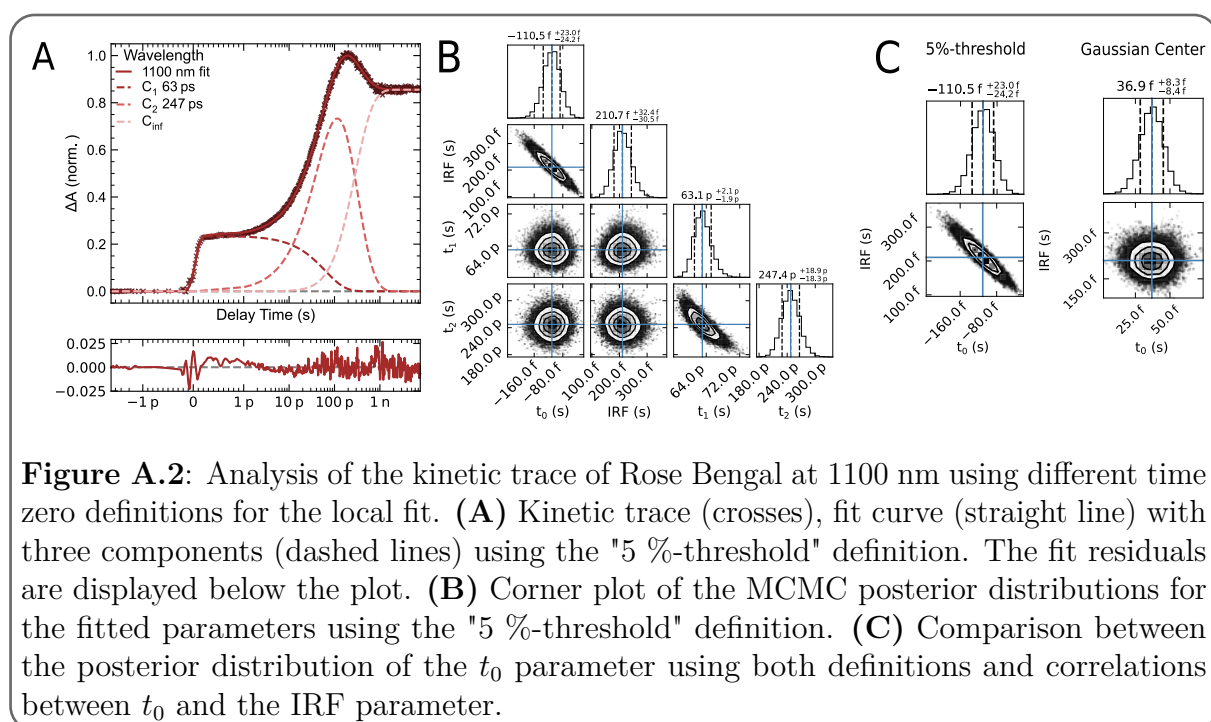


Figure A.2: Analysis of the kinetic trace of Rose Bengal at 1100 nm using different time zero definitions for the local fit. **(A)** Kinetic trace (crosses), fit curve (straight line) with three components (dashed lines) using the "5 %-threshold" definition. The fit residuals are displayed below the plot. **(B)** Corner plot of the MCMC posterior distributions for the fitted parameters using the "5 %-threshold" definition. **(C)** Comparison between the posterior distribution of the t_0 parameter using both definitions and correlations between t_0 and the IRF parameter.

A.4 Formulas Used to Calculate Fit Metrics

In the following, we list the equations used by TAPAS to calculate the goodness-of-fit and uncertainty estimates (see "Fit Metrics" in the main text). Here, $i = 1, \dots, N$ indexes the N delay points and $j = 1, \dots, L$ indexes the L wavelength channels.

Weighted residuals

$$r_{ij} = (\Delta A_{ij} - \Delta A_{\text{cal},ij}) \sqrt{W_{ij}}, \quad (\text{A.6})$$

where $W_{ij} \in [0, 1]$ is the weight applied to point (i, j) . If no weighting is applied, the same formulas below can be evaluated with $W_{ij} \equiv 1$. If a custom weighting array is applied, TAPAS also calculates the subsequent unweighted metrics.

Sum of squared residuals (SSR)

$$\text{SSR} = \sum_{i=1}^N \sum_{j=1}^L r_{ij}^2. \quad (\text{A.7})$$

Weighted total sum of squares (SST)

$$\overline{\Delta A} = \frac{\sum_{i=1}^N \sum_{j=1}^L W_{ij} \Delta A_{ij}}{\sum_{i=1}^N \sum_{j=1}^L W_{ij}}, \quad (\text{A.8})$$

$$\text{SST} = \sum_{i=1}^N \sum_{j=1}^L W_{ij} (\Delta A_{ij} - \overline{\Delta A})^2. \quad (\text{A.9})$$

Coefficient of determination (r^2)

$$r^2 = 1 - \frac{\text{SSR}}{\text{SST}}. \quad (\text{A.10})$$

Root-mean-square error (RMSE)

Let $M = N \times L$, then

$$\text{RMSE} = \sqrt{\frac{1}{M} \sum_{i=1}^N \sum_{j=1}^L r_{ij}^2} = \sqrt{\frac{\text{SSR}}{M}}. \quad (\text{A.11})$$

Mean absolute error (MAE)

$$\text{MAE} = \frac{1}{M} \sum_{i=1}^N \sum_{j=1}^L |r_{ij}|. \quad (\text{A.12})$$

Effective degrees of freedom (d.o.f.)

For each wavelength and delay-time channel, the integrated autocorrelation times $\tau_{\text{delay},j}$

and $\tau_{\text{wave},i}$ are calculated via a python function from `emcee.autocorr` followed by:

$$\tau_{\text{delay}} = \frac{1}{L} \sum_{j=1}^L \tau_{\text{delay},j}, \quad \tau_{\text{wave}} = \frac{1}{N} \sum_{i=1}^N \tau_{\text{wave},i}, \quad (\text{A.13})$$

$$N_{\text{eff,delay}} = \frac{N}{\tau_{\text{delay}}}, \quad N_{\text{eff,wave}} = \frac{L}{\tau_{\text{wave}}}, \quad (\text{A.14})$$

$$N_{\text{eff}} = N_{\text{eff,delay}} \cdot N_{\text{eff,wave}}, \quad (\text{A.15})$$

$$\text{d.o.f.} = N_{\text{eff}} - P, \quad (\text{A.16})$$

with the effective number of datapoints N_{eff} and the number of free parameters P .

Effective standard deviation σ

$$\sigma_{\text{eff}} = \sqrt{\frac{\text{SSR}}{\text{d.o.f.}}}. \quad (\text{A.17})$$

Covariance Cov, standard error (SE) of parameter θ , and correlation coefficients C_{pq}

Let $J \in \mathbb{R}^{M \times P}$ be the Jacobian of the residuals (calculated with the python library **JAX**).

$$H = J^T J, \quad (\text{A.18})$$

$$\text{Cov} = \sigma_{\text{eff}}^2 (H)^+, \quad (\text{A.19})$$

with $(H)^+$ the Moore-Penrose pseudoinverse of H .

$$\text{SE}(\theta_p) = \sqrt{\text{Cov}_{pp}}, \quad (\text{A.20})$$

$$C_{pq} = \frac{\text{Cov}_{pq}}{\text{SE}(\theta_p) \text{SE}(\theta_q)}. \quad (\text{A.21})$$

A.5 Tutorial: Case Study Rose Bengal

A.5.1 Experimental Section

Sample Preparation Rose Bengal (RB) (Dye content 95 %, ≥ 96 % HPLC) sodium salt from Sigma (product number: 330000) and sodium hydroxide pellets from Fisher Scientific were used without further purification. A 20 μ M RB solution was prepared in 0.01 M NaOH using distilled water. The solution was transferred into a 2 mm path-length quartz microcuvette (Hellma Analytics) with a custom-built opening and stopcock (see **Figure A.3**). Prior to all measurements, the cuvette was gently purged with argon to minimize dissolved oxygen. The absorbance at the pump wavelength (520 nm) was 0.10. A magnetic stir bar was added, and the sample was continuously stirred throughout the experiment to mitigate laser-induced photodegradation.



Figure A.3: Used 2 mm cuvette with custom-built opening.

Transient Absorption Measurements Transient absorption measurements were performed with two Ultrafast Systems instruments: the HELIOS Fire (femtosecond regime) and the EOS Fire (nanosecond regime). An Astrella-F Ti:sapphire amplifier (Coherent) produced 800 nm pulses, 90 fs in duration, at a 1 kHz repetition rate. The output was split into pump and probe beams; the pump wavelength was tuned to 520 nm via the sum frequency of the signal in the Apollo-T optical parametric amplifier (Ultrafast Systems). Pump pulse energies were kept at 1 μ J and stray excitation or scattered light was suppressed with the 650/SP BrightLine shortpass filter from Semrock (excitation filter) and the FELH0800 longpass filter from Thorlabs (emission filter during NIR experiments). For femtosecond experiments, a white-light continuum was generated with a sapphire plate (410 - 750 nm) and a proprietary material similar to YAG (830 nm - 1400 nm) whereas for nanosecond experiments the continuum was produced with a photonic crystal fiber. Pump-probe delay times were controlled by a mechanical delay stage to 7.5 ns (fs-TA) and electronically up to 450 μ s (ns-TA). Probe fluctuations were corrected using a reference channel, and the integrity of the sample was verified by comparing UV-vis spectra before and after each experiment.

Software All analyses and visualizations were generated entirely in TAPAS v1.1.4 (Python 3.11.11, PyQt 6.9).

A.5.2 Step-by-Step Guide: NIR Exploration and Sequential Kinetic Modeling

General Structure General Structure. TAPAS employs a tab-based interface in which each tab is dedicated to a distinct step of the analytical workflow. Global project operations including project save/load, GUI preferences, and plotting templates are accessible via the menu bar and toolbar positioned above the tab pane (**Figure A.4**).

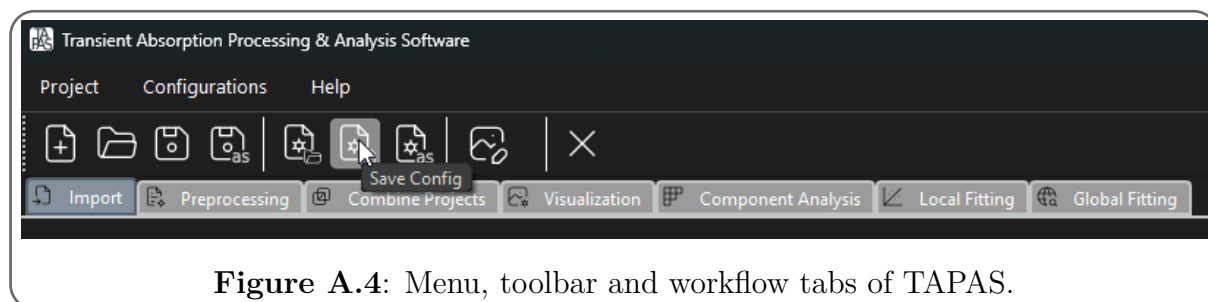


Figure A.4: Menu, toolbar and workflow tabs of TAPAS.

Data Import & Metadata.

- Open the **Import** tab.
- click **Browse** and select the TA data, paste the full path into the input field or Drag-and-drop the file onto the widget.
- Adjust the Import Settings as required (**Figure A.5**).
- Press **Load Data** to read the data into TAPAS.

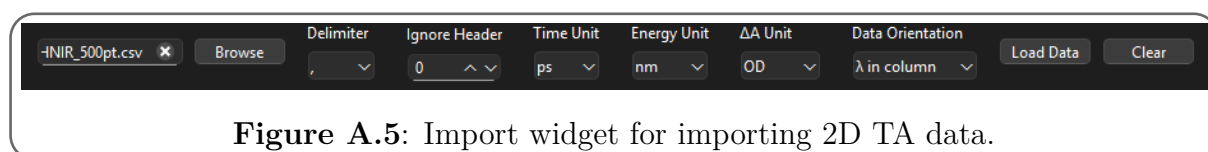


Figure A.5: Import widget for importing 2D TA data.

- Add structured metadata.

Background: Meaningful metadata are critical for reproducibility and automated processing, yet standard CSV files lack a uniform structure, making their extraction difficult without bespoke parsing. TAPAS therefore converts all datasets to HDF5 containers, which store numerical data and structured metadata in distinct, machine-readable sections. The software then leverages these metadata fields to generate plot titles, directory names, and other context-sensitive labels automatically.

- TAPAS scans any lines appended to the end of the .csv and stores them as unstructured Notes metadata.
- Populate the appropriate fields in the **Metadata** container (**Figure A.6**).

Processing.

Metadata

Experiment Name: Rose Bengal Case Study

Sample Name: 20 μ M fs-TA NIR

Excitation Wavelength: 520 nm

Excitation Intensity: 1 μ J/pulse

Solvent: H2O

Notes:

file info: Date: April 28, 2025
 Sample: Rose Bengal 20 μ M
 Solvent: H2O
 Pump energy (μ J): 1
 Pump wavelength (nm): 520
 Cuvette length (mm): 2
 Comments: Time Zero: 218.181 ps
 Averaging time: 2.0 s
 Number of scans: 2
 Measurement time: 00:41:26
 8 Apr 2025 13:23 • Data saved

Figure A.6: Metadata widget of the Import Tab.

- Interactive inspection.
 - Open the **Preprocessing** tab.
 - Position the cross-hair anywhere on the 2-D spectrum with the middle mouse button. The corresponding horizontal and vertical slices update automatically.
 - Scroll the mouse wheel to adjust the color scale (ΔA range) of the surface plot. Regions of detector insensitivity and the chirp are readily discernible in the raw map (**Figure A.7**).
- Trim the data cube.
 - Specify the desired delay and wavelength limits in the **Trim** panel (**Figure A.8**).
 - Observe the selected window highlighted in the canvas.
 - Click **Apply** to commit the trimmed dataset. It is now available to other tabs like **Visualization** and **Fitting** tabs.

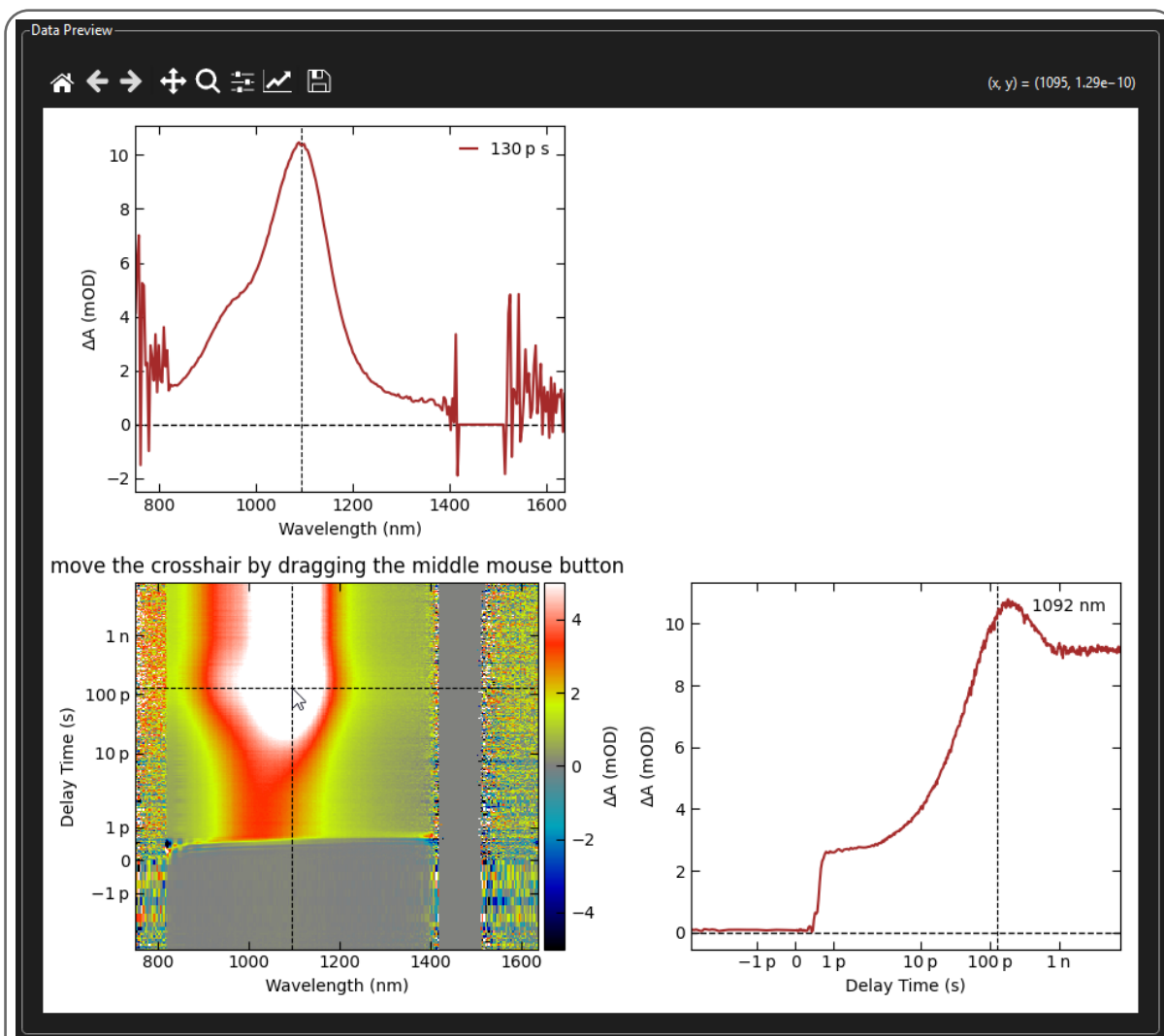


Figure A.7: Preprocessing Canvas showing ΔA spectral slices (top) and kinetic traces (bottom right) at the current position of the cross-hair in the 2D hyperspectrum (bottom left).

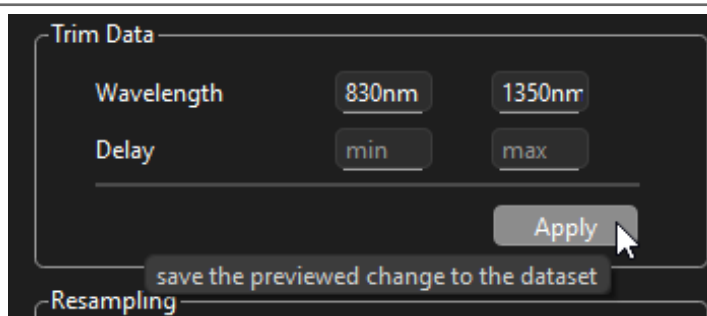


Figure A.8: Widget to trim the dataset.

- Resample the delay grid.

Background: The original delay axis is sparse and linear before time-zero, then becomes logarithmic. A direct chirp correction on this irregular grid can introduce artefacts

(e.g., a jagged rising edge). After the chirp correction, the data can be down-sampled to the original density again.

- In the **Resampling** widget section (**Figure A.9**), set the interval (e.g. min to 0), the up/down- sampling factor, the axis and the method.
- Press **Resample** to generate a subsampled grid up to 0 ps and **Apply**.
- Alternatively, **Regularize** redistributes a fixed number of points evenly (useful along the wavelength axis).

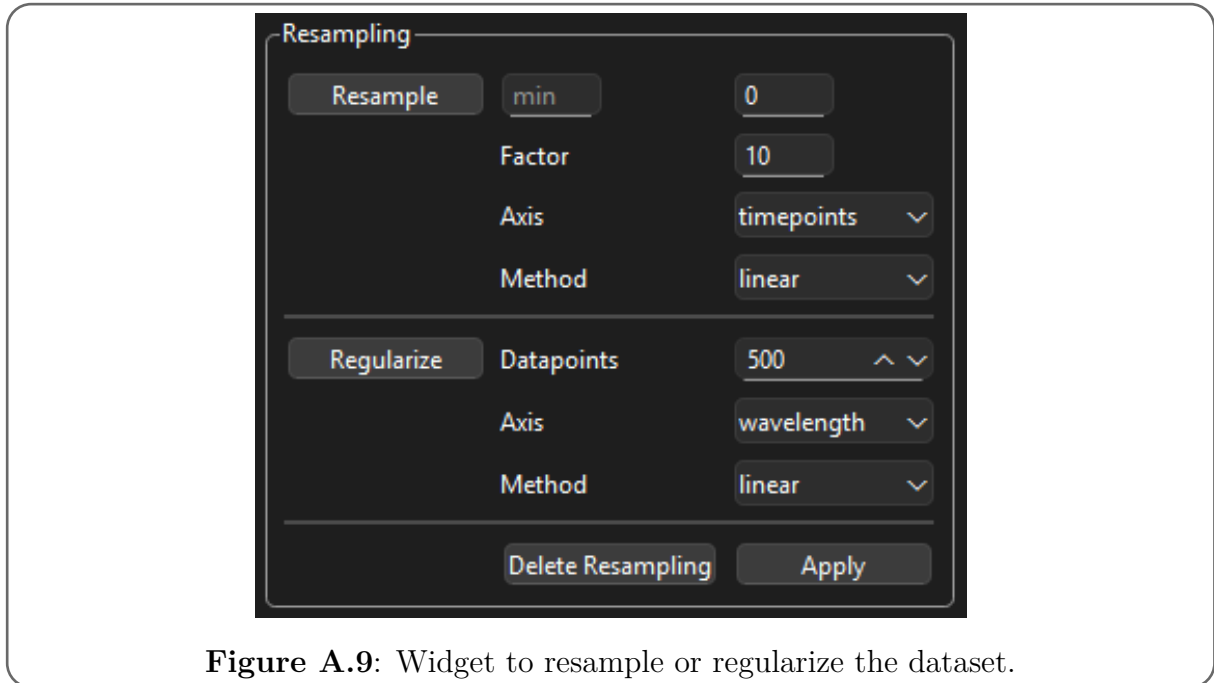


Figure A.9: Widget to resample or regularize the dataset.

- Chirp correction.
 - Set a heuristic threshold (e.g. 5 % rise, global maximum) and click **Autocorrect** (**Figure A.10**) TAPAS locates the corresponding time-of-arrival markers.
 - With **Manually Correct** active, left-click adds a point, right-click removes one.
 - Select **Fit** to pass a fourth-order polynomial through the chosen points (**Figure A.11**).
 - Click **Show Correction** to display the dispersion-corrected data interpolated back onto the original grid.
 - Alternatively, choose **Correct from Project** to import a fitted curve from another TAPAS project.

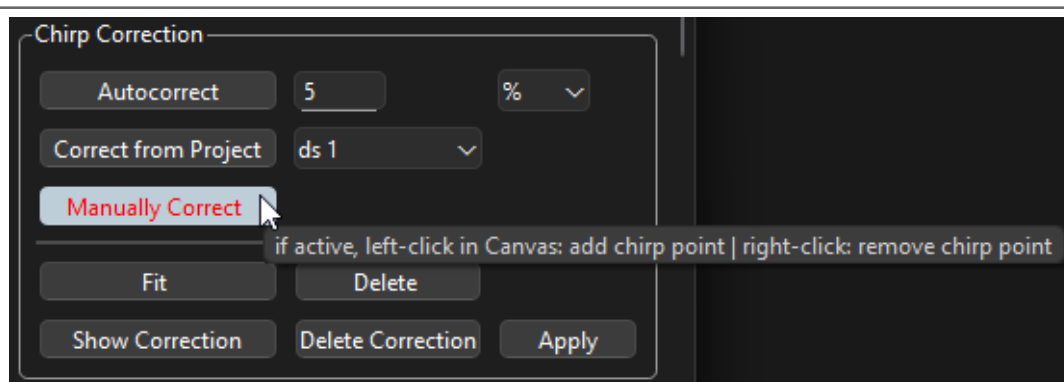


Figure A.10: Chirp-correction widget in TAPAS.

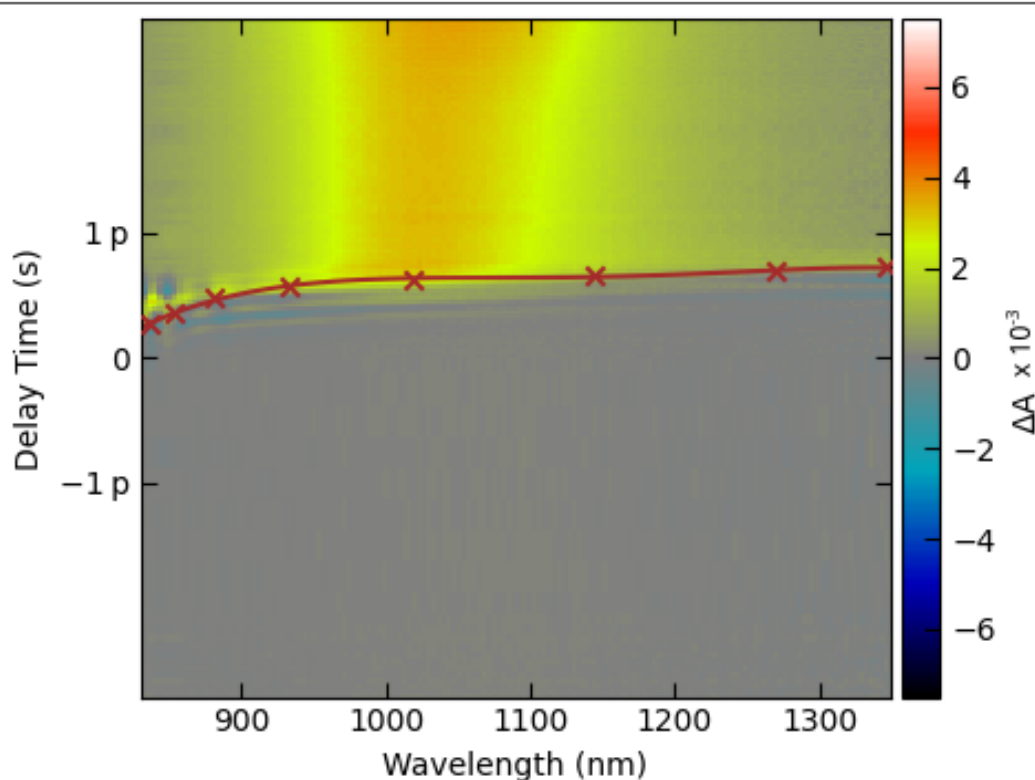


Figure A.11: Canvas during chirp correction. The points and the fitted 4th order polynomial are displayed.

- Background Correction.
 - Select the interval to be averaged as background (**Figure A.12**).
 - Select the averaging method (mean, median) and, if required, set an upper time limit beyond which no correction will be applied.
 - Click **Subtract Area** to view a preview of the corrected spectrum.
 - Click **Apply** to commit the background-corrected data to the dataset.
 - If a matching solvent map was imported in the **Import** tab, choose **Subtract Solvent** to eliminate the solvent contribution.

- Alternatively, select **Subtract from Project** to remove a compatible 2-D surface stored in another TAPAS project.

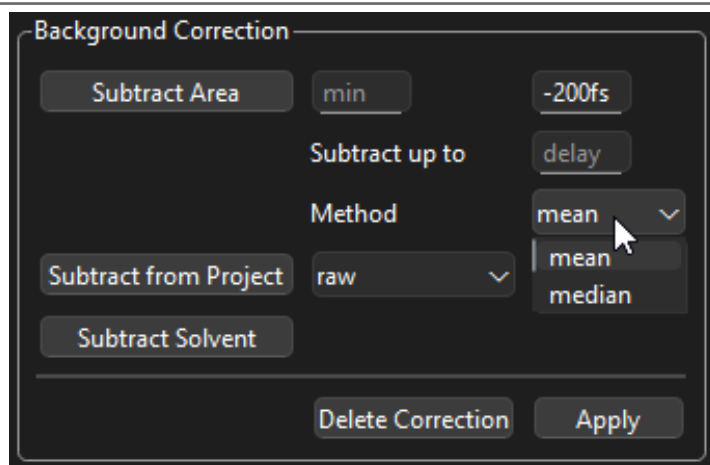


Figure A.12: Background correction widget.

- Time-Zero Correction (not applied to the present dataset).
 - Set a delay-time to be treated as $t = 0$ (**Figure A.13**).
 - Click **Apply** to shift the entire delay axis or **Delete Correction** to remove the shift.

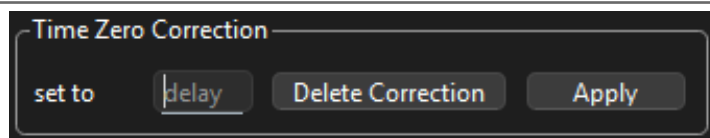


Figure A.13: Time-zero correction widget.

- Averaging and Filtering (not applied to the present dataset).
 - Select a filter type from the dropdown list (**Figure A.14**).
 - Set the window length and polynomial order for Savitzki-Golay filtering or the filter size for moving filters.
 - Specify the axis (delay or wavelength) over which the filter will operate.
 - **Show**, **Delete** or **Apply filter**.

In **Figure A.15** the final preprocessed dataset can be seen.

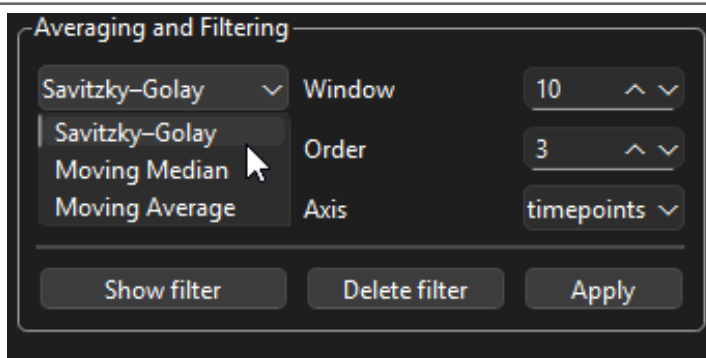


Figure A.14: Averaging and filtering widget

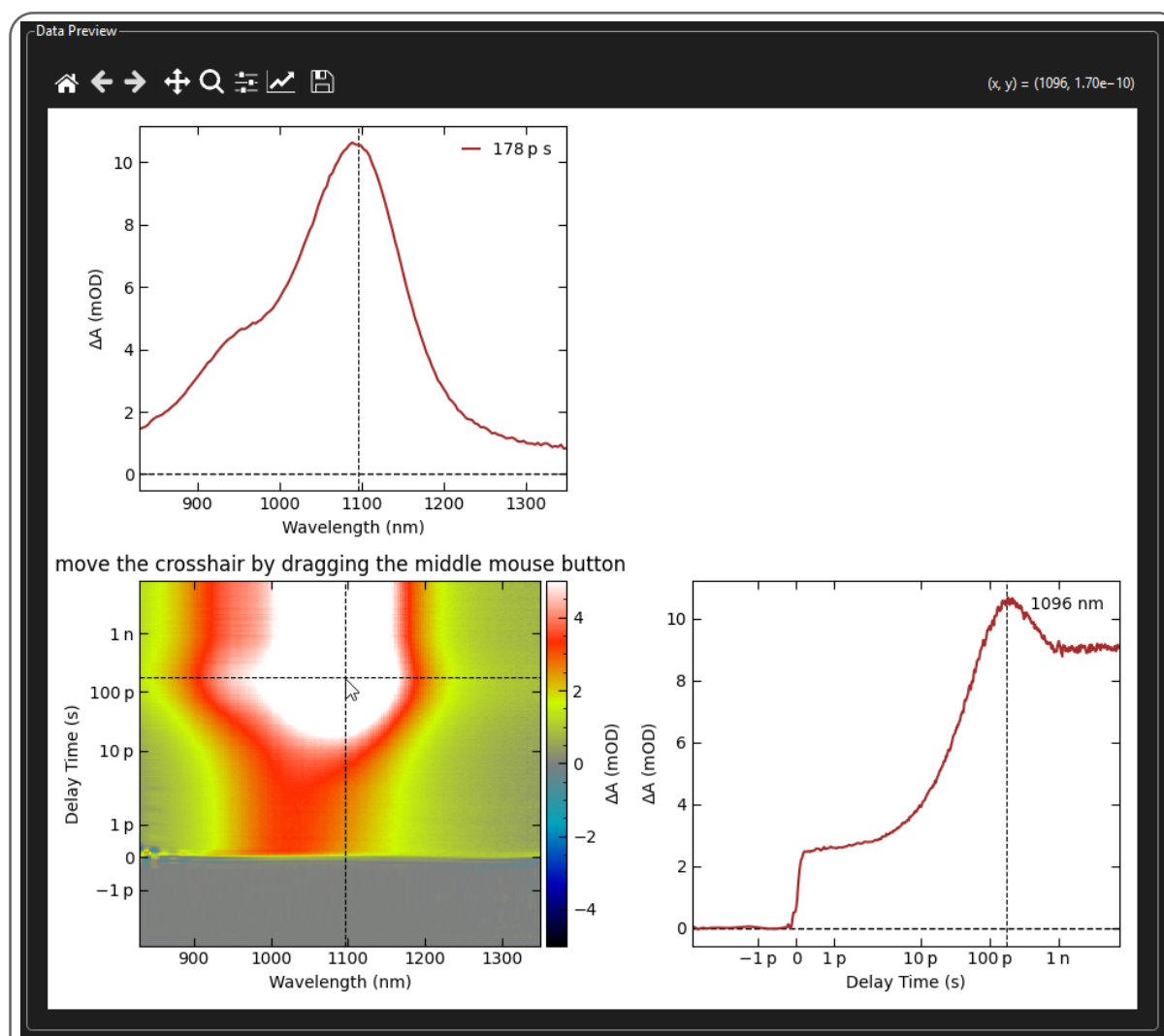


Figure A.15: Preprocessing Canvas after trim, chirp and background correction.

Component Analysis.

- SVD Analysis.
 - Select the **Component Analysis** tab.

- Select a dataset to be subjected to SVD.
- Adjust the number of principal components. TAPAS dynamically recalculates the spectral and temporal vectors, the singular values, and the two-dimensional residual map (**Figure A.16**).

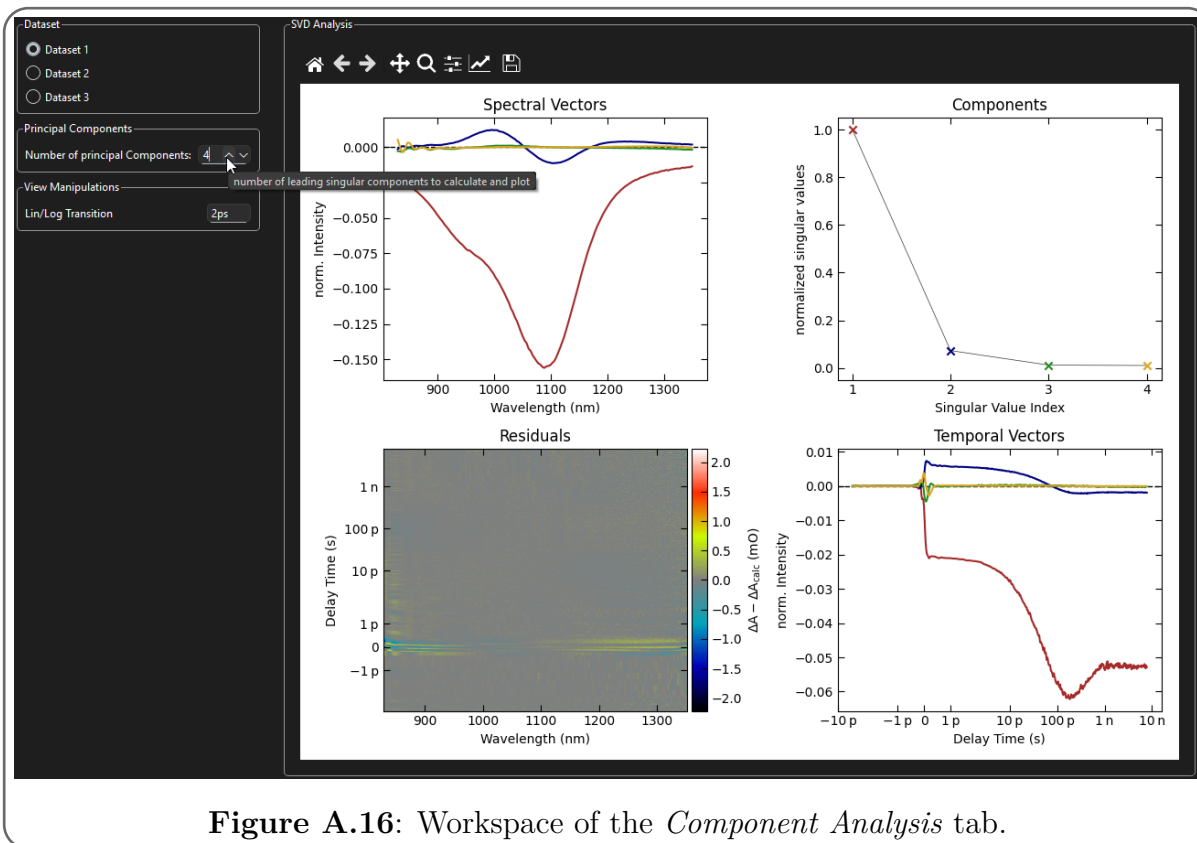


Figure A.16: Workspace of the *Component Analysis* tab.

Local Fit at 1200 nm.

- Prepare Fit.
 - Select the **Local Fit** tab.
 - Select the desired dataset.
 - Enter the target wavelength (1200 nm) and, if needed, define a spectral window for averaging (**Figure A.17**).
 - Configure the kinetic model:
 - * Number of components
 - * Optional infinite (offset) component
 - * CA modeling
 - * Kinetic model
 - * Time-zero definition
 - * Fitting algorithm
 - Supply initial parameter guesses and, where appropriate, bounds or fixed values.
 - Click **show initial fit** to visualize how well these starting estimates describe the data.

Fitting Parameters

Wavelength $\pm$ 0 nm ^ v

Components ^ v

☒ Infinite Component?

Fit CA v

Model v

time zero v

Method v

	value	min	max	vary
t0	20fs			
IRF	200fs			
τ_1	50ps			
τ_2	500ps			

modeling initial guess succeeded

Figure A.17: Input mask of the *Local Fit* Tab.

