

Synthesis and Characterization of Photoluminescent Tetrel(II) Complexes

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Abstract

Over the past few decades, the utilization of light has gained significant attention as an alternative for reducing fossil fuel consumption. Sunlight can be used as an energy source by converting solar energy into electricity as in photovoltaic technology or by switching solar energy to chemical energy as in photochemistry and photocatalysis. Further, energy efficient devices which transform electricity into light like light-emitting diodes reduce the general energy demand.

In these applications, highly efficient photoactive transition metal complexes are mostly implemented. They provide high photoluminescence quantum yields which are crucial for light-emitting devices and/or long-lived excited states that are necessary to achieve bimolecular reactions in photocatalysis. The prerequisite for the implementation of transition metal complexes in applications was the research and understanding of the fundamental photophysical properties. Accordingly, considerable progress has been made in recent years for transition metal complexes based on both precious and earth-abundant 3d metals.

However, similar understanding of the fundamental photophysical properties with heavy main group complexes is missing. Photoactive complexes based on group 14 elements, the so-called tetrel complexes, are particularly rare. The most notable oxidation states for tetrel complexes in this context are +IV and +II. Especially photoluminescent tetrel(II) complexes, i.e. tetrylenes, are very scarce, but enable a higher variety of specific excited state characters than tetrel(IV) complexes.

The known examples mostly show weak phosphorescence with fast and efficient non-radiative deactivation. Further, the knowledge about the respective photophysical processes, including the nature of the excited state with its relevant deactivation pathways, has remained essentially unknown.

This work deals with phosphorescent heavy tetrel(II) complexes and the investigation of their excited state dynamics, in particular with complexes based on tin(II) and lead(II). Both elements should enhance efficient intersystem crossing due to the heavy-atom effect and subsequently facilitate phosphorescence.

The first project explores the excited state energy landscape of the tin(II) and lead(II) complexes E(bpep) as intramolecularly donor-stabilized tetrylenes with the dianionic tripodal ligand bpep²⁻ (E = Sn, Pb; H₂bpep = 2-[1,1-bis(1*H*-pyrrol-2-yl)ethyl]pyridine). Detailed time-resolved and steady-state spectroscopic as well as (time-dependent) density functional theory studies provide new insights into the excited state dynamics of both complexes. The tin(II) complex displays green intraligand charge transfer phosphorescence in solution as well as in the solid state. Despite its larger heavy-atom effect, the lead(II) complex solely displays very weak red phosphorescence at low temperatures in the solid state, originating from strongly distorted ligand-to-metal charge transfer states. Quantum chemical calculations elucidate these observations and corroborate the deactivation pathways through strongly distorted excited states. These new findings basically help to establish rational ligand design concepts for tetrel(II) complexes with long-lived phosphorescence.

Based on the knowledge from the prior project, a conceptional topological approach combined with rational ligand design addresses specific excited state characters. The tripodal complex Sn(bpep) showed an intraligand charge transfer due to the additional

intramolecular donor. In opposition, the $\text{Sn}(\text{}^t\text{-BuPDP}^{\text{}^t\text{-Bu}})$ complex with the meridional coordinating pincer-type ligand $\text{}^t\text{-BuPDP}^{\text{}^t\text{-Bu}2-}$ ($\text{H}_2\text{}^t\text{-BuPDP}^{\text{}^t\text{-Bu}} = 2,6\text{-bis}(3,5\text{-di-}t\text{-butylpyrrol-2-yl})\text{pyridine}$) provides no additional donor stabilization and should show photoluminescence from a ligand-to-metal charge transfer. Indeed, the tin(II) complex displays red phosphorescence in the solid state from the assumed excited state, underlining the success of the conceptional approach. However, the phosphorescence is surprisingly weak, and its respective radiative rate presents unusual temperature dependence. This aspect can be explained by aggregation effects in the solid state, which are concluded from quantum chemical investigations.

The third project covers the well-known *Lappert's* diamino stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$, which was reported in 1974 for the first time. Since then, it has been broadly studied with respect to the ground state properties and reactivity. However, its photophysical properties have been overlooked for over fifty years. The molecule provides a sufficient stability in solution, which enables detailed spectroscopic investigations such as temperature-dependent and time-resolved emission or absorption spectroscopy. The results are further verified by quantum chemical calculations. The yellow-coloured *Lappert's* diamino stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ exhibits thermally activated dual orange/green phosphorescence with microsecond lifetimes in fluid solution at room temperature, which can be attributed to conformational changes on the excited state hypersurface. In addition, the mechanism of the photochemical radical formation of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_3$ has been elucidated. Two relevant excimers with second-order Jahn-Teller distorted structures are discussed in this aspect. Based on the results from this project, further rational ligand design concepts for tetrel(II) complexes with long-lived emissive excited states can be developed.

Alongside the stannylene, *Lappert's* diamino plumbylene $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ was also probed regarding the photophysical properties. In the first place, it provides strong thermal and photosensitivity with subsequent elemental lead formation. In the last project of the present work, this challenge was concerned with temperature-dependent emission and absorption spectroscopy. This plumbylene displays a weak red photoluminescence from possibly two triplet ligand-to-metal charge transfer states at low temperatures in frozen solution. Quantum chemical calculations indicate that a branching into two separated excited states takes place after photoexcitation. Furthermore, both excited states might play a role in the photodegradation mechanisms of $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ to elemental lead, which was also examined in this work.

Overall, the present work sheds more light on the fundamental photophysical and photochemical properties of heavy tetrel(II) complexes, including the investigation of the excited state characters and excited state dynamics or the examination of photochemical mechanisms. Complexes with several ligand geometries and coordination numbers were investigated with sophisticated spectroscopic experiments and quantum chemical calculations, to gather sufficient knowledge of the basic photophysics and their reactivities. The present studies revealed new results and challenges which might mark a step into the right direction for first applications.

Kurzzusammenfassung

Während der letzten Jahrzehnte hat die Verwendung von Licht als Alternative zur Reduzierung des Gebrauchs von fossilen Brennstoffen erhebliche Aufmerksamkeit erlangt. Sonnenlicht kann als Energiequelle bei der Umwandlung von Sonnenenergie in Elektrizität, wie in der Photovoltaik, oder in chemische Energie wie in der Photochemie oder Photokatalyse, dienen. Zudem können energieeffiziente Geräte, die Strom in Licht umwandeln, wie beispielsweise Leuchtdioden, den allgemeinen Energieverbrauch reduzieren.

Hoch effiziente photoaktive Übergangsmetallkomplexe werden in solchen Anwendungen meistens implementiert. Diese verfügen über hohe Photolumineszenz-Quantenausbeuten, die wichtig für Leuchtdioden sind, und/oder über langlebige angeregte Zustände, die benötigt werden, um bimolekulare Reaktion in der Photokatalyse zu erreichen. Die Voraussetzung, um solche Übergangsmetallkomplexe in der Anwendung zu implementieren ist die Erforschung und das Verständnis der fundamentalen photophysikalischen Eigenschaften. Entsprechend ist in den letzten Jahren bedeutender Fortschritt auf dem Gebiet der Übergangsmetallkomplexe basierend sowohl auf edlen als auch auf häufig vorkommenden 3d Metallen erreicht worden.

Allerdings liegt ein vergleichbares Verständnis der fundamentalen photophysikalischen Eigenschaften in schweren Hauptgruppenelementkomplexen nicht vor. Photoaktive Komplexe basierend auf Elementen der Gruppe 14, die sogenannten Tetrel Komplexe, sind wenig bekannt. In diesem Zusammenhang liegen die Komplexe meistens in der Oxidationsstufe +IV oder +II vor. Besonders photolumineszierende Tetrel(II) Komplexe, auch Tetrylene genannt, sind sehr selten. Im Gegensatz zu Tetrel(IV) Komplexen ist der Charakter der angeregten Zustände in Tetrel(II) Komplexen vielseitiger.

Die bekannten Beispiele weisen meist eine schwache Phosphoreszenz mit einer schnellen sowie effizienten strahlungslosen Desaktivierung auf. Ferner ist das Wissen über die jeweiligen photophysikalischen Prozesse, insbesondere die Natur des angeregten Zustands mit den relevanten desaktivierenden Pfaden, begrenzt.

Die vorliegende Arbeit beschäftigt sich mit phosphoreszierenden schweren Tetrel(II)-Komplexen und deren Dynamik im angeregten Zustand, insbesondere mit Komplexen basierend auf Zinn(II) und Blei(II). Beide Elemente sollten aufgrund des Schwer-Atom-Effektes effiziente Interkombination mit anschließender Phosphoreszenz ermöglichen.

Im ersten Projekt wird die Energie-Landschaft des angeregten Zustands der Zinn(II)- und Blei(II)-Komplexe E(bpep) als intramolekulare donor-stabilisierte Tetrylene mit dem dianionischen und tripodalen Liganden bpep^{2-} thematisiert (E(bpep), E = Sn, Pb; H_2bpep = 2-[1,1-bis(1*H*-pyrrol-2-yl)ethyl]Pyridin). Detaillierte Studien mittels zeitaufgelöster und stationärer Spektroskopie sowie (zeitabhängiger) Dichtefunktionaltheorie ermöglichen neue Einsichten in die Dynamik des angeregten Zustands beider Komplexe. Der Zinn(II)-Komplex strahlt sowohl in Lösung als auch im Festkörper grüne Phosphoreszenz über einen intraligand Ladungstransfer aus. Trotz des höheren Schwer-Atom-Effekts weist der Blei(II)-Komplex eine sehr schwache Phosphoreszenz im Festkörper bei niedrigen Temperaturen auf, die auf einem stark verzerrten Ligand-zu-Metall Ladungstransfer-Zustand beruhen. Quantenchemische Rechnungen stützen diese Beobachtungen und bekräftigen, dass stark verzerrte angeregte Zustände für die Desaktivierung verantwortlich sind. Diese neuen Erkenntnisse unterstützen die Entwicklung sinnvoller Liganden-Design-Konzepte für langlebige phosphoreszierende Tetrel(II)-Komplexe.