- Run the Optimization.
 - Press **Fit** to execute the routine with the current settings.
 - If the optimization fails, a diagnostic message appears in the status bar; revise starting values or bounds and retry.
 - On successful convergence, TAPAS displays the fitted curve together with a detailed statistical report.
 - Click **Save Fit to Dataset** to make the result available for later parameter analysis and for the **Visualization** tab.

```

local fit results: 1.2e-06m
Date: 250616
Experimental conditions: 20  $\mu$ M fs-TA NIR | 520 nm | 1  $\mu$ J/pulse | H2O |

-----

-- Results from Jacobian Analysis: --

problem seems well conditioned

-- PARAMETERS: --
t0: 71.4fs  $\pm$  9fs (12.37%)
IRF: 235.5fs  $\pm$  16fs (6.92%)
 $\tau$ 1: 17% 76.2ps  $\pm$  6ps (8.50%)
 $\tau$ 2: 49% 185.9ps  $\pm$  25ps (13.48%)
Ainf: 33 %

-- CORRELATIONS: --
t0 IRF  $\tau$ 1
IRF 0.63
 $\tau$ 1 -0.09 -0.06
 $\tau$ 2 0.06 0.04 -0.93

-- FIT METRICS: --
Model: sequential
 $r^2$ : 0.998
SSR: 0.52
RMSE: 0.032 mOD
MEA: 0.025 mOD
data points: 509 (total), 81 (effective)
eff residual var: 0.01
eff residual  $\sigma$ : 0.08 mOD
Jacobian cond num: 11
Avg lag-1 autocor y axis: 0.413
Method: Nelder-Mead
time zero: Gaussian centroid
# evaluations: 146
fit + diagnostics time: 0.22 s + 0.00 s

-----

-- Results from the MCMC Posterior Analysis --

Number of samples: 1000

-- PARAMETERS: --
Param -2 $\sigma$  -1 $\sigma$  Median +1 $\sigma$  +2 $\sigma$ 
-----
t0 -22fs -10fs 70.0fs 10fs 20fs
IRF -40fs -20fs 233.7fs 20fs 41fs
 $\tau$ 1 -12ps -7ps 78.3ps 15ps 80ps
 $\tau$ 2 -95ps -40ps 178.8ps 27ps 55ps
ln( $\sigma$ ) -0.16 -0.08 -2.50 0.09 0.18

-- CORRELATIONS: --
t0 IRF  $\tau$ 1  $\tau$ 2
IRF 0.74
 $\tau$ 1 -0.04 -0.07
 $\tau$ 2 0.06 0.07 -0.88
ln( $\sigma$ ) 0.01 0.01 0.05 -0.04

burn: 300, thin: 1

```

Figure A.18: Full output after a successful local fit in TAPAS including the results of the (unbound) posterior analysis. This is printed in the Results Widget and is exportable as a text file.

- Explore the posterior with MCMC (optional).
 - Highlight a saved fit in the fitting list (**Figure A.19**).
 - Define MCMC settings:
 - * Burn-in (samples to discard)
 - * Initial draw (starting sample size)
 - * Thinning ratio
 - * Stopping criterion
 - Click **Perform Analysis** to start the sampler; the canvas reports estimated run time, accepted samples, and interim statistics.
 - You may abort after any iteration block if convergence is satisfactory.
 - Once complete, press **Save Analysis** to attach the posterior results to the dataset, where they can be accessed in the **Visualization** tab.

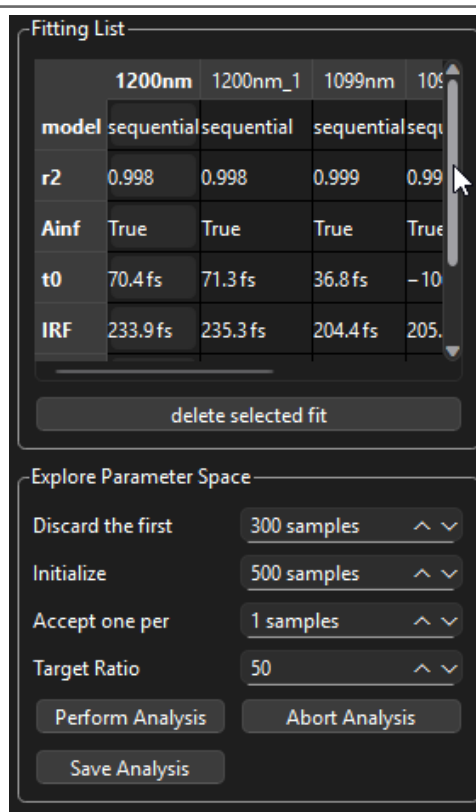


Figure A.19: Fitting List widget, where the user selects a presaved fit for the MCMC parameter space evaluation which can be defined in the lower widget.

Visualization of the Local Fit.

- Plot the kinetic trace.
 - Open the **Visualization** tab.
 - Click the **Local Fit** plot button and choose **Kinetic Trace**.

- In the **Plot Properties** panel, pick the desired fit (**Figure A.20**).
- Adjust colors, axis limits, and any additional plot settings.
- In the Figure Style panel (**Figure A.21**), define figure size, font, file format, and output folder.
- Click **Save** to write the figure with the chosen settings.
- Click **Export data** to save the underlying curve as a CSV file.

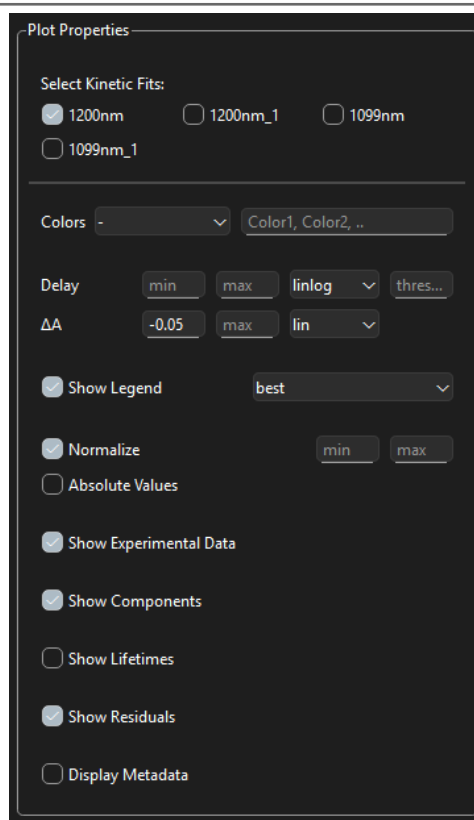


Figure A.20: Plot properties for the visualization of the local fit kinetic traces.

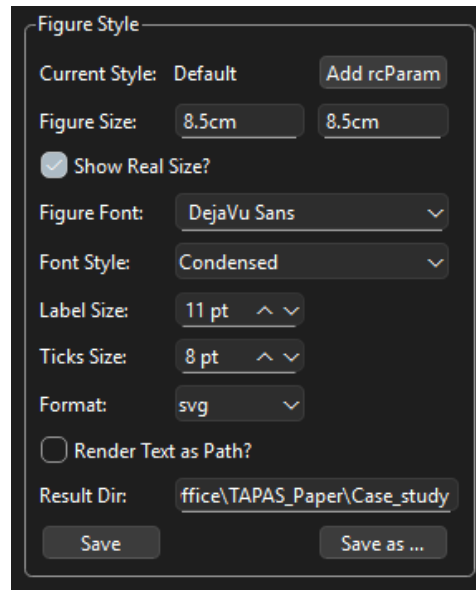


Figure A.21: Figure style panel used for the visualization and export of data and fit results.

- Display the parameter posteriors.
 - Select the **Visualization** tab.
 - Click **Local Fit** (or **Global Fit**) and select **Posterior dist.**
 - In Plot Properties (**Figure A.22**), choose the fit whose posterior you wish to inspect.
 - Set the number of histogram bins and toggle options for contours, data points, medians, etc.
 - Specify figure size, font, file format, and output directory in the Figure Style panel (**Figure A.21**).
 - Press **Save** to export the figure, or **Export data** to write the posterior samples to *.csv*.

Plot Properties

Select Fit:

☒ 1200nm ☐ 1200nm_1 ☐ 1099nm
☐ 1099nm_1

Bins 17 ^ v

Label Pad 58 ^ v

Subplot Pad 9 ^ v

Max # of Ticks 3 ^ v

☒ Show Values

☒ Show Errors

☒ Show Median $\pm \sigma$

☐ Show Datapoints

☒ Show Contours

☒ Plot Density

Figure A.22: Plot properties for the visualization of the parameter posteriors.

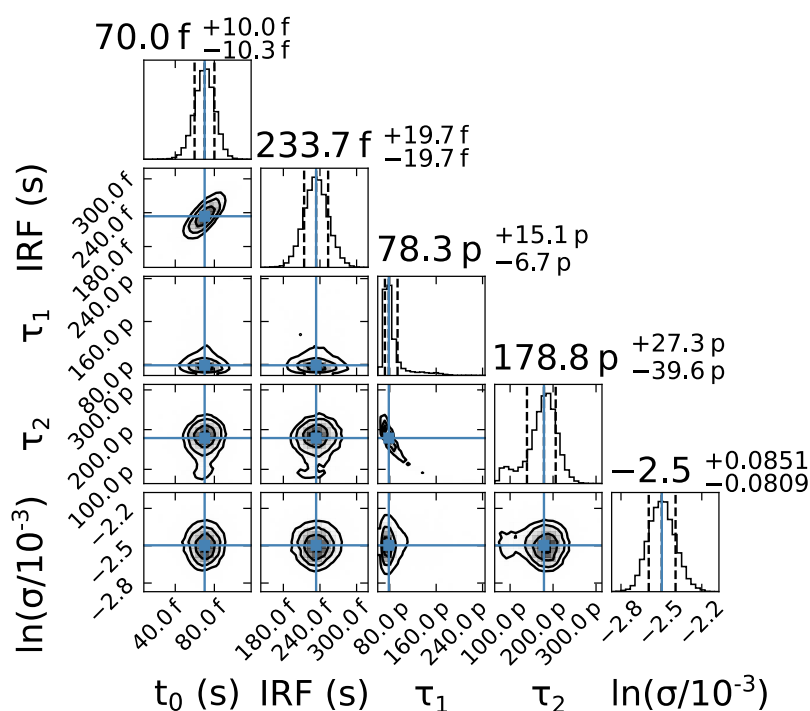


Figure A.23: Local sequential analysis of Rose Bengal in the NIR at 1200 nm (unbound). Corner plot of the MCMC posterior for the biexponential local fit. The main peaks lie at $\tau_1 \approx 80$ ps and $\tau_2 \approx 180$ ps, but weak secondary lobes are visible where τ_1 samples cluster near 200 ps and τ_2 near 80 ps. These minor modes arise from label-switching: because the likelihood is unchanged if the two exponential components are interchanged, the sampler occasionally swaps their identities when no bounds are imposed.

Global Sequential Fit.

The layout parallels the **Local Fit** tab, so the workflow described in Local fit at 1200 nm applies here as well.

Key additions are:

- Ground-state bleach component (not applied to the present dataset).
 - Tick **Explicit GSB** to include an explicit species with a fixed negative concentration to represent the ground-state population of excited molecules.
 - Tick **Use Steady-State** if the steady-state absorption trace should be used as the spectral shape for this component; the fit then allows a small wavelength shift and broadening around the template.
- Wavelength-dependent weighting (not applied to the present dataset).
 - Define multiple wavelength intervals with weights (0 – 100 %).

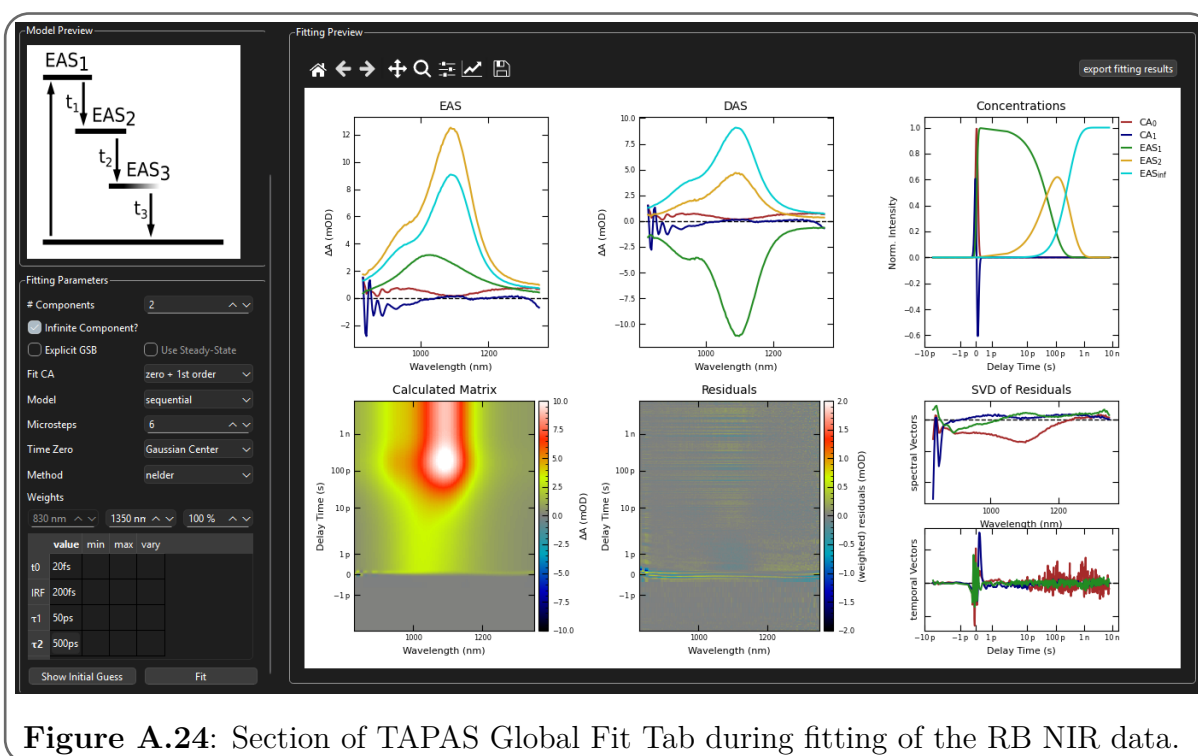


Figure A.24: Section of TAPAS Global Fit Tab during fitting of the RB NIR data.

Visualization of the Global Fit

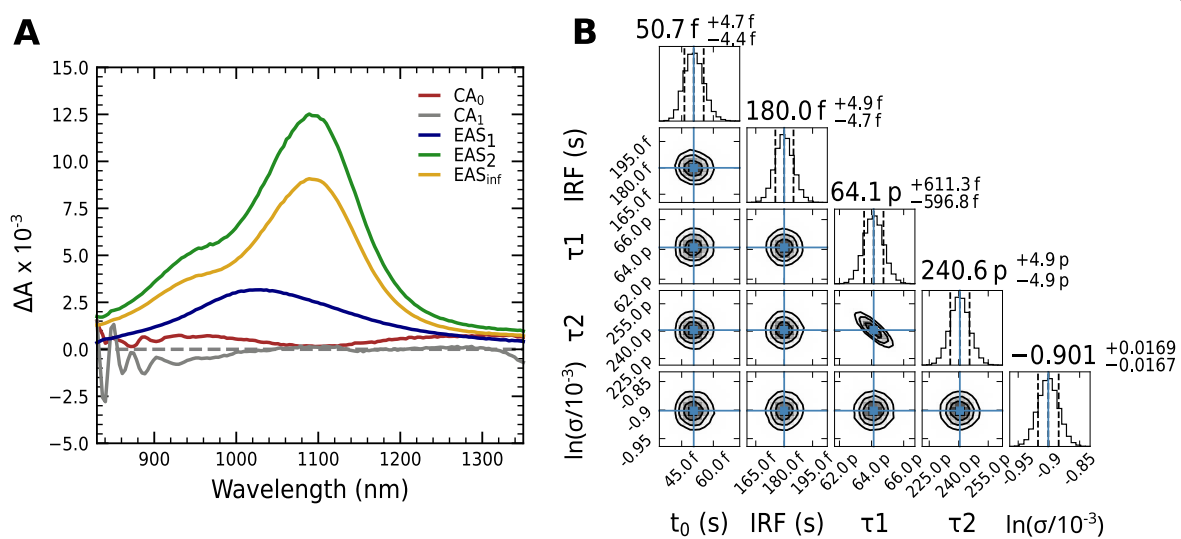


Figure A.25: Global sequential analysis of Rose Bengal in the NIR. **(A)** EAS obtained from the global fit, comprising the three kinetic components together with the zero- and first-order coherent-artifact terms that account for pump–probe overlap at early delays. **(B)** Corner plot of the MCMC posterior for the same model.

A.5.3 Step-by-Step Guide: Comprehensive Target Analysis

Preprocessing of the vis TA data. The visible fs-TA dataset was treated as outlined in **Appendix A.5.3**, except that solvent subtraction was performed first via the Background Correction widget in the Preprocessing tab. The human-readable metadata generated by TAPAS for each pre-processing step are summarized in **Table A.2**.

Table A.2: Preprocessing metadata of the vis fs-TA data created by TAPAS.

Step	Action
Preprocessing 1	Solvent subtracted.
Preprocessing 2	Data trimmed from 4.1e-07 m to 7.5e-07 nm and -5e-12 (s) to 7.77e-09 (s).
Preprocessing 3	resampled delay time from lowest value to highest value by multiplying by 10.0 and using linear interpolation.
Preprocessing 4	Chirp corrected using a 4th order polynomial. Fit coefficients in order of increasing degree [-2.36334637e-12 -2.00368478e-05 1.45834916e+02 -2.45504267e+08 1.31726486e+14].
Preprocessing 5	resampled delay time from lowest value to -2e-13 by multiplying by 0.1 and using linear interpolation.
Preprocessing 6	Background corrected by calculating the median from earliest time to -3.3e-13 (s) and subtracting it from the whole dataset.

Table A.3: Preprocessing metadata of the vis ns-TA data created by TAPAS.

Step	Action
Preprocessing 1	Data trimmed from 4.1e-07 m to 9.13e-07 nm and -2e-07 (s) to 0.000446 (s).
Preprocessing 2	Background corrected by calculating the mean from earliest time to -1e-09 (s) and subtracting it up to 1.9e-05 (s) from the dataset.
Preprocessing 3	Data trimmed from 4.1e-07 m to 9.13e-07 nm and 2e-09 (s) to 0.000446 (s).

Combining two projects.

- Preprocess both projects individually.
- Load both projects.
 - Open the **Combine** tab.
 - click **Browse** and select the TA data, paste the full path into the input field or Drag-and-drop the file onto the widget.
 - Press **Load** to read the project into TAPAS.
- Combine both projects.

- Choose how to handle the overlapping area.
- Select how the data is interpolated on the new grid.
- Select how to handle missing grid values.

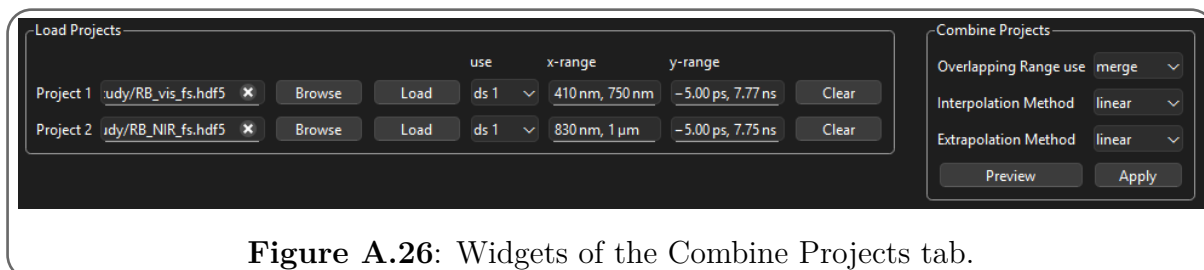


Figure A.26: Widgets of the Combine Projects tab.

Global Sequential Fit, Weights and explicit ground state model

- Explicit ground-state model.
 - Load steady-state absorbance data in the **Import** tab.
 - Regularize the wavelength grid in the **Preprocessing** tab.
Background: the optimization refines the GSB template by FFT-based shifting and broadening; this requires a regular grid.
 - Switch to the **Global Fit** tab and tick **Explicit GSB** as well as **Use Steady-State**.
- Define weighting windows.
 - In the **Fitting Parameters** panel, select a wavelength interval with the spin boxes.
 - Assign a weighting factor between 0 % (ignore) and 100 % (full weight). Down-weight regions dominated by scattered light, detector edges, or heavy interpolation artefacts to improve fit robustness (**Figure A.27**).

Fitting Parameters

Components

☒ Infinite Component?

☒ Explicit GSB ☒ Use Steady-State

Fit CA

Model

Microsteps

Time Zero

Method

Weights

410 nm	500 nm	100 %
500 nm	530 nm	0 %
530 nm	750 nm	100 %
750 nm	830 nm	0 %
830 nm	1350 nm	100 %

	value	min	max	vary
t0	20fs			
IRF	200fs			false
τ_1	2ps			
τ_2	60ps			
τ_3	200ps			

fitting algorithm finished successfully

Figure A.27: Fitting settings and parameters used for the global sequential fit.

Target Fit. The target fit was carried out with a built-in kinetic scheme selected from the **Model** drop-down in the Fitting Parameters widget; the remaining steps followed the standard global/local-fit workflow. Guidance on creating custom kinetic models and integrating them into TAPAS is provided in **Appendix A.5.4**.

Note that in the current target global fit example, CA modeling with a zero and first order Gaussian IRF led to a nearly singular Jacobian. As a result, TAPAS cannot derive standard errors from the covariance matrix (compare the output in **Figure A.30**). In this situation, however, the MCMC posterior routine still provides reliable error estimates.

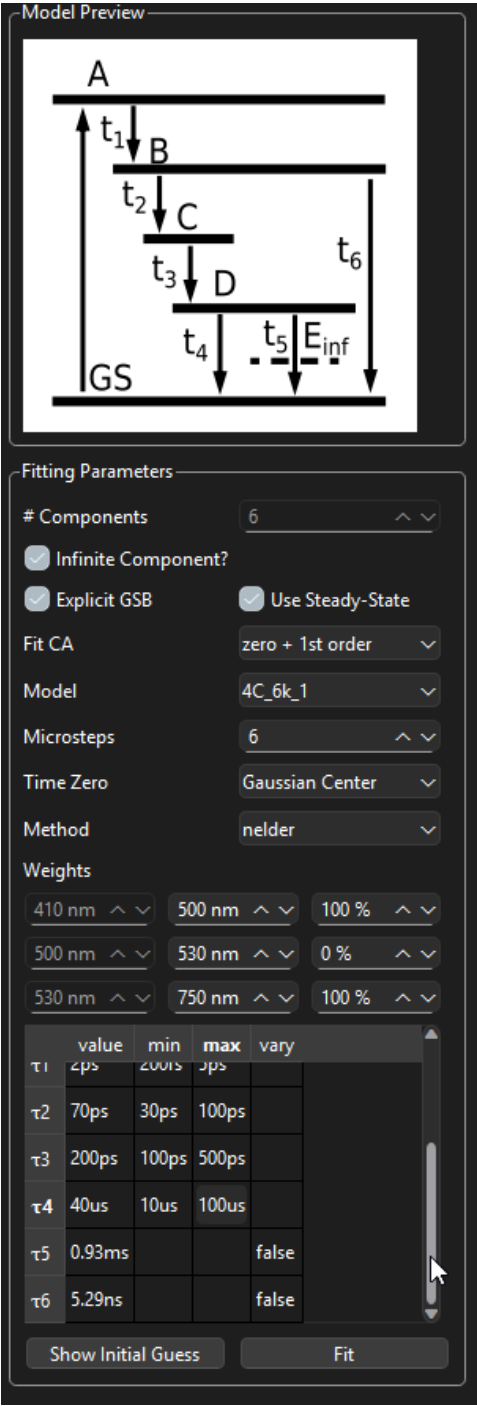


Figure A.28: Fitting settings and parameters used for the target fit.

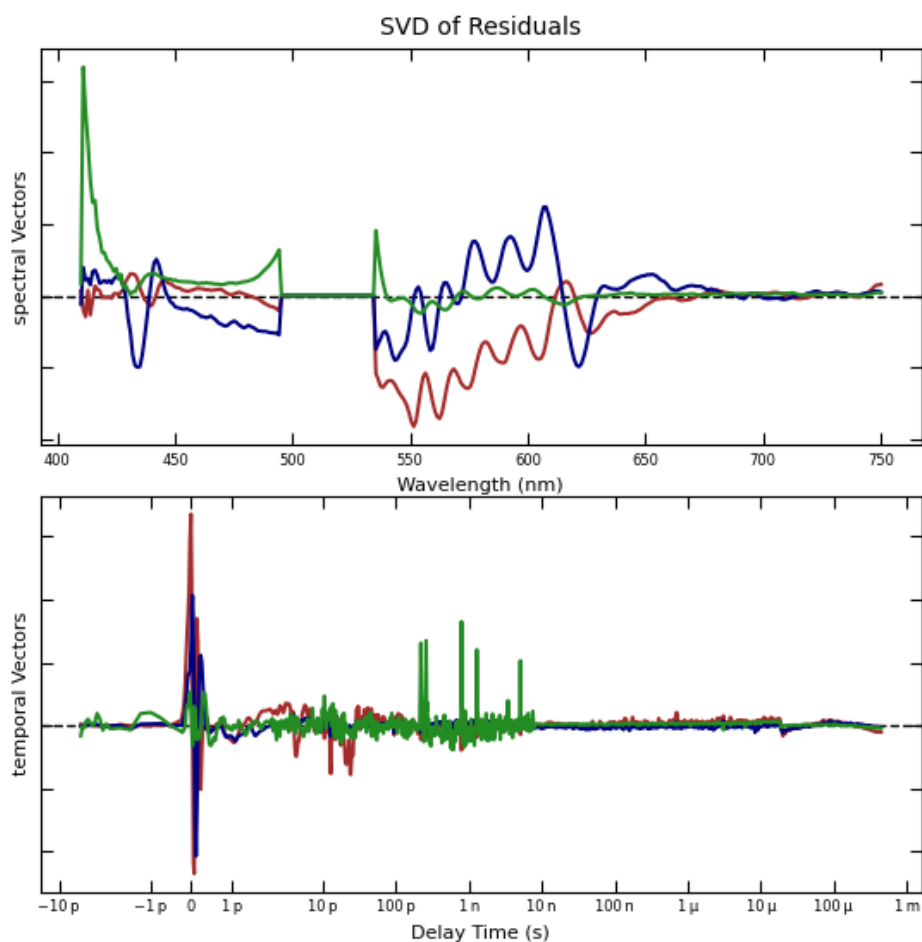


Figure A.29: SVD of the target-fit residuals. **Top:** First three spectral singular vectors highlighting narrow features at the detector edges and weak bands that match pump-fluctuation. **Bottom:** Corresponding temporal singular vectors. The leading vector peaks sharply at early delays, consistent with coherent-artifact remnants, whereas the second and third vectors exhibit low-amplitude, slowly varying behavior typical of pump-intensity noise.


```

global fit results:
Date: 250616
Experimental conditions: 20  $\mu$ M TA combined | 520 nm | 1  $\mu$ J/pulse | H2O |

-----

-- Results from Jacobian Analysis: --

errors could not be calculated:
non-stable derivatives

-- PARAMETERS: --
t0: 139.9fs
IRF: 200.0f(fixed)
 $\tau_1$ : 1.7ps
 $\tau_2$ : 71.1ps
 $\tau_3$ : 215.0ps
 $\tau_4$ : 41.8 $\mu$ s
 $\tau_5$ : 930.0 $\mu$ (fixed)
 $\tau_6$ : 5.3n(fixed)
gs_shift: 3.6n(fixed)
gs_sigma: 2.0n(fixed)
Ainf: True

-- FIT METRICS: --
Model: 4C_6k_1
r2: 1.000
SSR: 44317.76
RMSE: 0.311 mOD
MEA: 0.110 mOD
data points: 457640 (total), 8689 (effective)
eff residual var: 5.11
eff residual  $\sigma$ : 2.26 mOD
Avg lag-1 autocorr x axis: 0.549
Avg lag-1 autocor y axis: 0.712
Method: Nelder-Mead
time zero: Gaussian centroid
# evaluations: 535
fit + diagnostics time: 4.53 s + 2.04 s

-----

-- UNWEIGHTED RESULTS: --
errors could not be calculated:
non-stable derivatives

-- FIT METRICS: --
r2: 0.975
SSR: 3003145.75
RMSE: 2.562 mOD
MEA: 0.447 mOD
data points: 457640 (total), 8031 (effective)
eff residual var: 374.42 mOD
eff residual  $\sigma$ : 19.35

Avg lag-1 autocorr x axis: 0.942
Avg lag-1 autocor y axis: 0.715

-----

-- Results from the MCMC Posterior Analysis --

Number of samples: 1000

-- PARAMETERS: --
Param -2 $\sigma$  -1 $\sigma$  Median +1 $\sigma$  +2 $\sigma$ 
-----
t0 -3fs -1fs 139.9fs 1fs 3fs
 $\tau_1$  -108fs -56fs 1.7ps 58fs 118fs
 $\tau_2$  -684fs -344fs 71.1ps 340fs 682fs
 $\tau_3$  -5ps -3ps 215.3ps 3ps 5ps
 $\tau_4$  -585ns -303ns 41.8 $\mu$ s 305ns 605ns
ln( $\sigma$ ) -0.01 -0.01 0.81 0.01 0.02

-- CORRELATIONS: --
t0  $\tau_1$   $\tau_2$   $\tau_3$   $\tau_4$ 
 $\tau_1$  0.07
 $\tau_2$  0.05 0.11
 $\tau_3$  0.03 -0.27 0.25
 $\tau_4$  0.02 -0.01 0.02 0.10
ln( $\sigma$ ) 0.04 0.00 0.03 0.00 0.00

burn: 300, thin: 1

```

Figure A.30: Full output after the target global fit in TAPAS including the results of the posterior analysis. This is printed in the Results Widget and is exportable as a text file.

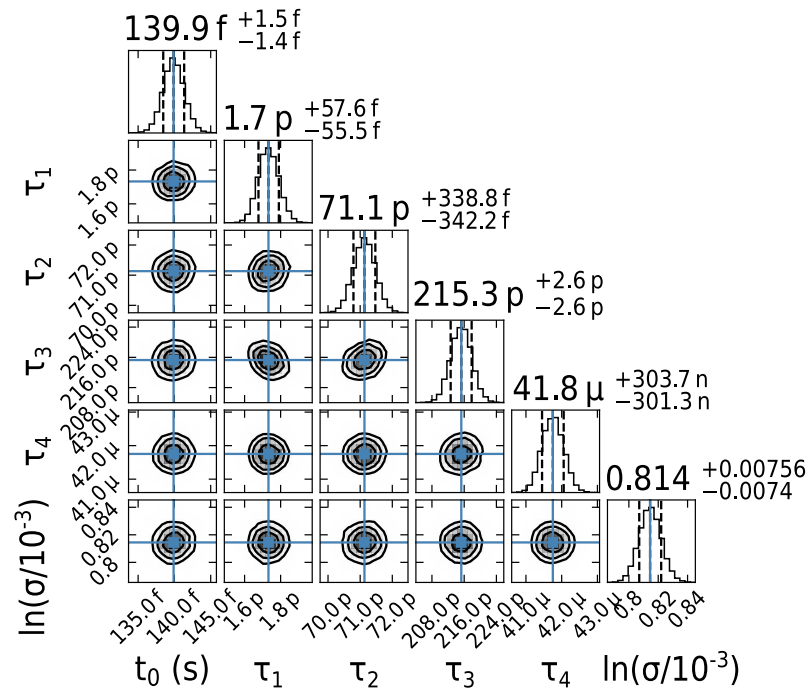


Figure A.31: Corner plot of the MCMC posterior for the target model.

HDF5 Container-File. Storing the TA data as an HDF5 container reduces disk usage and simplifies downstream processing. HDF5 keeps the numerical arrays in binary form, so a typical TA data set that occupies 4.58 MB in UTF-8 CSV format shrinks to only 1.98 MB, a reduction of about sixty percent. The format also allows us to attach structured metadata directly to each data set, which makes programmatic reading and writing straightforward. Figure S5.3.7 shows the HDF5 file using HDFView 3.3.1 produced for the present study together with the metadata that TAPAS adds automatically.

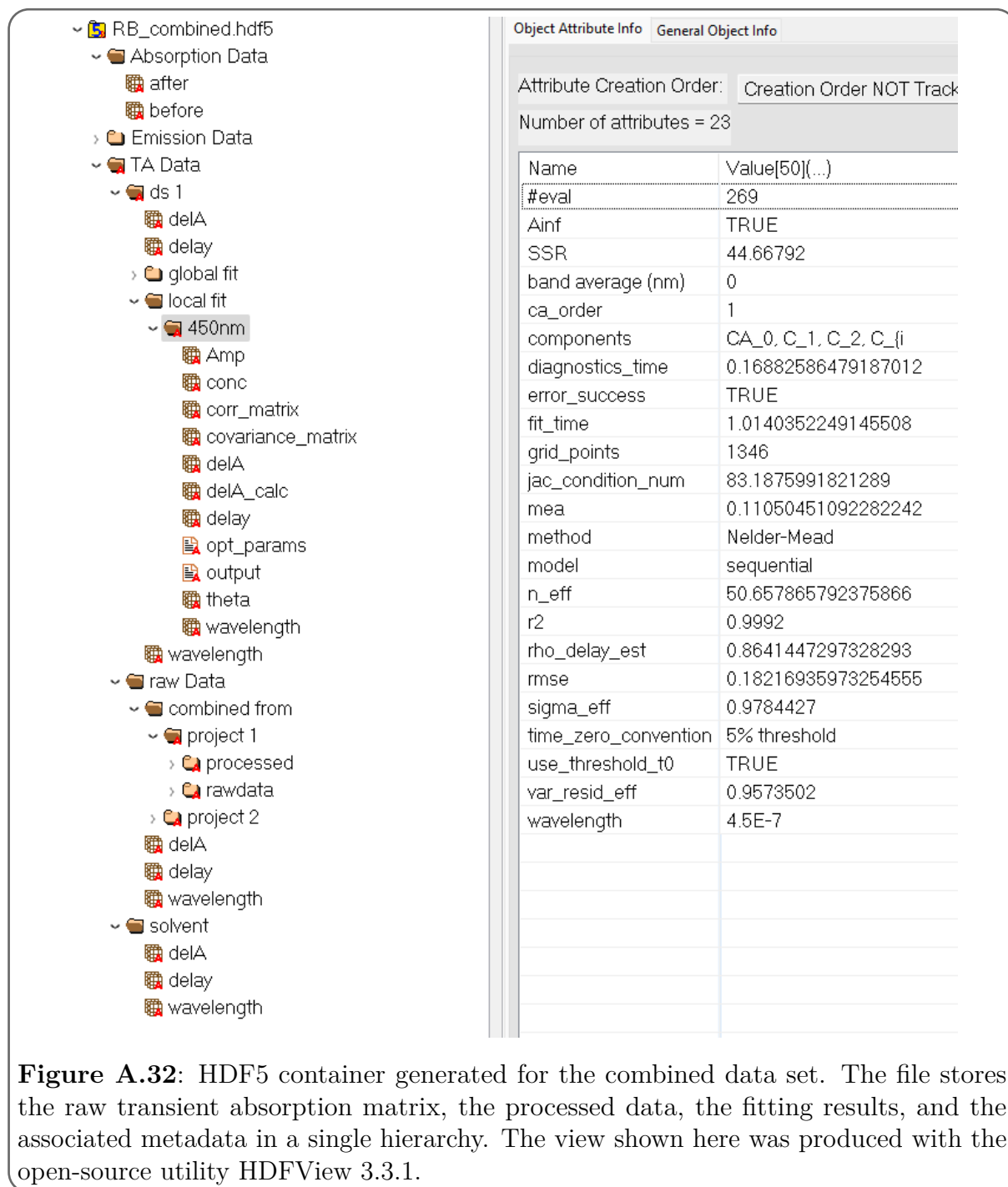


Figure A.32: HDF5 container generated for the combined data set. The file stores the raw transient absorption matrix, the processed data, the fitting results, and the associated metadata in a single hierarchy. The view shown here was produced with the open-source utility HDFView 3.3.1.

A.5.4 Define and Integrate a new Kinetic Model

The procedure involves three parts: (1) coding the kinetics, (2) exposing the model in the GUI, and (3) optionally teaching the controller how to label the compartments.

- Define the kinetics.

File: `tapas/utils/model_function.py`

Depending on the kinetic model, TAPAS needs to treat and display different amounts of components and rates. These must not only be defined inside the model function itself, but also encoded in a standardized way in the function name, so that TAPAS knows, before evaluating the kinetics, how many variables to expect.

- Duplicate an existing template: Inside the `ModelFunctions` class, copy-paste any target-model function as a starting point. Each function consists of a name that follows a specific naming pattern, two sections where the parameters and kinetics are defined, respectively, and three subsequent sections containing the core algorithm, which remain unchanged between models. It is crucial that the number of components and rates encoded in the function name exactly matches the parameters (rates and components) defined in the parameter section. This one-to-one correspondence ensures that TAPAS can correctly interpret and process the model.
- Rename the function. Use exactly the pattern `model_<n>C_<m>k_<j>`, where
 - * n = number of compartments (excluding A_{inf}),
 - * m = number of (first-order) rate constants,
 - * j = arbitrary identifier.

Background: TAPAS parses this name to prefill the rate-constant input masks.

- Edit the parameter block: In the `# parameters` section, set rates $k_1, k_2 \dots k_n$ and `n_pool = <n>`.

```
# ----- parameters -----
t0, irf = theta[0], theta[1]
k1, k2, k3, k4, k5, k6 = 1.0 / theta[2:-2] if use_bleach else 1 / theta[2:]

n_pool = 5 if Ainf else 4
c0 = jnp.zeros(n_pool)
```

- Build the rate matrix: Modify the `kinetics()` sub-function to assemble the rate matrix that integrates to concentration profiles.

```
# ----- kinetics -----
def kinetics(c, g):
    A = c[0]
    B = c[1]
    C = c[2]
    D = c[3]

    dA = g - k1 * A
    dB = k1 * A - (k2 + k6) * B
    dC = k2 * B - k3 * C
    dD = k3 * C - (k4 + k5) * D

    if Ainf:
        E = c[4]
        dE = k5 * D
        return jnp.array([dA, dB, dC, dD, dE])
    else:
        return jnp.array([dA, dB, dC, dD])
```

- Leave everything else unchanged.
- Expose the model in the GUI.
File: `tapas/views/tabwidgets/global_fit_tabwidget.py`
 - Add the signature to the **combobox**: Within `InputWidget._initUI()`, append the model name string to `self.cb_model`.

```
self.cb_model = QComboBox()
self.cb_model.addItem(
    ['parallel', 'sequential', '2C_3k_1', '3C_5k_1', '3C_4k_1', '4C_6k_1', ])
```

- (Optionally) label the compartments.
File: `tapas/controller/global_fit_controller.py`
 - Update the label map: in `GlobalFitController.get_component_labels()`, insert:

```
elif model == '4C_6k_1':
    labels += ['A', 'B', 'C', 'D']
    if Ainf:
        labels.append('E_{inf}')
```

- Compartment labels then propagate to plots, tables, and exported CSV files.

A.6 Comparison TAPAS, Glotaran and KiMoPack

This section benchmarks TAPAS, Glotaran, and KiMoPack with respect to raw fitting speed, error estimation speed and fidelity. TAPAS and Glotaran return first-order standard errors, while KiMoPack derives confidence limits from an F-test that requires many re-fits. The latter is statistically superior for strongly correlated or asymmetric parameters, but the extra work inevitably inflates the wall-clock time. TAPAS can also perform Bayesian MCMC sampling, but those runtimes are not included here because they exceed even the F-test and serve a different diagnostic purpose.

We evaluated the programs on two pre-processed pump-probe data sets: The RB NIR set recorded on a coarse wavelength grid that contains three sequential kinetic components, the slowest of which is effectively infinite, and the RB vis set recorded on a fine grid that requires four components (again with one infinite lifetime) together with wavelength-dependent weighting and CA modelling. On the first dataset, we used poor initial guesses while on the second dataset, the initial parameters are closer to the expected lifetimes. Each sequential-decay model was fitted five times with every program to average out variability from caching and operating-system scheduling. Wherever possible, we matched the initial parameter guesses, kinetic scheme, weighting strategy, and convergence tolerances across the three interfaces. All runs were performed on a Windows 11 workstation equipped with an Intel Core i5-9500 CPU (3.00 GHz, six physical cores) and 16 GB of DDR4-2667 RAM.

Because Glotaran is operated through a GUI, we could only record the overall wall-time (button click → “Finished”). This value includes plotting, repainting, disk I/O, and other GUI overhead. The underlying fit and error estimation steps are therefore somewhat faster than the figures we report.

A.6.1 NIR Dataset: Performance and Fit Statistics

The three programs were supplied with identical kinetic schemes and identical initial parameter guesses (see **Figures A.33 to A.35**). KiMoPack offers two flavors of the sequential model, `consecutive` and `full_consecutive`. `consecutive` performs most of the optimization with a faster parallel-decay model and switches to the true sequential rate equations only in the final refinement step, whereas `full_consecutive` works with the genuine sequential equations throughout, mirroring the strategy used by TAPAS. Although the two KiMoPack options converge to essentially the same parameter values, the `consecutive` route triggered floating-point overflows during the error calculation, producing unrealistically wide confidence intervals. In addition, its parallel-model shortcut cannot be applied when fitting more elaborate target schemes. For completeness, we list timings for both KiMoPack variants.

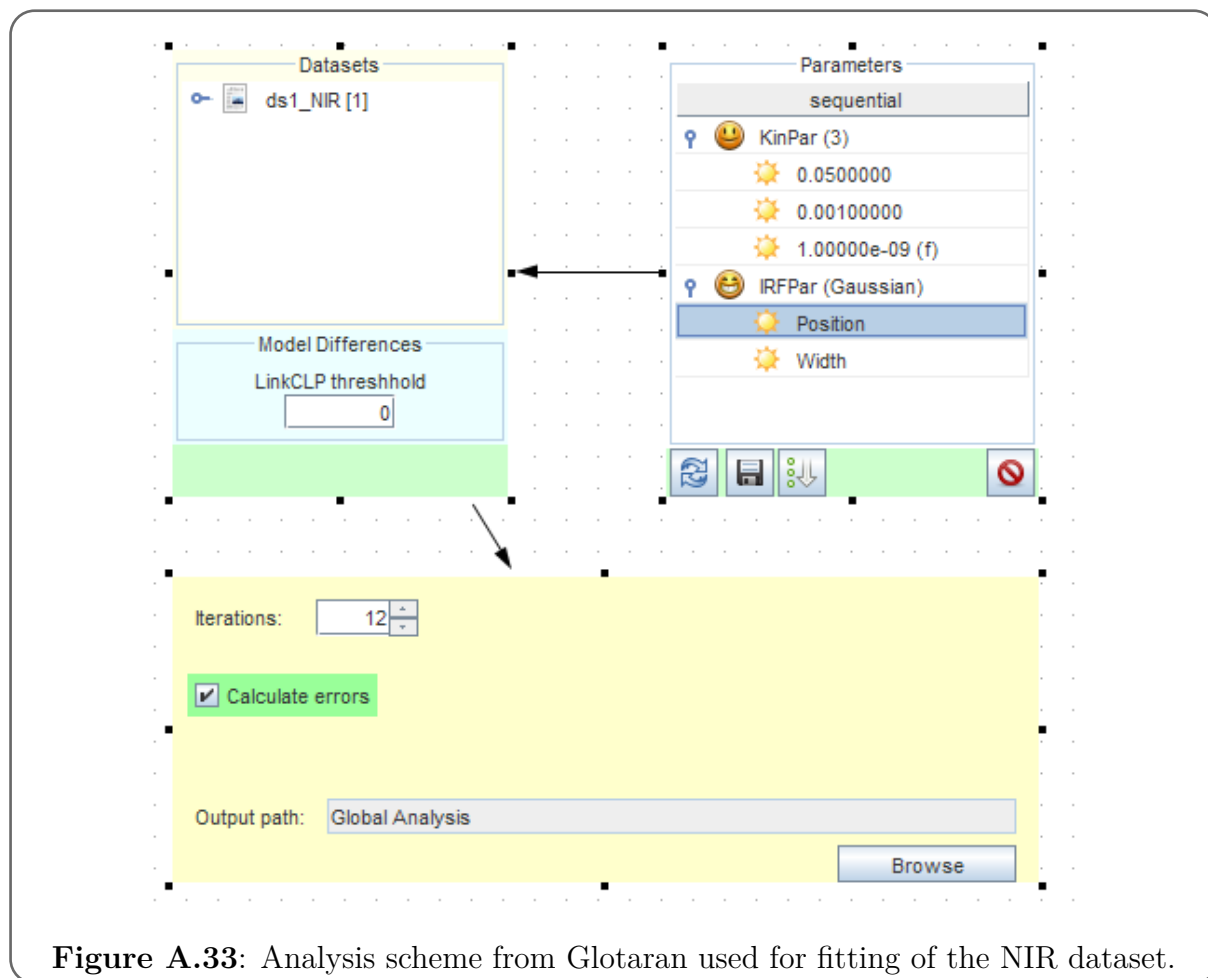


Figure A.33: Analysis scheme from Glotaran used for fitting of the NIR dataset.

```

ta = KiMoPack.plot_func.TA(filename)

# ta.mod = 'consecutive'
ta.mod = 'full_consecutive'

par = lmfit.Parameters()
par.add('k1', value=1 / 20, vary=True)
par.add('k2', value=1 / 1000, vary=True)
par.add('infinite')
par.add('t0', value=0.1, min=-.2, max=.2, vary=True)
par.add('resolution', value=0.2, min=0.1, max=0.3, vary=True)
ta.par = par
ta.Fit_Global(confidence_level=0.68)

```

Figure A.34: Script used for NIR sequential fitting and error estimation using KiMoPack.

Fitting Parameters

Components

☒ Infinite Component?

☐ Explicit GSB ☐ Use Steady-State

Fit CA

Model

Microsteps

Time Zero

Method

Weights

	value	min	max	vary
t0	100fs			
IRF	200fs			
τ_1	20ps			
τ_2	1ns			

Figure A.35: Fitting parameter widget of TAPAS used for the NIR sequential fit.

Table A.4 lists the wall-times recorded in the five replicate runs together with their averages. For TAPAS and KiMoPack two numbers are reported: the first is the time parameter optimization and caching and the second is the additional time needed to compute the parameter uncertainties. For Glotaran, only a single, approximate figure is given with the total wall-time from pressing Run to completion since its GUI makes it impractical to separate optimization, error calculation, and plotting overhead.

Table A.4: Runtimes for optimization and uncertainty estimation in five replicate fits of the NIR data set.

Software	Run 1 / s	Run 2 / s	Run 3 / s	Run 4 / s	Run 5 / s	Average / s
TAPAS 1.1.4	0.54 + 0.16	0.53 + 0.17	0.56 + 0.16	0.56 + 0.16	0.55 + 0.15	0.55 + 0.16
Glotaran 1.5.1	2.86	2.89	2.68	2.74	2.82	2.80
KiMoPack 7.12.9 (consecutive)	1.70 + 43.97	1.63 + 45.12	1.93 + 43.67	1.71 + 56.51	1.97 + 43.61	1.79 + 46.58
KiMoPack 7.12.9 (full_consecutive)	11.83 + 116.46	11.87 + 119.01	11.90 + 122.45	11.65 + 120.78	12.20 + 116.23	11.89 + 118.99

TAPAS exports each lifetime already in the form $\tau \pm \sigma_{\tau}$ (one-sigma, 68 % coverage). Glotaran, in contrast, prints the rate constants k together with their standard errors σ_k (see **Figure A.36**). The corresponding lifetime uncertainty is obtained by ordinary error propagation

$$\sigma_{\tau} = \left| \frac{\partial \tau}{\partial k} \right| \sigma_k = \frac{\sigma_k}{k^2} \quad (\text{A.22})$$

so that $\tau \pm \sigma_{\tau}$ can be reported on the same basis. KiMoPack, run with `confidence_level = 0.68`, returns the lower and upper profile-likelihood limits directly (**Figures A.36 to A.38**), giving the desired 68 % confidence interval without further conversion. The results are summarized in **Table A.5**.

Table A.5: Parameter estimates and 1σ uncertainties ($\approx 68\%$ confidence interval) calculated by different software.

Software	τ_1/ps	τ_2/ps
TAPAS 1.1.4	63.9 ± 1	242.1 ± 9
Glotaran 1.5.1	63.9 ± 0.13	242.1 ± 1.1
KiMoPack 7.12.9 (consecutive)	$63.9 + 44 / - 28$	$242.1 + 1600 / - 137$
KiMoPack 7.12.9 (full_consecutive)	$63.8 + 2.9 / - 2.5$	$242.8 + 23.4 / - 22.2$

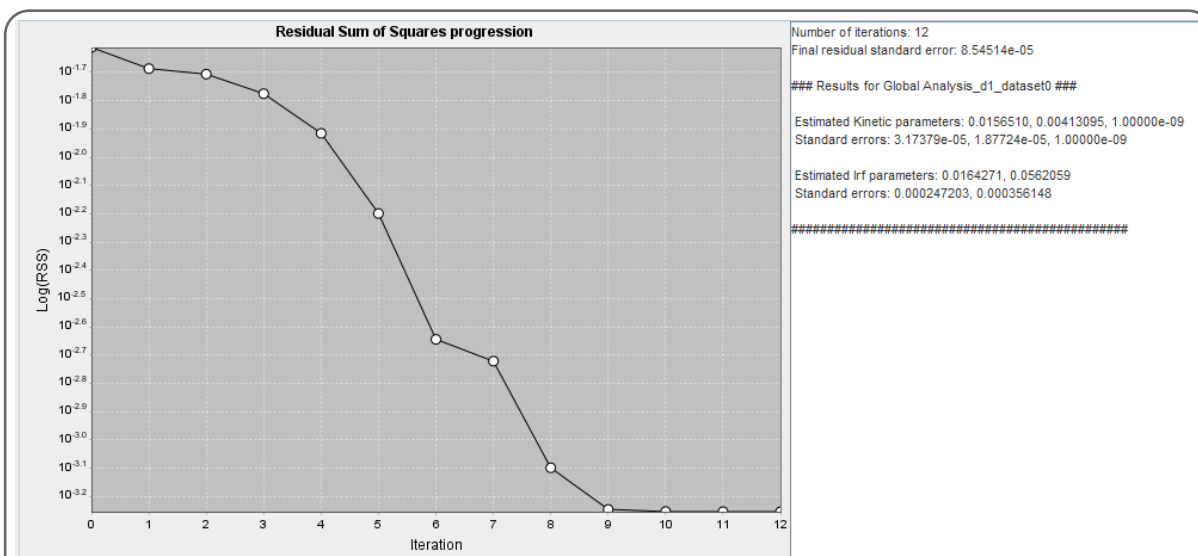


Figure A.36: Glotaran overview output after a successful fit using the analysis scheme in Figure A.33.

The rates converted to times with unit ps with confidence interval to level of 68.0

	value	lower_limit	upper_limit	init_value	vary	min	max	expr
k1	242.083	104.876	1818.89	20	True	0	inf	
k2	63.893	35.8827	108.343	1000	True	0	inf	
infinite	1			1	False	-inf	inf	
t0	-0.0956301	-0.0956301	0.0252694	0.1	True	-0.2	0.2	
resolution	0.112053	0.105142	0.37974	0.2	True	0.1	0.3	

consecutive

Figure A.37: Console output of KiMoPack after analyzing the NIR dataset with a confidence interval of 0.68 using the consecutive model.

The rates converted to times with unit ps with confidence interval to level of 68.0

	value	lower_limit	upper_limit	init_value	vary	min	max	expr
k1	63.8375	61.3193	66.7739	20	True	0	inf	
k2	242.778	220.581	266.187	1000	True	0	inf	
infinite	1			1	False	-inf	inf	
t0	0.0278695	0.0222377	0.0333283	0.1	True	-0.2	0.2	
resolution	0.132411	0.112537	0.152479	0.2	True	0.1	0.3	

full_consecutive

Figure A.38: Console output of KiMoPack after analyzing the NIR dataset with a confidence interval of 0.68 using the full-consecutive model.

A.6.2 Vis Dataset: Performance and Fit Statistics

We followed the same workflow as in **Appendix A.6.1**. For the vis data set, we additionally enabled CA modeling in Glotaran and TAPAS (KiMoPack does not offer this feature in its core distribution) and applied zero-weighting to the 353–495 nm region to suppress strong scattered-light artifacts. **Figures A.39 to A.41** illustrate the input dialogs and model definitions, and **Table A.6** report the timing benchmarks and the fitted parameters with the uncertainties. It is worth noting that the discrepancy in the fast component between KiMoPack and TAPAS/Glotaran is entirely due to the lack of CA modeling which is compensated by τ_1 .

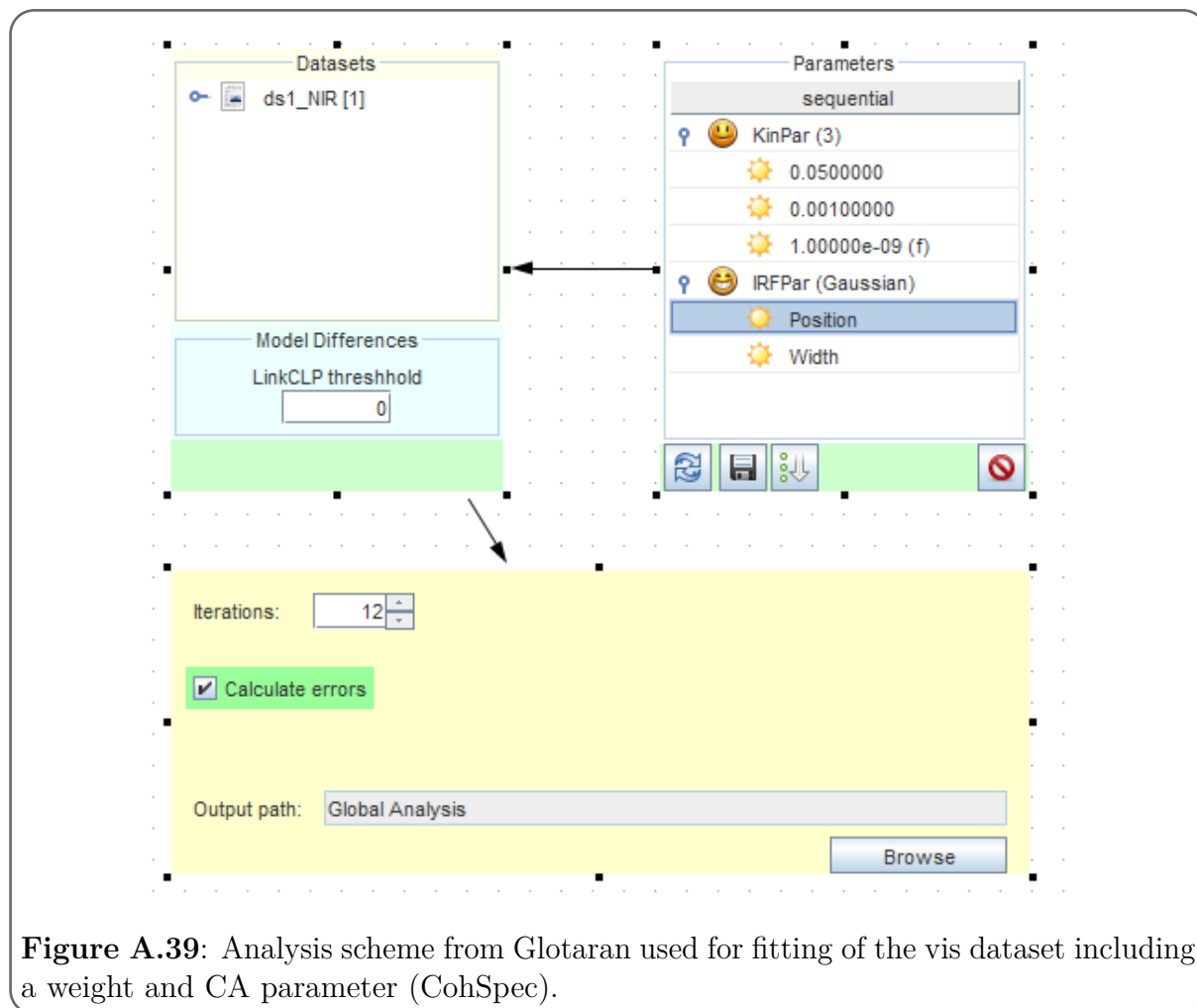


Figure A.39: Analysis scheme from Glotaran used for fitting of the vis dataset including a weight and CA parameter (CohSpec).

```

ta = KiMoPack.plot_func.TA(filename)

# ta.mod = 'consecutive'
ta.mod = 'full_consecutive'

par = lmfit.Parameters()
par.add('k1', value=1 / 20, vary=True)
par.add('k2', value=1 / 1000, vary=True)
par.add('infinite')
par.add('t0', value=0.1, min=-.2, max=.2, vary=True)
par.add('resolution', value=0.2, min=0.1, max=0.3, vary=True)
ta.par = par
ta.Fit_Global(confidence_level=0.68)

```

Figure A.40: Script used for sequential fitting and error estimation using KiMoPack.

Fitting Parameters

Components: 3

☒ Infinite Component?

☐ Explicit GSB ☐ Use Steady-State

Fit CA: zero order

Model: sequential

Microsteps: 6

Time Zero: Gaussian Center

Method: nelder

Weights

	value	min	max	vary
IRF	200fs			
τ_1	2ps			
τ_2	70ps			
τ_3	200ps			

Show Initial Guess Fit

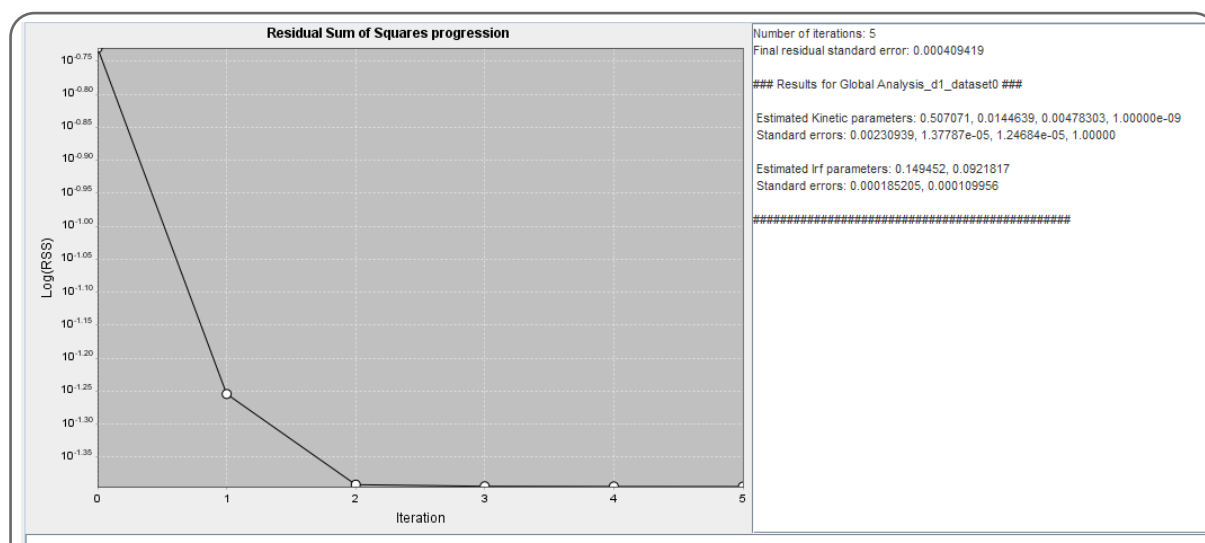
Figure A.41: Fitting parameter widget of TAPAS used for the NIR sequential fit.

Table A.6: Runtimes for optimization and uncertainty estimation in five replicate fits of the vis data set.

Software	Run 1 / s	Run 2 / s	Run 3 / s	Run 4 / s	Run 5 / s	Average / s
TAPAS 1.1.4	1.61 + 1.08	1.83 + 1.09	1.62 + 1.07	1.59 + 1.09	1.62 + 1.09	1.65 + 1.08
Glotalan 1.5.1	12.92	12.31	11.89	12.08	12.32	12.30
KiMoPack 7.12.9 (consecutive)	3.42 + 579.19	3.74 + 545.15	3.92 + 553.21	3.75 + 556.73	3.98 + 581.81	3.76 + 563.22
KiMoPack 7.12.9 (full_consecutive)	12.23 + 464.31	11.95 + 468.71	11.99 + 468.35	11.53 + 466.22	11.49 + 465.28	11.84 + 466.57

Table A.7: Parameter estimates and 1σ uncertainties ($\approx 68\%$ confidence interval) calculated by different software.

Software	τ_1/ps	τ_2/ps	τ_3/ps
TAPAS 1.1.4	2.1 ± 0.4	69.2 ± 3	209.0 ± 20
Glotalan 1.5.1	2.0 ± 0.009	69.1 ± 0.1	209.1 ± 0.5
KiMoPack 7.12.9 (consecutive)	$0.5 + 30.5 / - 0.5$	$68.2 + 30.2 / - 47.8$	$235.8 + \infty / - 137.4$
KiMoPack 7.12.9 (full_consecutive)	$0.4 + 0.1 / - 0.2$	$68.1 + 3.6 / - 3.7$	$236.6 + 40.4 / - 33.4$

**Figure A.42:** Glotaran overview output after a successful fit using the analysis scheme in **Figure A.39**.

```

The rates converted to times with unit ps with confidence interval to level of 68.0
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
|         | value | lower_limit | upper_limit | init_value | vary | min | max | expr |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| k0      | 0.460579 | 0.00412344 | 31.0098 | 2 | True | 0 | inf |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| k1      | 68.2141 | 20.3779 | 98.3757 | 70 | True | 0 | inf |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| k2      | 235.828 | 98.4442 | 9.37961e+11 | 200 | True | 0 | inf |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| infinite | 1 | | | 1 | False | -inf | inf |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| t0      | -0.0789345 | -0.0789345 | 0.274738 | 0.1 | True | -2 | 2 |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| resolution | 0.176572 | 0.0340119 | 0.397163 | 0.2 | True | 0.04 | 0.5 |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
consecutive

```

Figure A.43: Console output of KiMoPack after analyzing the vis dataset with a confidence interval of 0.68 using the consecutive model.

```

The rates converted to times with unit ps with confidence interval to level of 68.0
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
|         | value | lower_limit | upper_limit | init_value | vary | min | max | expr |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| k0      | 0.441812 | 0.31397 | 0.646249 | 2 | True | 0 | inf |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| k1      | 68.1255 | 64.4554 | 71.6958 | 70 | True | 0 | inf |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| k2      | 236.573 | 203.203 | 277.027 | 200 | True | 0 | inf |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| infinite | 1 | | | 1 | False | -inf | inf |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| t0      | 0.107499 | 0.103526 | 0.111908 | 0.1 | True | -2 | 2 |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
| resolution | 0.208355 | 0.196404 | 0.220814 | 0.2 | True | 0.04 | 0.5 |
+-----+-----+-----+-----+-----+-----+-----+-----+-----+
full_consecutive

```

Figure A.44: Console output of KiMoPack after analyzing the vis dataset with a confidence interval of 0.68 using the full-consecutive model.

A.6.3 Discussion

On both data sets, TAPAS outperformed the other packages by factors of 2–20x in wall-time, with the exact speed-up depending on model complexity, grid density, and the quality of the initial guesses. This improvement arises primarily from TAPAS’s JAX implementation which uses XLA compilation and just-in-time execution to accelerate the calculations.

All three programs produced parameter values that agree within their statistical uncertainties. The only clear divergence appears in the vis data set, where KiMoPack assigns a shorter lifetime to the fastest component. This difference is explained by the absence of CA modeling in KiMoPack, which forces the first lifetime to absorb the uncorrected signal. The remaining lifetimes, including the slow tail, differ only within the reported error bars.

TAPAS computes first-order standard errors during a single optimization pass. These uncertainties match the confidence intervals obtained with KiMoPack’s profile-likelihood procedure, even though the KiMoPack routine requires roughly 500 times more wall time. The KiMoPack intervals are about twice as wide because they account for the full correlation among parameters. Glotaran reports much narrower errors. Those values are unrealistically small on dense time grids because Glotaran treats every time point as an independent observation. TAPAS corrects this problem by scaling the covariance matrix with an effective sample size derived from the integrated autocorrelation of the residuals. (Compare **Section 3.4.3** in the main manuscript and **Appendix A.4**)

Only TAPAS presents the complete correlation matrix. In the NIR experiment, the correlation coefficient between the first two lifetimes is -0.86. This strong anticorrelation explains why very different lifetime pairs (e.g. 64 ps and 242 ps versus 80 ps and 163 ps) yield fits of virtually identical quality (r^2 : 0.999, $\text{RMSE}(\Delta A)$: $8.5 - 8.9 \times 10^{-5}$). Without access to correlation information, the confidence intervals supplied by all three programs would overestimate the level of robustness.

Supplementary Information for Chapter 4

Preparation, Photoluminescence and Excited State Properties of the Homoleptic Cluster Cation $[(W_6I_8)(CH_3CN)_6]^{4+}$

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Figure B.1: Crystals of **III** under VIS (left side) and UV (right side) irradiation.

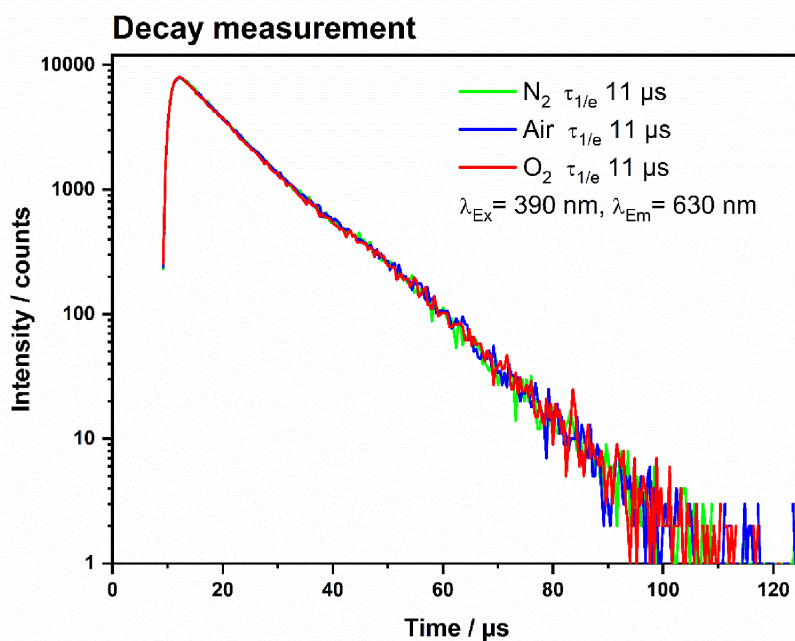


Figure B.2: Decay measurement of solid **III**.

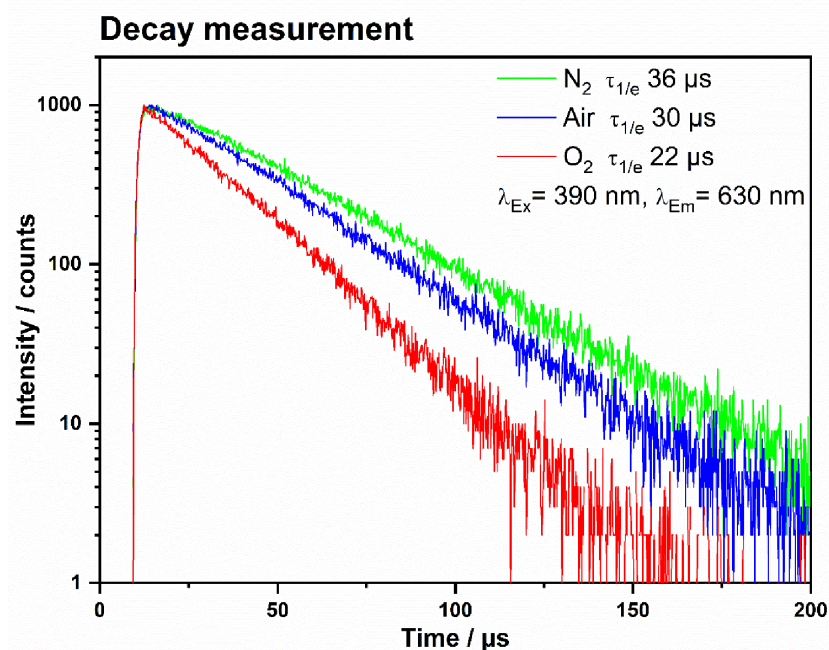


Figure B.3: Decay measurement of solid $(\text{TBA})_2[\text{W}_6\text{I}_8(\text{CO}_2\text{C}_3\text{F}_7)_6]$.

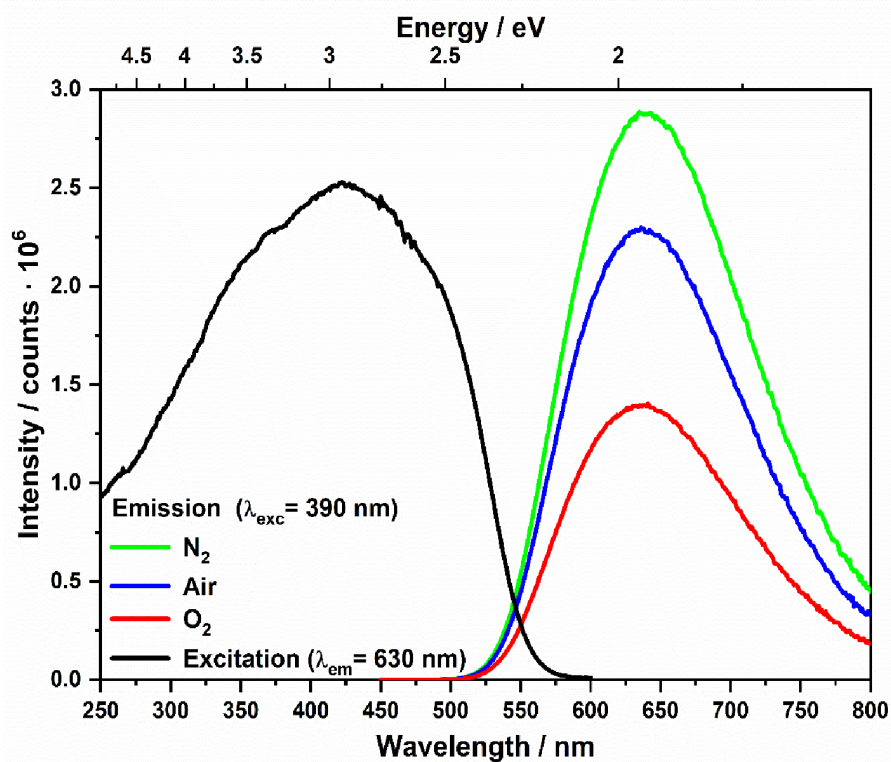
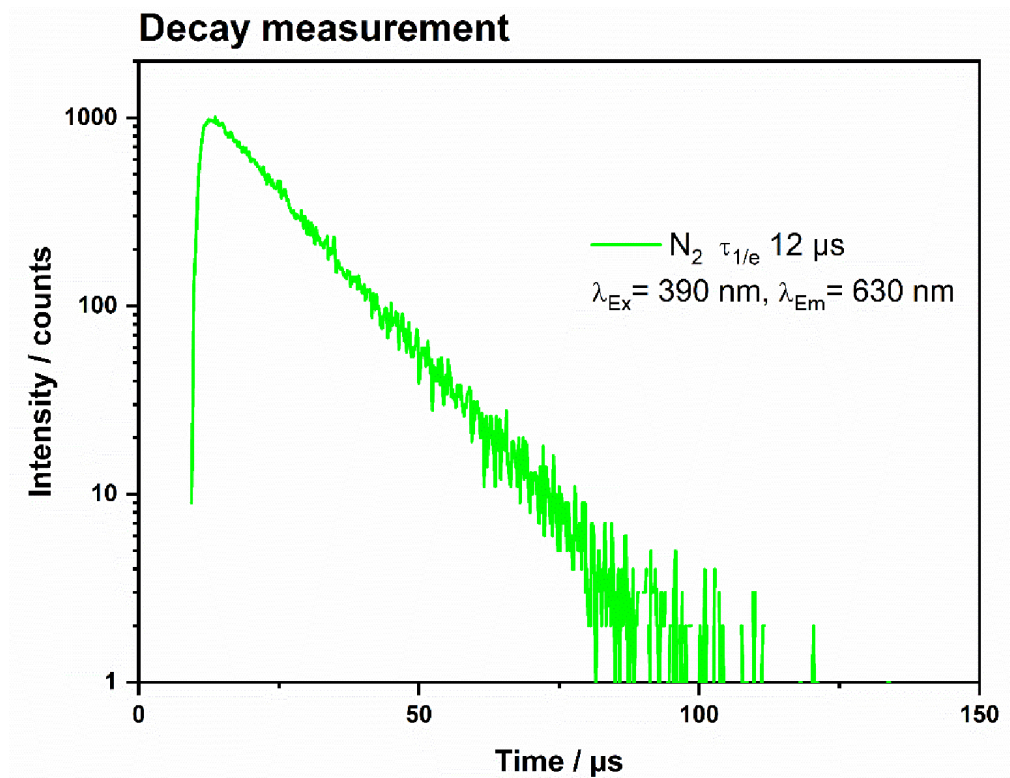
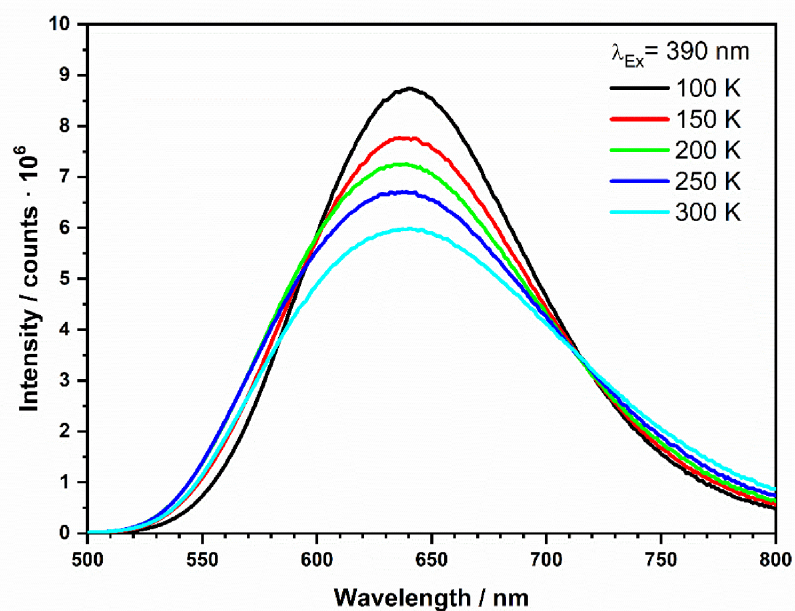


Figure B.4: Excitation and emission spectra of solid $(\text{TBA})_2[\text{W}_6\text{I}_8(\text{CO}_2\text{C}_3\text{F}_7)_6]$ under nitrogen, air and oxygen atmosphere.

Figure B.5: Decay measurement of **III** in acetonitrile.Figure B.6: Emission spectra of solid $(\text{TBA})_2[\text{W}_6\text{I}_8(\text{CO}_2\text{C}_3\text{F}_7)_6]$ at different temperatures.