Basierend auf den Erkenntnissen des vorherigen Projekts, so führt ein konzeptioneller topologischer Ansatz, beruhend auf der gezielten Einstellung der Liganden-Geometrie, zur Anregung spezifischer angeregter Zustände. Der tripodale Komplex $\text{Sn}(\text{bpep})$ wies aufgrund des zusätzlichen intramolekularen Donors einen intraligand Ladungstransfer auf. Im Gegensatz dazu, verfügt der Komplex $\text{Sn}(\text{}^t\text{-BuPDP}^{\text{}^t\text{-Bu}})$ mit dem meridionalen Pincer-artigen Liganden $\text{H}_2\text{}^t\text{-BuPDP}^{\text{}^t\text{-Bu}} = 2,6\text{-bis}(3,5\text{-di-}t\text{-butylpyrrol-2-yl})\text{Pyridin}$ über keine zusätzliche Donor-Stabilisierung und müsste Photolumineszenz über eine Ligand-zu-Metall Ladungstransfer zeigen. Ausgehend vom vermuteten angeregten Zustand, strahlt dieser Zinn(II)-Komplex rote Phosphoreszenz im Festkörper aus, eine Tatsache, die den konzeptionellen Erfolg zunächst unterstreicht. Allerdings ist die Phosphoreszenz überraschend schwach und die dazugehörigen Strahlungsraten zeigen ungewöhnliche Temperaturabhängigkeit auf. Dies ist auf unerwartete Aggregations-Effekte im Festkörper zurückzuführen, die aus quantenchemischen Rechnungen schlussgefolgert wurden.

Das dritte Projekt beschäftigt sich mit dem sehr bekannten *Lappert's* diamino Stannylen $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$, von dem im Jahr 1974 zum ersten Mal berichtet wurde. In seinen Grundzustandseigenschaften sowie in seiner Reaktivität wurde es seitdem umfangreich untersucht. Bis heute unbeachtet bleiben allerdings dessen photophysikalische Eigenschaften. Das Molekül weist eine ausreichende Stabilität in Lösung auf, was es für eine detaillierte spektroskopische Untersuchung wie zum Beispiel temperaturabhängige und zeitaufgelöste Emissions- oder Absorptionsspektroskopie zugänglich macht. Des Weiteren sind die Ergebnisse durch quantenchemische Rechnungen gestützt. Das gelbe *Lappert's* diamino Stannylen $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$, strahlt in Lösung und bei Raumtemperatur thermisch aktivierte mikrosekundenlange grüne bzw. orangene duale Phosphoreszenz aus, die aufgrund von Konformationsänderungen auf der Hyperfläche des angeregten Zustands stattfindet. Zusätzlich wurde der Mechanismus der photochemisch generierten Radikalbildung von $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_3$ erläutert. Dabei wurden zwei Excimere, deren Strukturen aufgrund von Jahn-Teller Effekte zweiter Ordnung verzerrt sind, in dem Kontext diskutiert. Basierend auf den Ergebnissen dieses Projekts können weitere Liganden-Design Konzepte für langlebige emissive Tetrel(II)-Komplexe entwickelt werden.

Neben dem Stannylen, wurde auch *Lappert's* diamino Plumbylen $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ bezüglich der photophysikalischen Eigenschaften untersucht. In erste Linie weist es starke thermische und photolytische Labilität vor, die mit anschließender Bildung von elementarem Blei daherkommt. Im letzten Projekt der vorliegenden Arbeit wurde diese Herausforderung anhand temperaturabhängiger Emissions- und Absorptionsspektroskopie angegangen. Bei niedrigen Temperaturen und gefrorener Lösung zeigt das Plumbylen schwach rote Photolumineszenz aus womöglich zwei Triplett-Zuständen über Ligand-zu-Metall Ladungstransfers auf. Quantenchemische Rechnungen deuten darauf hin, dass zwei separate angeregte Zustände nach Anregung bevölkert werden. Zusätzlich könnten beide angeregten Zustände im untersuchten Photolyse-Mechanismus vom $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ zu elementarem Blei, eine Rolle spielen.

Zusammenfassend lässt sich festhalten, dass die vorliegende Arbeit tiefergehende Informationen über die fundamentalen photophysikalischen sowie photochemischen Eigenschaften in schweren Tetrel(II)-Komplexen darlegt. Dies beinhaltet sowohl die Aufklärung des Charakters vom angeregten Zustand und dessen Dynamik als auch die

Untersuchung photochemischer Mechanismen. Komplexe mit verschiedenen Liganden-Geometrien und Koordinationszahlen wurden mit aufwendigen spektroskopischen Experimenten und quantenchemischen Rechnungen untersucht, um ein ausreichendes Wissen der grundlegenden Photophysik und derer Reaktivität zu erhalten. Die vorliegenden Studien deckten überraschend neue Ergebnisse und Herausforderungen auf, die einen einleitenden Schritt zur ersten Anwendung darstellen könnten.

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List of Abbreviations & Physical Quantities

A	absorption
a.u.	arbitrary units
Ar	aryl substituent
B	distortional mode
BiDIPY	bismuth-dipyrromethene
BODIPY	boron-dipyrromethene
bpy	2,2'-bipyridine
c	concentration
c	speed of light
C	coordination number
CT	charge transfer
δ	chemical shift
DCM	dichloromethane
ΔE	energy difference
deg	degradation
ΔE_{HL}	HOMO-LUMO gap
ΔE_{ST}	singlet-triplet energy separation
ΔG	Gibbs free energy
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
Δ_o	ligand field splitting in octahedral coordination
E	energy
E	group 14 element
e	elementary charge
e.g.	exempli gratia
E_a	activation barrier
em	emission

ε	molar absorption coefficient
ε_0	permittivity of the vacuum
ES	excited state
ESI	electron spray ionization
$E_{\sigma+\pi}$	Energy of the double bond in the classical planar form
eV	electron volt
Eq	equation
exc	excitation
f	fluorescence
Φ	quantum yield
f	oscillator strength
FCWD	Franck-Condon weighted density of states
Φ_{deg}	photodegradation quantum yield
Φ_{PL}	photoluminescence quantum yield
ΔG	Gibbs free energy
GS	ground state
h	Planck constant
$\hbar$	reduced Planck constant
$\hat{H}$	Hamiltonian
H ₂ bpep	2-[1,1-bis(1 <i>H</i> -pyrrol-2-yl)ethyl]pyridine
H ₂ ^{<i>t</i>-Bu} PDP ^{<i>t</i>-Bu}	2,6-bis(3,5-di- <i>tert</i> -butylpyrrol-2-yl)pyridine
HMGC	heavy main group complex
HOMO	highest occupied molecular orbital
Hppy	2-phenyl-pyridine
IC	internal conversion
ILCT	intraligand charge transfer
ISC	intersystem crossing
k_{obs}	observed rate constant

k_B	Boltzmann constant
k_f	fluorescence rate constant
k_{IC}	internal conversion rate constant
k_{ISC}	intersystem crossing rate constant
k_{nr}	non-radiative rate constant
k_p	phosphorescence rate constant
k_q	quenching rate constant
k_r	radiative rate constant
k_{VR}	vibrational relaxation rate constant
L	ligand
λ	wavelength
LC	ligand centered
λ_{em}	emission wavelength
λ_{exc}	excitation wavelength
LL'CT	ligand-to-ligand charge transfer
LMCT	ligand-to-metal charge transfer
LUMO	lowest unoccupied molecular orbital
μ	electric transition dipole moment
m	mass
M	molar mass
M	metal
MC	metal centered
m_e	electron mass
Me	methyl
Mes	mesityl
MLCT	metal-to-ligand charge transfer
n	amount of substance
n	non-bonding

ν	frequency
NMR	nuclear magnetic resonance
nr	non-radiative
n _s -orbital	tetrel centered non-bonding orbital with high s-character
OLED	organic light emitting diode
OTf ⁻	triflate
p	phosphorescence
<i>P</i>	Power
PbH	Pb[N(SiMe ₃) ₂] ₂
Ph	phenyl
phen	1,10-phenanthroline
PHOLED	phosphorescent organic light emitting diode
π_L	ligand centered π -orbital
p π -orbital	tetrel centered π -orbital with high p-character
[Q]	quencher concentration
r	radiative
R	alkyl substituents
<i>r</i>	distance
r.t.	room temperature
ref.	reference
S	singlet
S	total spin
sh	shoulder
SOC	spin-orbit coupling
SOJT	second-order Jahn-Teller
τ	lifetime
T	triplet
<i>T</i>	temperature

t	time
TA	transient absorption
TADF	thermally activated delayed fluorescence
TADP	thermally activated delayed phosphorescence
t Bu	<i>tert</i> -butyl
(TD)-DFT	(time-dependent) density functional theory
THF	tetrahydrofuran
TMC	transition metal complex
τ_q	quenched lifetime
TS	transition state
UV	ultraviolet
Vis	visible
VR	vibrational relaxation
vs.	versus
ζ	SOC constant

1 Introduction

1.1 Photoactive Materials – A Sustainable Alternative?

Since the Industrial Revolution, energy usage has increased massively and economic output has risen accordingly.^[1] This has gone hand in hand with a huge exploitation of limited fossil fuels like petroleum, coal or natural gas that has grown tremendously over the past centuries.^[2] Combustion processes based on these energy sources produce large amounts of air pollutants, including carbon dioxide, nitric oxides or sulphur dioxide.^[3] Therefore, sustainable and environmentally friendly alternatives are more necessary than ever and have already gained a significant surge in attention.^[4,5]

One possible alternative to reduce dependency on fossil fuels is to use sunlight as an energy source, either by transforming solar energy into electricity as in photovoltaic technology^[6–10] or by converting it into chemical energy through photochemical or photocatalytic reactions.^[11–14] Alongside changing the energy source, it is also required to diminish the consumers energy demand by utilizing energy-efficient devices like organic light-emitting diodes (OLEDs) or phosphorescent organic light-emitting diodes (PHOLEDs) as light sources (Figure 1.1).^[15–17]

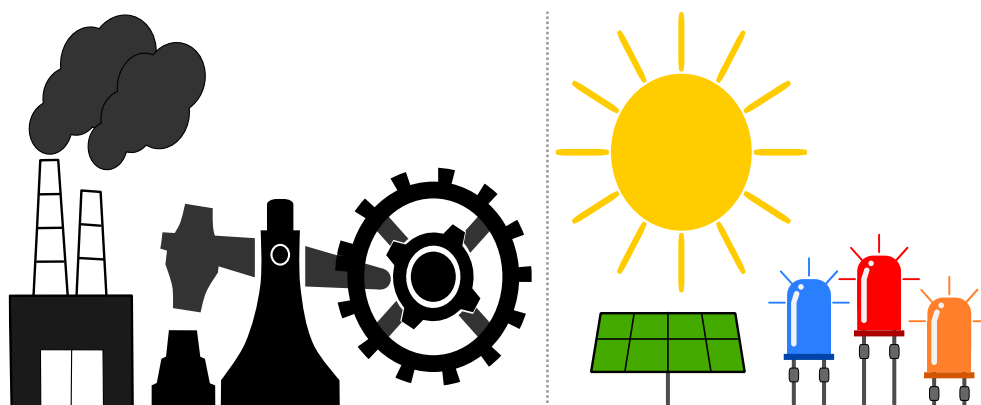


Figure 1.1: Figurative representation of the common fossil fuels in opposition to the sustainable clean energy sources.

Notably, photoactive transition metal complexes (TMCs) have gained a huge interest in research and application as versatile materials over the last few decades.^[13,18–21] Their distinctive and tunable structure allows access to a huge selection of properties for specific purposes. Research and application have focused mainly on photoactive TMCs based on precious metals like ruthenium, iridium, platinum or rare-earth elements (lanthanides). The most prominent examples are the complexes $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) or $\text{Ir}(\text{ppy})_3$ (Hppy = 2-phenyl-pyridine).

Especially, $[\text{Ru}(\text{bpy})_3]^{2+}$ has been meticulously investigated in several studies involving areas such as fundamental photophysics,^[22–25] dye-sensitized solar cells,^[26] photocatalysis^[11,13] or even medical applications like photodynamic therapy^[27].

A key factor for its utilization is a sufficiently long lifetime of the excited state, that usually occurs when the spin multiplicity of the excited state differs from the ground state. This aspect induces spin-forbidden nonradiative and radiative processes between excited state and ground state, which extends the excited state lifetime. To obtain excited states with different spin multiplicities to the ground state, efficient intersystem crossing is

necessary which is driven by strong spin-orbit coupling and can be induced by the heavy-atom effect.^[28–30]

Regardless of the superb performance, the main issue of ruthenium as well as iridium is the extremely low earth abundancy (Table 1.1).^[31] Due to the low abundance and resulting high costs in mining, this issue hampers an affordable and global transition to sustainable energy sources. Thus, these precious metals must be replaced with earth abundant elements.

An alternative, which has been explored and evolved remarkably well in the past few decades, is the implementing of TMCs based on first row transition metals (3d elements).^[32–38] First promising applications with 3d TMCs have already been established for instance in dye-sensitized solar cells,^[39] in OLEDs^[40–43] or in photocatalysis.^[44–47]

This progress has been accomplished through the development of clear design concepts and structure property relationships, concomitantly diminishing nonradiative processes. In 3d TMCs, the emissive/photoactive excited states ought to be undistorted either directly by the character of the excited state as in the case of pseudo-octahedral chromium(III) and iron(II) complexes^[35–38] or by rigidification in case of pseudo-tetrahedral d¹⁰ copper(I) complexes preventing the flattening distortion.^[48–51] Further, excited states which are responsible for nonradiative deactivation should be energetically separated from emissive/photoactive states by tuning the ligand field splitting and the energy of the relevant excited states.^[35–38]

Table 1.1: Earth abundance of selected elements in the earth's crust in mg/kg.^[31]

Element	Ru/Ir	Fe	Cr	Cu	Sn	Pb	Si
Abundance	0.001	56300	102	60	2.3	14	282000

On the contrary, comparable design concepts and structure property relationships for photoluminescent complexes based on heavy main group elements are missing, although these elements possess a high earth abundance, as well (Table 1.1). Generally, the idea of heavy main group complexes (HMGCs) in the context of photophysics or photochemistry has been neglected in the past decades and examples of photoactive HMGCs are rather seldom.^[52]

Especially, photoactive HMGCs based on group 14 elements in the oxidation state +II, referred to as tetrel(II) complexes, are very scarce. Photoluminescence is mostly limited to frozen solutions or to the solid state.^[53–55] Most strikingly, the nature of the excited states in photoluminescent tetrel(II) complexes has remained usually unknown. Knowledge and understanding of that is a key prerequisite for developing and rationalizing design concepts for specific purposes. Particularly, the elements tin and lead could provide excited states with different spin multiplicities to the ground state via the heavy-atom effect.^[28,29]

The present work focuses on development and characterization of photoluminescent heavy tetrel(II) complexes with tin(II) and lead(II) followed by a detailed investigation of their photophysics. This effort is not only driven by replacing TMCs with precious metals but instead by enhancing a rather underexplored field within the research of molecular photophysics and photochemistry.

The following introduction will first give a short overview of the relevant photophysical processes and excited state properties. These aspects are further explained and exemplified by the photophysics in TMCs, with a particular focus on the well-known $[\text{Ru}(\text{bpy})_3]^{2+}$ complex. Thereafter, some few examples of photoluminescent HMGCs of different classes and their photophysical properties are briefly reviewed.

Finally, the basic knowledge of heavy tetrel(II) complexes is pointed out, including their structural properties and ground state reactivity. In addition, the current state of research in photoactive heavy tetrel(II) complexes is summarized and discussed.

1.2 Photophysical Background

1.2.1 Fundamental Photophysical Processes

A molecule can absorb a photon of a certain energy to induce an electronic transition (resonance condition, $E = h\nu$). Once a photon is absorbed, the molecule turns from its ground state (GS) to an excited state (ES), concomitant with a redistribution of electron density within the molecule (absorption A, photoexcitation). From the ES after photoexcitation, the molecule has different pathways to relax into the GS, either by radiative (r) processes like an emission of a photon also named photoluminescence or by non-radiative (nr) processes, described by the rate constants k_r and k_{nr} . These processes follow first-order kinetics in the first place.^[56,57]

The radiative processes can be separated into spin-allowed fluorescence k_f , defined by an unchanged total spin $\Delta S = 0$ and spin-forbidden phosphorescence k_p , defined by a change in total spin $\Delta S = 1$. In the case of a molecule with a singlet GS (S_0), fluorescence occurs from an energetically higher-lying singlet state (S_1) and phosphorescence from an energetically higher-lying triplet state (T_1) (Figure 1.2).

The non-radiative processes can be divided into spin-allowed internal conversion (IC) and spin-forbidden intersystem crossing (ISC) as well as vibrational relaxation (VR) with its respective rate constants k_{IC} , k_{ISC} and k_{VR} .

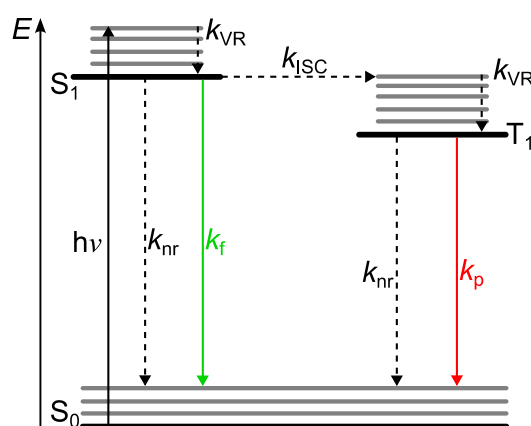


Figure 1.2: Simplified Jablonski diagram with selected relaxation pathways beginning from the singlet (S_0) ground state to the energetically lowest triplet (T_1) excited state.

Neglecting other (bimolecular) processes, such as photoinduced electron or energy transfer, the ES lifetime τ is determined by the mentioned processes and is described as the reciprocal sum over all relevant rates deactivating the ES and corresponds to the observed rate constant k_{obs} [Eq (1)]. Experimentally, the ES lifetime τ can be obtained either by time-resolved emission or transient absorption (TA) spectroscopy.

$$\tau = \frac{1}{k_r + k_{nr}} = \frac{1}{\sum_i k_i} = \frac{1}{k_{obs}} \quad (1)$$

The efficiency of a certain process is determined by the quantum yield Φ which is the ratio between the rate constant of the considered process and the sum over all rate constants. For example, the photoluminescence quantum yield Φ_{PL} is described by the ratio between k_r and all other rate constants that deactivate the ES [Eq (2)].^[56,57]

$$\phi_{\text{PL}} = \frac{k_r}{k_r + k_{\text{nr}}} = k_r \cdot \tau \quad (2)$$

The photoluminescence quantum yield ϕ_{PL} can also be expressed as the ratio between the number of emitted photons and number of absorbed photons [Eq (3)]. This aspect is crucial in cases of practical measurements of ϕ_{PL} and subsequent k_r determination.^[56,57]

$$\phi_{\text{PL}} = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}} \quad (3)$$

1.2.2 The Nature of Phosphorescence

An electronic transition between an initial state (i) and final state (f) depends, inter alia, on the electric transition dipole moment $\mu_{i,f}$ of two wavefunctions Ψ_i and Ψ_f with the dipole moment operator $\hat{\mu}$ for the electronic part [Eq (4)]. The probability of an electronic transition between a state i and state f is proportional to the square of the absolute value of the electric transition dipole moment $|\mu_{i,f}|^2$.^[58,59]

$$\mu_{i,f} = \langle \Psi_f | \hat{\mu} | \Psi_i \rangle = \int \Psi_f^* \hat{\mu} \Psi_i dr \quad (4)$$

If the electric transition dipole moment $\mu_{i,f}$ differs from zero, the electronic transition from the GS to ES (absorption) or from the ES to GS (emission) becomes allowed. If $\mu_{i,f}$ equals zero, the transition is forbidden.