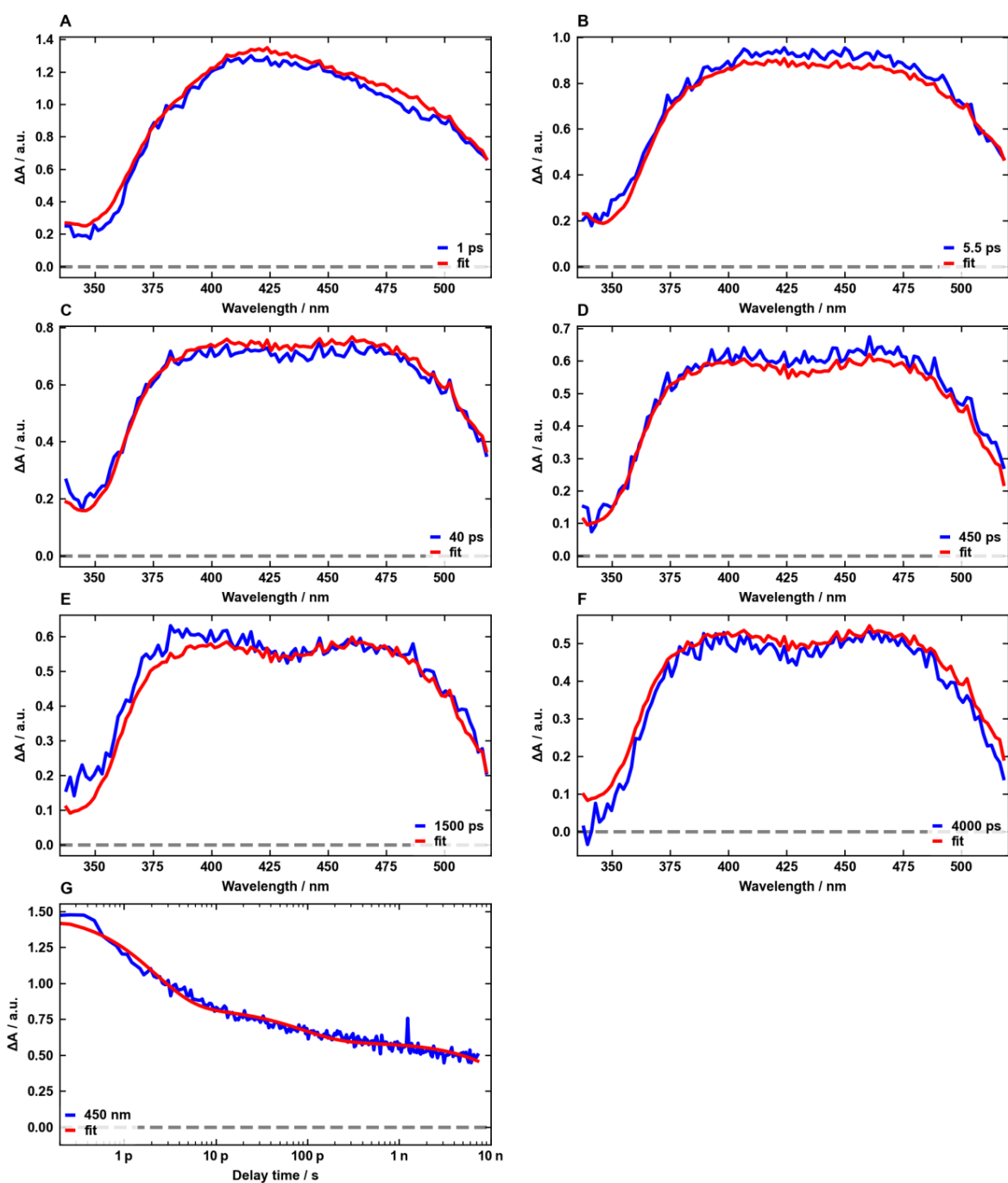


Figure B.7: Selected ΔA spectra (A-F) of **III** at different time delays (blue) after excitation at 300 nm and kinetic trace at 450 nm (G). The corresponding fit spectra and traces of the global analysis are shown in red.

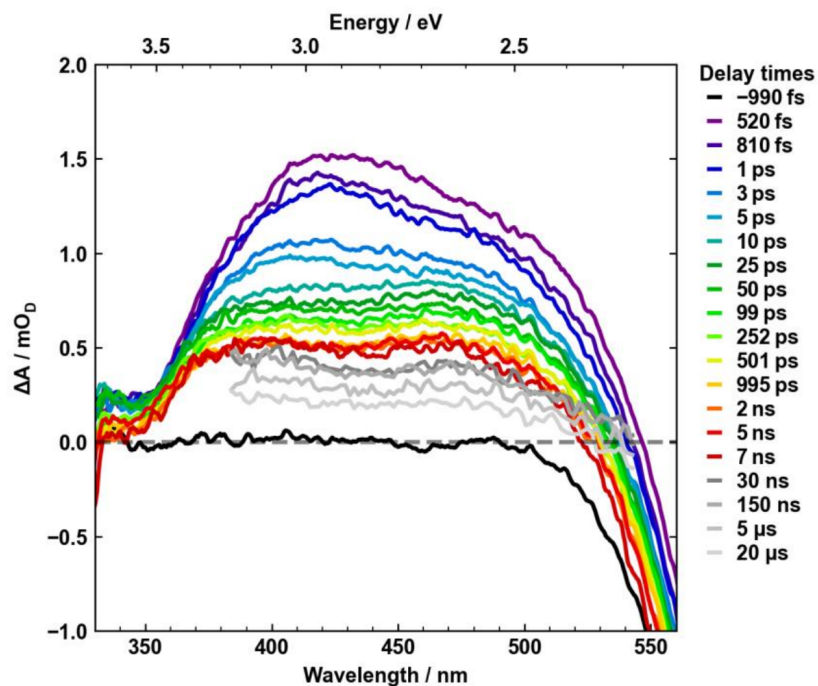


Figure B.8: Selected ΔA spectra of **III** at different delay times after excitation at 300 nm. A femtosecond transient absorption spectrometer was used for delay times up to 7.5 ns. For the long-lived species longer than 7 ns, a different nanosecond pump probe spectrometer was used (grey scale). The negative signals at wavelengths higher than 520 nm are due to strong luminescence.

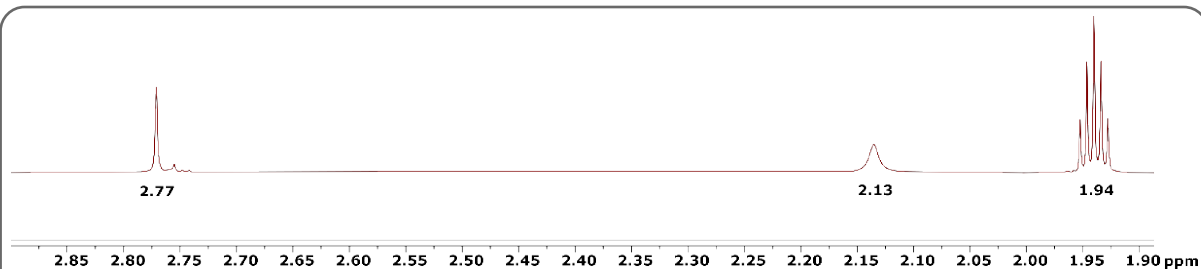


Figure B.9: Section of the ^1H -NMR of **III** in CD_3CN showing the signal for the CH_3 -group at 2.77 ppm and a signal of H_2O at 2.13 ppm.

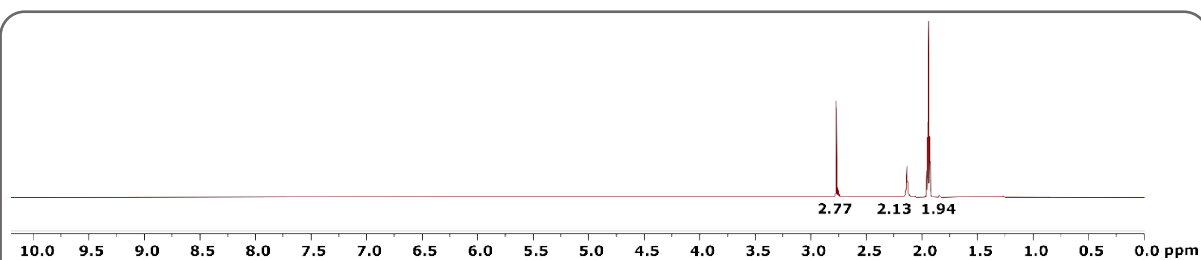


Figure B.10: Greater section of the ^1H -NMR of **III** in CD_3CN between 0.0 and 10 ppm.

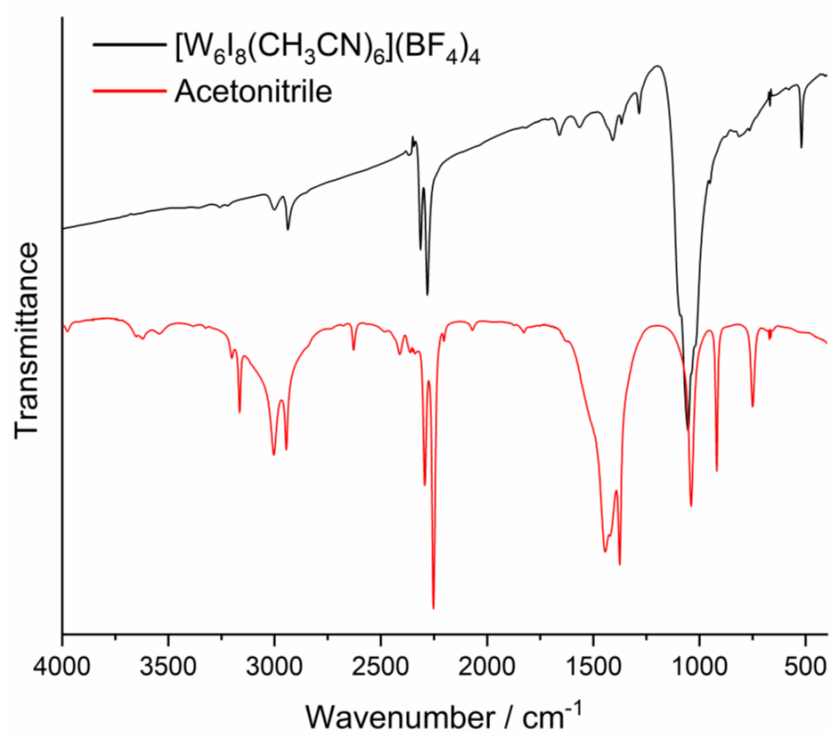


Figure B.11: Infrared spectrum of **III** in black and of acetonitrile in red.

Supplementary Information for Chapter 5

Time- and Temperature-Resolved Triplet Dynamics in Tungsten Iodide Clusters

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C.1 Additional Experimental Information



Figure C.1: PMMA film of **1** under UV light.

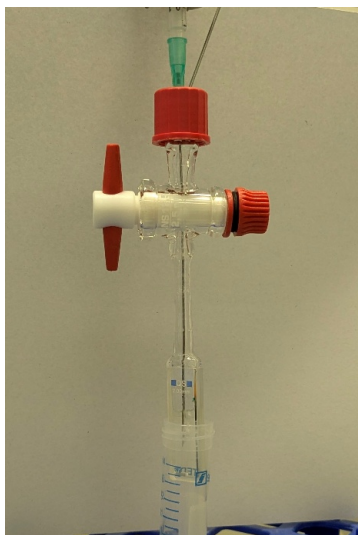


Figure C.2: Microcuvette with homebuilt opening to control the atmosphere within the cuvette.

C.2 Transient Absorption Data

C.2.1 Analysis of **2**

The analysis of the fs TA experiments of **2** in MeCN ($\lambda_{\text{exc}} = 350$ nm) are shown in **Figure C.3**. The procedure is the same as described in the main manuscript. In **Figure C.3 A** the background corrected 2D hyperspectrum is depicted. A sequential fit at 500 nm (**Figure C.3 B**) required 3 components with lifetimes of 270 fs, 4 ps and a lifetime longer than our measurement window of 2 ns ($r^2 = 0.99$). Global fitting over the whole spectral range gave comparable lifetimes of 370 fs (red) and 5.6 ps (blue) and a coefficient of determination of 0.98. The corresponding EADS are shown in **Figure C.3 C**.

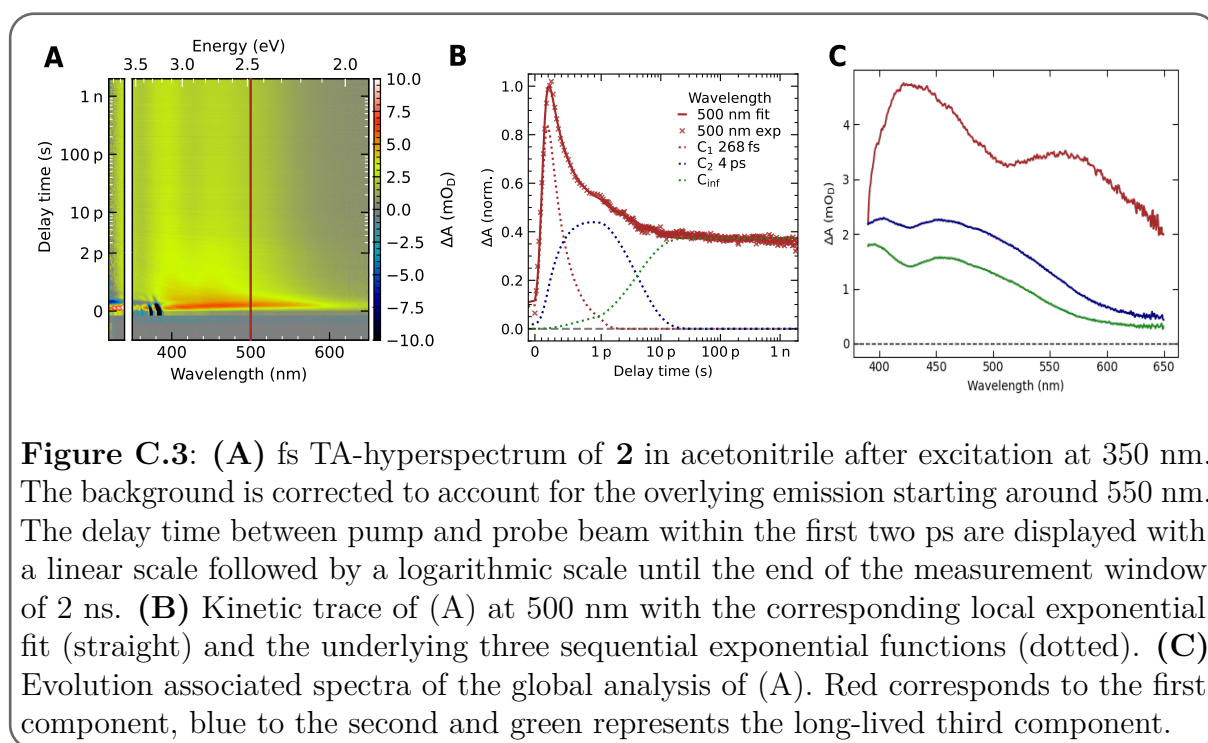


Figure C.3: (A) fs TA-hyperspectrum of **2** in acetonitrile after excitation at 350 nm. The background is corrected to account for the overlying emission starting around 550 nm. The delay time between pump and probe beam within the first two ps are displayed with a linear scale followed by a logarithmic scale until the end of the measurement window of 2 ns. (B) Kinetic trace of (A) at 500 nm with the corresponding local exponential fit (straight) and the underlying three sequential exponential functions (dotted). (C) Evolution associated spectra of the global analysis of (A). Red corresponds to the first component, blue to the second and green represents the long-lived third component.

C.2.2 Analysis of the IRF and Solvent Response

Figure C.4 presents the fs TA data of pure acetonitrile under the same experimental conditions as for the ultrafast experiments of **1** and **2**. In **Figure C.4 A**, the 2D spectrum is depicted while the kinetic trace at 500 nm as well as the fit is shown in **Figure C.4 B**. Here, we find a main component decaying with 90 fs and a second weak decay of 900 fs ($r^2 = 0.96$). The same results can be reproduced by global fitting giving lifetimes of 140 fs and 900 fs ($r^2 = 0.91$). The corresponding EADS with the first component in red and the second component in blue is shown in **Figure C.4 C**. Since MeCN does not absorb the excitation wavelength, we contribute these signals to the IRF, solvent response and coherent artifacts.

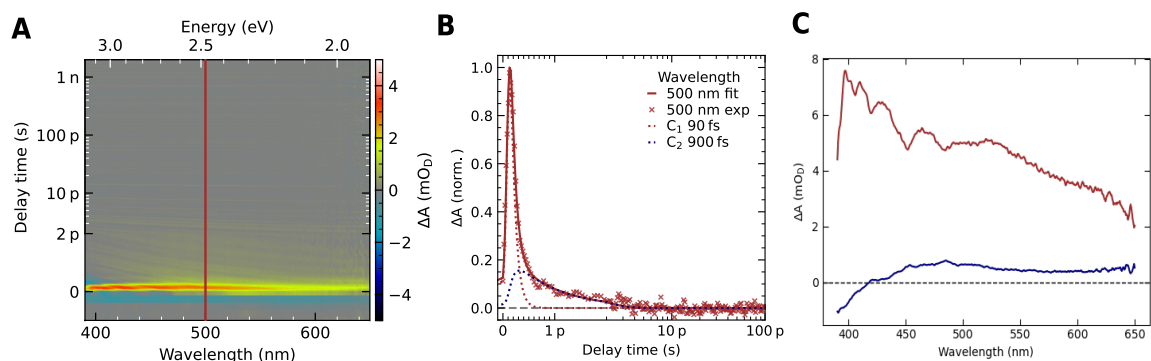


Figure C.4: (A) fs TA-hyperspectrum of acetonitrile after excitation at 350 nm. The delay time between pump and probe beam within the first two ps are displayed with a linear scale followed by a logarithmic scale until the end of the measurement window of 2 ns. (B) Kinetic trace of (A) at 500 nm with the corresponding local exponential fit (straight) and the underlying three sequential exponential functions (dotted). (C) Evolution associated spectra of the global analysis of (A). Red corresponds to the first (140 fs) and blue to the second component (900 fs).

C.2.3 Fitting Model and Variability

Local and global fitting analysis was performed using a sequential model with three components $A \rightarrow B \rightarrow C$ convoluted with the instrument response function (IRF). The IRF was modeled with a Gaussian function and C was set to a non-decaying constant term. **Table C.1** lists the statistical 1σ uncertainties obtained from the Jacobian together with the Pearson correlation coefficients that most affect those uncertainties. Global fitting tightens the confidence intervals relative to the local fits, but strong anti-correlation between the IRF width and the fastest time constant τ_1 (up to -0.75) remains unavoidable because the IRF (~ 200 fs FWHM) is of the same order as τ_1 . This coupling implies that the practical uncertainty of τ_1 is somewhat larger than its formal 1σ value, whereas τ_2 is less affected. Accordingly, we estimate the uncertainty of the relevant ISC parameter τ_2 extracted from global analysis at a conservative 10 to 15 %.

Table C.1: Parameter uncertainties and parameter–parameter correlations of the local (500 nm) and global fits of the TA data.

Compound	Fit	τ_1	τ_2	IRF– τ_1 corr.	τ_1 – τ_2 corr.
1 (TBA) ₂ [(W ₆ I ₈)I ₆]	local	55 %	15 %	-70 %	40 %
1 (TBA) ₂ [(W ₆ I ₈)I ₆]	global	12 %	6 %	-70 %	24 %
2 (TBA) ₂ [(W ₆ I ₈)(TFA) ₆]	local	23 %	30 %	-60 %	55 %
2 (TBA) ₂ [(W ₆ I ₈)(TFA) ₆]	global	5 %	7 %	-50 %	50 %
Acetonitrile	local	8 %	11 %	-75 %	55 %
Acetonitrile	global	4 %	7 %	-60 %	30 %

C.2.4 Analysis of the long-lived Component with ns-TA

In Table **Table C.2**, the monoexponential fits of the kinetic traces at 500 nm of **Figure 5.3 A** of the main manuscript are shown.

Table C.2: Monoexponential fits of **1** and **2** at different oxygen concentrations corresponding to **Figure 5.3 A** in the main manuscript. Errors are estimated to be within 10 %.

Compound	τ (0 % O ₂) / μ s	τ (8 % O ₂) / μ s	τ (21 % O ₂) / μ s	τ (100 % O ₂) / μ s
1 (TBA) ₂ [(W ₆ I ₈)I ₆]	22	1.1	0.43	0.09
2 (TBA) ₂ [(W ₆ I ₈)(TFA) ₆]	33	2.7	1.13	0.24

C.3 Emission Data at 295 K and Oxygen Quenching

In **Figure C.5** the emission lifetime traces of **1** and **2** in MeCN at different oxygen concentrations are depicted ($\lambda_{\text{exc}} = 375 \text{ nm}$, $\lambda_{\text{em}} = 680 \text{ nm}$). They were fitted monoexponentially giving lifetimes shown in **Table C.3**. The corresponding emission spectra are shown in **Figure C.6**.

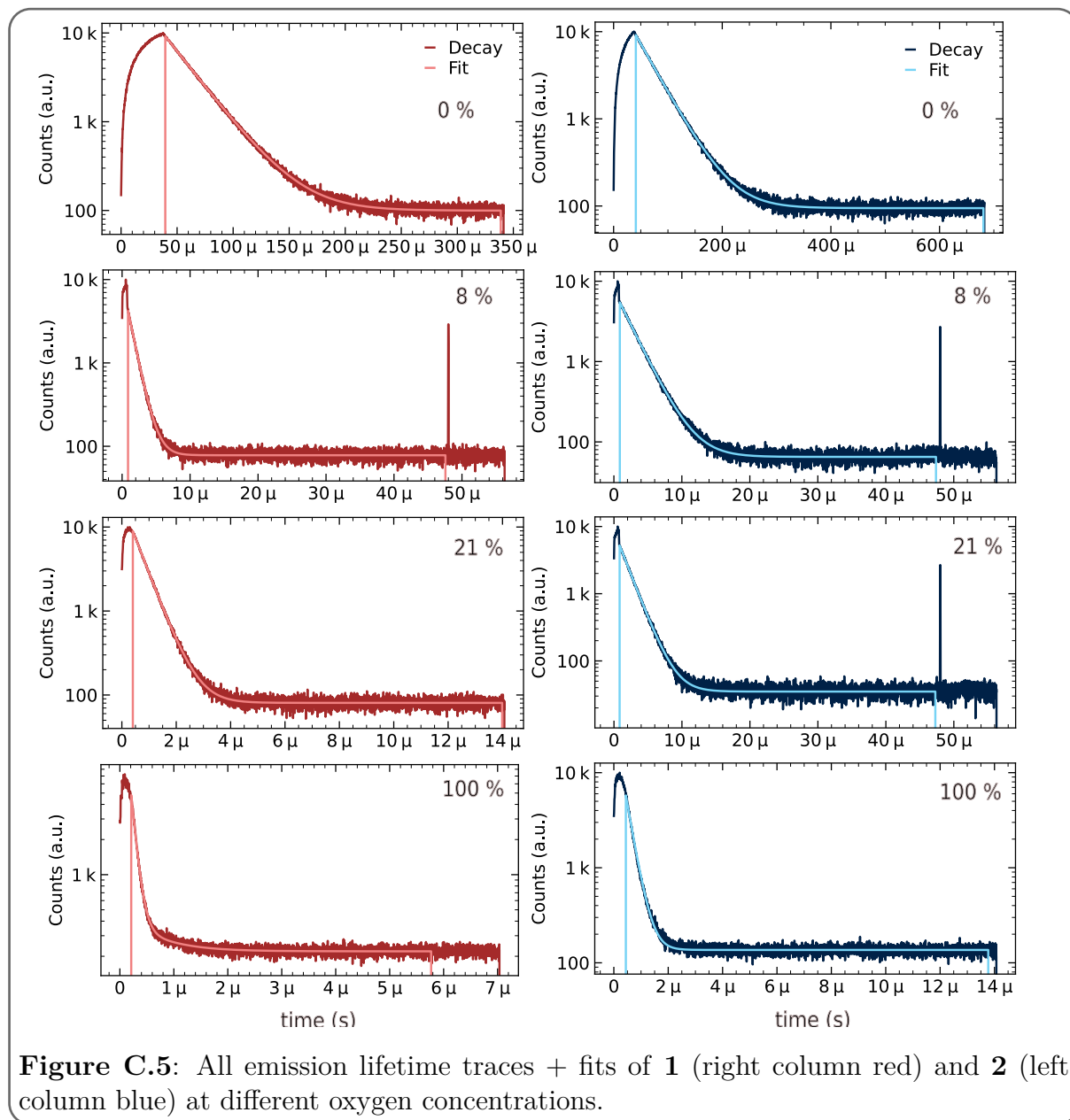


Figure C.5: All emission lifetime traces + fits of **1** (right column red) and **2** (left column blue) at different oxygen concentrations.

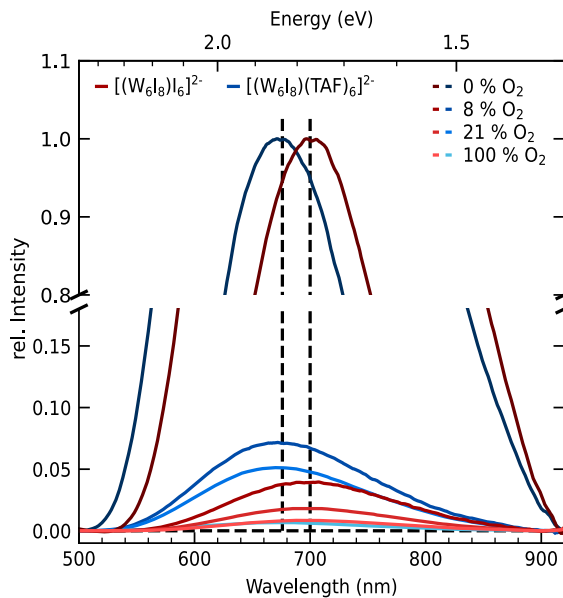


Figure C.6: Emission Spectra of **1** and **2** at different oxygen concentrations.

Table C.3: Table S3.1. Monoexponential lifetime fits of **1** and **2** at different oxygen concentrations. Errors are estimated to be within 5 %.

Compound	$\tau(0\% \text{ O}_2) / \mu\text{s}$	$\tau(8\% \text{ O}_2) / \mu\text{s}$	$\tau(21\% \text{ O}_2) / \mu\text{s}$	$\tau(100\% \text{ O}_2) / \mu\text{s}$
1 (TBA) ₂ [(W ₆ I ₈)I ₆]	26.8	1.08	0.51	0.09
2 (TBA) ₂ [(W ₆ I ₈)(TFA) ₆]	38.67	2.49	1.66	0.26

C.4 Analysis of the T-Dependent Emission Data of **1** in Solution

In **Figure C.7**, the lifetimes and emission spectra of **1** in MeCN as a function of temperature are displayed as well as the phase transition at 228 K with a dashed line. In **Figure C.7 A**, the lifetimes were fitted with two components showing a clear biexponential decay in the solid state which transitions to the expected monoexponential decay above the melting point. The emission spectra in **Figure C.7 B** show an emission maximum of 700 nm in the liquid state and a maximum centered at 685 nm when frozen. Beside that shift of 40 meV at the phase transition, the spectral characteristics resemble the dynamics found in a PMMA matrix. Although a blueshift of the emission maximum can be expected due to a decreased stabilization of the triplet in the solid state, the drastic changes in the emission lifetime are unlikely to only originate from the different state of matter. A possible explanation could be a dynamic equilibrium which is disturbed and eventually frozen while falling below the melting point. Especially the *apical* ligands are only weakly bound to the $[\text{W}_6\text{I}_8]^{4+}$ core and can be exchanged easily with silver carboxylates under the formation of AgI .^{19,296} Recently, we synthesized the cationic $[(\text{W}_6\text{I}_8)(\text{CH}_3\text{CN})_6]^{4+}$ and $[(\text{W}_6\text{I}_8)\text{I}(\text{CH}_3\text{CN})_5]^{3+}$, proving that acetonitrile can also stabilize the cluster with a suitable counter ion.³⁶⁷ Although $(\text{TBA})_2[(\text{W}_6\text{I}_8)\text{I}_6]$ would be the thermodynamic stable configuration, $(\text{TBA})[(\text{W}_6\text{I}_8)\text{I}_5(\text{CH}_3\text{CN})] + (\text{TBA})\text{I}$ or even $[(\text{W}_6\text{I}_8)\text{I}_4(\text{CH}_3\text{CN})_2] + 2 (\text{TBA})\text{I}$ could be kinetically trapped at the phase transition leading to a drastic quenching of the lifetimes.

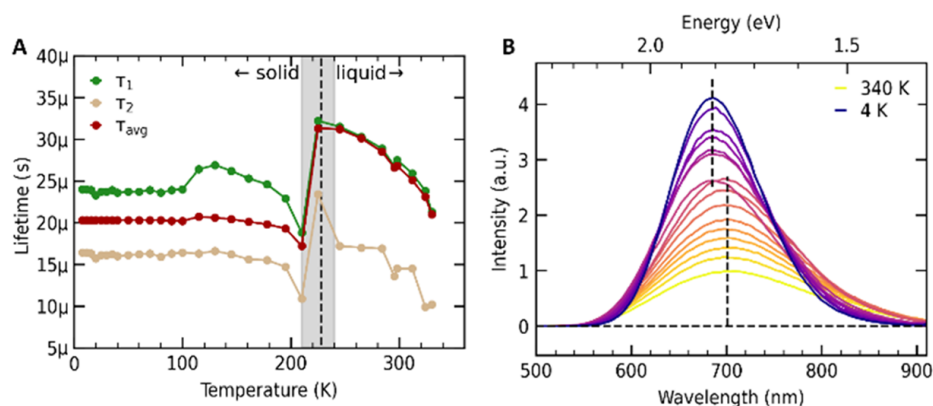


Figure C.7: (A) Biexponential and average lifetimes of **1** in MeCN extracted at different temperatures. The gray area represents the phase transition of MeCN at 228K. (B) Corresponding emission spectra at each temperature step. The dashed line marks the emission maximum.

This interpretation would have multiple consequences. First, the resulting biexponential lifetimes in the frozen state would change when changing the temperature gradient used to freeze the sample. Second, the addition of $(\text{TBA})\text{I}$ should reduce the biexponential behavior according to Le Chatelier's principle and third, the different binding situation of TFA in **2** should also change the dynamic exchange reactions. **Figure C.8 A** shows the biexponential lifetime of **1** at room temperature and 77 K as a function of addition of $(\text{TBA})\text{I}$. In the upper panel at room temperature, we found the expected monoexponential lifetime of 26 μs which is stable against small amounts of additional $(\text{TBA})\text{I}$. If frozen with

liquid nitrogen, we again find a biexponential behavior resulting in an overall lower average lifetime of 24 μs , although the lifetimes and amplitudes are slightly different compared to the experiments performed in a cryostat. Upon addition of large amounts of (TBA)I (e.g. 1000 : 1 or higher) at room temperature, we detect an increased quenching introduced by (TBA)I leading to a lifetime drop by 12 % to 23 μs . Besides that, we find no additional influence of (TBA)I at room temperature, which can also be seen in the emission spectra in **Figure C.8 B**. This changes drastically at 77 K. Here we find that the addition of (TBA)I (1000 equivalents) reduces the biexponential behavior and leads to an increase in lifetime. This is consistent with our hypothesis, that exchanged or missing apical iodide is not only the cause of the different dynamics observed below the melting point but also can be addressed with competing ligands. This is supported by the small changes in the emission spectra in **Figure C.8 B** at 77 K which point to a different composition of frozen cluster species because of different (TBA)I amounts.

In case of **2**, we find no significant biexponential character at 77 K in solution with a monoexponential decay of 40 μs , which only differs by 5 % compared to the experiments in PMMA. This leads us to the conclusion that TFA- is less susceptible to exchange reactions compared to I-, probably due to its bidentate nature.

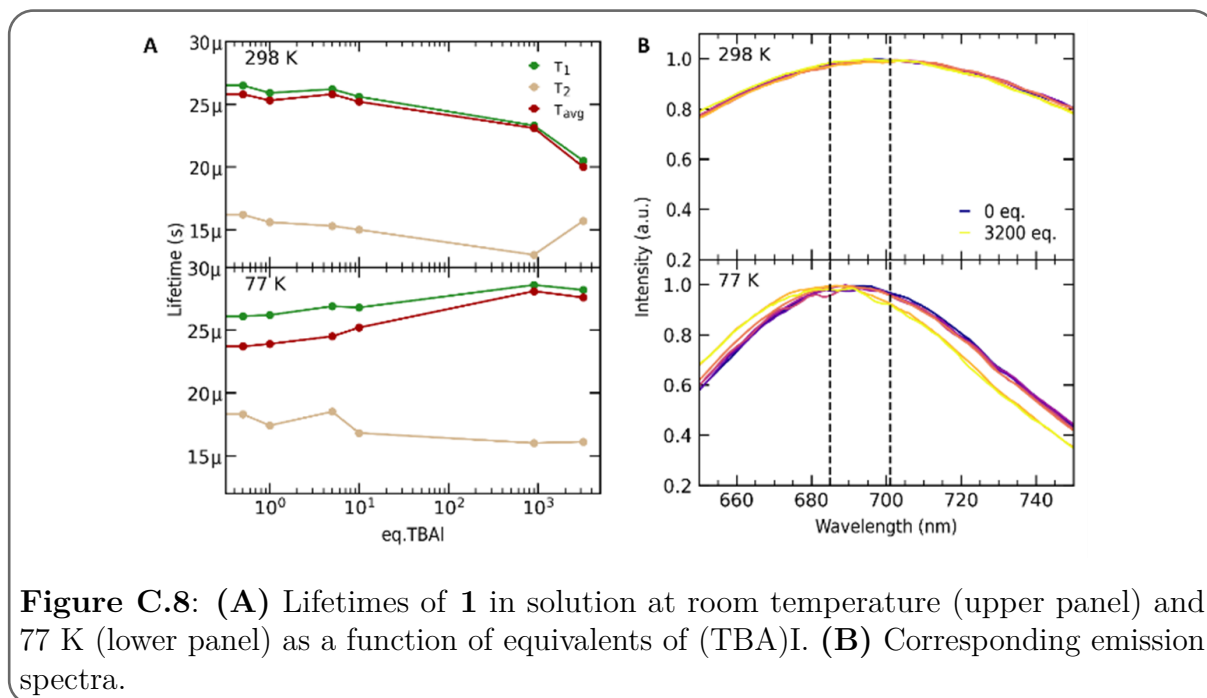


Figure C.8: (A) Lifetimes of **1** in solution at room temperature (upper panel) and 77 K (lower panel) as a function of equivalents of (TBA)I. (B) Corresponding emission spectra.

C.5 T-Dependent Emission Data of **1** and **2** in PMMA

To extract the emission maximum and FWHM at every temperature step for **1** and **2**, a single Gaussian function was fitted at every temperature. Although this did not fit the emission well over the whole spectral range, especially at higher temperatures, it gives a systematic measure of the emission maximum and FWHM values. The results are shown in **Figure C.9**.

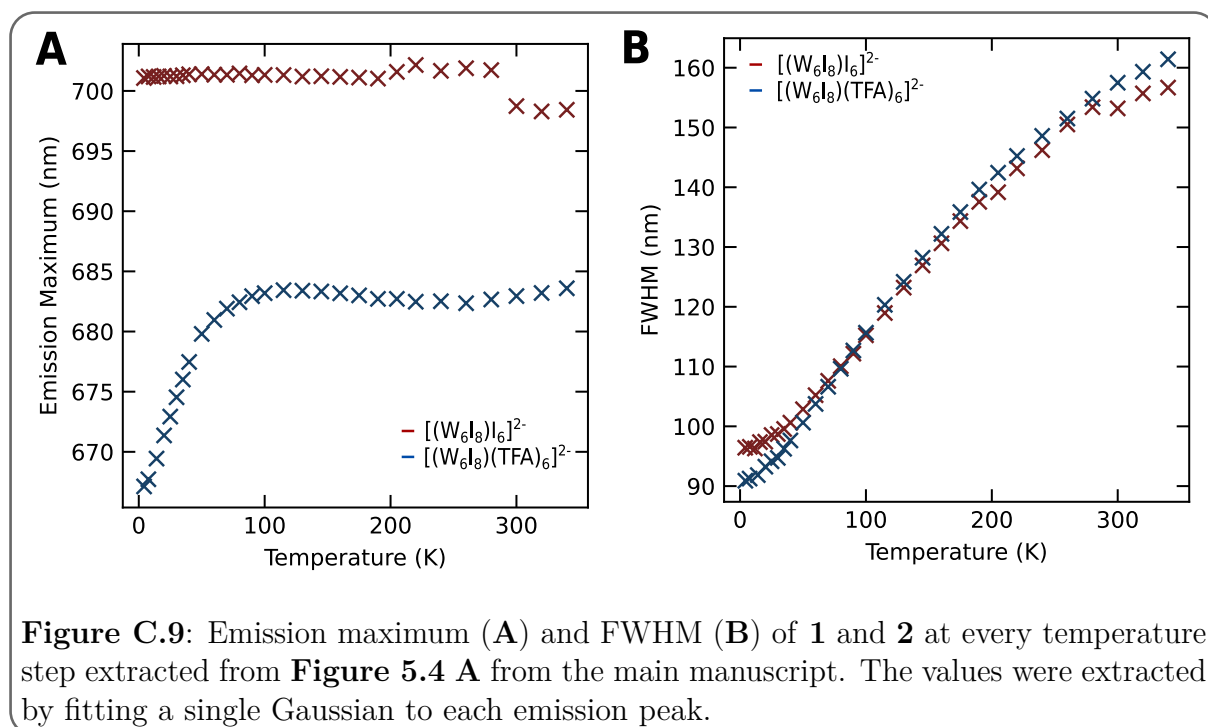


Figure C.9: Emission maximum (A) and FWHM (B) of **1** and **2** at every temperature step extracted from **Figure 5.4 A** from the main manuscript. The values were extracted by fitting a single Gaussian to each emission peak.