The square of the absolute value of the electric transition dipole moment $|\mu_{i,f}|^2$ is connected to the oscillator strength $f_{i,f}$ of a transition and the energetic difference $\Delta E_{i,f}$ between the initial and final state [Eq (5)].^[58] The oscillator strength $f_{i,f}$ can be obtained by time-dependent density functional theory (TD-DFT) calculations. Note, the higher the oscillator strength $f_{i,f}$ amounts, the more intense the signal in the absorption or emission spectrum becomes.

$$f_{i,f} = \frac{2m_e}{3e^2\hbar^2} \cdot \Delta E_{i,f} \cdot |\mu_{i,f}|^2 \quad (5)$$

The radiative rate constant k_r of an emission depends on the square of the absolute value of the electric transition dipole moment $|\mu_{i,f}|^2$ and the energetic difference $\Delta E_{i,f}$ between final and initial state (emission energy) in third order of magnitude [Eq (6)].^[58]

$$k_r = \frac{\Delta E_{i,f}^3}{6\pi\epsilon_0\hbar^4c^3} \cdot |\mu_{i,f}|^2 \quad (6)$$

Additionally, several selection rules come up which determine whether an electronic transition is allowed or forbidden. One of them is the spin selection rule which declares, the total spin S cannot change during electronic transitions. Consequently, one has to distinguish between spin-allowed $\Delta S = 0$ and spin-forbidden $\Delta S = 1$ transitions.^[58,59]

However, spin-forbidden transitions like phosphorescence appear and this rule is only valid for systems with weak or negligible spin-orbit coupling (SOC). The SOC constant ζ scales roughly with the effective nuclear charge in the fourth order of magnitude within the hydrogenic approximation ($\zeta \sim Z_{\text{eff}}^4$).^[29,58] This means if heavy elements are present

in the system, they can efficiently accelerate spin-forbidden processes (heavy-atom effect).^[29,58,59]

In the case of a phosphorescence from the lowest triplet ES (T_1) to the singlet GS (S_0), the SOC impacts the electric transition dipole moment.^[60,61] First, SOC lifts the degeneracy of the three spin-sublevels of T_1 . Therefore, all spin-sublevel wavefunctions must be considered in the triplet wavefunction and are expressed by the zero projection of the total spin on the Cartesian axes in T_1^α ($\alpha = x, y, z$).^[60,61] Second, the wavefunctions of S_0 and all T_1 sublevels are perturbed by admixing of another triplet (T_m) and singlet (S_n) states, resulting in the SOC corrected wavefunctions $\tilde{T}_1^\alpha$ and $\tilde{S}_0$ [Eq (7), ((8))].^[60,61]

$$\tilde{T}_1^\alpha = T_1^\alpha + \sum_{n=0}^{\infty} \frac{\langle S_n | \hat{H}_{SO} | T_1^\alpha \rangle}{E(T_1) - E(S_n)} S_n \quad (7)$$

$$\tilde{S}_0 = S_0 + \sum_{\beta}^{x,y,z} \sum_{m=1}^{\infty} \frac{\langle T_m^\beta | \hat{H}_{SO} | S_0 \rangle^*}{E(S_0) - E(T_m)} T_m^\beta, \beta = x, y, z \quad (8)$$

Hence, the electric transition dipole moment must be considered for the SOC corrected wavefunctions $\tilde{T}_1^\alpha$ and $\tilde{S}_0$ [Eq (9)].^[60,61]

$$\mu_{\tilde{T}_1^\alpha \tilde{S}_0} = \langle \tilde{S}_0 | \hat{\mu} | \tilde{T}_1^\alpha \rangle = \sum_{n=0}^{\infty} \frac{\langle S_n | \hat{H}_{SO} | T_1^\alpha \rangle}{E(T_1) - E(S_n)} \langle S_0 | \hat{\mu} | S_n \rangle + \sum_{m=1}^{\infty} \frac{\langle T_m^\alpha | \hat{H}_{SO} | S_0 \rangle^*}{E(S_0) - E(T_m)} \langle T_m^\alpha | \hat{\mu} | T_1^\alpha \rangle \quad (9)$$

In other words, triplet to triplet and singlet to singlet transitions with high transition dipole moments mix to and permit the T_1 to S_0 transition. Further, the transition dipole moment depends on the certain SOC matrix elements [$\langle S_n | \hat{H}_{SO} | T_1^\alpha \rangle$ and $\langle T_m^\alpha | \hat{H}_{SO} | S_0 \rangle^*$, $\hat{H}_{SO}$ = SOC Hamiltonian] and scales with the reciprocal singlet-triplet energy differences between the respective states.^[60,61]

The SOC-mediated perturbation can also induce direct singlet to triplet absorption, as already observed in TMCs employing heavy metal centers such as platinum(II) and osmium(II).^[62–64] Finally, the expression of the SOC corrected phosphorescence rate k_p^α for the T_1 to S_0 transition can be obtained by combining Eq (6) and Eq (9).

$$k_p^\alpha = \frac{\Delta E_{T_1, S_0}^3}{6\pi\epsilon_0 \hbar^4 c^3} \cdot |\mu_{\tilde{T}_1^\alpha \tilde{S}_0}|^2 \quad (10)$$

In most cases, the splitting of the T_1 sublevels is small and the observed phosphorescence rate constant k_p is an arithmetic average of the respective rate constants from each sublevel. Further, the phosphorescence rate k_p should show no temperature dependence as Eqs (6) and (9) indicate. However in cases, the splitting of the T_1 sublevels is non-negligible with respect to the temperature T , the final phosphorescence rate $k_{p,av}$ is an average over the three sublevels following a Boltzmann distribution [Eq (11)].^[65] This equation is also valid, if different emissive ESs are energetically close to each other and establish a thermal equilibrium.

$$k_{p,av} = \frac{k_{p,1} + k_{p,2}e^{-(\Delta E_2/k_B T)} + k_{p,3}e^{-(\Delta E_3/k_B T)}}{1 + k_{p,2}e^{-(\Delta E_2/k_B T)} + k_{p,3}e^{-(\Delta E_3/k_B T)}} \quad (11)$$

So far, the nuclear motions, which follow the electronic transitions, have not been considered in the previous descriptions. For nonlinear molecules with N atoms, every

electronic state consists of a certain electron configuration and a series of $3N-6$ vibrational sublevels with respective vibrational wavefunctions. In case of an electronic transition between an initial state (i) and final state (f), the electron movement happens instantaneously compared with the time scale of nuclear motions and the geometry of the molecule does not change during excitation. Transitions where the nuclear motion is preserved are called vertical transitions and are described by the Franck-Condon principle.^[56,57]

The total wave function $\Psi_{n,v}(\mathbf{r}, \mathbf{R})$ ($\mathbf{r}$ = electron- and $\mathbf{R}$ = nuclear-coordinates) is a product between the electronic wavefunction $\psi_n(\mathbf{r}, \mathbf{R})$ depending on the electronic state n and the nuclear wavefunction $\chi_{n,v}(\mathbf{R})$ depending on n and on the vibrational state(s) v (Born-Oppenheimer approximation).^[58,59] Thus, the electric transition dipole moment is modified with the nuclear part [Eq (12)].

$$\mu_{(i,v),(f,v')} = \langle \Psi_{f,v'} | \hat{\mu} | \Psi_{i,v} \rangle = \langle \psi_f \chi_{f,v'} | \hat{\mu} | \psi_i \chi_{i,v} \rangle = \mu_{i,f} \cdot \langle \chi_{f,v'} | \chi_{i,v} \rangle = \mu_{i,f} \cdot S(v', v) \quad (12)$$

$S(v', v)$ is the overlap integral between the vibrational wavefunctions of the initial and final state. Hence, the intensity of an absorption or emission is proportional not only to $|\mu_{i,f}|^2$ but also to $|S(v', v)|^2$, which is called Franck-Condon factor.^[58,59] Finally, all beforementioned processes, which depend on the electric transition dipole moment, for instance k_r , must be adjusted by the Franck-Condon factors $|S(v', v)|^2$, as well.

How sharp or broad an absorption or emission band is, depends on the respective geometrical displacement between GS and ES and, hence, on the considered Franck-Condon factors (Figure 1.3).