C.5.1 Variability of the Lifetime Fits

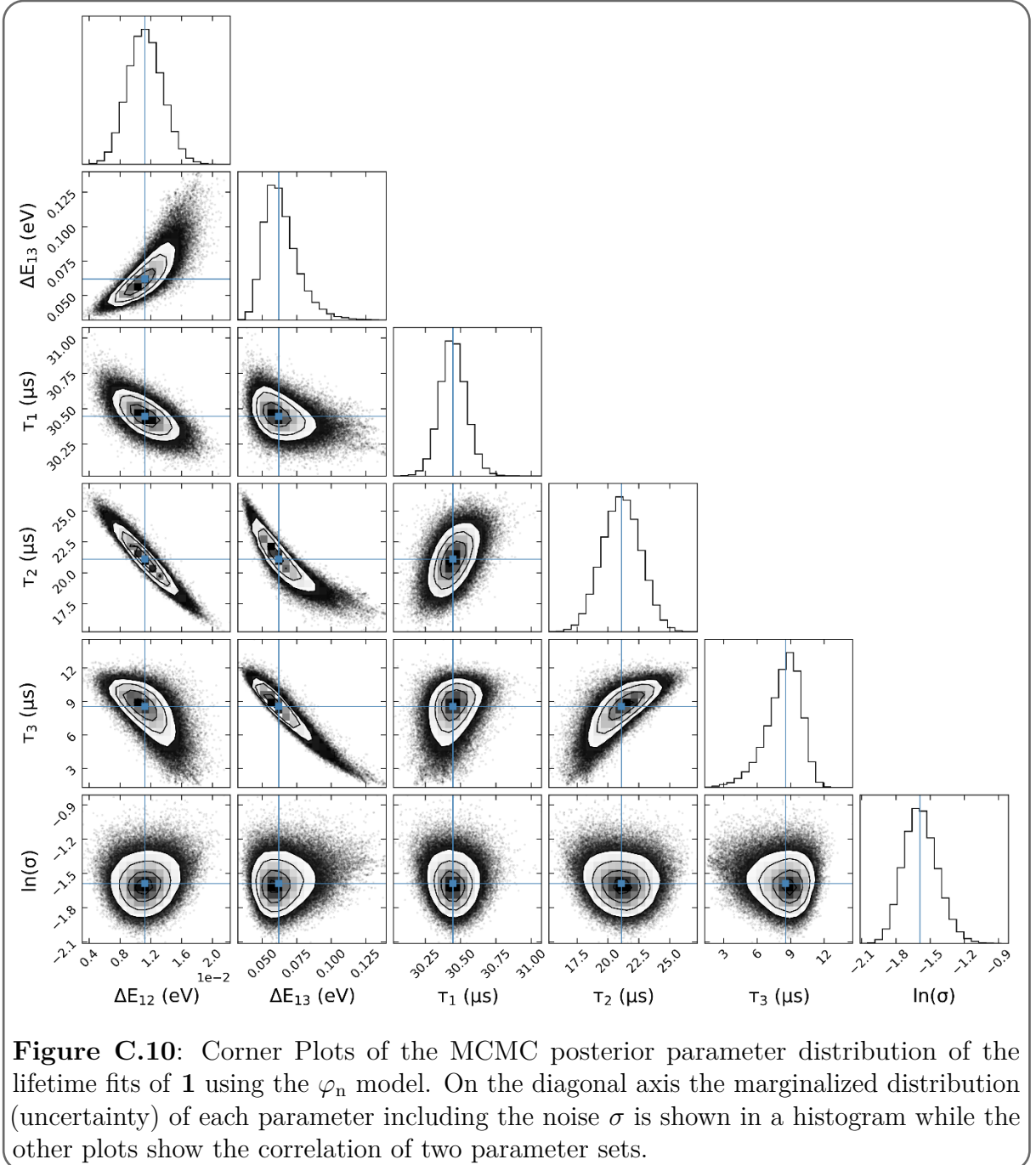
The relative parameter uncertainties of the fitted models are summarized in **Table C.4**. They were estimated by the covariance matrices provided by the python module lmfit.

Table C.4: Parameter uncertainties of the T-dependent lifetime fit estimated from the covariance matrices for **1** and **2**.

Model	Cluster	E_{12}	E_{13}	E_{14}	τ_1	τ_2	τ_3	τ_4
φ_n	1	22 %	23 %	—	1 %	9 %	25 %	—
ϕ_n	1	fixed	24 %	22 %	1 %	4 %	9 %	20 %
φ_n	2	8 %	14 %	—	1 %	2 %	24 %	—
ϕ_n	2	fixed	9 %	12 %	1 %	4 %	2 %	31 %

We used a python implementation of the Markov chain Monte Carlo (MCMC) called emcee³⁷³ to study the posterior distributions of the fitting parameters and to extract correlations between those. **Figures C.10 to C.13** shows the results of the MCMC study

using a corner plot representation.⁴⁸⁰ Here, the histograms on the diagonal axis show the marginalized distribution of each parameter (uncertainty) and the standard deviation of the noise σ separately, while the other plots depict the joint distribution of a pair of parameters (correlation). We find negative correlations between the splitting of each sublevel and the corresponding lifetime for both models. This is especially true for the highest sublevel which is also reflected in the high uncertainty values in **Table C.4**. This can be rationalized by the lack of datapoints above 340 K. In the ϕ_n model, we determine additionally high negative correlation between τ_1 and τ_2 mainly because of the proximity in energy and lifetime. We could not find a correlation between the noise level and parameter estimates. Based on this analysis, the values for the energy splitting and sublevel lifetimes should be understood as rough estimates especially for **1**.



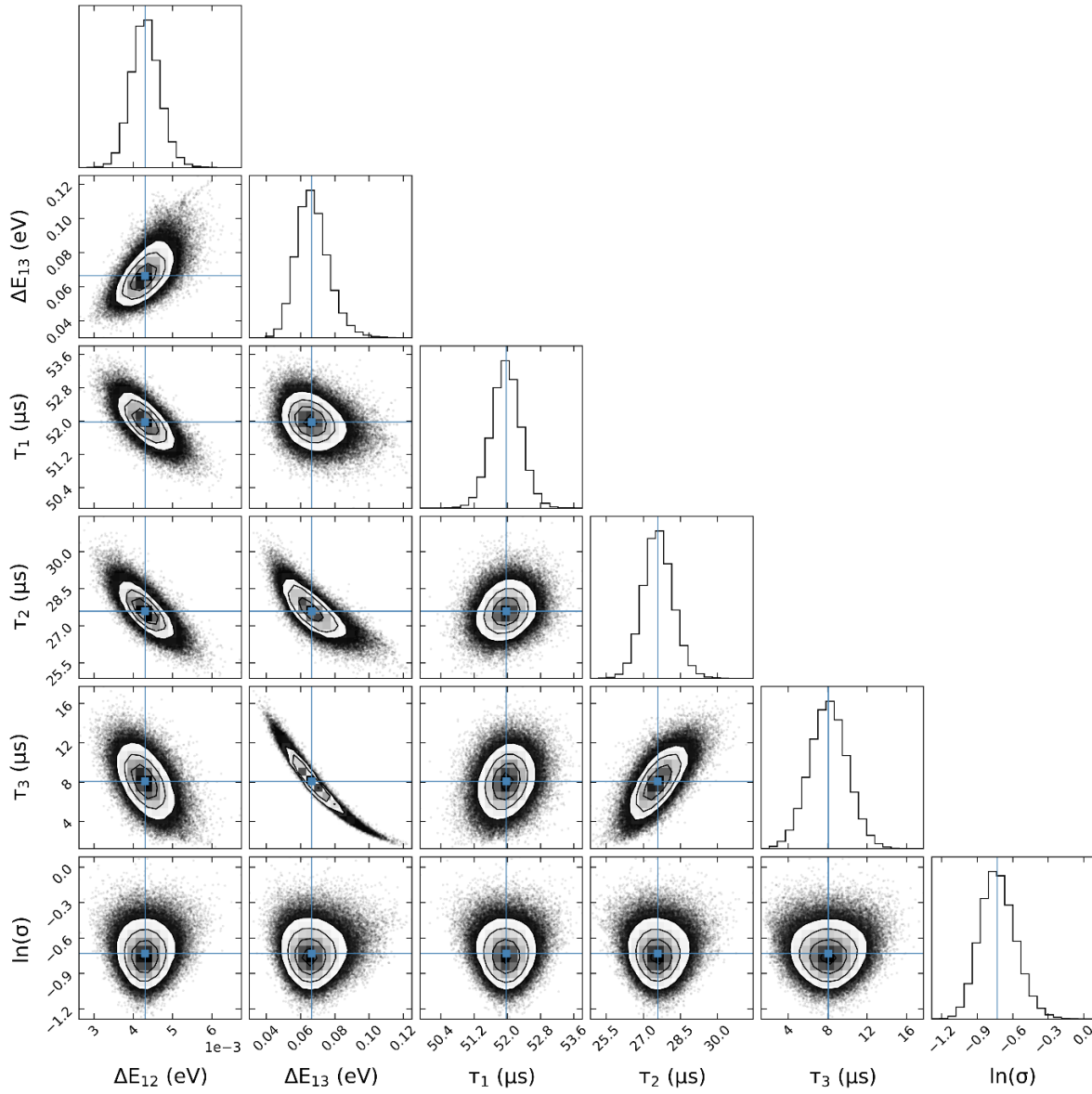
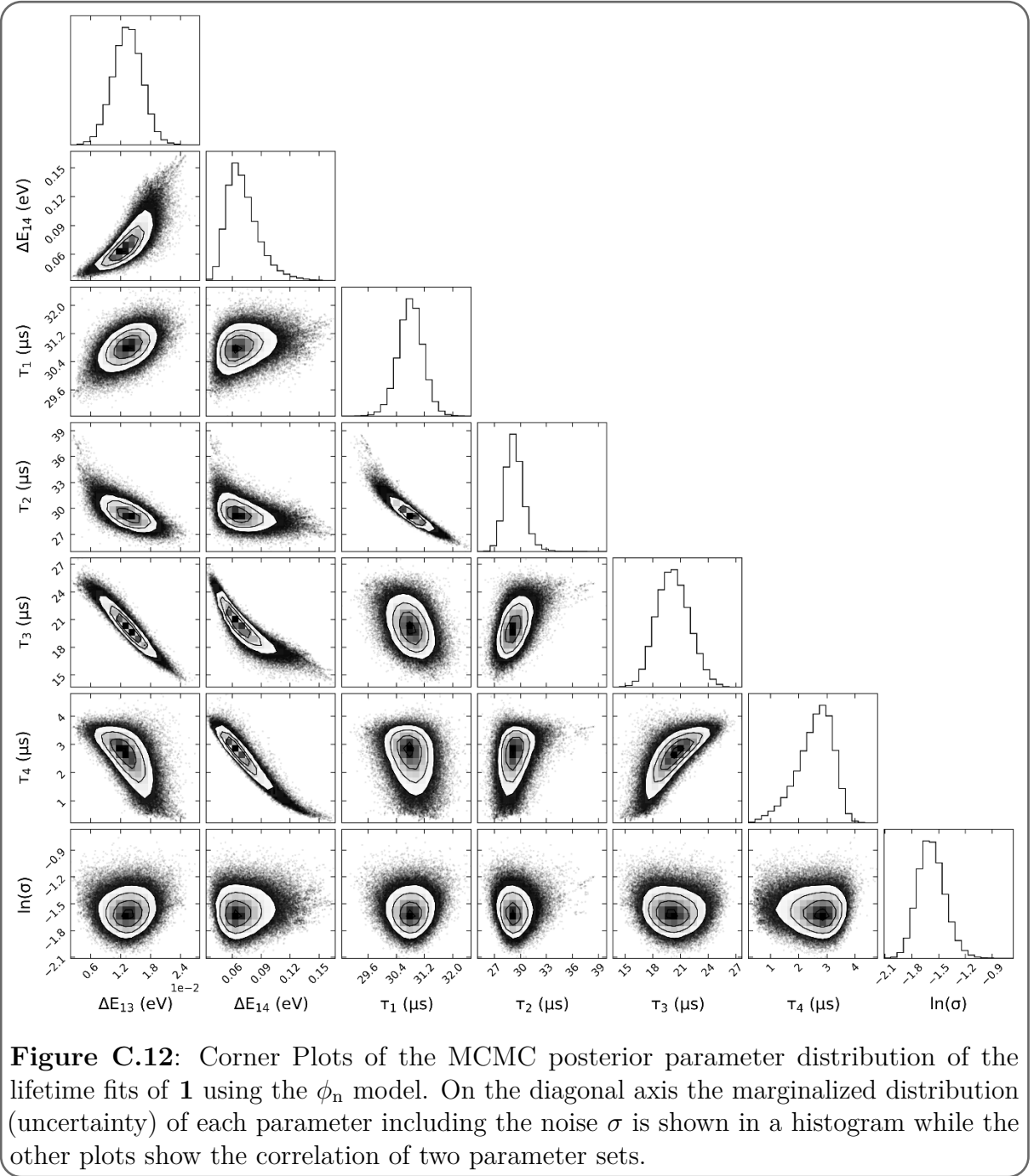


Figure C.11: Corner Plots of the MCMC posterior parameter distribution of the lifetime fits of **2** using the φ_n model. On the diagonal axis the marginalized distribution (uncertainty) of each parameter including the noise σ is shown in a histogram while the other plots show the correlation of two parameter sets.



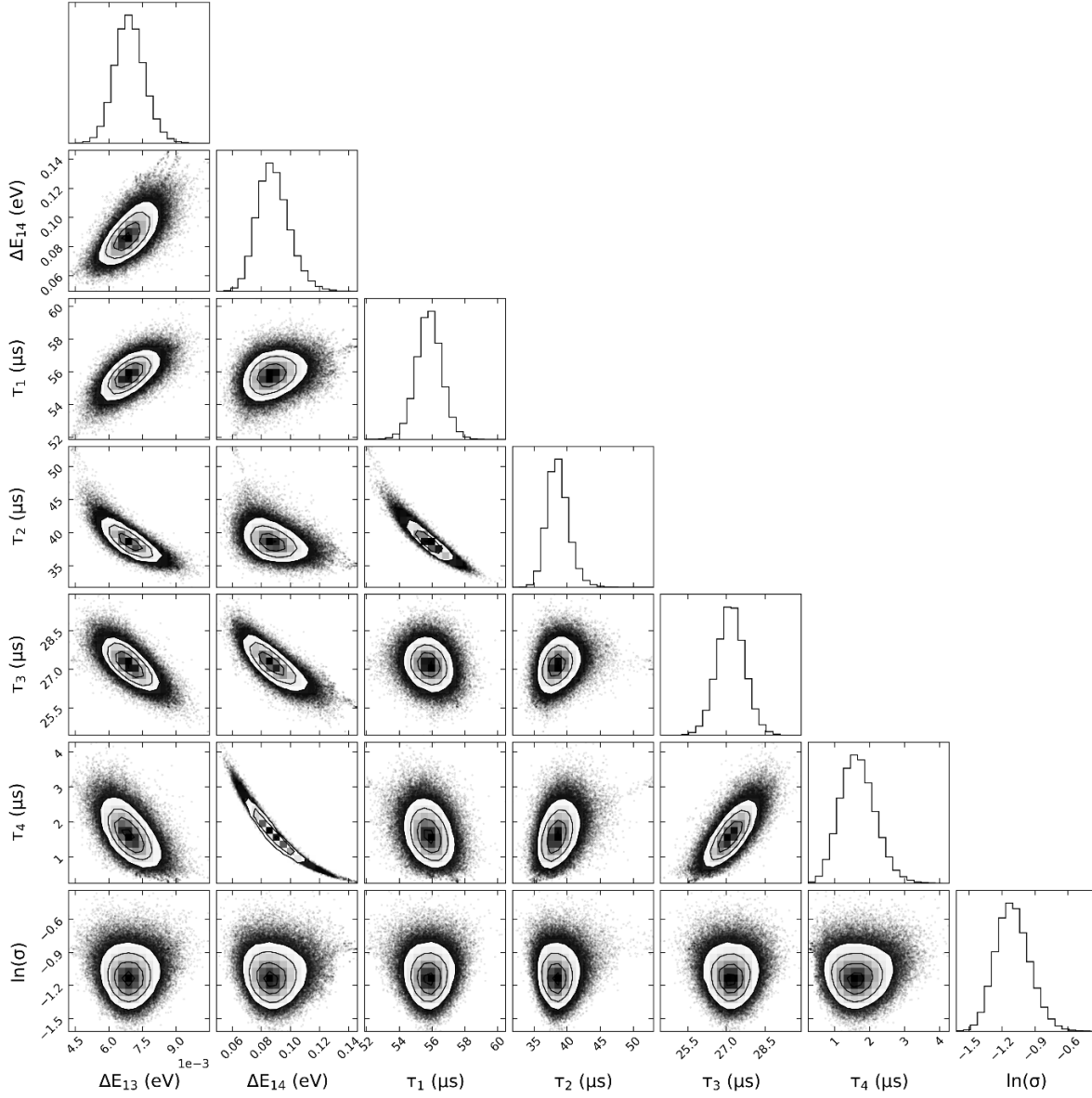


Figure C.13: Corner Plots of the MCMC posterior parameter distribution of the lifetime fits of **2** using the ϕ_n model. On the diagonal axis the marginalized distribution (uncertainty) of each parameter including the noise σ is shown in a histogram while the other plots show the correlation of two parameter sets.

C.5.2 Fitting Results of the Spectral Emission Fits

Table C.5: Fitting results of the T-dependent spectral measurements for **1** and **2**. Parameter names refer to equations **Equations C.1 to C.4**.

Model	Cluster	E_1/eV	E_2/eV	E_3/eV	E_4/eV	k_2/Hz	k_3/Hz	k_4/Hz	FWHM_0^a / meV	$k_{\text{broadening}}^a$ / meV
φ_n	1	1.78	1.78	1.96	–	26	32	–	177	8
ϕ_n	1	1.63	1.78	1.78	1.93	26	10 000	11 000	165	9
φ_n	2	1.87	1.82	2.01	–	4	7	–	177	9
ϕ_n	2	1.73	1.88	1.83	1.95	15	332	1 000	155	11

^aFWHM₀ refers to the theoretical FWHM at 0 K, and $k_{\text{broadening}}$ is the proportionality constant of Doppler broadening (see **Equation C.4**).

Table C.6: Fitting results of the T-dependent spectral measurements for **1** and **2**. E_n refers to the emission maximum, and FWHM_{*x*K} represents the temperature-dependent broadening according to **Equation C.4**.

Model	Cluster	E_1/nm	E_2/nm	E_3/nm	E_4/nm	FWHM _{4K} / meV	FWHM _{77K} / meV	FWHM _{200K} / meV	FWHM _{300K} / meV
φ_n	1	698	697	630	–	193	247	290	315
Φ_n	1	759	695	697	641	183	244	292	321
φ_n	2	664	682	615	–	195	256	304	333
Φ_n	2	718	659	678	637	177	252	311	346

C.5.3 Variability of the Spectral Emission Fits

The fits of the models on the spectral emission shape are analyzed as above. The calculated uncertainties of every E_n value are smaller than 1 % while the difference between the radiative rates Δk_{1n} can have larger uncertainties. The relative parameter uncertainties are summarized in **Table C.7**.

Table C.7: Parameter uncertainties of the T-dependent spectral fit estimated from the covariance matrices for **1** and **2**.

Model	Cluster	E_{1-4}	Δk_{12}	Δk_{13}	Δk_{14}	FWHM_0^a / meV	$k_{\text{broadening}}^a$ / meV
φ_n	1	<1 %	20 %	20 %	–	<1 %	<1 %
ϕ_n	1	<1 %	2 %	10 %	15 %	<1 %	<1 %
φ_n	2	<1 %	3 %	3 %	–	<1 %	<1 %
ϕ_n	2	<1 %	2 %	2 %	5 %	<1 %	<1 %

^aFWHM₀ refers to the theoretical FWHM at 0 K, and $k_{\text{broadening}}$ is the proportionality constant of Doppler broadening (see **Equation C.4**).

As discussed above in the analysis of the lifetime fits, we explore the posterior parameter distribution using MCMC. The corner plot representation of the analysis is shown in

Figures C.14 to C.17. We find strong negative correlation between the initial FWHM and the FWHM broadening factor which is expected. These values are of limited interest, and they do not strongly affect the estimation of the other parameters. For some fits, an increased correlation between Energy positions E_n and the corresponding rates can be found, also reflected in the uncertainty estimates in **Table C.7**. Especially, a strong correlation between the rates of the second and third sublevel in the φ_n model of **1** can be found. Based on these results, the parameter estimates of the emissive rates and FWHM broadening should be handled with caution while the relaxation Energies of each sublevel are more stable.

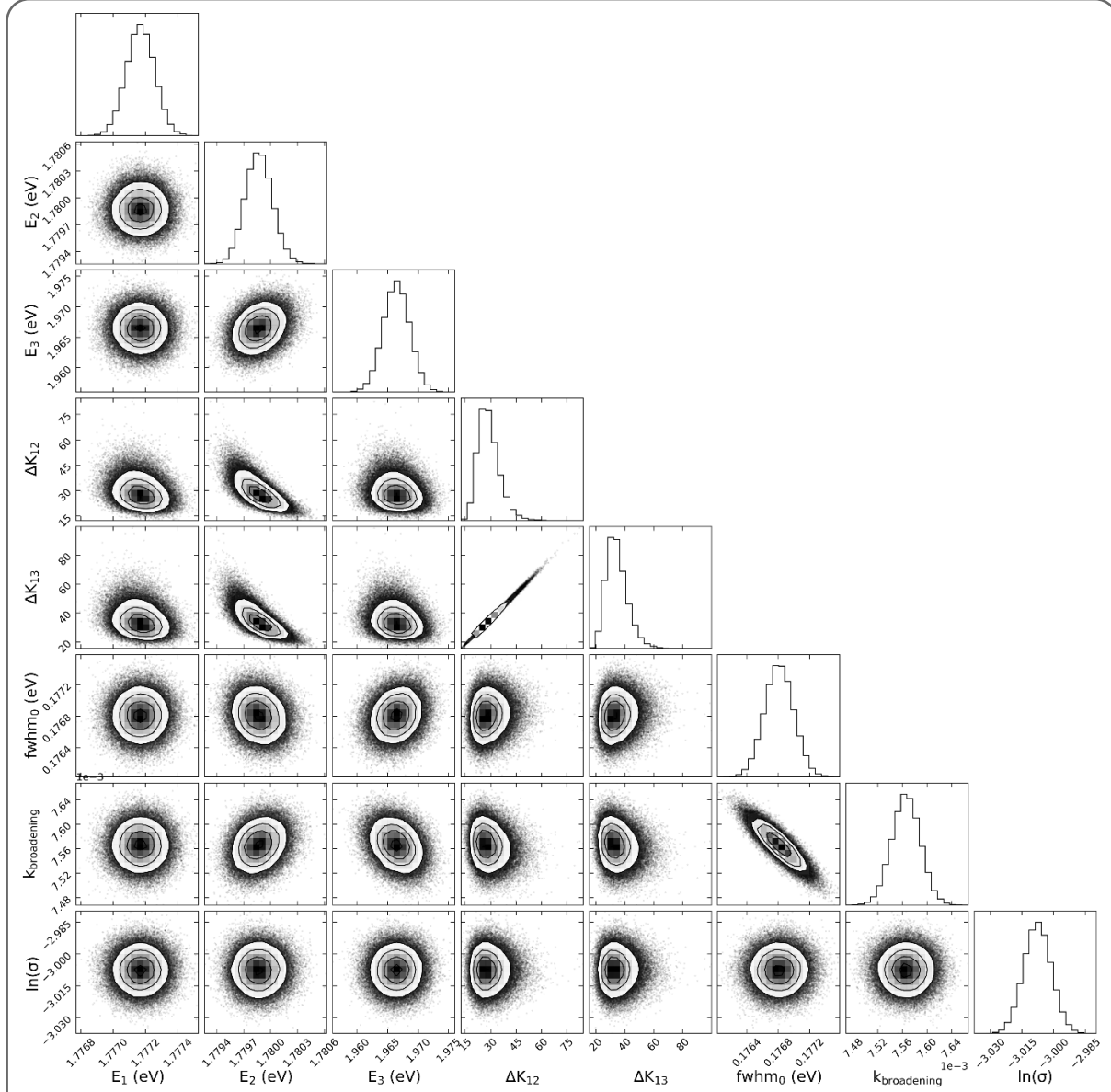
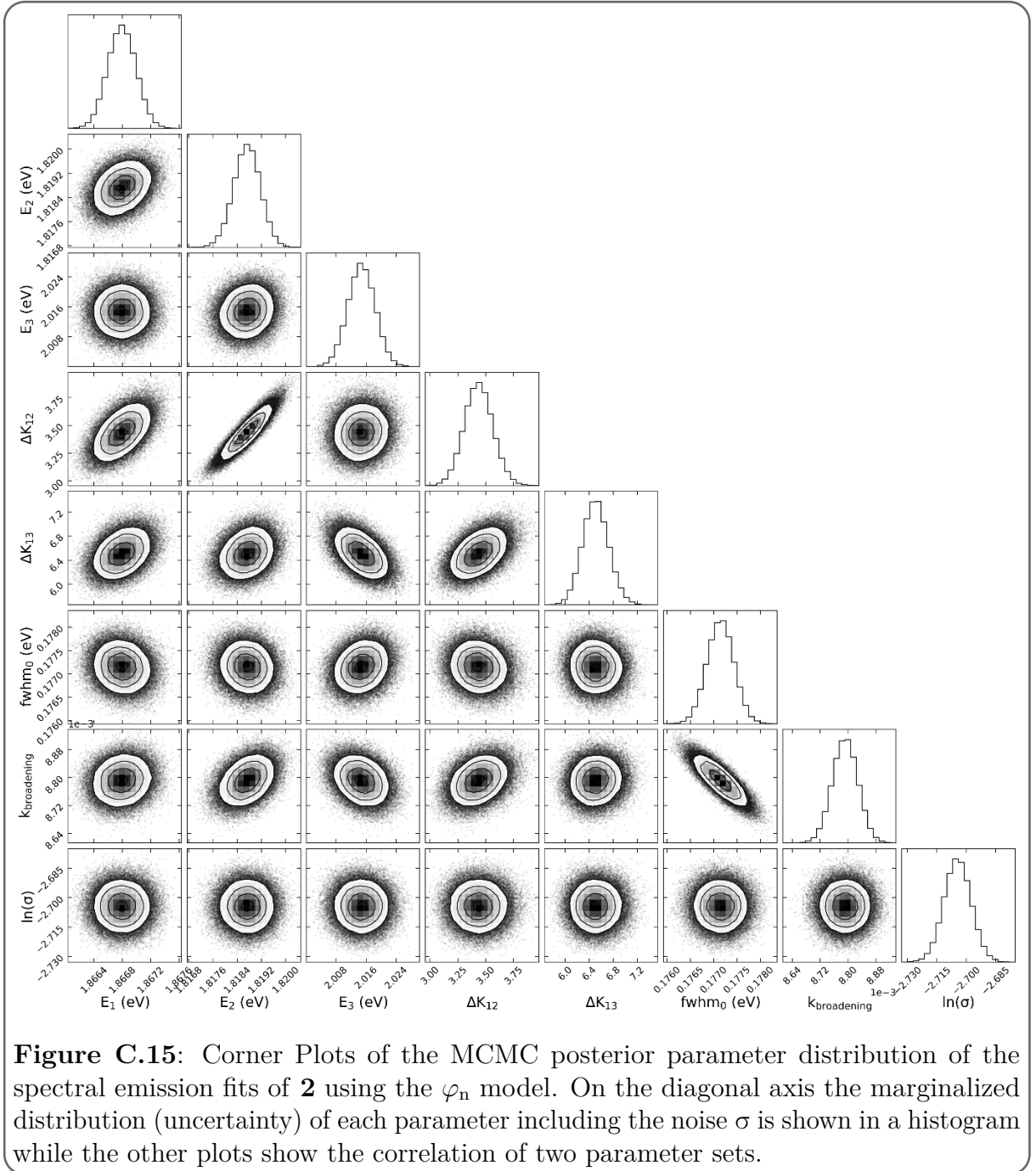
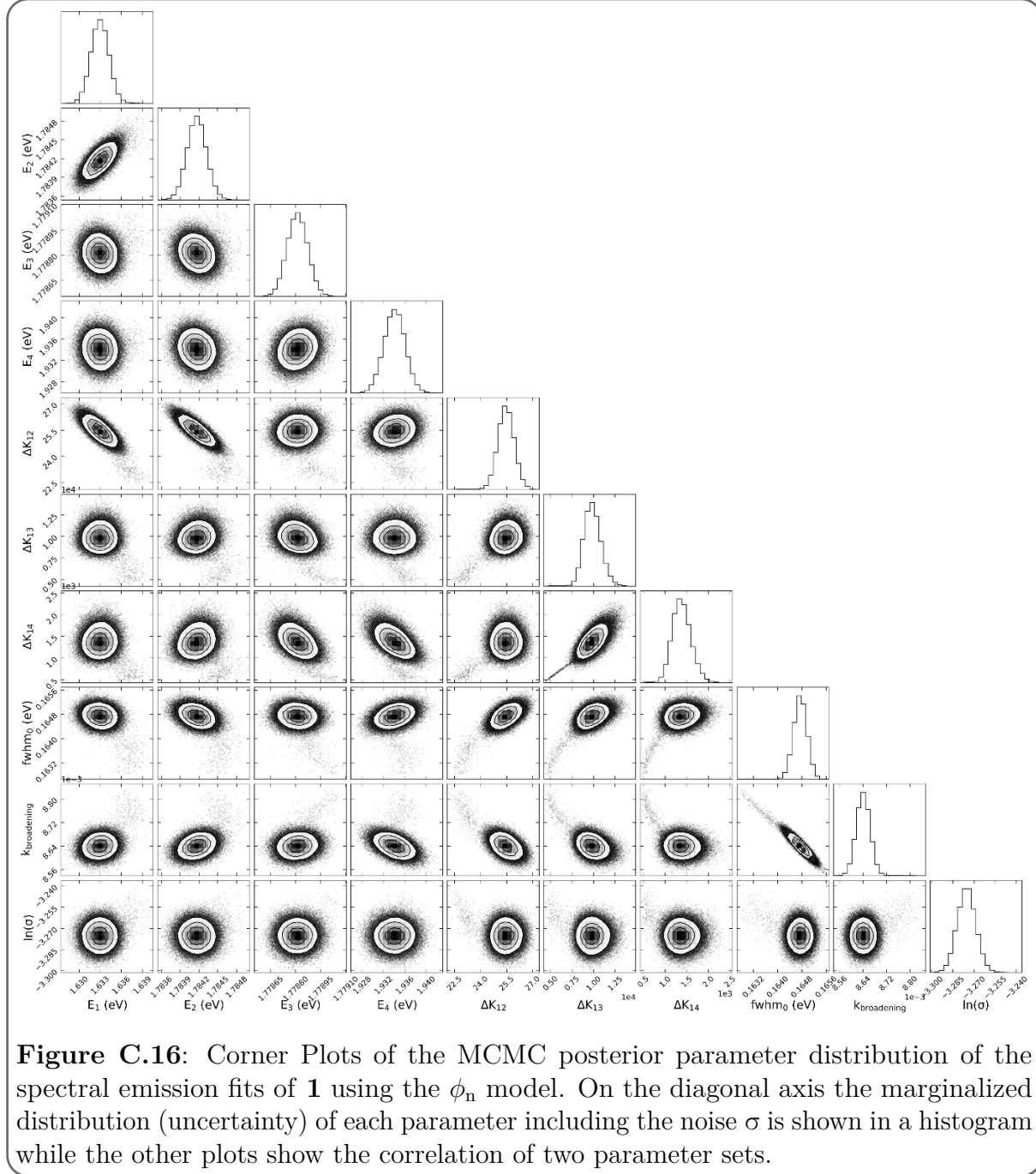


Figure C.14: Corner Plots of the MCMC posterior parameter distribution of the spectral emission fits of **1** using the φ_n model. On the diagonal axis the marginalized distribution (uncertainty) of each parameter including the noise σ is shown in a histogram while the other plots show the correlation of two parameter sets.





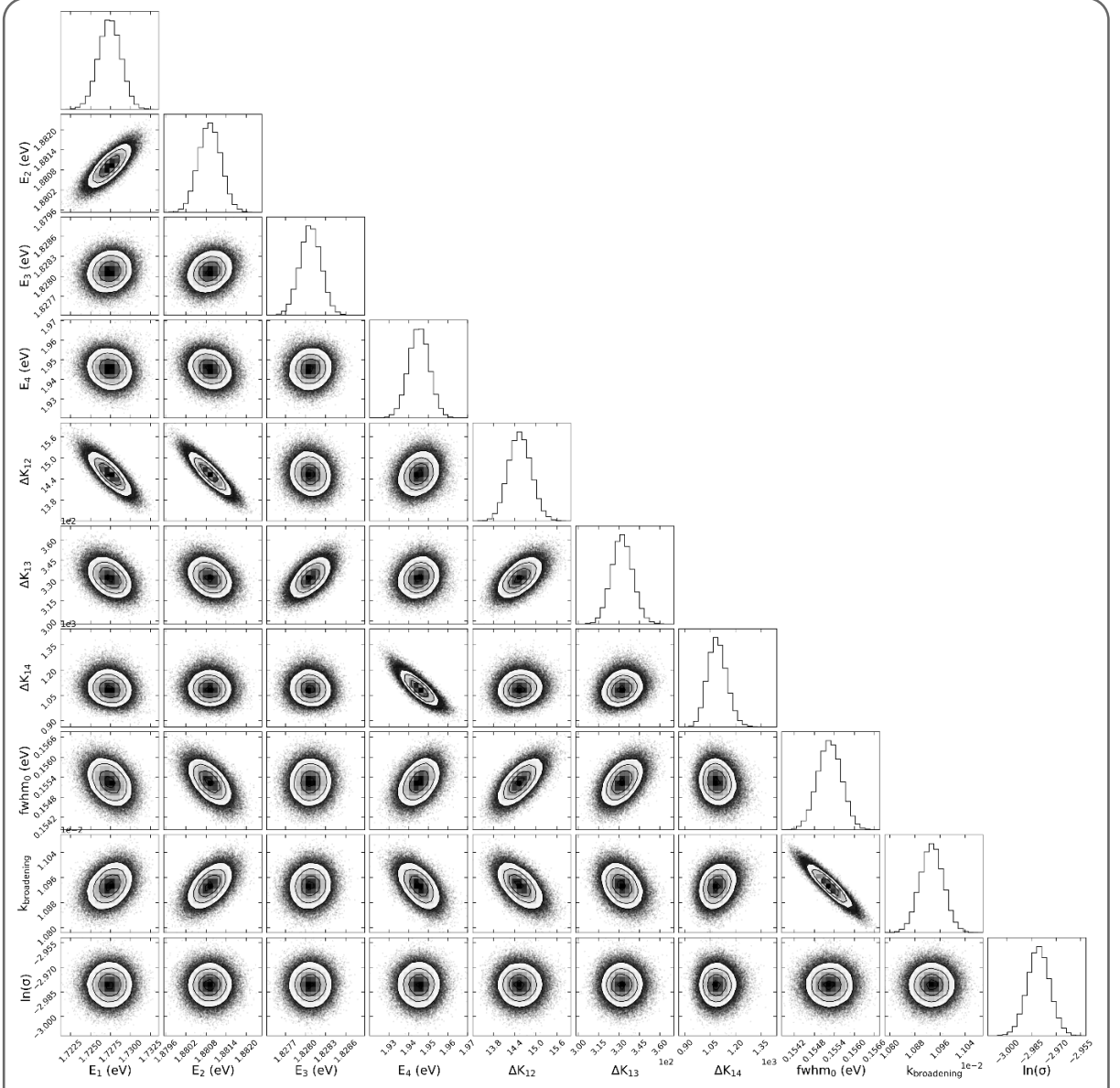


Figure C.17: Corner Plots of the MCMC posterior parameter distribution of the spectral emission fits of **2** using the ϕ_n model. On the diagonal axis the marginalized distribution (uncertainty) of each parameter including the noise σ is shown in a histogram while the other plots show the correlation of two parameter sets.

C.6 Additional Information on the φ_n/ϕ_n model

C.6.1 Model Assumptions and Comparison

The models irrespective of the number of sublevels assume that at every temperature, every emissive sublevel is in a Boltzmann equilibrium. Additionally, the spectral shape of the phosphorescence of every sublevel is similar and constant at a given temperature and may only vary in their peak position E_n . In its initial implementation by Azumi and colleagues, it was further assumed that the emission spectrum is independent of the temperature, meaning that the FWHM is constant over the whole temperature range.³¹⁷ As mentioned by Kitamura and coworkers, this is not warranted and temperature dependent spectral broadening should be considered.²² Therefore, in their model implementation, they kept the FWHM constant for every sublevel at a given temperature but allowed a variation with temperature. However, they did not mention restrictions or a temperature dependence of the broadening. In our implementation of the φ_n/ϕ_n model, we assumed a homogeneous Doppler broadening leading to a monotonous increase in FWHM proportional to $\sqrt{T}$.

The degrees of degeneracy used for **Equation 5.2** in the main manuscript are based on the assumed geometries by the φ_n/ϕ_n models. They are summarized in **Table C.8**.

Table C.8: Degree of degeneracy for the sublevels according to the geometry assumed by the φ_n and ϕ_n models.