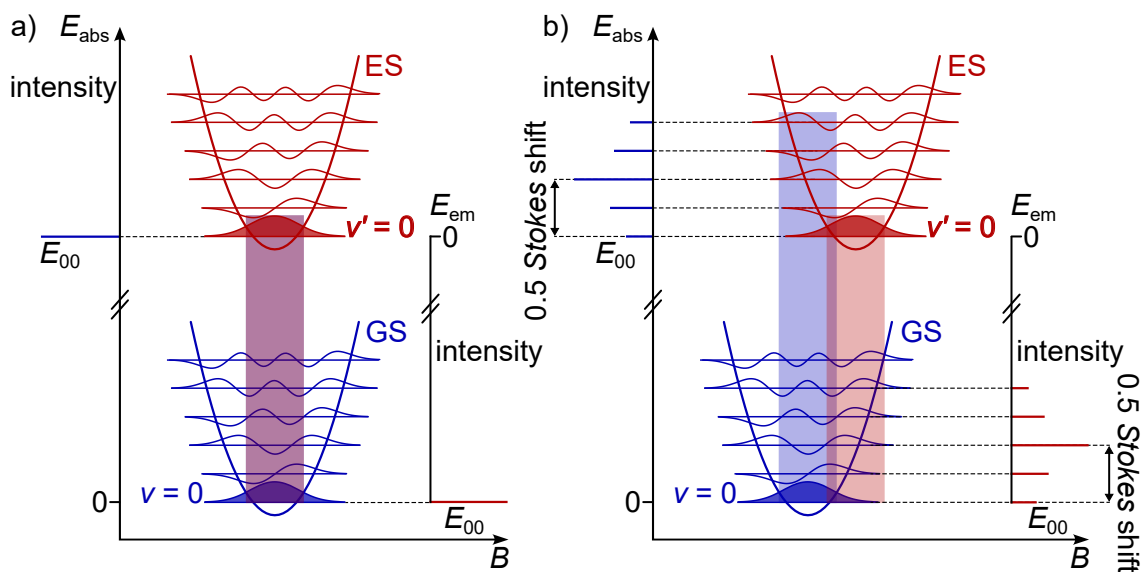


Figure 1.3: Schematic representation of the potential energy surface diagrams of ground state (GS) in blue and excited state (ES) in red along a distortion mode B with relevant vibrational wavefunctions for a) a nested ES and b) a distorted ES with intensities of vibronic transitions as projection for absorption (blue) and emission (red). Adapted from ref.^[57,66]

If the ES provides a small geometrical distortion to the GS, the ES is called nested state. In this case the absorption and emission bands are sharp (illustrated as projection on y axes for absorption (blue) and emission (red) in Figure 1.3a). Here, the vibrational overlap between the zero vibrational levels of the respective state ($S(0,0)$ $v=v'=0$) is only considered, resulting in a match between absorption and emission energy (E_{00}). The energy difference between the absorption and emission band maximum of transitions

involving the same GS and ES is defined as Stokes shift, which is small for nested ES. If the ES provides a large geometrical distortion to the GS, the respective transitions consist of several vibrational overlaps ($S(v',0)$, $S(0,v)$), which result in a broadening of the absorption and emission bands (Figure 1.3b). Due to the displacement the Franck Condon factors involving the higher vibrational levels are larger than the overlap between the zero vibrational levels, which moves the absorption and emission band maxima at higher and lower energy than E_{00} , respectively. Therefore, a large Stokes shift results. Half of the Stokes shift evolves from the hypsochromically shifted absorption band maximum, and the other half from the bathochromically shifted emission band maximum. In general, the Stokes shift stems from the geometrical displacement of the respective states and is experimentally easily accessible, which makes it a good indicator for ES distortions.

1.2.3 Non-radiative Processes

After an electronic transition (A) from a singlet GS (S_0) to an energetically higher-lying singlet ES (S_2) occurred, subsequently non-radiative isoenergetic internal conversion (k_{IC}) into a higher vibrational state of the ES S_1 takes place (Figure 1.4).^[57] The electronic change happens fast and the nuclei must adapt to the new electron density distribution and establish a new minimum geometry of S_1 by vibrational relaxation (k_{VR}). Formally forbidden intersystem crossing (k_{ISC}) from a S_1 to a T_1 state with its respective three sublevels can occur subsequently.

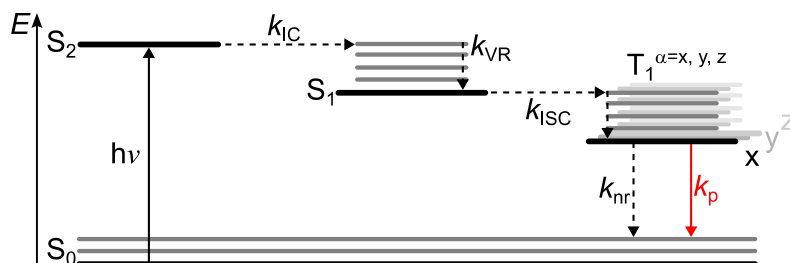


Figure 1.4: Schematic Jablonski diagram with selected relaxation pathways beginning from the singlet ground state S_0 to the lowest triplet excited state T_1^α with the triplet sublevels $\alpha = x, y, z$.

In general, processes like IC or ISC can be understood with Fermi's golden rule, describing a transition from an initial state (i) to a continuum of final states (f) [Eq (13)].^[58,59,67] The rate constant k_{nr} depends on the coupling between the initial and a sum of all final states, which is driven by the Hamiltonian $\hat{H}_{i \rightarrow f}$. Further, the initial and final states ought to be of same energy $E_i \approx E_f$, which is considered in the Dirac delta function $\delta(E_{i,v} - E_{f,j,v'})$.^[67] The Dirac delta function enforces energy conservation.^[29] Taking the vibrational levels v of the relevant states into account, the latter aspect can be summarized with the Franck-Condon factors, giving the Franck-Condon weighted density of states (FCWD). Note, the higher the density of states, the more efficient the respective process is.

$$\begin{aligned}
 k_{nr} &= \frac{2\pi}{\hbar} \sum_j |\langle \psi_{f,j} | \hat{H}_{i \rightarrow f} | \psi_i \rangle|^2 \cdot \sum |\langle \chi_{f,v'} | \chi_{i,v} \rangle|^2 \cdot \delta(E_{i,v} - E_{f,j,v'}) \\
 &= \frac{2\pi}{\hbar} \sum_i |\langle \psi_{f,i} | \hat{H}_{i \rightarrow f} | \psi_i \rangle|^2 \cdot \text{FCWD}
 \end{aligned} \tag{13}$$

Finally, the Hamiltonian must be adjusted accordingly, depending on which process is considered. In case of internal conversion (k_{IC}), the process is driven by vibronic coupling and the nuclear motion must be included.^[68]

Intersystem crossing (k_{ISC}), for example from a S_1 state to a T_1 state with its respective three sublevels ($\alpha = x, y, z$) (Figure 1.4), is driven by SOC, which can be induced by the heavy-atom effect.^[28–30] Therefore, the SOC Hamiltonian $\hat{H}_{SOC}$ is applied and Eq (13) can be modified to Eq (14).^[28,29]

$$k_{ISC} = \frac{2\pi}{\hbar} \sum_{\alpha} |\langle T_1^{\alpha} | \hat{H}_{so} | S_1 \rangle|^2 \cdot \text{FCWD} \quad (14)$$

Besides the heavy-atom effect, efficient and fast ISC processes can appear in purely organic molecules without any heavy atoms. It can be induced if the orbital symmetry between the involved singlet and triplet states changes which is described by the El Sayed rules.^[69,70] Here, the change in spin must be accompanied by a change in angular momentum, so that the total angular momentum is preserved.^[28,29] This means that e.g. in organic π -systems containing nitrogen atoms with located non-bonding (n) orbitals the $^1(n-\pi^*) \rightarrow ^3(\pi-\pi^*)$ ISC is more efficient and faster than the $^1(\pi-\pi^*) \rightarrow ^3(\pi-\pi^*)$ ISC which includes the same type of orbitals.

How effective the final triplet ES T_1 deactivates non-radiatively depends on the molecular geometric distortion of T_1 compared to the GS S_0 . If T_1 is a nested state to S_0 , the vibrational wavefunction overlap between the lowest vibrational level of T_1 and the higher vibrational level of S_0 is poor, leading to small Franck-Condon factors and less probable non-radiative decay (weak coupling limit, Figure 1.5a).^[29,57,71] Here, k_{nr} is mainly dominated by the energy difference ΔE between T_1 and S_0 , as described by the energy gap law, which implies that k_{nr} increases exponentially as ΔE decreases ($k_{nr} \sim e^{-\Delta E}$).^[71,72]

On the contrary, if the T_1 geometry is strongly distorted compared to the S_0 geometry the vibrational wavefunction overlap is large and the non-radiative $T_1 \rightarrow S_0$ transition is enhanced (strong coupling limit, Figure 1.5b).^[29,57,71] Further, if the potential energy surfaces cross, the non-radiative deactivation can become a thermally activated process additionally, which hinges on the activation barrier E_a between the ES minimum and the potential energy surface crossing point.^[57] This process can be described as an Arrhenius-like behavior [Eq (15)].^[73,74]

$$k_{nr}(T) = A \cdot e^{-\frac{E_a}{k_B T}} \quad (15)$$

With A expressing the pre-exponential factor, k_B the Boltzmann's constant and T the temperature.

Note, the illustrated parabolas are cross-sections of the global potential energy hypersurface along a certain distortional mode. The hypersurface includes all possible vibrational modes of the molecule.