φ_n Model			ϕ_n Model			
Degree of degeneracy g_n			Degree of degeneracy g_n			
$n = 1$	$n = 2$	$n = 3$	$n = 1$	$n = 2$	$n = 3$	$n = 4$
3 (T_{2u})	2 (E_u)	3 (T_{1u})	2 (E_u)	1 (B_u)	2 (E_u)	3 (T_{1u})

C.6.2 Derivation of the Spectral Fit

Based on the calculated zero-magnetic-field splitting of the sublevels and the φ_n/ϕ_n model, the emission spectra of **Figure 5.4 A** can be simulated with the following equation

$$I(E, T) = \sum_n k_n * G(E - E_n) * P(T, \Delta E_{1n}), \quad (C.1)$$

where each sublevel n contributes with the product of the emissive rate constant k_n relative to φ_1 or ϕ_1 , the normalized gaussian function $G(E - E_n)$ and the probability of overcoming the energy barrier ΔE_{1n} due to thermal energy $P(T)$. $G(E - E_n)$ and $P(T)$ are defined as follows:

$$G(E - E_n, n) = \frac{1}{\text{FWHM}(\phi_n) \sqrt{\pi/2}} e^{-2 \frac{(E - E_n)^2}{\text{FWHM}^2}} \quad (C.2)$$

$$P(T, n) = e^{-\frac{\Delta E_{1n}}{k_B T}} \quad (C.3)$$

with E and T being the spectral energy and temperature. E_n and $\text{FWHM}(\phi_n)$ describe the emission maximum energy and full width at half maximum of φ_n/ϕ_n respectively. ΔE_{1n} refers to the energy difference between φ_1 or ϕ_1 and φ_n or ϕ_n (e.g. $\Delta E_{11}=0$) similar to **Equation 5.2** in the main manuscript. The FWHM for every sublevel is kept constant at a given temperature and a homogenous Doppler broadening ($\propto \sqrt{T}$) is assumed, leading to the following model of the FWHM:

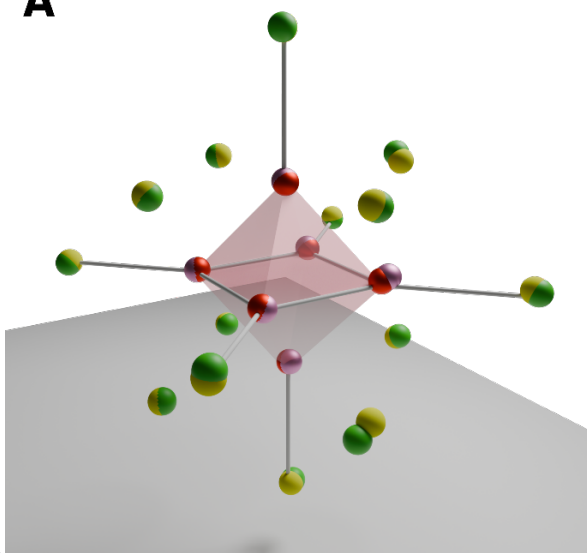
$$\text{FWHM} = \text{FWHM}_n + k_{\text{broadening}} \cdot \sqrt{T} \quad (\text{C.4})$$

C.7 TDDFT Analysis

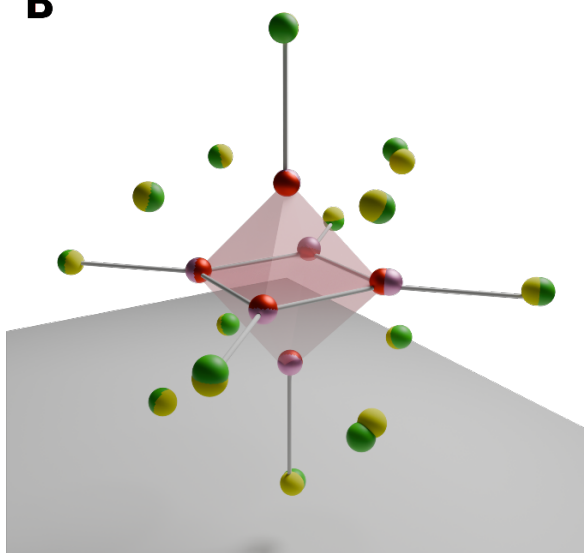
C.7.1 Optimized Geometries for the SOC2 and SOC3 states of 1

Chart C.1: Distortions found in the SOC2 (**A**) and SOC3 (**B**) geometry (W = purple, I = green) compared to SOC0 geometry (W = red, I = yellow).

A



B



C.7.2 Eigenvectors of the SOC0-3 matrices of 1

Table C.9: Eigenvectors of the SOC0 matrices for 1.						
SOC0	Energy (eV)	ΔE_{1n} (meV)	State Mixing ^a			
			R	S	M _s	%
0	0	–	0	0	0	94 %
1	2.86	0	1	1	0	47 %
			1	1	–1	47 %
			1	1	1	5 %
2	2.86	0.2	1	1	1	42 %
			1	1	–1	42 %
			1	0	0	15 %
3	2.86	0.4	1	1	0	80 %
			1	1	–1	10 %
			1	1	1	10 %
4	2.90	38	3	1	0	39 %
			2	1	1	15 %
			2	1	–1	15 %
			2	1	0	10 %

^aR represents the root or index of the non-relativistic state, S denotes the spin and M_s corresponds to the spin magnetic number.

Table C.10: Eigenvectors of the SOC1 matrices for **1**.

SOC1	Energy (eV)	ΔE_{1n} (meV)	State Mixing ^a			
			R	S	M _s	%
0	0	–	0	0	0	94 %
1	1.99	0	1	1	0	64 %
			1	1	1	16 %
			1	1	–1	16 %
2	2.00	4	1	1	1	48 %
			1	1	–1	48 %
			2	0	0	2 %
3	2.01	16	1	1	1	32 %
			1	1	–1	32 %
			1	1	0	30 %
4	2.34	350	1	0	0	84 %
			2	1	1	4 %
			2	1	–1	4 %
			3	1	0	3 %

^aR represents the root or index of the non-relativistic state, S denotes the spin and M_s corresponds to the spin magnetic number.

Table C.11: Eigenvectors of the SOC2 matrices for **1**.

SOC2	Energy (eV)	ΔE_{1n} (meV)	State Mixing ^a			
			R	S	M _s	%
0	0	–	0	0	0	94 %
1	1.98	0	1	1	0	36 %
			1	1	1	30 %
			1	1	–1	30 %
2	1.98	4	1	1	1	48 %
			1	1	–1	48 %
			1	1	0	1 %
3	1.99	14	1	1	0	58 %
			1	1	–1	19 %
			1	1	1	19 %
4	2.32	347	1	0	0	86 %
			4	1	1	2 %
			4	1	–1	2 %
			3	1	–1	2 %

^aR represents the root or state index, S denotes the spin, and M_s corresponds to the spin magnetic number.

Table C.12: Eigenvectors of the SOC3 matrices for **1**.

SOC3	Energy (eV)	ΔE_{1n} (meV)	State Mixing ^a			
			R	S	M _s	%
0	0	–	0	0	0	94 %
1	2.00	0	1	1	0	64 %
			1	1	1	16 %
			1	1	–1	16 %
2	2.00	4	1	1	1	48 %
			1	1	–1	48 %
			2	0	0	2 %
3	2.02	17	1	1	1	32 %
			1	1	–1	32 %
			1	1	0	30 %
4	2.35	349	1	0	0	84 %
			2	1	1	4 %
			2	1	–1	4 %
			3	1	0	3 %

^aR represents the root or index of the non-relativistic state, S denotes the spin, and M_s corresponds to the spin magnetic number.

Table C.13: Cartesian coordinates in Å of the optimized SOC0 geometry of **1**.

I	10.51409878302265	15.03847191756634	0.20347215420503
I	10.12102030888199	15.72163732445811	4.03836786959419
I	7.42518882839472	13.56627602624270	2.10682590902797
I	9.64682752085683	18.65374628557627	1.42637117379342
I	6.95029126355422	16.49975576133775	–0.50378650106645
I	6.54443941312038	20.38568655447897	–0.21446926213751
I	3.89436113455103	14.31160799344930	0.59300176901459
I	7.67278943436324	13.38331413275191	6.00675996831038
I	10.32286314852287	19.45733600960282	5.19930388700604
I	4.09618936426873	18.04731646015082	1.75394844815905
I	4.57038983560981	15.11522275012976	4.36593817886835
I	7.26692645527650	17.26921484447534	6.29608943552474
I	6.79203384644629	20.20269412266689	3.68548588976401
I	3.70311862892982	18.73053309986188	5.58886078456506
W	8.45854515954427	16.15213162137497	1.82792755938521
W	6.88423643389314	18.27125509617078	1.66145510835013
W	5.83350767679465	15.86534758524160	1.98307706456901
W	8.38370974379449	17.90360992949121	3.80922976458479
W	7.33298247202941	15.49771120546363	4.13085176656154
W	5.75868054814480	17.61683127950862	3.96438903192037

Table C.14: Cartesian coordinates in Å of the optimized SOC1 geometry of **1**.

I	10.52738571216460	15.03239448699424	0.19596483000912
I	10.12636263723803	15.71876019465783	4.02794051447128
I	7.41907068390729	13.57544490923704	2.11372300086308
I	9.63765341750521	18.65192873860963	1.43300572202866
I	6.96280120508602	16.49421233864647	-0.50703267362456
I	6.59509949593212	20.43390557502452	-0.16470320253365
I	3.89522268213675	14.25877794042944	0.65601854982862
I	7.60447368798389	13.34663789357841	5.97288499569907
I	10.30136831976004	19.52405804948257	5.14629255456436
I	4.06378786867142	18.02220649499691	1.44190591213995
I	4.54750679722975	15.17904158704813	4.39069847656751
I	7.54607792801706	17.16590923383515	6.42210170423598
I	6.73142560382292	20.18136639692413	3.72316630568370
I	3.64832222674874	18.75488176432787	5.63400847355186
W	8.46977559918278	16.14574065151214	1.81926756208626
W	6.87484700819918	18.26811748671446	1.65156188072237
W	5.82774382695162	15.87201764360003	1.97150303397368
W	8.38702881987432	17.89724729502251	3.82026583687782
W	7.34066977640725	15.50192845572710	4.14100916002821
W	5.66557670318063	17.66512286363069	4.03351736282649

Table C.15: Cartesian coordinates in Å of the optimized SOC2 geometry of **1**.

I	10.50897902495057	15.04008846342761	0.16748395085157
I	10.14492102633883	15.70762046346178	4.01026823585061
I	7.41711174881893	13.57594501848987	2.10583320485055
I	9.63427372788446	18.65409613134115	1.42778195983372
I	6.94219200359880	16.50475057087487	-0.49348625399788
I	6.60441440910880	20.43942391134083	-0.14959775072309
I	3.89988777800718	14.24719440004639	0.67722078617179
I	7.62908483879891	13.35289951279238	5.98714237472682
I	10.31492405809041	19.49930927382655	5.17106154924143
I	4.04975940601002	18.01513902936544	1.37277695642215
I	4.55309107310486	15.17901095413045	4.39432770878174
I	7.45711269893598	17.19714948245275	6.38770550839196
I	6.73969174202670	20.18063825207384	3.72393803824824
I	3.62493620205682	18.76721177190653	5.59226221413980
W	8.46782638218377	16.14689798613635	1.81614452944396
W	6.86411529717155	18.26868362734729	1.67137554341840
W	5.82273557244438	15.88335884968404	1.98991965010687
W	8.41121588679456	17.89341251212783	3.81916300220026
W	7.35975442126326	15.48555273368033	4.14044826589033
W	5.72617270241077	17.65131705549272	4.11133052615056

Table C.16: Cartesian coordinates in Å of the optimized SOC3 geometry of **1**.

I	10.52679561045318	15.03358605078175	0.19589510543466
I	10.12650620072251	15.71890135393289	4.02782498549781
I	7.41907033837782	13.57553461133979	2.11333903783289
I	9.63723246498221	18.65278738437124	1.43378488676591
I	6.96241200287767	16.49428837183643	-0.50680417261076
I	6.59416089267519	20.43271646724594	-0.16684565027807
I	3.89528098301892	14.25839477667693	0.65611882628100
I	7.60629549343272	13.34545701767922	5.97256642004991
I	10.30180928628762	19.52207689877469	5.14857736818093
I	4.06290568171603	18.02211638470659	1.44371118443695
I	4.54831910151454	15.17846231674968	4.39114978087431
I	7.54239568137980	17.16564816206722	6.42195841854580
I	6.73346886589011	20.18228886998781	3.72154247237317
I	3.64969274907505	18.75648452090796	5.63225891208607
W	8.46956001748266	16.14625651671996	1.81950680134102
W	6.87430350036185	18.26853684952030	1.65116701376172
W	5.82735171804911	15.87220257775240	1.97163225749458
W	8.38698235381535	17.89727103999266	3.82117328567431
W	7.34107243039201	15.50108908401826	4.14165775517855
W	5.66658462749533	17.66560074493761	4.03288531107910

Table C.17: Structural parameters in Å of the optimized SOC0, SOC1, SOC2 and SOC3 geometries of **1**.

Distances in Å	SOC0	SOC1	SOC2	SOC3
W–W average	2.6452	2.6837	2.6841	2.6839
W–W min	2.6450	2.6335	2.6222	2.6341
W–W max	2.6455	2.7396	2.7632	2.7388
W–I _{inner} average	2.7988	2.8254	2.8042	2.8253
W–I _{inner} min	2.7984	2.7492	2.7511	2.7504
W–I _{inner} max	2.7993	3.0807	2.8956	3.0784
W–I _{apical} average	2.8470	2.8343	2.8348	2.8341
W–I _{apical} min	2.8468	2.7962	2.8024	2.7957
W–I _{apical} max	2.8472	2.8475	2.8477	2.8472

C.7.3 Optimized Geometries for the S_0 and T_1 states of **2**

Chart C.2: Distortions found in the T_1 geometry (W = purple, I = green, C = light gray, O = pink) compared to S_0 geometry (W = red, I = yellow, C = dark gray, O = orange). Fluorine atoms are omitted for clarity.

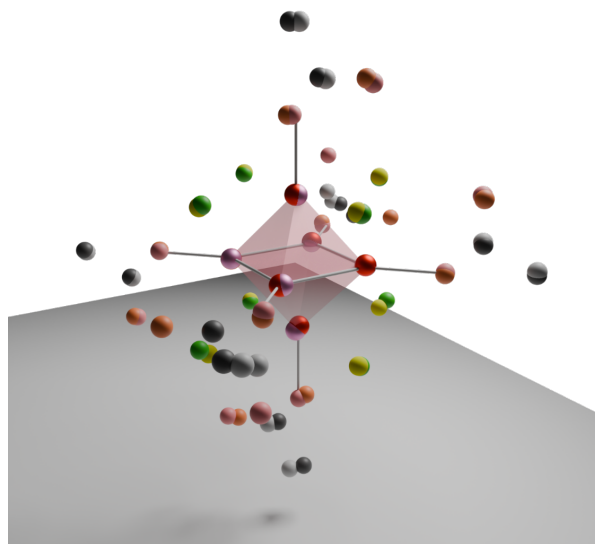


Table C.18: Cartesian coordinates in Å of the optimized S_0 geometry of **2**.

W	1.43535822261459	0.34368398027799	1.16731691661541
W	-0.01980848108324	-1.80435013857941	0.55600365561818
W	-1.21134735691340	0.43127372730314	1.36208970771758
I	2.79287651654736	-2.01382519865113	0.38154066834231
I	0.21606526274075	-1.07633055238847	3.24978980380333
I	0.25455766433193	2.71508769526192	2.09753407948120
I	2.81879061092566	1.82717080869732	-0.79432802313493
O	3.13637620496732	0.69168888926466	2.36801484885251
C	3.31536901269670	1.06067455902001	3.57659666976323
O	2.51698085521143	1.34350473004459	4.43782271105440
C	4.83320003662091	1.12812008170849	3.89817972600455
F	5.46411508156469	1.99726202894874	3.09482835155112
F	5.42079989362914	-0.06600471036528	3.73177446376704
F	5.06606261966084	1.51083149268614	5.15362758685136
O	0.03675516427401	-3.85052207681359	1.09399560312678
C	-0.52917150871450	-4.53764760506169	2.00660356038509
O	-1.31399196532418	-4.20956861092149	2.86647296632497
C	-0.07919250952608	-6.02160883054888	1.92196403564589
F	-0.64884889880009	-6.77570730480577	2.8624153367687
F	-0.39597273234195	-6.56036049863146	0.73557452040699
F	1.24844245872655	-6.13778531101321	2.07041005991159
O	-2.68419755170348	0.89737433139014	2.79549078756252
C	-2.65433123148445	1.26964175161517	4.01658703201633
O	-1.71782042153757	1.46660874431881	4.75322854049113
C	-4.09718483093659	1.48629262754734	4.54784427389841
F	-4.72502329460631	2.45265185934631	3.85996981484624
F	-4.11248443324853	1.84317764296706	5.83200810161958
F	-4.83558301785910	0.37399199417018	4.43509027297521
W	-1.43536221413462	-0.34368357305982	-1.16731307764444
W	0.01980391450641	1.80435128593728	-0.55599943286558
W	1.21134349684642	-0.43127307366725	-1.36208562463083
I	-2.79288078209530	2.01382441071866	-0.38153350434539
I	-0.21606872925268	1.07633190766972	-3.24978494949548
I	-0.25456288329436	-2.71508711376782	-2.09752903820659
I	-2.81879602134063	-1.82716853838420	0.79433118710521
O	-3.13637363832371	-0.69168900630156	-2.36801639737692
C	-3.31535730876878	-1.06067535402855	-3.57659879995543
O	-2.51696339564787	-1.34349616170035	-4.43782230736204
C	-4.83318610661349	-1.12813255851245	-3.89818927903420
F	-5.46410177247272	-1.99727126085756	-3.09483492695811
F	-5.42079236294494	0.06599087117264	-3.73179606311685
F	-5.06604044026736	-1.51085438111281	-5.15363520165576
O	-0.03675732499961	3.85052317967194	-1.09398951429001
C	0.52916803658785	4.53764536761797	-2.00660062640540
O	1.31398469617036	4.20956293358228	-2.86647171829192
C	0.07918885103210	6.02160673115613	-1.92196537726855
F	0.64886770462118	6.77570947194166	-2.86239930313339
F	0.39593731172377	6.56035539697069	-0.73556637106980
F	-1.24844303795877	6.13778092537809	-2.07044513941470
O	2.68419591193027	-0.89737217116947	-2.79548599929444
C	2.65432775908005	-1.26964222928880	-4.01658135918194
O	1.71781579337198	-1.46661604916623	-4.75321902708458
C	4.09718114312602	-1.48628030549730	-4.54784348855036
F	4.72504599913847	-2.45260690426472	-3.85994790598648
F	4.11247845768917	-1.84319987693186	-5.83199771352421
F	4.83555557185840	-0.37396003089400	-4.43512511323670

Table C.19: Cartesian coordinates in Å of the optimized T_1 geometry of **2**.

W	1.40944827849183	0.32992321336323	1.16991488173629
W	-0.03065856292294	-1.79937263827109	0.54968338943503
W	-1.24937210496657	0.41414223344245	1.48952891668598
I	2.77857587698001	-2.00980260860493	0.37110568900087
I	0.42058618573276	-1.28090773431972	3.29372553295073
I	0.15837196479311	2.73191836733587	2.07491253245906
I	2.80612457262711	1.81723575031530	-0.76646019697292
O	3.07309733386996	0.74575982707131	2.40388229825260
C	3.20157312810654	1.19401521049833	3.58969433049784
O	2.35744405883513	1.47355945325566	4.41318443357327
C	4.69968568351920	1.39018930395362	3.93755043849218
F	5.26812450375408	2.26837162939087	3.10100659574693
F	5.37437640374640	0.23896248287258	3.83044711969953
F	4.86965838910280	1.84476118241556	5.17580756921484
O	-0.03618923290362	-3.85251654884165	1.06360785909176
C	-0.67225213758653	-4.53242453299321	1.93296395342609
O	-1.47748237570756	-4.17452133457761	2.76524115050471
C	-0.30811384884682	-6.03537790315265	1.82597796194895
F	-0.92486961173269	-6.76531281056191	2.75105135839633
F	-0.65606159904928	-6.52074117283727	0.62667380640237
F	1.00876603850979	-6.22529975712305	1.96989313273982
O	-2.66031910517404	0.86334238534564	2.96393807210867
C	-2.54880337895292	1.22553122443929	4.18428579736588
O	-1.55163109606000	1.41322302613632	4.84427849245410
C	-3.94346507874395	1.43499709980726	4.82694752444660
F	-4.61417438480755	2.40484136376107	4.19267021072170
F	-3.85525064371469	1.77695308505147	6.10881066978462
F	-4.68013664040781	0.32031093077988	4.75285968461140
W	-1.42421137900590	-0.32010435282223	-1.17898659529481
W	-0.00207002709109	1.78443061065199	-0.57133051013366
W	1.21003509024400	-0.43711227196654	-1.36379814750861
I	-2.84163569079120	2.13284219649638	-0.74985576786413
I	-0.18606109898257	1.07732701529276	-3.25625609585307
I	-0.26476216098524	-2.72227860518761	-2.08376589781438
I	-2.87252182491969	-1.74612410117811	0.78830882827792
O	-3.06511887005791	-0.74882774162335	-2.43279394959816
C	-3.19710103939893	-1.11699821837816	-3.64532436227131
O	-2.35800917841641	-1.29574174635101	-4.50112150122464
C	-4.69301918666075	-1.34417725402536	-3.98390183017880
F	-5.23841148389395	-2.24723748093957	-3.15994336577616
F	-5.38875280827055	-0.20758080039748	-3.85145190886032
F	-4.86270284356491	-1.77913290697439	-5.22930596339079
O	0.02466951133186	3.82675969380464	-1.11430659855406
C	0.61372143224402	4.50150535541873	-2.01989495786201
O	1.36101399929919	4.13717249685879	-2.90187657250782
C	0.26501426637623	6.00683344840217	-1.89325537446020
F	0.86382225871797	6.73797126415555	-2.82915083674671
F	0.64332877066159	6.48391130078803	-0.70056054128246
F	-1.05425526167185	6.20453506147090	-2.00566352248227
O	2.66656219594165	-0.90418429555806	-2.82797851386919
C	2.59166038716292	-1.26221443824750	-4.04878291667262
O	1.61875248870865	-1.46133273145444	-4.74341309768264
C	4.00790218732006	-1.45324480667047	-4.65077191860936
F	4.67267478025991	-2.41714186813503	-4.00049637092263
F	3.96354769554469	-1.79175531435517	-5.93617233110333
F	4.72887517340651	-0.32986023702813	-4.55133258452905

Table C.20: Structural parameters in Å of the optimized S_0 and T_1 geometries of **2**.

Distances in Å	S_0	T_1
W–W average	2.6602	2.6769
W–W min	2.6549	2.6117
W–W max	2.6659	2.7732
W–I _{inner} average	2.8163	2.8238
W–I _{inner} min	2.8000	2.7743
W–I _{inner} max	2.8365	2.9861

Supplementary Information for Chapter 6

The Lowest Excited State of Heptacenes Is Dark

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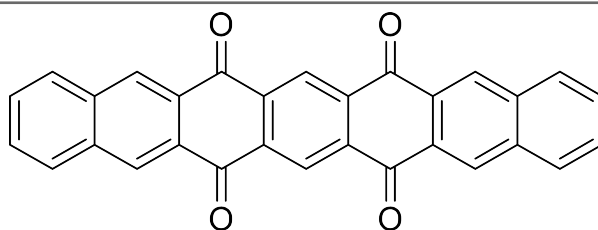
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D.1 General

All reactions were run under inert gas (Ar) conditions. THF and *n*-hexane were taken from a SPS-800 from *MBraun*. Chemicals were purchased from *Acros*, *Sigma-Aldrich*, *TCI Chemicals* and *fluorochem* and used without further purification. NMR spectra were recorded on a *BRUKER Avance 400* and a *Bruker Avance 700* at 400/700 MHz (^1H NMR) and 100/176 MHz (^{13}C NMR). Chemical shifts for ^1H NMR spectra are reported in ppm relative to TMS using the residual signals of chloroform-*d* (δ 7.26) and benzene-*d*₆ (δ 7.16) as reference. Chemical shifts for ^{13}C NMR spectra are reported in ppm relative to TMS using the signal of chloroform-*d* (δ 77.00) and benzene-*d*₆ (δ 128.1) as reference. Mass spectra with high resolution were recorded on a *maXis-4G*-spectrometer from *Bruker Daltonics* (ESI or APCI) with a TOF analyzer.

D.2 Synthesis

D.2.1 Heptacene-6,8,15,17-diquinone (1)

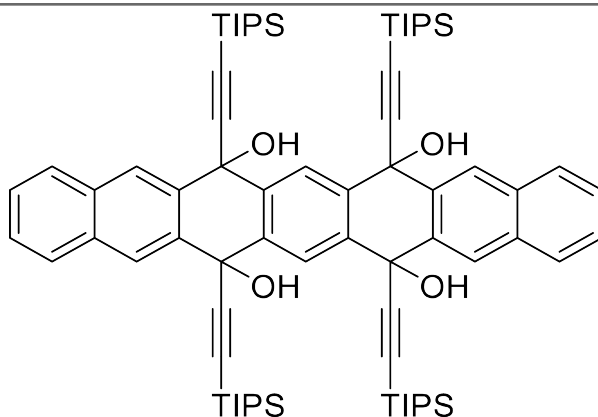


Heptacene-6,8,15,17-diquinone was synthesized following Baxter et al.⁴⁶⁴

HRMS (APCI): $[\text{M}+\text{H}]^+$ calculated m/z 439.09649, measured m/z 439.09638

^1H NMR (400.16 MHz, D_2SO_4): δ (ppm) 9.46 (s, 2H, H7), 9.18 (s, 4H, H5), 8.34-8.25 (m, 4H, H1), 8.06-7.98 (m, 4H, H2).

D.2.2 Tetra-6,8,15,17-TIPS-ethynyl Heptacene (Tetrol 2)



(Triisopropylsilyl)acetylene (333 μ L, 1.48 mmol, 13 eq.) was dissolved in 12 mL dry *n*-hexane and *n*-BuLi (547 μ L (2.5 M in *n*-hexane), 1.37 mmol, 12 eq.) was slowly added at rt. After stirring for 1 h, 0.5 mL dry THF was added and afterwards heptacene-6,8,15,17-diquinone (50.0 mg, 114 μ M, 1 eq.). The mixture was heated and stirred at 50 °C for 20 h. The reaction was quenched with sat. aq. NH₄Cl, the phases were separated, and the organic phase dried over MgSO₄. After removing the solvent, the residue was purified by column chromatography (DCM/EtOAc 19:1, R_f = 0.3). Tetrol **2** was isolated as a light brown solid (24 mg, 20.5 μ M, 18 %) that was not completely pure, but of sufficient quality for the next step.

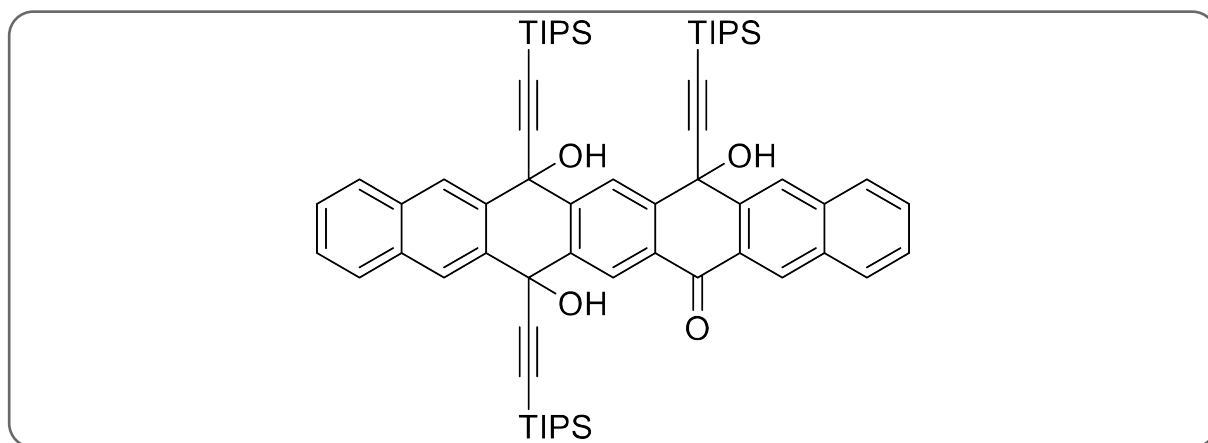
¹H NMR (400.16 MHz, CDCl₃): δ (ppm) 8.74 (s, 2H, H7), 8.60 (s, 4H, H5), 7.89-7.87 (m, 4H, H1), 7.55-7.51 (m, 4H, H2), 4.21 (br, 4H, OH), 1.09-1.04 (m, 84H, (CH₃)₂CHSi).

¹³C NMR (176.09 MHz, C₆D₆): δ (ppm) 138.5, 135.8, 133.3, 128.2, 127.2, 126.9, 126.4, 107.9 (Ar-C-C-TIPS), 90.5 (Ar-C-C-TIPS), 69.3 (C-OH), 18.9 ((CH₃)₂CHSi), 18.8 ((CH₃)₂CHSi), 11.5 ((CH₃)₂CHSi)

HRMS (ESI): [M+Na]⁺ calculated m/z 1189.67474, measured m/z 1189.67326

As a side product threefold substitution leads to triol **3** which was also isolated.

D.2.3 Tri-8,15,17-TIPS-ethynyl Heptacene-6-one (Triol 3)



Obtained as by-product in the synthesis of tetra-6,8,15,17-TIPS-ethynyl heptacene (DCM, R_f = 0.2, 23 %).

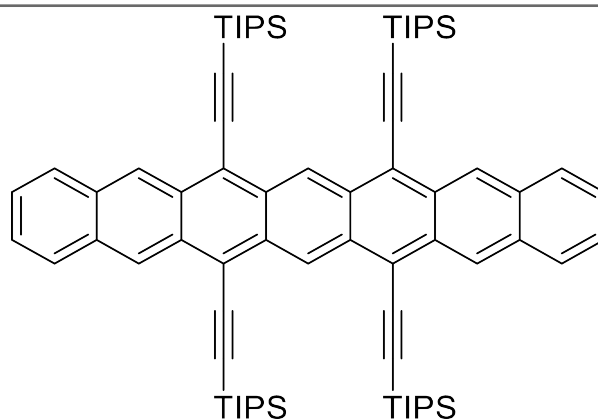
¹H NMR (400.16 MHz, 298.15 K, CDCl₃): δ (ppm) 9.10 (s, 1H), 9.00 (s, 1H), 8.87 (s, 1H), 8.70 (s, 1H), 8.66 (2s, 2H), 8.03-8.01 (m, 1H), 7.96-7.92 (m, 3H), 7.64-7.60 (m, 1H), 7.58-7.51 (m, 3H), 3.26 (br, s, 1H, OH), 3.17 (br, s, 1H, OH), 2.97 (br, s, 1H, OH), 1.12-1.05 (m, 63H, (CH₃)₂CHSi).

¹³C NMR (176.09 MHz, C₆D₆): δ (ppm) 182.8, 144.7, 139.5, 139.3, 136.0, 135.8, 135.4, 133.4, 133.4, 132.9, 130.4, 130.0, 129.5, 129.1, 128.4, 128.3 (2C), 128.1, 127.5, 127.4, 127.1 (2C), 127.0, 126.6, 126.6, 126.2, 109.2 (2C), 108.7, 90.6, 90.0, 89.3, 69.2, 69.0, 67.2, 18.8, 11.4, 11.3

HRMS (ESI): [M+Na]⁺ calculated m/z 1007.52566, measured m/z 1007.52548

D.2.4 Tetra-6,8,15,17-TIPS-ethynyl Heptacene (TIPS4Hep)

Tetra-6,8,15,17-TIPS-ethynyl heptacene tetrol **2** (48 mg, 41.1 μ M, 1 eq.) was dissolved in degassed THF (10 mL). Degassed (Ar bubbled) aq. HCl (10 %, 0.5 mL) and SnCl₂ · 2 H₂O



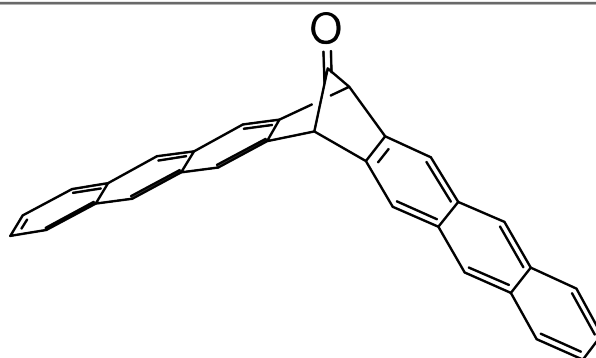
(186 S5 mg, 824 μ M, 20 eq.) was added and the reaction vessel was covered with aluminum foil. The mixture was stirred at 30 °C for 3 h. Argon was bubbled through the solution while the vessel is open to remove all the solvent in the absence of oxygen. Then a mixture of *n*-hexane/DCM (9:1) was added and the mixture poured onto a thick silica plug (7 cm height) in the dark. More solvent (*n*-hexane/DCM (9:1)) was added (400 mL) and it was quickly pushed through the plug via vacuum into an aluminum foil covered round bottom flask. The solvent was quickly removed on a rotary evaporator and the resulting light brown solid was quickly stored under Ar (19.9 mg, 44 %).

$^1\text{H NMR}$ (700.29 MHz, C_6D_6): δ (ppm) 10.14 (s, 2H, H7), 9.55 (s, 4H, H5), 8.00-7.99 (m, 4H, H1), 7.14-7.12 (m, 4H, H2), 1.46-1.45 (m, 84H, $(\text{CH}_3)_2\text{CHSi}$).

$^{13}\text{C NMR}$ (176.09 MHz, C_6D_6): δ (ppm) 133.5, 132.8, 131.0, 128.9 (C1), 127.3 (C5), 126.7 (C7), 126.7 (C2), 119.2 (C6), 109.2 (Ar-C-C-TIPS), 106.5 (Ar-C-C-TIPS), 19.4 ($(\text{CH}_3)_2\text{CHSi}$), 12.5 ($(\text{CH}_3)_2\text{CHSi}$)

HRMS (APCI): $[\text{M}+\text{H}]^+$ calculated m/z 1099.68184, measured m/z 1099.68336

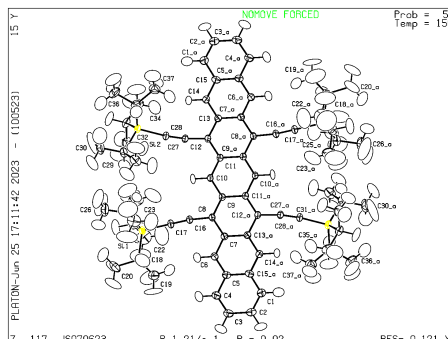
D.2.5 Monocarbonyl Heptacene COHep



The synthesis of heptacene mono carbonyl precursor **COHep** was performed following the route of Gourdon et al.⁴⁷³ The $^1\text{H NMR}$ spectrum was consistent with that reported by Gourdon et al.⁴⁷³

D.3 Crystallography

D.3.1 Tetra-6,8,15,17-TIPS-ethynyl Heptacene (TIPS4Hep)



Formula	C ₇₄ H ₉₈ Si ₄
CCDC	2272243
$D_{\text{calc}} / \text{g cm}^{-3}$	1.083
μ / mm^{-1}	1.103
Formula weight	1099.944
Colour	clear colourless
Shape	block-shaped
Size / mm ³	0.19 × 0.19 × 0.15
T / K	150.01(10)
Crystal system	monoclinic
Space group	P2 ₁ /c
$a / \text{\AA}$	16.0576(1)
$b / \text{\AA}$	15.3073(1)
$c / \text{\AA}$	14.9738(1)
$\alpha / ^\circ$	90
$\beta / ^\circ$	113.644(1)
$\gamma / ^\circ$	90
$V / \text{\AA}^3$	3371.57(5)
Z	2
Z'	0.5
Wavelength / $\text{\AA}$	1.54184
Radiation type	Cu K α
$\theta_{\text{min}} / ^\circ$	3.00
$\theta_{\text{max}} / ^\circ$	79.94
Measured Refl's	167 341
Indep't Refl's	7 360
Refl's $I \geq 2\sigma(I)$	7 215
R_{int}	0.0151
Parameters	794
Restraints	0
Largest Peak	0.2239
Deepest Hole	−0.2160
GooF	1.0773
wR_2 (all data)	0.0472
wR_2	0.0470
R_1 (all data)	0.0196
R_1	0.0192

D.4 Additional Information

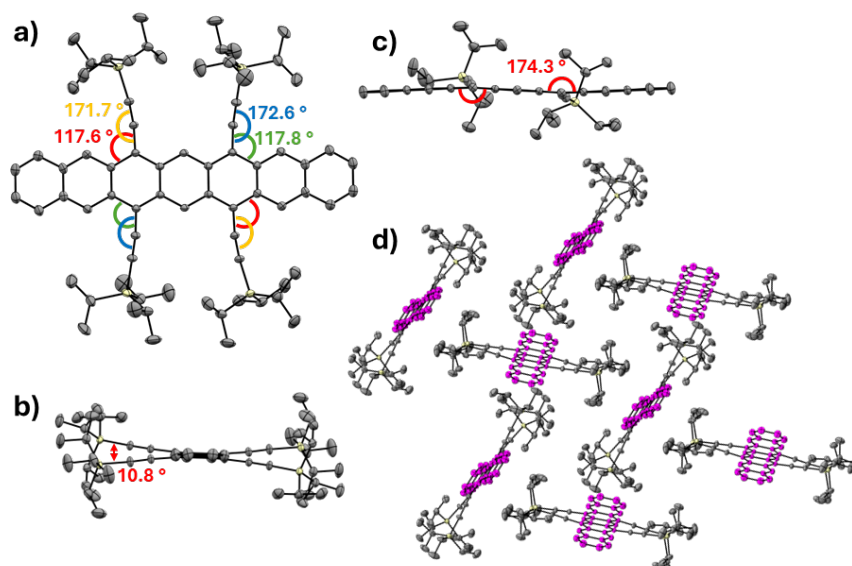


Figure D.1: a) Molecular structure of **TIPS4Hep** in the solid state, b) and c) side view to emphasize the steric demand of the TIPS groups and the resulting distortion, d) herringbone packing of **TIPS4Hep**. Anisotropic displacement parameters are depicted at the 50 % probability level, hydrogen atoms are omitted for clarity.

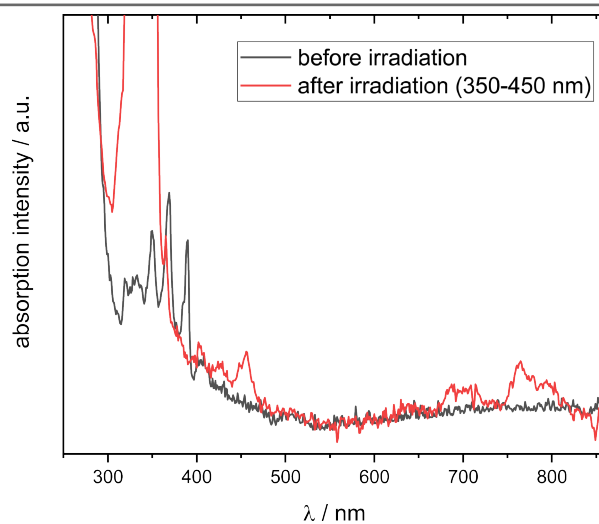


Figure D.2: Absorption spectrum of the formation of heptacene **Hep** via mono carbonyl photo precursor **COHep** in 2-MeTHF at 77 K inside a J.-Young tube.

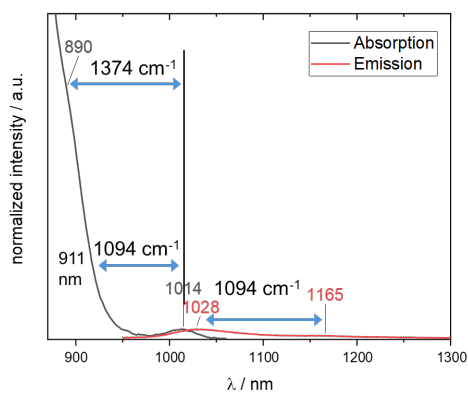


Figure D.3: Distances of vibrational progression of absorption and emission of TIPS4Hep in *n*-hexane compared to each other.

D.4.1 Literature-Known Spectra of Heptacene Derivatives

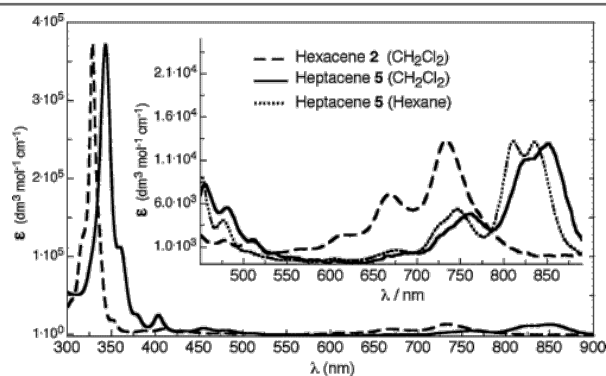


Figure D.4: Absorption spectra of 7,16-silylethynylheptacene. Reprinted with permission from *J. Am. Chem. Soc.* **2005**, 127, **22**, 8028–8029.⁴⁶² Copyright 2005 American Chemical Society.

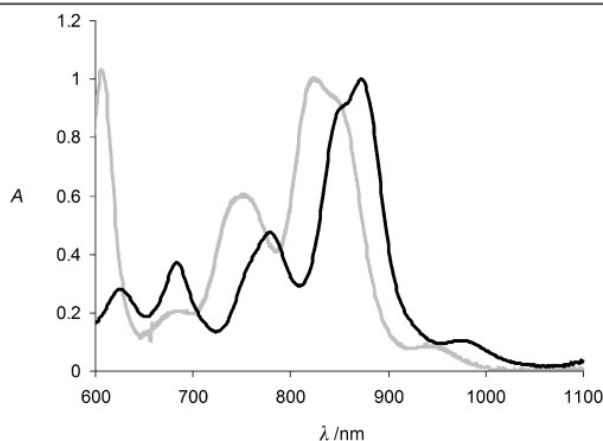


Figure D.5: Absorption spectra of two heptacene derivatives reported by Wudl et al.³⁴² Reprinted with permission from *John Wiley and Sons* (License Number 5975811183536).

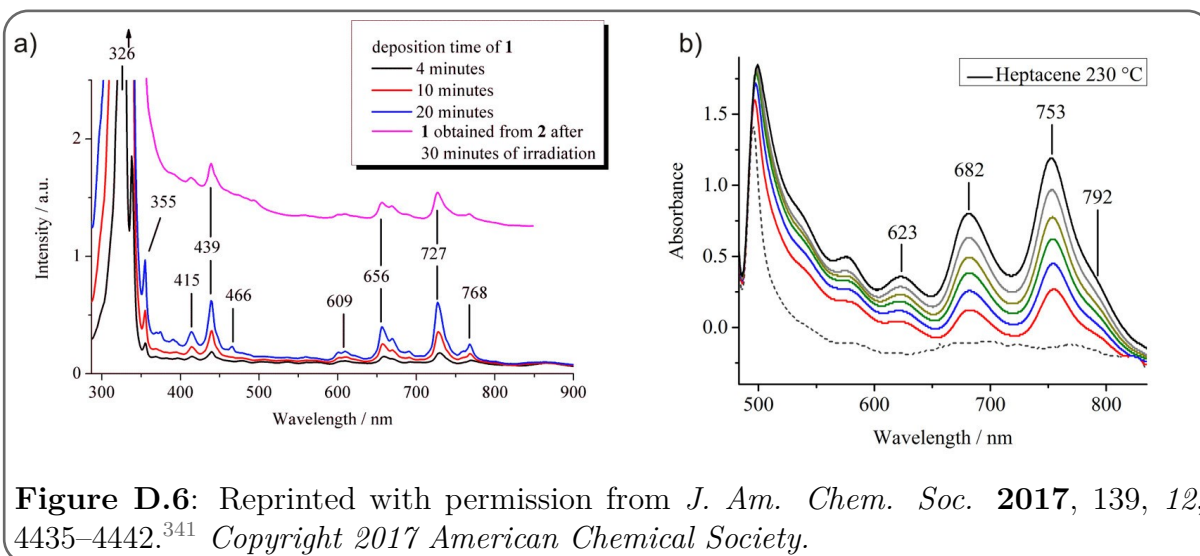


Figure D.6: Reprinted with permission from *J. Am. Chem. Soc.* **2017**, 139, 12, 4435–4442.³⁴¹ Copyright 2017 American Chemical Society.

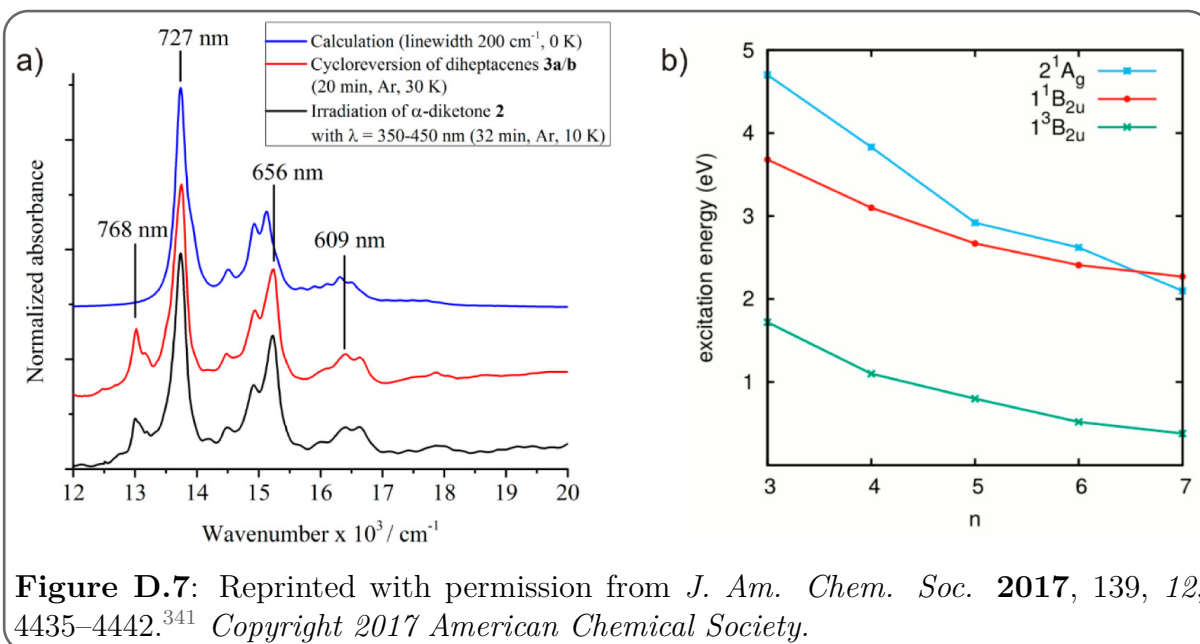


Figure D.7: Reprinted with permission from *J. Am. Chem. Soc.* **2017**, 139, 12, 4435–4442.³⁴¹ Copyright 2017 American Chemical Society.

D.4.2 Steady State Absorption Spectroscopy

Absorption spectroscopy was performed on a Lambda 1050 spectrometer from *PerkinElmer* with a *PerkinElmer* 3D WB Det module in the double beam modus. Temperature dependent measurements were performed with an *Oxford Optistat DN2* with a *Mercury iTC* temperature controller. 110-QS cuvettes made of quartz glass from *Hellma* with a light path of 10 mm were used. Typically, all samples were prepared in a glove box under argon atmosphere. Liquid samples were prepared with concentrations of about 10 $\mu\text{mol/L}$. The solvents applied were at least of HPLC grade and if necessary, they were dried by common lab methods or were taken from a solvent purifications system (MBraun). If not stated otherwise all spectra were recorded at room temperature (20 – 25 °C). For the irradiation a medium pressure mercury vapor lamp (USHIO, USH-508S) combined with a dichroic mirror was used.

Solvents in the Vis and NIR:

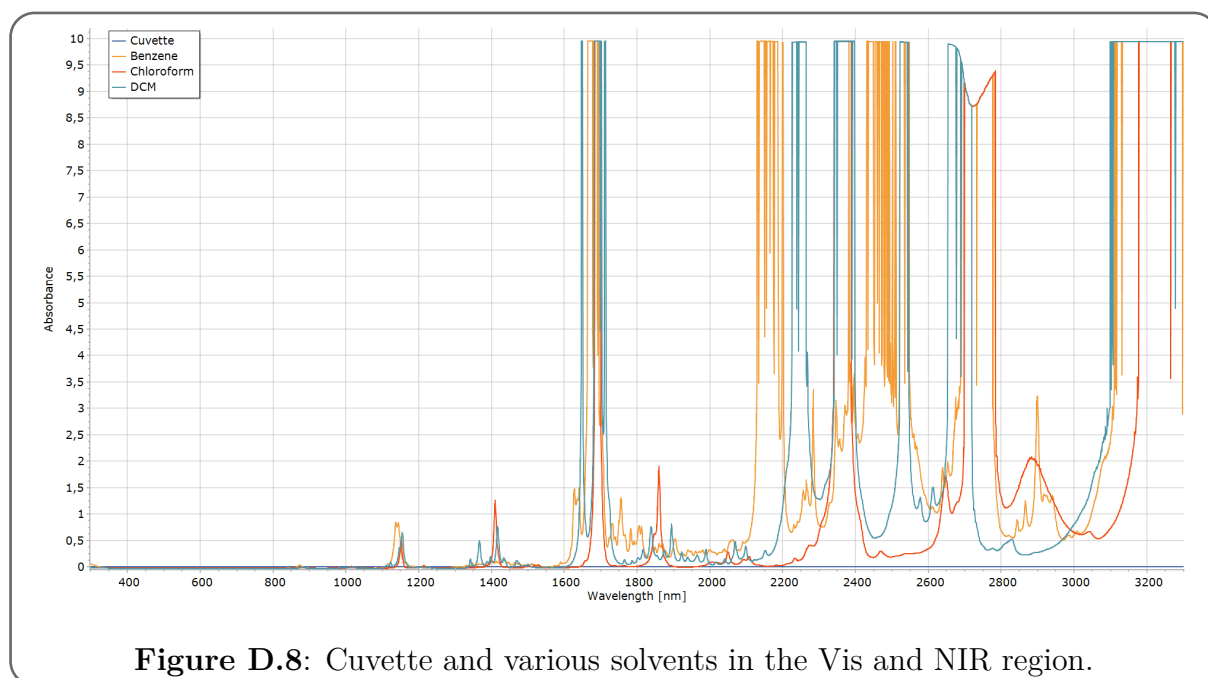
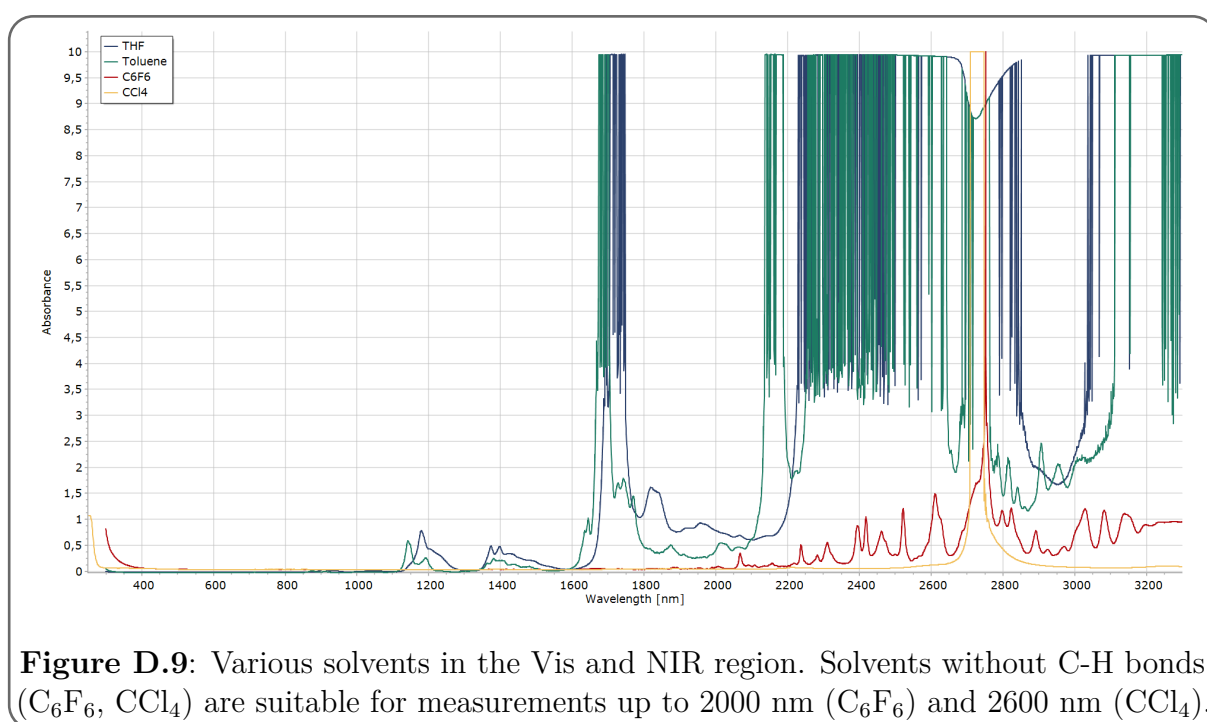


Figure D.8: Cuvette and various solvents in the Vis and NIR region.



D.4.3 Fluorescence Spectroscopy

Steady-state spectra were measured on a Horiba Fluorolog-3 spectrofluorimeter equipped with a 450 W xenon lamp for steady-state measurements. Emitted light was detected by a Hamamatsu R13456 PMT (UV/vis/NIR, $200\text{ nm} < \lambda_{\text{em}} < 1000\text{ nm}$) or a Hamamatsu H1033075 PMT (NIR, $900\text{ nm} < \lambda_{\text{em}} < 1700\text{ nm}$) detector. A double grating monochromator 320DFX (1200 grooves/nm, blazed at 330 nm or 600 grooves/nm, blazed at 750 nm) was used for spectral selection in the excitation path, while in the visible and near infrared emission path the single grating monochromators iHR550 (1200 grooves/mm, blazed at 500 nm; 950 grooves/mm, blazed at 900 nm; 1800 grooves/mm, blazed at 500 nm) and iHR320 (600 grooves/mm, blazed at 1000 nm) were used. To avoid higher order excitation light, long pass filter glass plates (Schott, 3 mm thickness) were used in the emission beam path when needed. Excitation spectra were recorded using two gratings for the excitation wavelength and later merged.

Measurements at 77 K were performed in regular borosilicate glass J. Young NMR tubes (5 mm outer diameter). For cooling and spectrum detection the sample tube within a quartz dewar (Horiba/PTI) filled with liquid nitrogen was placed into the light path. If necessary to reduce artifacts in the spectra from bubbles in the liquid nitrogen at least two consecutive spectra were averaged.

Typically, all samples were prepared in a glove box under argon atmosphere. Liquid samples were prepared with concentrations of about $10\text{ }\mu\text{mol/L}$ or with an absorbance of around 0.1 and if further degassing was necessary, the samples were degassed prior to measurement by at least three pump-freeze-thaw cycles. The solvents applied were at least of HPLC grade and if necessary, they were dried by common lab methods or were taken from a solvent purifications system (MBraun). If not mentioned otherwise a quadratic 1 cm suprasil© quartz cuvette was used for sample solutions measurements in the standard cuvette-holders. If not stated otherwise all spectra were recorded at room temperature ($20 - 25\text{ }^{\circ}\text{C}$).



Figure D.10: Red coloring of a solution of **TIPS4Hep** in CCl_4 after attempted fluorescence spectroscopy. Only the part where the excitation light beam hit the sample a red coloration is visible.

D.4.4 Transient Absorption Spectroscopy (TAS)

TAS measurements were performed on a HELIOS Fire fs TA spectrometer and EOS Fire ns spectrometer, both from Ultrafast Systems. The one box femtosecond amplifier Astrella-F-1K Ti:sapphire from Coherent was used to produce 90 fs laser pulses at 800 nm and a repetition rate of 1 kHz. The fundamental beam was split into a probe and a pump beam for the fs TAS experiments, while for the ns experiments, only the pump was used. The wavelength of the pump was mixed to monochromatic 900 nm inside the Apollo-T optical parametric amplifier from Ultrafast Systems using the second harmonic of the idler. For the fs experiments, a whitelight continuum probe (WLC) from 340 to 640 nm, 420 to 780 nm and 820 to 1600 nm was generated by focussing the 800 nm probe beam onto a CaF₂ plate, sapphire plate and proprietary plate similar to YAG, respectively. The delay between pump and probe was controlled mechanically by a delay-line from Ultrafast Systems. For the ns experiments, the delay was controlled electronically and a WLC from 380 to 850 nm and 750 to 1600 nm was generated within a photonic crystal fiber.

All samples were prepared under inert conditions in a glovebox. 2 mm quartz glass cuvettes from Hellma were used equipped with a homebuilt screw cap to prevent oxygen infiltration during the measurements. The samples were diluted to approximately 50 μM (0.045 OD at 900 nm) and stirred during the experiments. For the fs TAS experiments, 0.9 μJ per pulse were used while for the ns experiments, the pump power was increased to 8 μJ per pulse to account for the weaker transient signals at longer delay times. We could not observe any non-linear S14 effects or saturation at these experimental conditions. Steady-state absorbance and emission spectra were taken before and after the experiments to confirm that no degradation happened during the experiments.

The data were exported using the software Surface Explorer from Ultrafast Systems. Data processing, visualization and fitting were performed using Python 3.11 and libraries such as Matplotlib, NumPy, SciPy and lmfit.³⁷⁸

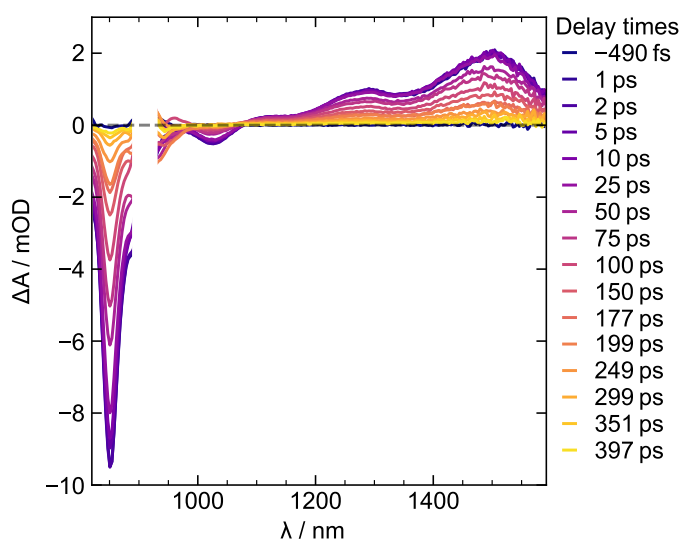


Figure D.11: NIR transient absorption spectra of **Figure 6.5 A** at selected delay times of **TIPS4Hep** in C₆F₆ ($\lambda_{\text{exc}} = 900\text{nm}$, 0.9 μJ / pulse).

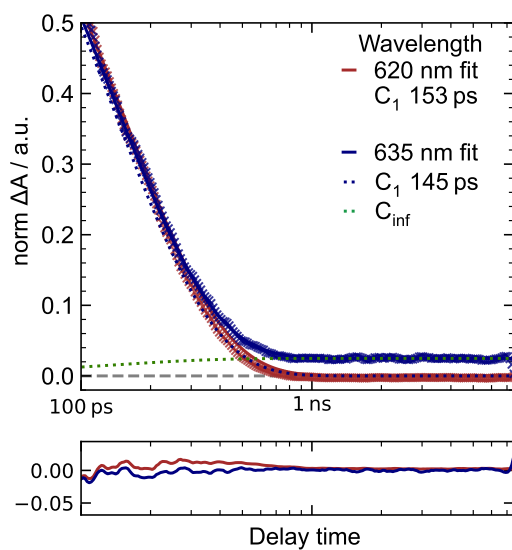


Figure D.12: Kinetic traces at 620 nm and 635 nm of **Figure 6.5 A** in the main manuscript and their corresponding fits ($\lambda_{\text{exc}} = 900\text{nm}$, $0.9 \mu\text{J} / \text{pulse}$). and their corresponding fits at selected wavelengths. The residuals of the fits are displayed below the graphs. At 635 nm, a sequential biexponential model is used as explained in the main text.

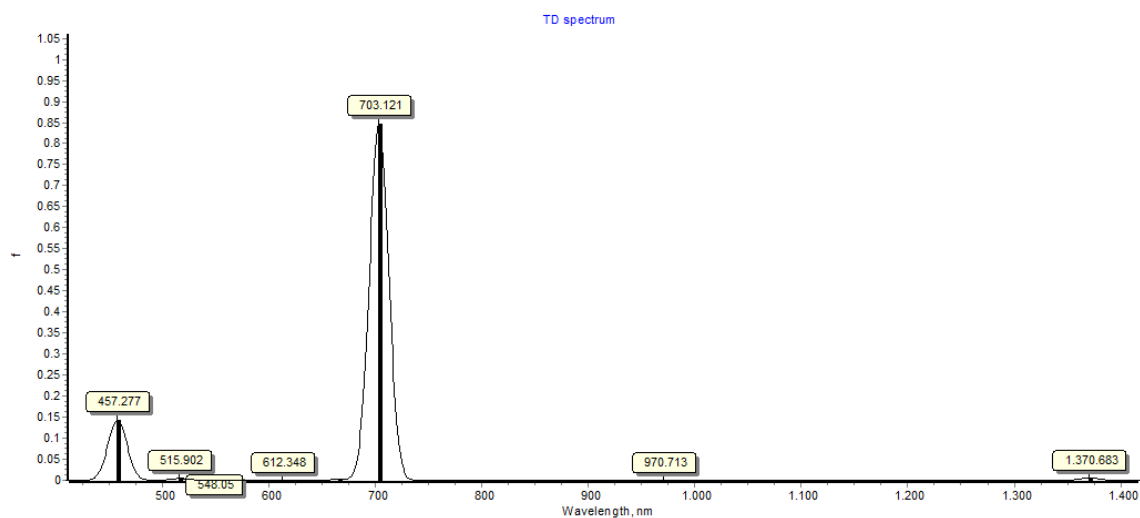


Figure D.13: Calculated vertical electronic absorption spectrum of the T_1 state of TIPS4Hep (UB3LYP/6311+G**//UM06-2X/def2-SVP).

D.4.5 Matrix Isolation

Experimental Details Matrix isolation experiments were performed using standard techniques^{481,482} with a CTI Cryogenics 8200 compressor (Brooks Automation) combined with a CCS-350R vacuum shroud (Janis Research) to achieve temperatures as low as 7 K. The precursor **COHep** was put into a quartz tube that was resistively heated and the sublimation product, heptacene, was deposited along with an excess of argon onto a cold sapphire window (7 K). Argon 6.0 (Westfalen AG, 99.9999 %) flow was maintained at 2.0 sccm using a mass flow controller (MKS mass flow PR400B). Quartz external windows were used to measure UV-Vis spectra using a Perkin Elmer Lambda 1050 spectrometer.

Results Heptacene was produced by heating the precursor at 280 °C, leading to decarbonylation and its sublimation. It was thereby deposited on a sapphire window in an excess of argon at 7 K and then characterized by UV-Vis spectroscopy. The UV-Vis spectrum is in good agreement with previous reports on the generation of heptacene via photochemical bisdecarbonylation of a bridged α -diketone precursor.³³⁰

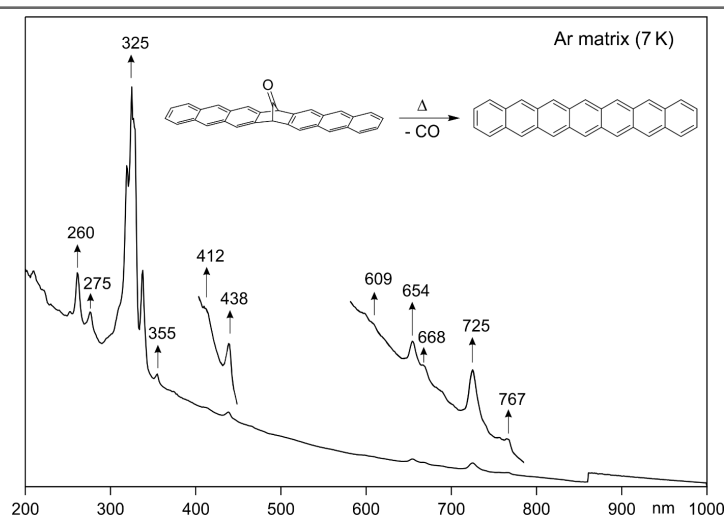


Figure D.14: UV-Vis spectrum measured in solid argon at 7 K, showing the formation of heptacene generated from **COHep**.

D.4.6 EPR

EPR experiments have been performed on a *Bruker EMXmicro* with *PremiumX* microwave bridge.

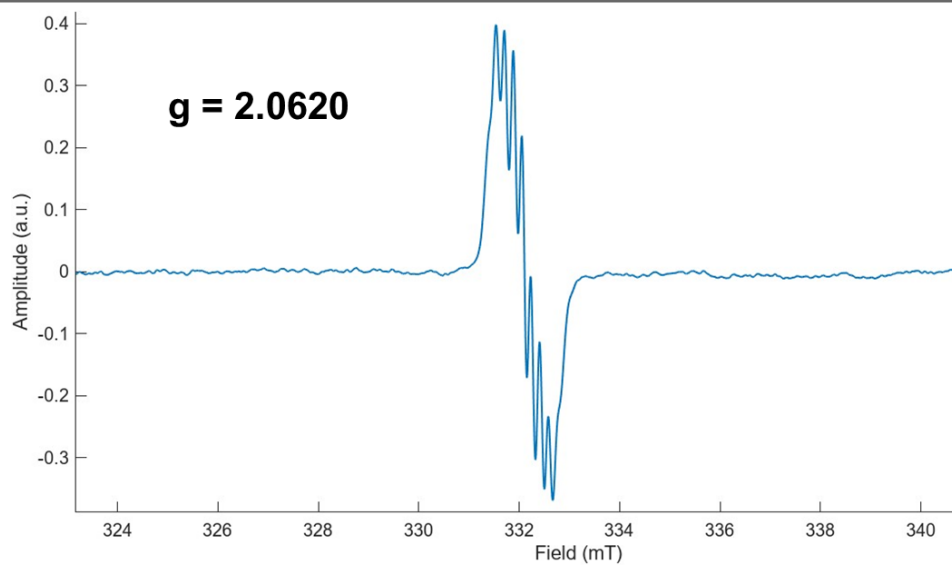


Figure D.15: EPR spectrum of radical cation of **TIPS4Hep**, oxidized by $\text{Ag}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ at rt in C_6F_6 .

D.5 Computations

D.5.1 TD-UDFT

Using the molecular crystal structure as initial guess, the structure of the singlet ground state of **TIPS4Hep** was computed using Gaussian 16⁴⁸³ and the M06-2X⁴⁸⁴ functional using the spinunrestricted treatment in conjunction with the def2-SVP basis set.⁴⁸⁵ The obtained structure was used for the subsequent geometry optimization of the lowest energy triplet state of TIPS4Hep at UM06-2X/def2-SVP. Likewise, the geometry of the T_1 state (1^3B_{2u}) of heptacene was computed at the M06-2X/def2-SVP level. Computation of harmonic vibrational frequencies confirmed that the triplet structures correspond to minima. The excitation energies were calculated using the UB3LYP^{486,487} functional in conjunction with the 6-311+G** basis set.⁴⁸⁸

The electronic absorption spectrum of the lowest energy triplet state of heptacene was computed previously using the PPP-MRSDCI approximation, and it was found that double excitations are important for some of the excited states.⁴⁷⁵ As double excitations are challenging to deal with in TDDFT, we computed parent heptacene for comparison. At UB3LYP/6-311+G**//M06-2X/def2SVP, the strong feature (oscillator strength $f = 1.14$) is at 601 nm (2.06 eV) that agrees well with the previous PPP-MRSDCI and experimental results (both 580 nm)^{339,475} despite some large de-excitation value associated with this excited state. The corresponding excited triplet state of **TIPS4Hep** is at 703 nm (1.76 eV, $f = 0.85$) and has large de-excitation values. We think that the trend of bathochromic shift of the intense band by around 0.2 eV observed in our experiment compared to that of Mondal et al.³³⁹ due to the TIPS groups is nonetheless supported by the TD-DFT calculations.

Lowest energy triplet state geometry of TIPS4Hep (UM06-2X/def2-SVP)

176 SCF Done: E(UM062X) = -4032.99201873 A.U. after 7 cycles

C	-0.71065000	8.61455500	-0.37890800
C	-1.40662800	7.42785700	-0.31512700
C	-0.71849700	6.18213200	-0.24823700
C	0.71854100	6.18213000	-0.24817300
C	1.40668100	7.42785300	-0.31500200
C	0.71071300	8.61455300	-0.37884500
C	-1.39706100	4.94859800	-0.18263800
C	1.39709500	4.94859300	-0.18252100
C	0.72305600	3.72751600	-0.12115000
C	-0.72303300	3.72751700	-0.12120200
C	-1.43630500	2.46830400	-0.05706200
C	-0.72963200	1.23949000	-0.03116300
C	0.72963500	1.23948700	-0.03114400
C	1.43631700	2.46829900	-0.05698200
H	-2.48163800	4.94900100	-0.18296900
H	-1.24649200	9.55787100	-0.42960500
H	-2.49341100	7.42563200	-0.31510900
H	2.49346500	7.42562500	-0.31488900
H	1.24656200	9.55786700	-0.42949400
H	2.48167300	4.94899200	-0.18276000
C	-0.72963800	-1.23951200	0.03104400
C	-1.43631700	-2.46832300	0.05698200

C	-0.72305200	-3.72753500	0.12122200
C	0.72303800	-3.72754000	0.12117900
C	1.43630500	-2.46833200	0.05691500
C	0.72962900	-1.23951700	0.03103100
C	-1.39708600	-4.94860700	0.18275600
C	1.39707000	-4.94861600	0.18265500
C	0.71850900	-6.18214400	0.24840900
C	-0.71852800	-6.18213900	0.24846400
C	-1.40666500	-7.42785500	0.31546000
H	-2.49344900	-7.42562400	0.31543600
C	-0.71069400	-8.61455000	0.37935000
C	0.71066900	-8.61455500	0.37929500
C	1.40664300	-7.42786400	0.31535100
H	-2.48166300	-4.94900400	0.18308000
H	2.48164700	-4.94902000	0.18289800
H	-1.24654100	-9.55785900	0.43012800
H	1.24651300	-9.55786800	0.43003100
H	2.49342700	-7.42564100	0.31524500
C	1.39896300	-0.00001700	-0.00006400
H	2.48330800	-0.00002000	-0.00006200
C	-1.39896600	-0.00001000	-0.00007000
H	-2.48331200	-0.00000700	-0.00007200
C	-2.85345900	2.50391900	-0.01464700
C	-4.07224400	2.63141700	0.03596600
C	-2.85347000	-2.50393500	0.01452900
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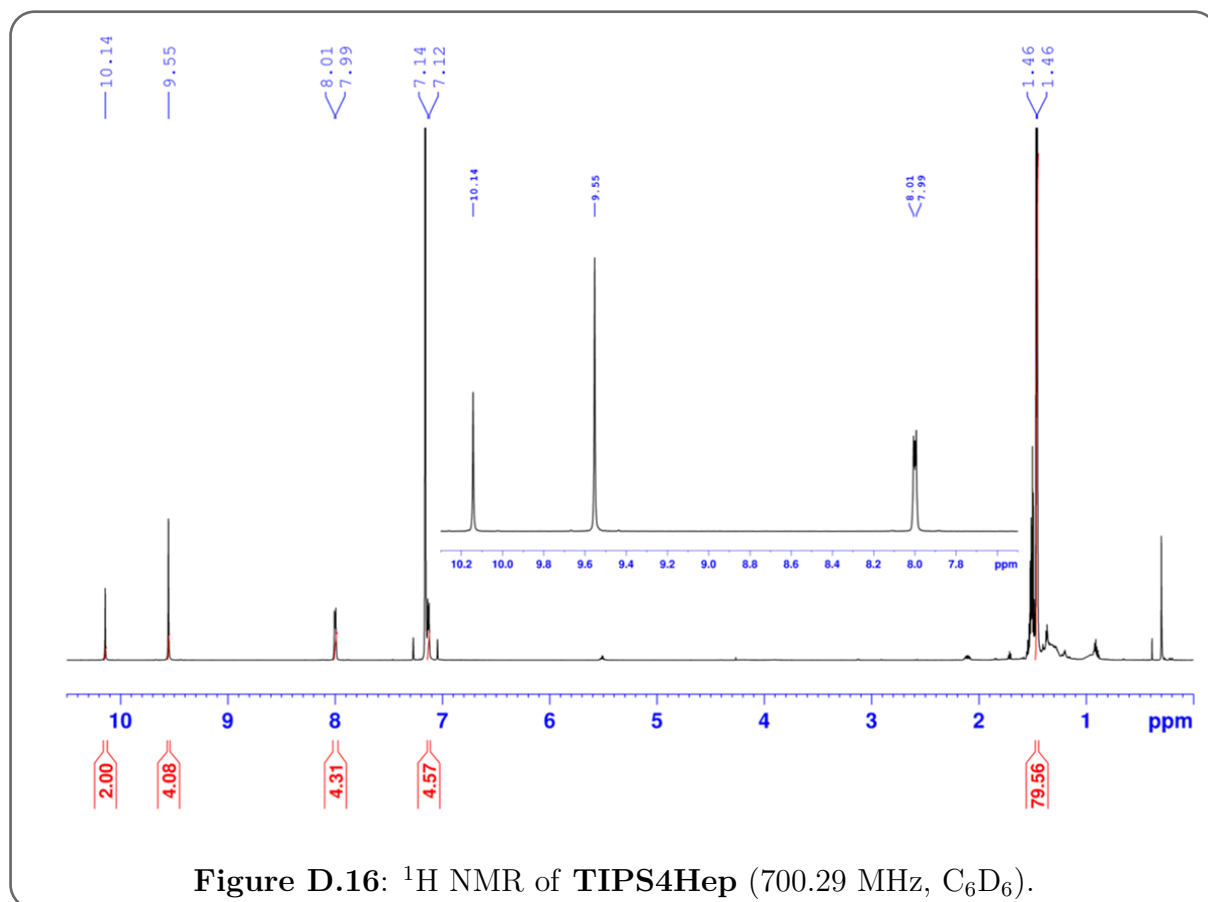
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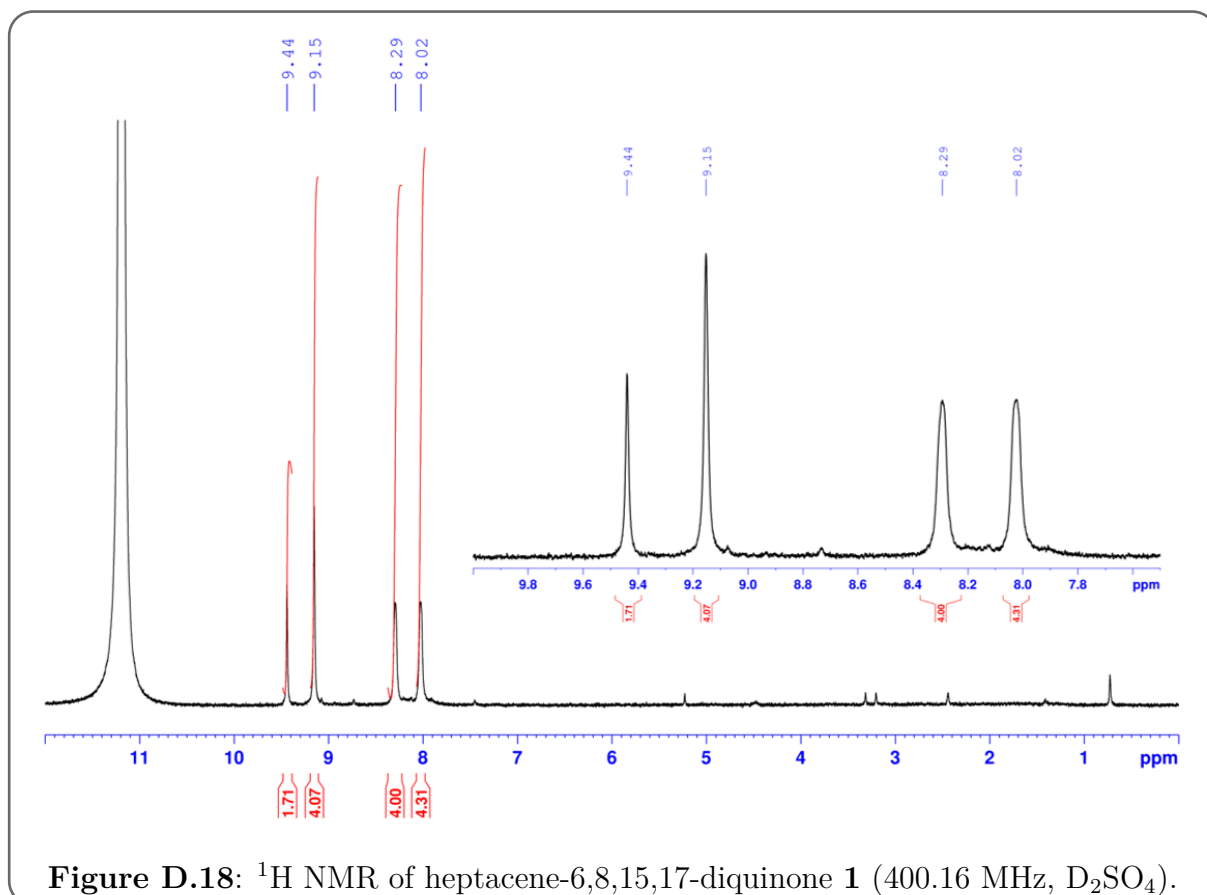
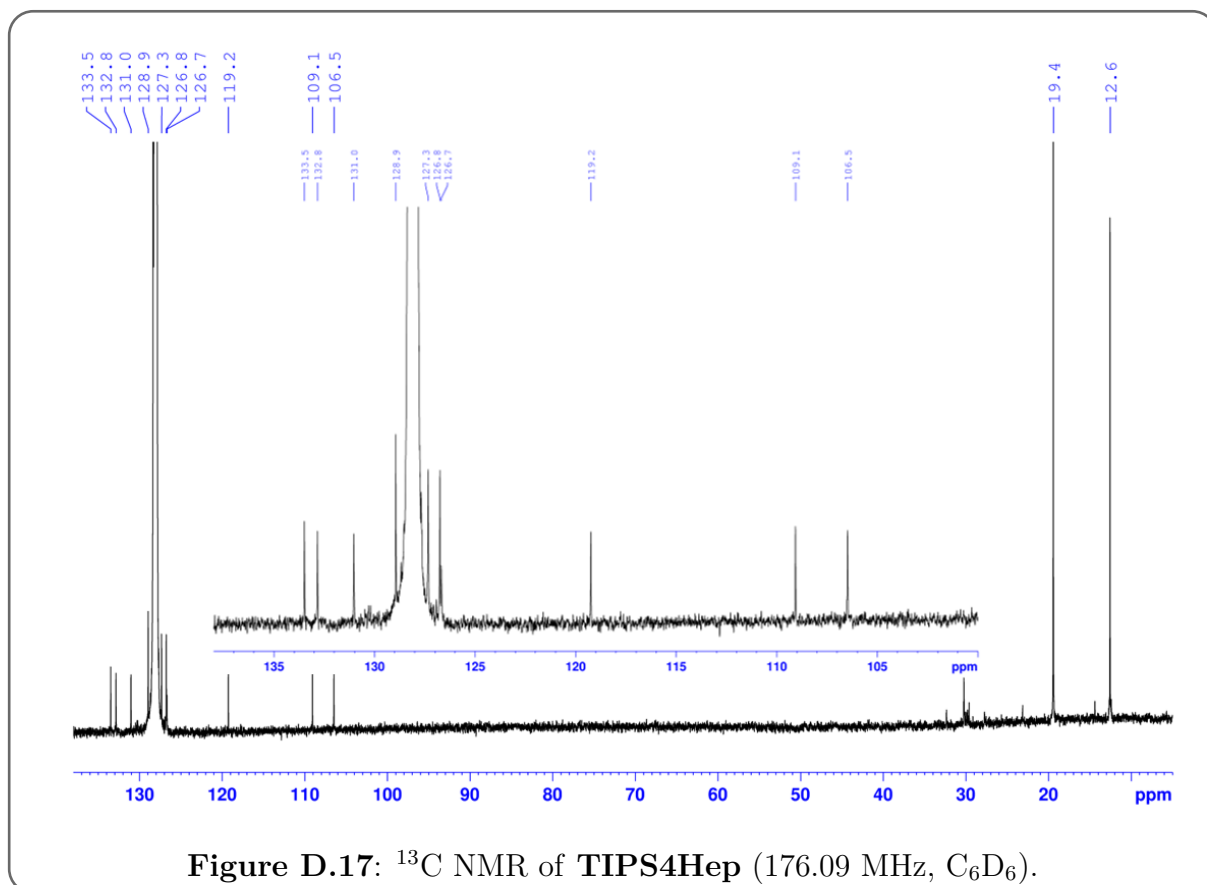
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6	0.000000000	6.153398000	-0.716740000
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1	0.000000000	4.923291000	-2.494990000
1	0.000000000	7.398014000	-2.495715000
6	0.000000000	3.707009000	0.723013000
1	0.000000000	4.923291000	2.494990000
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D.6 Experimental Spectra