The rules and processes presented here are also valid between different ESs e.g. S_1 to T_2 . Generally, non-radiative rates between different ESs are mostly higher than those between GS and ES, because of the smaller energy gaps separating the ESs, which is often referred to as Kasha's rule.^[57,75]

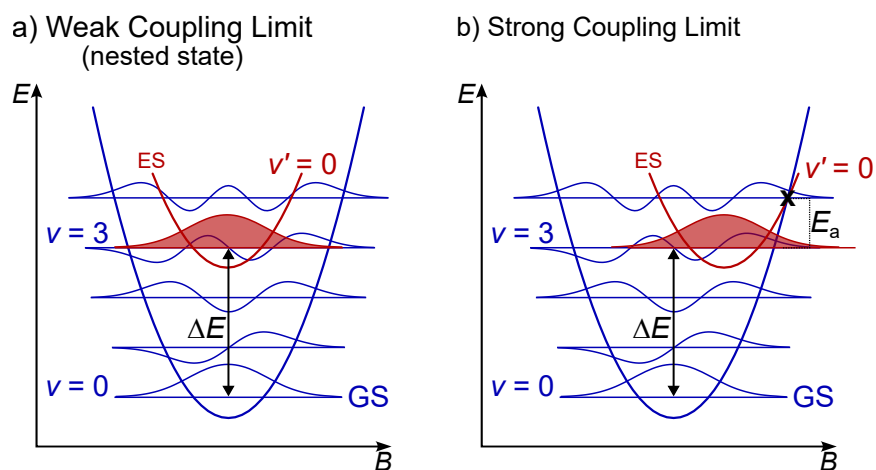


Figure 1.5: Potential energy surface diagrams of ground state (GS) in blue and excited state (ES) in red along a distortion mode B with relevant vibrational wavefunctions for a) weak coupling limit (nested ES, weak vibrational wavefunction overlap) and b) strong coupling limit (strongly distorted ES, strong vibrational wavefunction overlap). ΔE is the gap between GS (v_0) and ES (v_0), E_a activation barrier between ES minimum and the potential energy surface crossing point in black. Adapted from ref.^[29,57,66]

1.2.4 Excitonic Interactions

In a single molecule the electric transition dipole moment μ is the crucial quantity describing a vertical electronic transition (section 1.2.2). It can be considered as a vector corresponding along the oscillating electron displacement within a transition. However, in aggregates, where the molecules stay in close spatial proximity, the individual electric transition dipole moments μ of each molecule couple, resulting in excitonic interactions.^[76–78] As a simple example of a dimer, two molecules with their respective electric transition dipole moment μ interact with each other. This interaction gives a set of two new non-degenerate states.^[76] The mutual orientation of the electric transition dipole moments determines the resulting aggregate type, giving rise to either H- or J-aggregates. In addition, the oscillatory nature of the electric transition dipole moment becomes important and the relative phases of motion between these two dipoles defines the ESs (Figure 1.6).

If the dipoles couple in phase, the resulting state becomes optically allowed with respect to the GS and is denoted as ES_+ . In contrast, anti-phase coupling leads to an optically forbidden state, that is denoted as ES_- .^[77,78] Furthermore, the oscillator strength amounts to zero for the $GS \rightarrow ES_-$ transition and to twice that of the individual molecule for the $GS \rightarrow ES_+$ transition. This is an aspect, which may also influence the decay back to the GS after photoexcitation.^[76,77]

In H-aggregates, the transition dipoles provide a “side-by-side” orientation and the energetically higher state becomes allowed due to the in-phase relation of the respective dipoles (Figure 1.6a). Experimentally, this effect is visible in a blue-shift in the absorption spectrum of the relevant electronic transition compared to the absorption of the single molecule. Conversely, J-aggregates keep a “head-to-tail” orientation, and the lower state becomes allowed (Figure 1.6b). In this case, the aggregation causes a red-shift of the relevant absorption band.^[76,77]

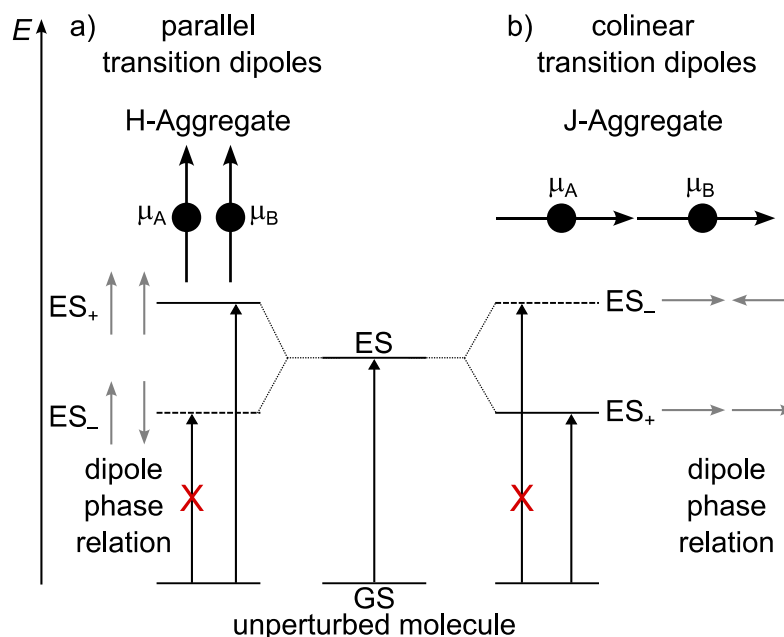


Figure 1.6: Schematic energy level diagram for a) H- and b) J-aggregate dimer with their respective orientation of their electric transition dipole moments μ . Transitions from the GS are permitted if the transition dipole moments couple in phase, indicated by the plus symbol. For H-aggregates the energetically higher and for J-aggregates the energetically lower ES becomes allowed.

1.3 Photophysics in Transition Metal Complexes

1.3.1 Electronic Transitions

When a TMC absorbs a photon, an electron from a certain orbital is promoted to an energetically higher-lying one. The direction of the electron- or charge transfer (CT) defines the ES.^[57] In the case of an octahedral coordinated metal complex ML_6 with only σ donating ligands, the five d-orbitals split into a set of three non-bonding t_{2g} and two antibonding e_g^* orbitals, establishing the ligand field splitting (Δ_o).^[79] These metal centered orbitals in combination with ligand orbitals form donor-acceptor systems that enable a variety of different CT transitions (Figure 1.7).

In TMCs mostly reducible and oxidizable metals or ligands are implemented leading to metal-to-ligand or ligand-to-metal CT states (MLCT or LMCT).^[56] In large ligand systems with electron-rich and electron-poor moieties an intraligand CT (ILCT) occurs from one ligand moiety to another.^[80,81] Further, in TMCs with donating and accepting ligands a ligand-to-ligand CT (LL'CT) appears.^[81,82] Ligands with π -systems can also exhibit ligand centered (LC) π - π^* transitions.

Metal centered (MC) transitions within the d manifold can arise, although they are formally forbidden in complexes with inversion symmetry because of Laporte's rule. However, these transitions may become allowed by vibrational modes, which lift the inversion symmetry dynamically or by utilizing ligand systems that do not provide inversion symmetry.^[79,83]

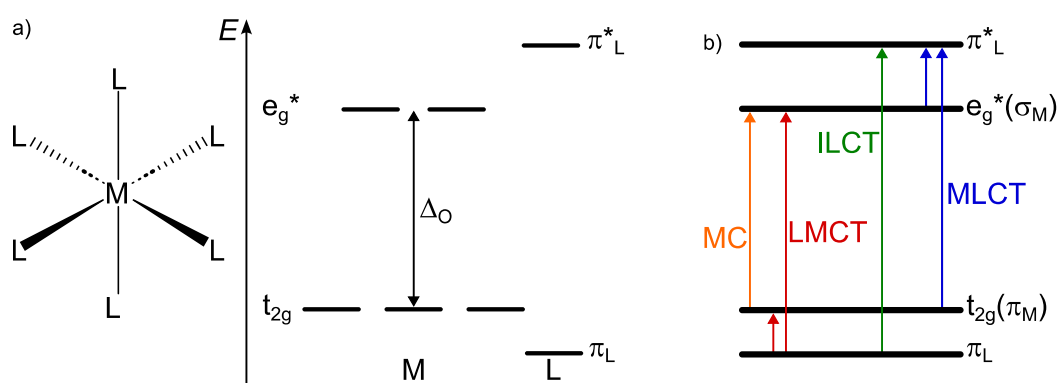


Figure 1.7: Schematic representation of a) the energy levels in an octahedral TMC (ML_6) and b) relevant electronic transitions. Ligand-to-ligand CT (LL'CT) and ligand centered (LC) transitions are omitted.

The pseudo-octahedral TMC $[Ru(bpy)_3]^{2+}$ is the most well-known example in the context of photochemistry, especially regarding phosphorescence and photocatalysis (Figure 1.8a).^[84] This complex features a 1GS with a $(t_{2g})^6(e_g^*)^0$ electron configuration. Upon photoexcitation with blue light, a 1MLCT state is initially populated, characterized by a formally oxidized metal center (Ru^{III}) and a reduced bipyridine ligand with a singly occupied π^* -orbital ($bpy^{\cdot-}$) (Figure 1.8b).

The ruthenium center provides strong SOC because of the heavy-atom effect ($\zeta = 1042 \text{ cm}^{-1}$)^[85]. Therefore, ultrafast and quantitative k_{ISC} to the 3MLCT state within less than 110 fs occurs as the follow-up process.^[86,87] Subsequent vibrational relaxation k_{VR} establishes the relaxed 3MLCT geometry on a picosecond timescale.^[88]

The $^3MLCT \rightarrow ^1GS$ transition takes place either via phosphorescence k_p or non-radiatively k_{nr} . The phosphorescence is observed with an emission maximum at $\lambda_{em} = 620 \text{ nm}$ in

acetonitrile at room temperature and a lifetime of $\tau_p = 930$ ns.^[84] Furthermore the photoluminescence quantum yield Φ_{PL} can reach values up to 0.095 in deaerated acetonitrile.^[89] The $^3\text{MLCT}$ state provides a small structural distortion relative to the ^1GS , i.e. nested state (weak coupling limit, Figure 1.5a), due to the almost non-bonding character of the metal centered t_{2g} -orbitals and the resulting delocalization of the electron in the ligand π^* -orbitals. Therefore, a long lifetime and high photoluminescence quantum yield results.