D.6.1 NMR





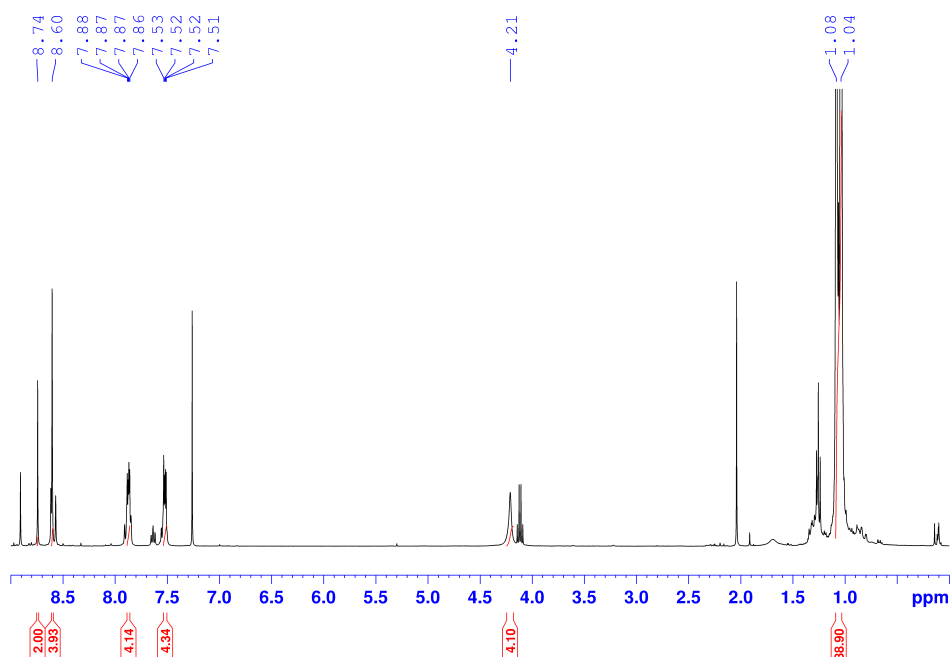


Figure D.19: ¹H NMR of tetra-6,8,15,17-TIPS-ethynyl heptacene tetrol **2** (400.16 MHz, CDCl₃).

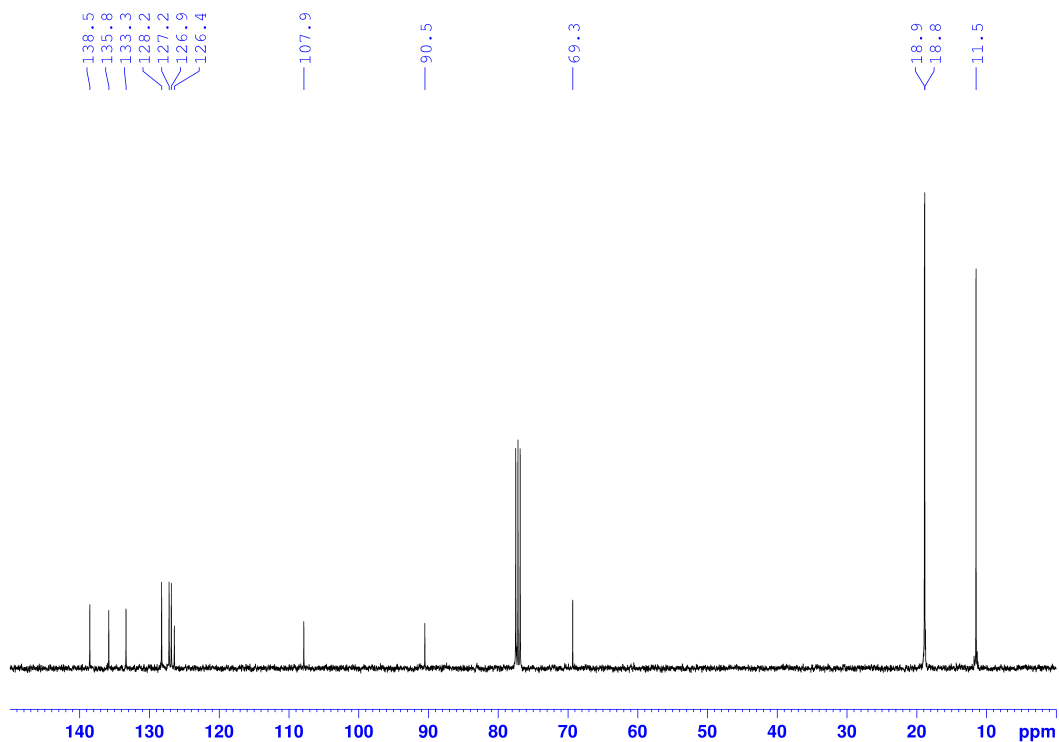


Figure D.20: ¹³C NMR of tetra-6,8,15,17-TIPS-ethynyl heptacene tetrol **2** (400.16 MHz, CDCl₃).

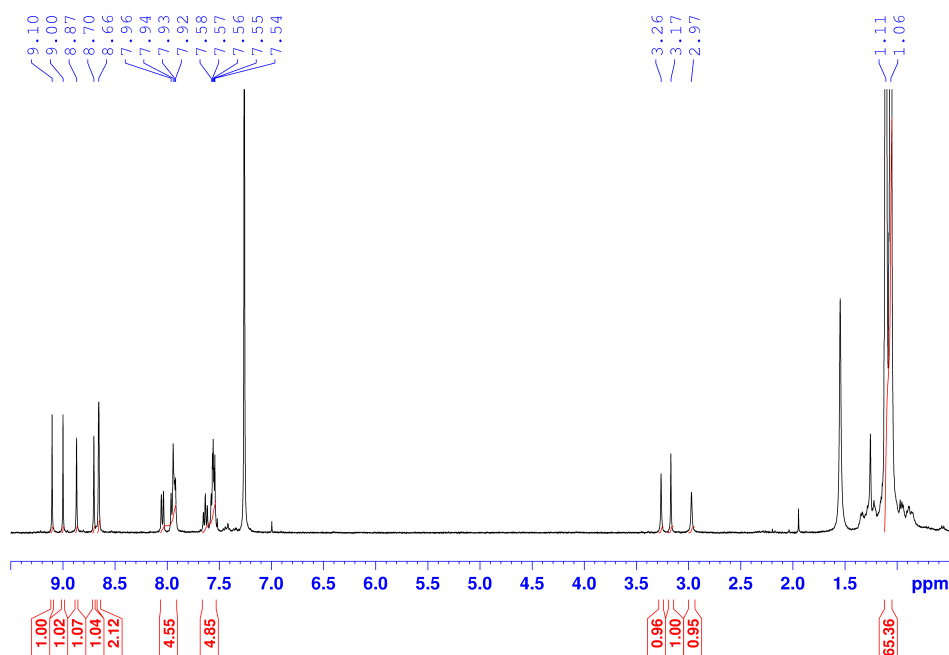


Figure D.21: ¹H NMR of tri-8,15,17-TIPS-ethynyl heptacene-6-one triol **3** (400.16 MHz, CDCl₃).

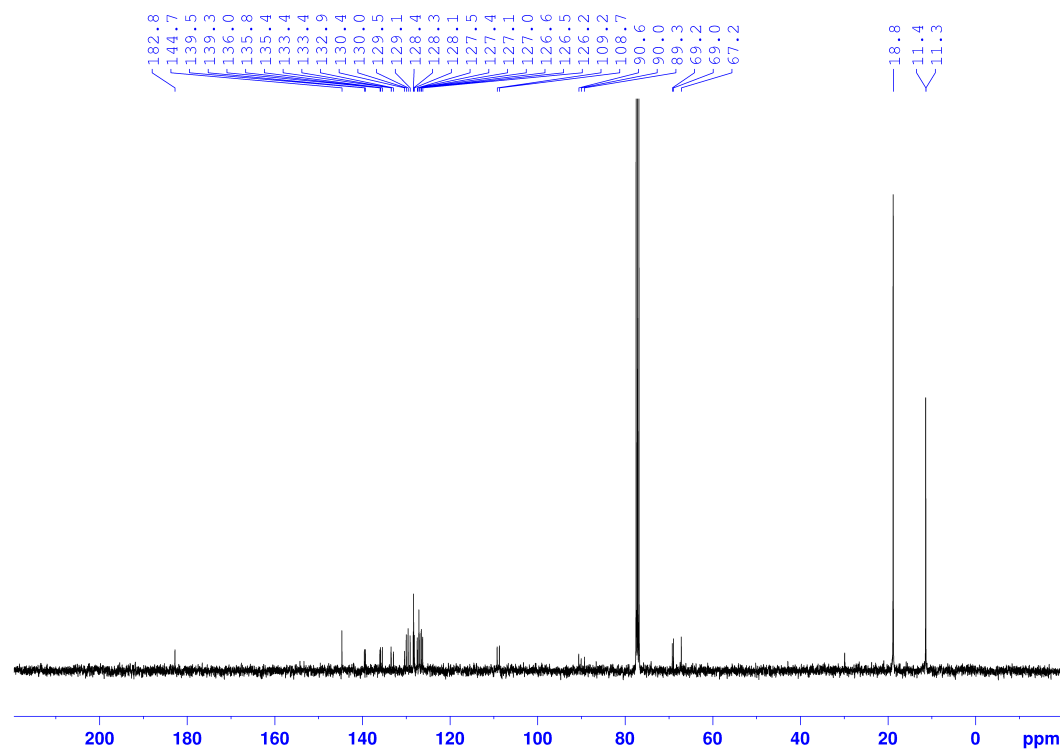
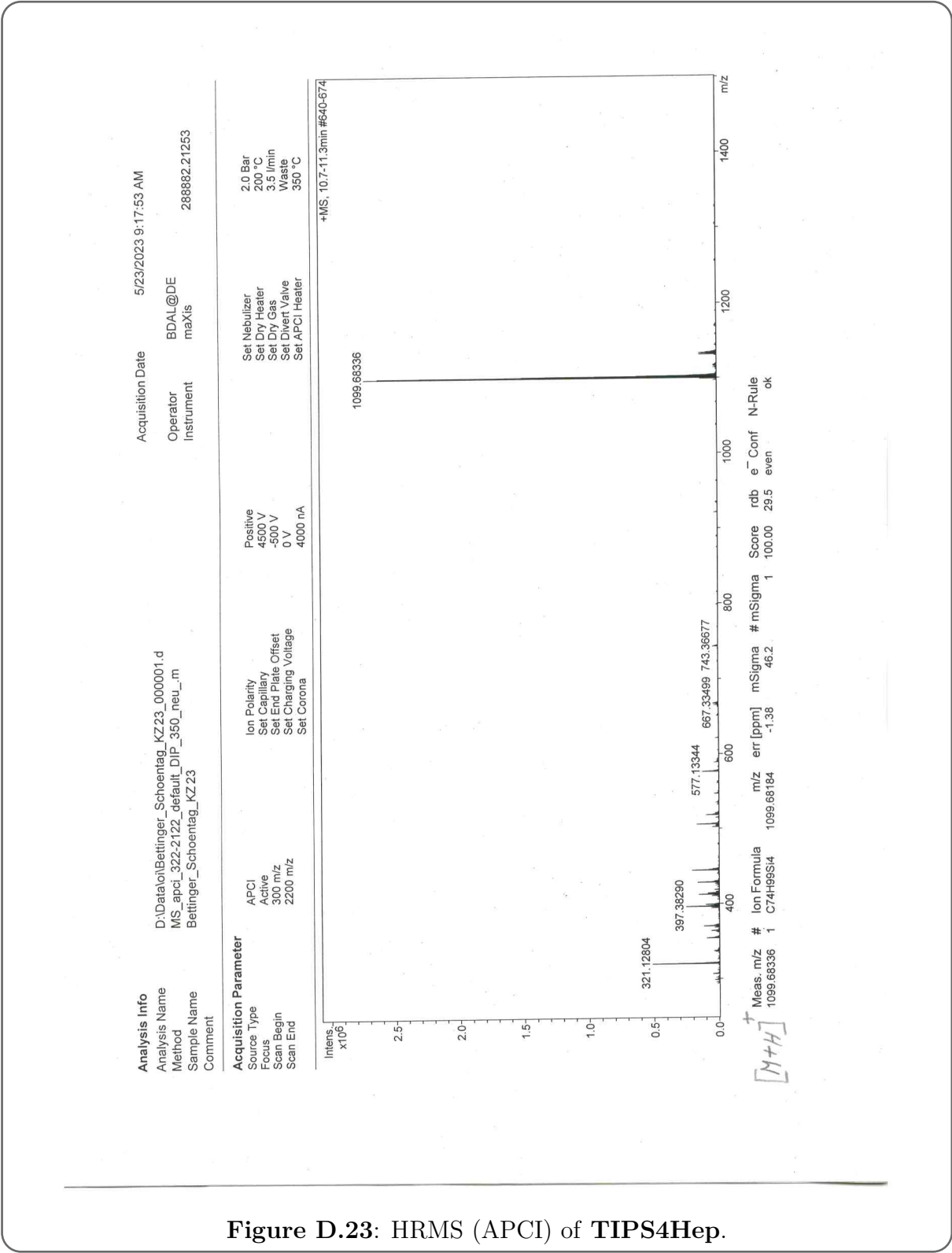


Figure D.22: ¹³C NMR of tri-8,15,17-TIPS-ethynyl heptacene-6-one triol **3** (400.16 MHz, CDCl₃).

D.6.2 Mass Spectrometry



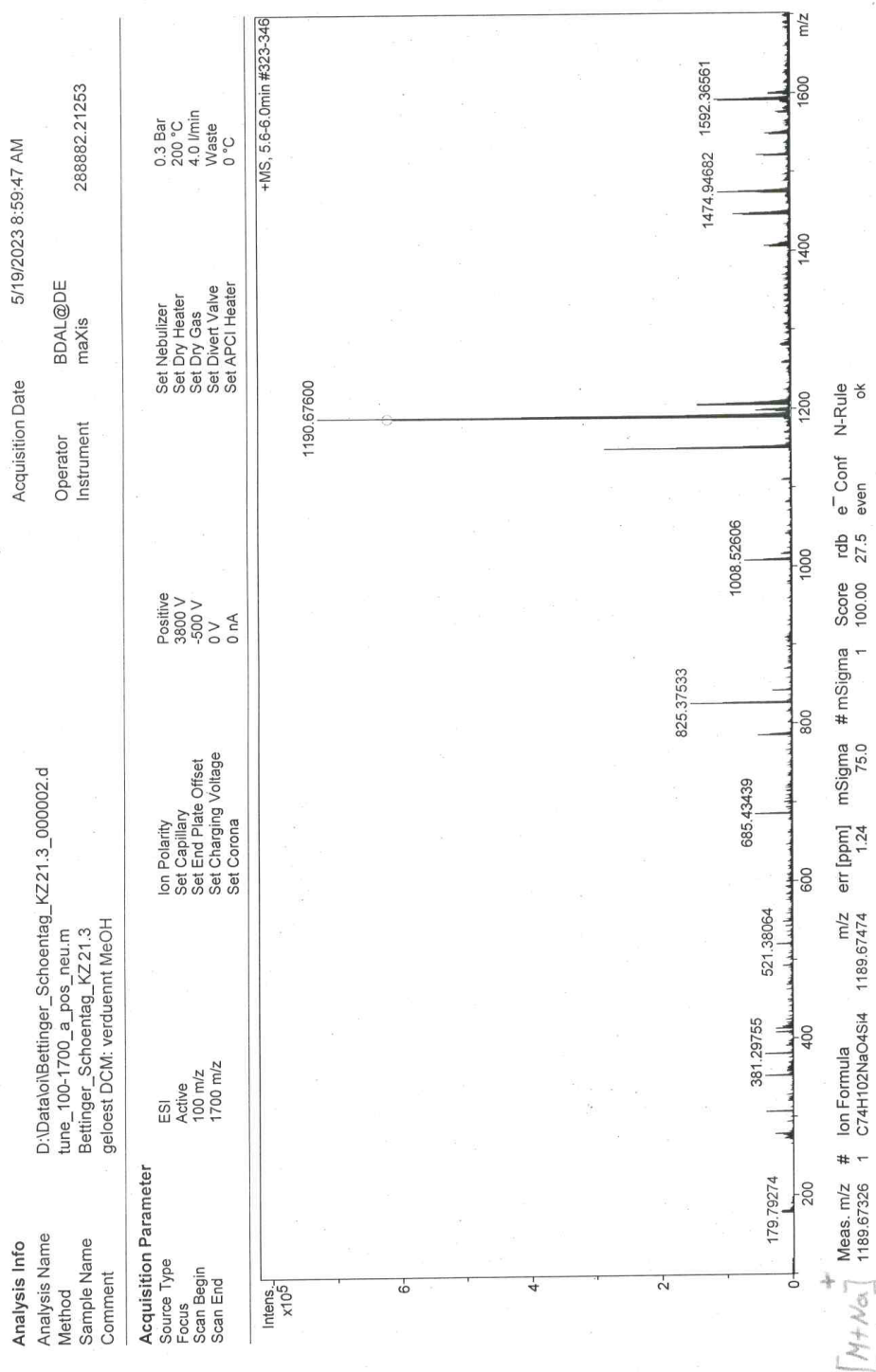


Figure D.24: HRMS (ESI) of tetra-6,8,15,17-TIPS-ethynyl heptacene tetrol **2**.

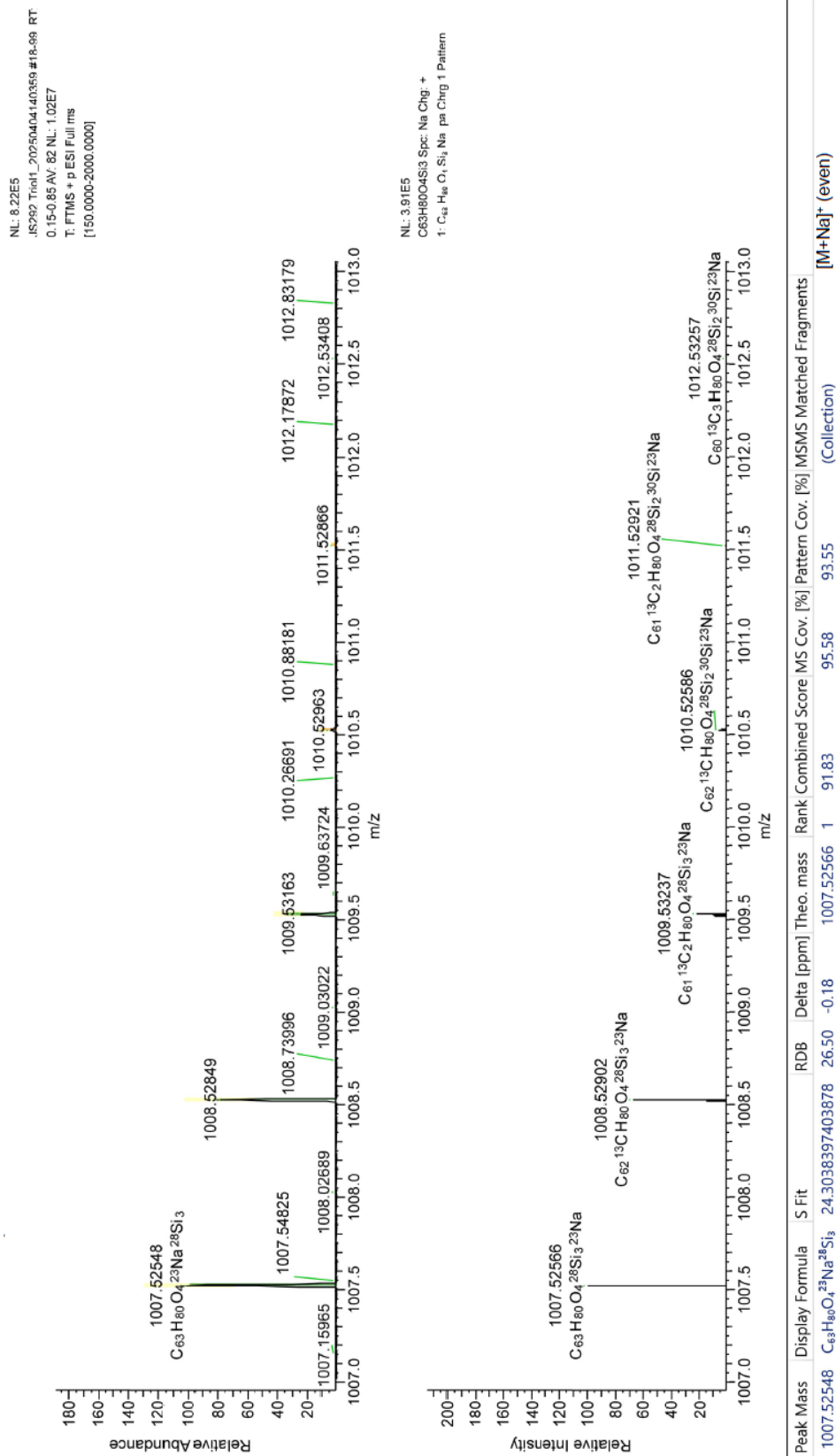


Figure D.25: HRMS (ESI) of tri-6,8,15-TIPS-ethinyl heptacene-6-one triol **3**.

Mass Spectrum SmartFormula Report

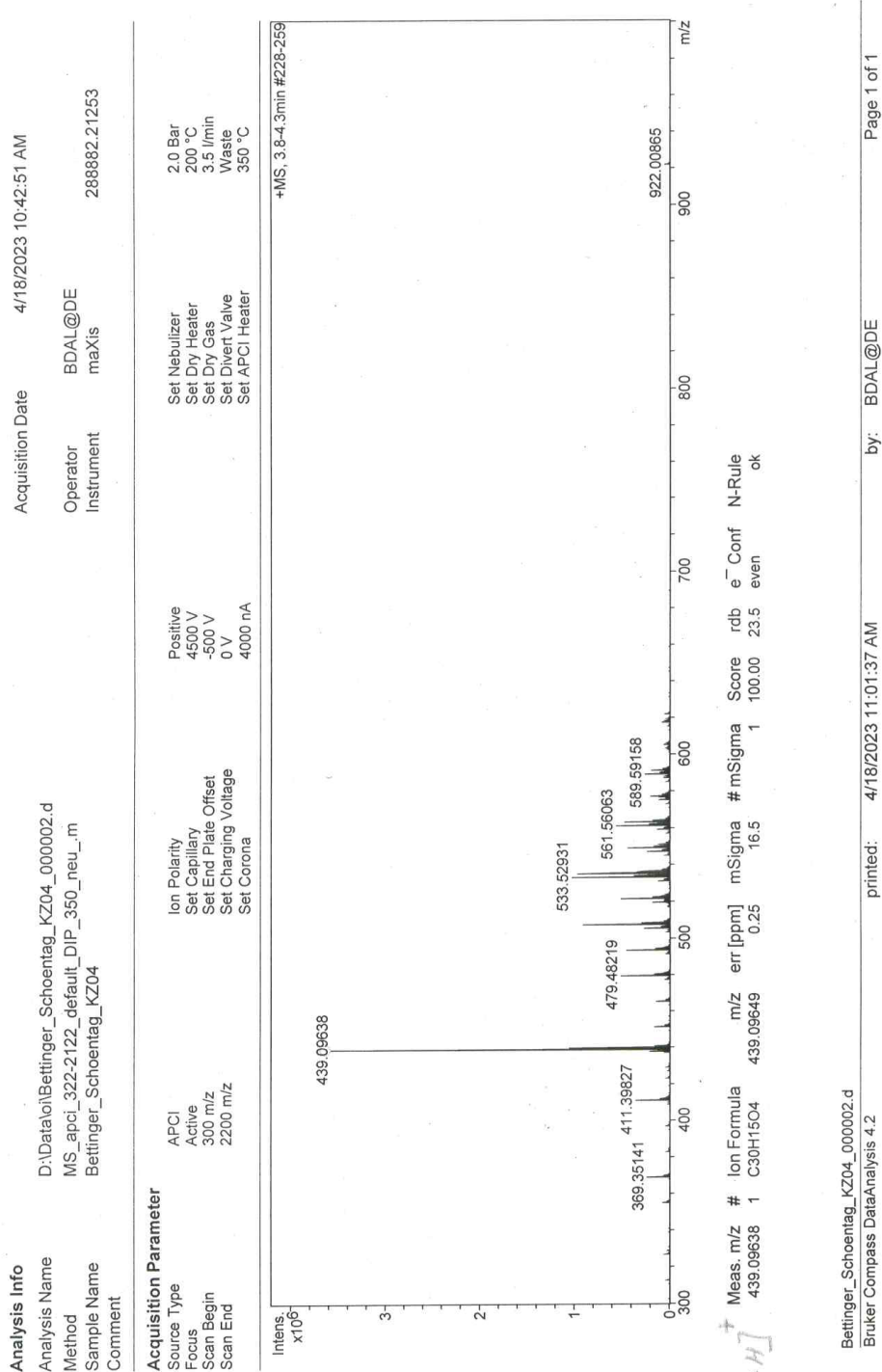


Figure D.26: HRMS (APCI) of heptacene-6,8,15,17-diquinone 1.

List of Publications & Scholarly Contributions

E.1 List of Publications

This thesis is based on the following peer-reviewed publications:

1. **Philipp Frech** and Marcus Scheele.
"TAPAS: Transient Absorption Processing and Analysis Software"
ChemPhotoChem **2026**, 10, e202500236
<https://doi.org/10.1002/cptc.202500236>
2. Florian Pachel, **Philipp Frech**, Markus Ströbele, David Enseling, Carl P. Romao, Thomas Jüstel, Marcus Scheele, and Hans-Jürgen Meyer
"Preparation, Photoluminescence and Excited State Properties of the Homoleptic Cluster Cation $[(W_6I_8)(CH_3CN)_6]^{4+}$ "
Dalton Transactions **2023**, 52, 3777-3785
<https://doi.org/10.1039/D2DT04063H>
3. **Philipp Frech**, Wolfgang Leis, Florian Pachel, Michael Seitz, Hans-Jürgen Meyer, and Marcus Scheele
"Time- and Temperature-Resolved Triplet Dynamics in Tungsten Iodide Clusters"
Inorganic Chemistry **2025**, 64, 20584-20595
<https://doi.org/10.1021/acs.inorgchem.5c02344>

4. Johannes Schöntag, **Philipp Frech**, Kathrin Zwettler, Navid Fardan, Ankit Soman, Wolfgang Leis, Markus Ströbele, Michael Seitz, Marcus Scheele, and Holger F. Bettinger
"The Lowest Excited State of Heptacenes Is Dark"
The Journal of Physical Chemistry Letters **2025**, *16*, 9479-9487
<https://doi.org/10.1021/acs.jpcllett.5c01314>
- Other scholarly publications including the author:
5. Onno Strolka, Pascal Rauthe, Tim Muschkin, **Philipp Frech**, André Niebur, Andreas-N. Unterreiner and Jannika Lauth
"Continuous Tuning of Intersystem Crossing Times in Rose Bengal Water/Methanol Solutions"
The Journal of Physical Chemistry B **2024**, *128*, 12189-12196
<https://doi.org/10.1021/acs.jpcb.4c07449>
6. Miriam Bassler, Jonas Hiller, Frank Wackenhut, Sven zur Oven-Krockhaus, **Philipp Frech**, Felix Schmidt, Christoph Kertzsch, Tim Rammner, Rainer, Ritz, Kai Braun, Marcus Scheele, Alfred J. Meixner, Marc Brecht
"Fluorescence Lifetime Imaging Unravels the Pathway of Glioma Cell Death upon Hypericin-Induced Photodynamic Therapy"
RSC Chemical Biology **2024**, *5*, 1219-1231
<https://doi.org/10.1039/D4CB00107A>
7. Christopher Kirsch, Tassilo Naujoks, Philipp Heizmann, **Philipp Frech**, Heiko Peisert, Thomas Chassé, Wolfgang Brütting, Marcus Scheele
"Zwitterionic Carbazole Ligands Enhance the Stability and Performance of Perovskite Nanocrystals in Light-Emitting Diodes"
ACS Applied Materials & Interfaces **2023**, *15*, 32744-32752
<https://doi.org/10.1021/acsami.3c05756>
8. Theo Maulbetsch, **Philipp Frech**, Marcus Scheele, Karl W. Törnroos, Doris Kunz
"A Saddle-Shaped Expanded Porphyrinoid Fitting C₆₀"
Chemistry – A European Journal **2023**, *29*, e202302104
<https://doi.org/10.1002/chem.202302104>
9. Andre Maier, Dimitry Lapkin, Nastasia Mukharamova, **Philipp Frech**, Dameli Assalauova, Alexandr Ignatenko, Ruslan Khubbutdinov, Sergey Lazarev, Michael Sprung, Florian Laible, Ronny Löffler, Nicolas Previdi, Annika Bräuer, Thomas Günkler, Monika Fleischer, Frank Schreiber, Ivan A. Vartanyants, Marcus Scheele
"Structure–Transport Correlation Reveals Anisotropic Charge Transport in Coupled PbS Nanocrystal Superlattices"
Advanced Materials **2020**, *32*, 2002254
<https://doi.org/10.1002/adma.202002254>

Declaration of Authorship & Contribution

F.1 Declaration of Authorship

The following declaration is reproduced from the "Guidelines on Artificial Intelligence in Teaching and Examination Contexts" from the University of Tübingen and applies in full to this thesis:⁴⁸⁹

- Hiermit versichere ich, dass ich die vorgelegte Arbeit selbst verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe. Die aus fremden Quellen direkt oder indirekt übernommenen Texte, Gangen, Konzepte, Grafiken usw. habe ich als solche gekennzeichnet und mit vollständigen Verweisen auf die jeweilige Quelle versehen.
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Ich versichere außerdem, dass ich mich generativer KI-Tools lediglich als Hilfsmittel bedient habe und in der vorliegenden Arbeit mein gestalterischer Einfluss überwiegt.

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¹This paragraph was added by the author.

- Die vorliegende Arbeit wurde bisher weder im In- noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.
- Mir ist bekannt, dass ein Verstoß gegen die genannten Punkte prüfungsrechtliche Konsequenzen haben und insbesondere dazu führen kann, dass die Prüfungsleistung mit „nicht ausreichend“ bzw. die Studienleistung mit „nicht bestanden“ bewertet wird und bei mehrfachem oder schwerwiegendem Täuschungsversuch eine Exmatrikulation erfolgen bzw. ein Verfahren zur Entziehung eines eventuell verliehenen akademischen Titels eingeleitet werden kann.

Philipp Frech

F.2 Publication Contributions

In the following, the authors' contributions to the publications discussed in this thesis are declared.

Publication 1 "TAPAS: Transient Absorption Processing and Analysis Software"³⁵⁶

I developed and distributed the software and provided the online resources such as documentation, source code, tutorials, license etc. I performed, visualized and analyzed the TA experiments and complementary measurements. I wrote the initial draft of the manuscript. M. Scheele supervised the project, revised the manuscript, and supported interpretation and design choices. O. Strolka and M. Fröhlich tested the software and proposed features and design choices.

Total estimated contribution: 90 %

Publication 2 "Preparation, Photoluminescence and Excited State Properties of the Homoleptic Cluster Cation $[(W_6I_8)(CH_3CN)_6]^{4+}$ "³⁶⁷

F. Pachel performed all the reactions reported as well as the NMR and infrared (IR) experiments and their interpretation. I planned, performed visualized and interpreted the TA experiments. I also performed complementary TA and steady-state experiments of the cluster and solvent. C. Romao carried out the electron localization function (ELF) calculations and M. Ghani carried out the elemental analysis. M. Ströbele and F. Pachel performed X-ray diffraction analysis, structure solution and refinement of single crystals. D. Enseling recorded the photoluminescence and lifetime measurements. F. Pachel, in collaboration with H.-J. Meyer, wrote the manuscript. I wrote the part on the excited-state properties and C. Romoa wrote the part on the ELF calculations. F. Pachel, M. Scheele, C. Romao, H.-J. Meyer, T. Jüstel and I edited and revised the manuscript.

Total estimated contribution: 20 %

Publication 3 "Time- and Temperature-Resolved Triplet Dynamics in Tungsten Iodide Clusters"⁴³⁰

I designed the experiments, performed and interpreted the steady-state absorbance and emission, and time-resolved emission and TA experiments. I also performed model fitting, statistical evaluation and visualization. W. Leis supported steady-state and time-resolved emission experiments, provided training, helped preparing the samples, helped interpreting the data and performed the TDDFT calculations. F. Pachel synthesized the clusters and helped with interpretation. I wrote the manuscript, and W. Leis, F. Pachel, H.-J. Meyer, M. Seitz and M. Scheele reviewed and edited it. H.-J. Meyer and M. Seitz supported interpretation. M. Scheele conceived and supervised the whole project and helped with interpretation.

Total estimated contribution: 75 %

Publication 4 "The Lowest Excited State of Heptacenes Is Dark"⁴⁵²

J. Schöntag developed and performed the synthesis, carried out NMR, mass, absorption and emission spectroscopy. I performed TA experiments as well as complementary steady-state experiments and evaluated, interpreted and visualized the data. K. Zwettler and A. Somani helped with the characterization and matrix isolation. N. Fardan synthesized a precursor. W. Leis supported emission experiments and interpretation. M. Ströbele carried out X-ray diffraction experiments, structure solution and refinement. H. Bettinger and J. Schöntag wrote the manuscript. I wrote the part on the excited-state properties and parts of the conclusion. M. Scheele reviewed and edited the manuscript. M. Scheele and M. Seitz supervised and helped interpreting the TA and emission experiments, respectively. H. Bettinger conceived and supervised the whole project.

Total estimated contribution: 25 %

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