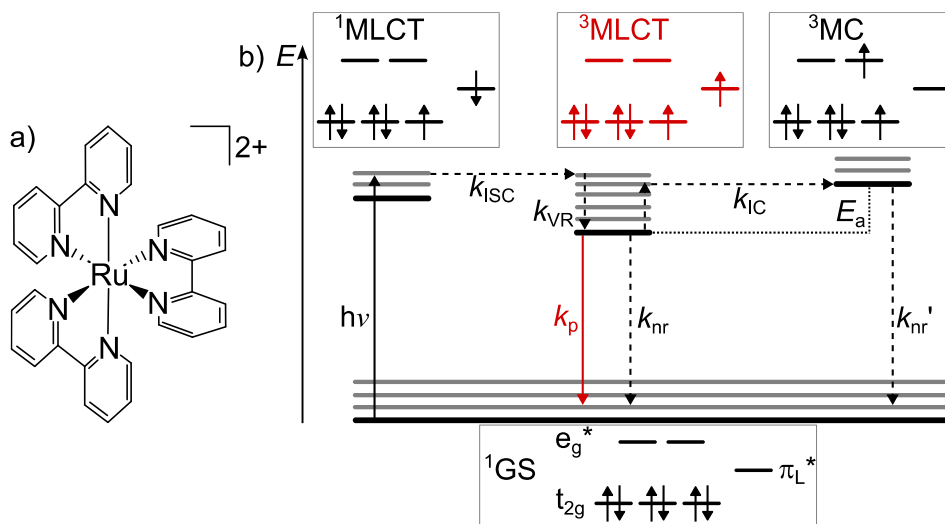


Figure 1.8: a) Molecular structure of $[\text{Ru}(\text{bpy})_3]^{2+}$, b) schematic Jablonski diagram with the relative relaxation pathways and respective electron configurations.

A major deactivation pathway of the $^3\text{MLCT}$ state in $[\text{Ru}(\text{bpy})_3]^{2+}$ is the thermally activated population of ^3MC states with a $(t_{2g})^5(e_g^*)^1$ electron configuration.^[35] The occupation of the antibonding e_g^* -orbitals toward the metal-ligand σ -bonds, with parallel Jahn-Teller distortions and concomitant energy decrease, drive the ES distortion and lead to fast GS recovery, according to the energy gap law.^[72] Thus, the ^3MC vibrational wavefunctions strongly overlap with ^1GS vibrational wavefunctions which facilitates the non-radiative relaxation (strong coupling limit, Figure 1.5b).^[35] In the case of $[\text{Ru}(\text{bpy})_3]^{2+}$, the thermally activated $^3\text{MLCT} \rightarrow ^3\text{MC}$ transfer is connected to an activation barrier E_a of roughly 3600 cm^{-1} (Figure 1.8b).^[90] The phosphorescence lifetime τ shows a strong temperature dependence, accordingly.^[90] Assuming a thermal equilibrium between the $^3\text{MLCT}$ and ^3MC state, the observed photoluminescence rate constant k , obtained from the $^3\text{MLCT}$ lifetimes, can be modeled with three rate constants [Eq (16)].^[90,91]

$$k = \frac{1}{\tau} = k_p + k_{\text{nr}} + k_{\text{nr}}' \cdot e^{-\frac{E_a}{k_B T}} \quad (16)$$

With k_p and k_{nr} expressing the phosphorescence and non-radiative rate constant for the $^3\text{MLCT} \rightarrow ^1\text{GS}$ relaxation as well as k_{nr}' the non-radiative rate constant for the $^3\text{MC} \rightarrow ^1\text{GS}$ transfer (Figure 1.8b). The exponential term, which reflects the thermal activation over the activation barrier E_a is derived from an Arrhenius-type modelling [see Eq (15)].^[90,91]

Beyond the non-radiative $^3\text{MC} \rightarrow ^1\text{GS}$ pathway, the strong geometric distortion in the ^3MC states may induce ligand loss by photodissociation which is the primary mechanism for the photodecomposition of $[\text{Ru}(\text{bpy})_3]^{2+}$.^[92,93] For example, the photodegradation quantum yield Φ_{deg} of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in acetonitrile at room temperature amounts to $\Phi_{\text{deg}} = 0.00024$.^[94] In cases of coordinating counterions, the photodegradation can be induced by their coordination and rise to $\Phi_{\text{deg}} \leq 0.001$.^[93–95]

1.3.2 Self-Quenching of Excited States

A molecule in its ES can undergo reactions with other molecules. The prerequisite for a bimolecular reaction between the photoexcited molecule and a substrate Q (quencher) is a sufficient long ES lifetime, basically on the nanosecond timescale or longer, in a diffusion-controlled reaction (dynamic quenching).^[84] The lifetime τ might be lower in case of static quenching if the quencher and the photoactive molecule are preorganized before excitation. Both types of quenching can be distinguished by a Stern-Volmer analysis [Eq(17)].^[96] Whereas dynamic quenching reduces the lifetime and the detected emission intensity, in static quenching only the detected emission intensity decreases with increasing concentration.

$$\frac{\phi_{PL}}{\phi_{PL,q}} = \frac{\tau}{\tau_q} = 1 + k_q \tau [Q] \quad (17)$$

The quenching process becomes an additional deactivation pathway of the ES [Eq (1)] and depends on the quenching rate constant k_q , the concentration of the quencher $[Q]$, the reduced ES lifetime τ_q and the unquenched ES lifetime τ .

During the quenching, the excited molecule itself can be transformed into a new species. Typical examples are square planar platinum(II) complexes, where a molecule in the $^3\text{MLCT}$ state reacts with a respective GS complex forming excimer adducts (self-quenching).^[97–100] The observed lifetimes τ_q show a dependence on concentration of the platinum(II) complexes. The resulting quenching rate constants k_q range mostly from 10^9 to $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for neutral platinum(II) complexes, indicating an efficient reaction.^[100] The excimer formation often occurs with $\text{Pt}^{\text{II}} \cdots \text{Pt}^{\text{II}}$ associations as well as with π - π interactions between the ligand moieties if ligands with huge π -systems are used (Figure 1.9).^[100–103]

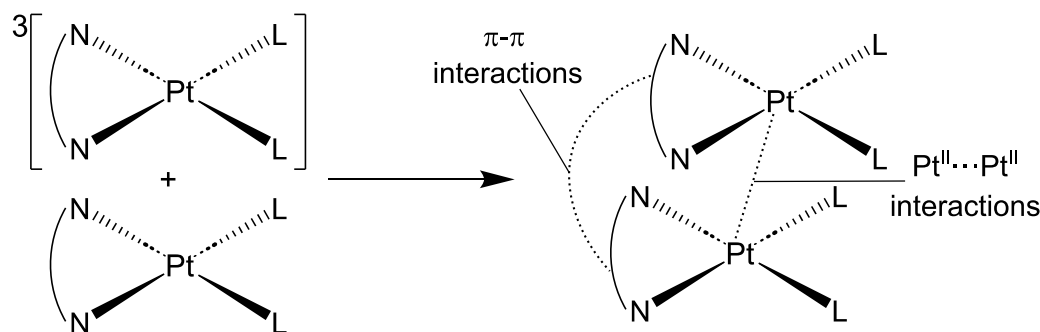


Figure 1.9: Schematic representation of a self-quenching reaction and excimer formation between a platinum(II) complex in the $^3\text{MLCT}$ state and a GS molecule forming an excimer adduct with $\text{Pt}^{\text{II}} \cdots \text{Pt}^{\text{II}}$ and π - π interactions.

Regarding self-quenching, the unquenched ES lifetime τ of the analyzed complex is unknown. A plot of the experimentally determined lifetimes τ_q or the relative quantum yields $\phi_{PL,q}$ against the concentration of the respective complex gives the quenching constant k_q from the slope and the unquenched lifetime τ from the intercept. Therefore, Eq (17) must be modified accordingly [Eq (18)(19)].

$$\frac{1}{\tau_q} = \frac{1}{\tau} + k_q [Q] \quad (18)$$

$$\frac{1}{\phi_{PL,q}} = \frac{1 + k_q \tau [Q]}{\phi_{PL}} \quad (19)$$

1.4 Photoluminescent Heavy Main Group Complexes

1.4.1 Examples of Bismuth(III) and Tetrel(IV) complexes

The photophysics of TMCs based on precious metals like ruthenium or platinum provided remarkable properties regarding long-lived ESs and phosphorescent materials. Alternatively, photoactive HMGCs containing group 15 (pnictogen) or group 14 (tetrel) elements are slowly gaining attention.^[52–55] Especially, complexes with heavy elements like bismuth, tin or lead should provide efficient ISC with subsequent phosphorescence due to the heavy-atom effect (section 1.2.2).

HMGCs based on bismuth(III) with a $(6s)^2$ electron configuration can show phosphorescence, but this is mostly limited to frozen solutions or the solid state.^[54,104–109]

For example, the $\text{Bi}(\text{phen})_2\text{Cl}_3$ complex (phen = 1,10-phenanthroline) shows phosphorescence peaking at $\lambda_p = 590$ nm with two lifetimes of $\tau_{p,1} = 14$ μs and $\tau_{p,2} = 241$ μs originating from a (XM)LCT state in the solid state at room temperature (Figure 1.10a).^[110] Likewise, $^3\text{MLCT}$ ($\text{Bi} \rightarrow \text{L}$) phosphorescence was reported by Marshak and coworkers in a six-coordinated complex $\text{Bi}(\text{bzq})_3$ (Hbzq = benzo[*h*]quinoline), which exhibits a broad emission band centered at 525 nm in THF solution at room temperature.^[111] The lifetime and photoluminescence quantum yield was determined to $\tau_p = 35$ μs and $\Phi_{\text{PL}} = 0.1$, respectively (Figure 1.10b). In addition, photodegradation of $\text{Bi}(\text{bzq})_3$ to $[\text{Bi}(\text{bzq})_2]^+$ and a free bzq ligand was observed upon UV excitation.^[111]

On the other hand, boron-dipyrromethene (BODIPY)^[112] analogs with bismuth(III) (BiDIPY) show no emission or just weak fluorescence originating from π - π^* transitions within the dipyrromethene unit.^[113–116] For example, the BiDIPY with anisoyl substituents exhibits weak fluorescence at $\lambda_f = 590$ nm in DCM solution with a quantum yield of $\Phi_{\text{PL}} = 0.002$ (Figure 1.10c).^[116]

Recently, Winter and coworkers reported a series of bismuth(III) complexes with pincer-type pyridine dipyrrolide (PDP) and halogenido ligands (Figure 1.10d).^[117] All complexes show phosphorescence at $\lambda_p = 606$ – 645 nm in 2-methyl-THF at 77 K. The origin of this emission was ascribed to a mixed LMCT/ILCT state with contribution of the bismuth centered vacant p-type orbital.^[117] The phosphorescence decay is biexponential with lifetimes in the μs regime.

Heterocycles containing bismuth(III) recently gained attention regarding their photoluminescent properties and their promising implementation into optoelectronic applications.^[118] Similar to the BiDIPY compounds, the ES usually consist of π - π^* character within their aromatic backbone with no or minimal bismuth participation. For instance, the bismuth(III) rhodamine equivalent displays weak fluorescence at $\lambda_f = 658$ nm with a fluorescence quantum yield of $\Phi_f = 0.039$ in aqueous buffer (pH = 7.4) at room temperature (Figure 1.10e).^[119] Though, the presence of a long-lived dark triplet state was determined by photo-generation of $^1\text{O}_2$ with a respective quantum yield of $\Phi(^1\text{O}_2) = 0.66$, making its useful as a potential photosensitizer.^[119,120]

Also, photoluminescent bismoles (bismuth(III) pyrrole congeners) have gained attention in research and application over the past few decades.^[118,121–124] One example is a series of phosphorescent dithienobismoles displaying phosphorescence at $\lambda_p = 601$ – 635 nm with lifetimes of $\tau_p = 2.1$ – 6.3 μs in chloroform at room temperature (Figure 1.10f). However, in the solid state only the SiMe_3 derivatives show phosphorescence. The authors argued that ES quenching effects due to π - π stacking are prevented by the bulky SiMe_3 groups.^[124]

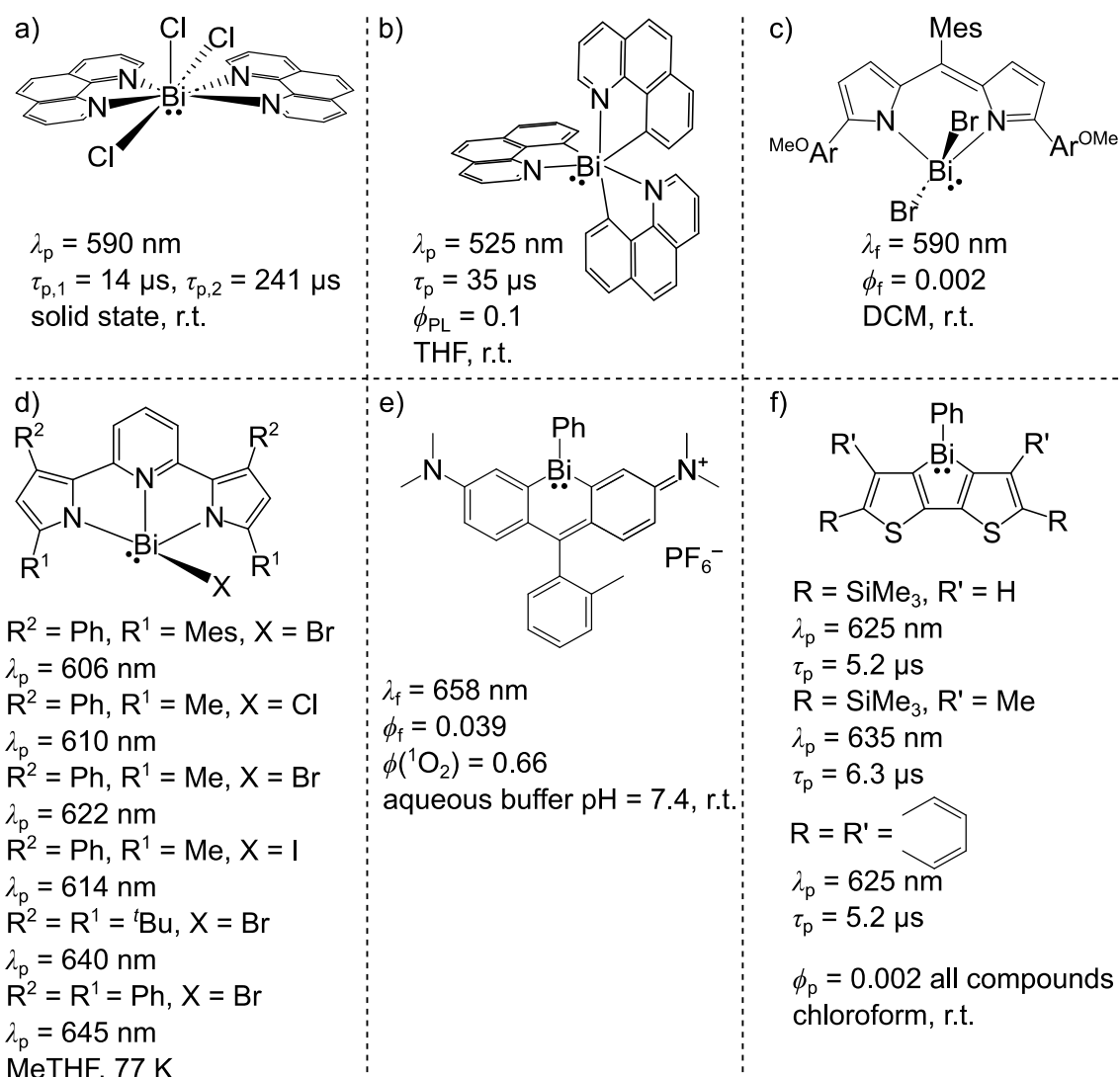


Figure 1.10: Selected photoluminescent bismuth(III) complexes with their photophysical data.

Overall, the field of photoluminescent bismuth(III) complexes is evolving concerning long-lived ESs and potential phosphorescent materials. Therefore, isoelectronic lead(II) complexes might possess similar properties. However, only a few examples of photoactive lead(II) compounds have been reported so far and their photophysical performance does not compete with the mentioned bismuth(III) examples (section 1.5.3).

One reason for that could be the different toxicity levels between lead and bismuth compounds. Whereas bismuth is considered nontoxic, the consumption of lead causes devastating effects in the human body.^[125,126] On the other hand, the lighter tin and its most compounds are regarding toxicity on an acceptable level.^[127]

Regardless of the central element, the research of photoactive tetrel complexes is slowly developing, as well.^[52] Currently, the oxidation state +IV dominates in photoluminescent tetrel complexes. Several examples have been reported in the last decades, displaying potentially photoactive triplet states and fluorescence.^[118,128,129]

Milsmann and coworkers reported a series of hexacoordinated PDP tetrel(IV) ($E = \text{Si-Sn}$) complexes exhibiting strong thermally activated delayed fluorescence (TADF) at room temperature in THF solution (Figure 1.11a).^[130] The emissive S_1 state possesses LL'CT character, describing the transfer from one ligand to another, whereas the T_1 state is described as an ILCT state with a pyrrolate to pyridine charge transfer within the ligand moiety. The detected TADF centers at $\lambda_{em} = 519\text{--}527 \text{ nm}$ with lifetimes in the ms regime

and photoluminescence quantum yields up to 0.49, giving promising prerequisites for the design of light-emitting diodes. Comparable hexacoordinated silicon(IV) complexes with 2,6-bis(benzimidazol-2-yl)pyridine ligands also demonstrate promising potential for electron transport and electroluminescence applications.^[131,132]

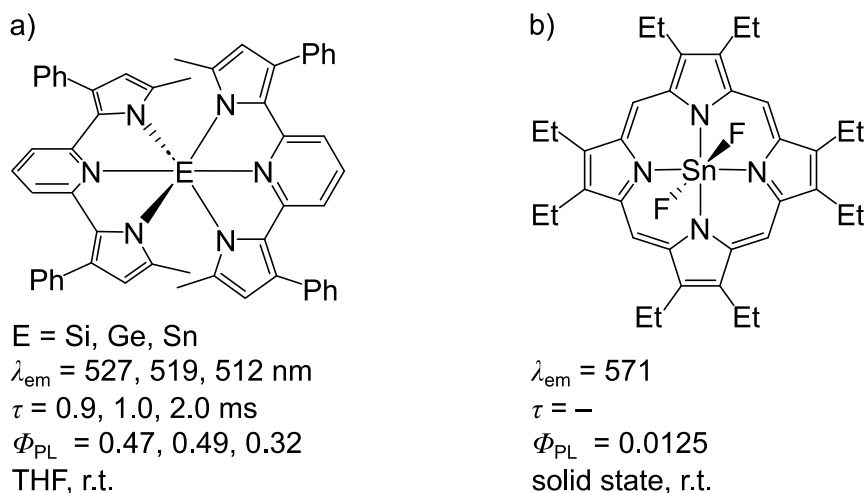


Figure 1.11: Molecular structures of selected tetrel(IV) TADF emitters incorporated in a) dipyrrolo-pyridine and b) octaethylporphyrin frameworks.

Beside these, the octaethylporphyrin difluorido tin(IV) complex also shows weak TADF at $\lambda_{em} = 571 \text{ nm}$ with a photoluminescence quantum yield of roughly $\Phi_{PL} = 0.0125$ in the solid state at room temperature (Figure 1.11b).^[133] These properties permitted triplet exciton harvesting in electroluminescent devices.

Cyclometalated tin(IV) and lead(IV) complexes with bis(indolyl)pyridine ligands exhibit fluorescence and LC phosphorescence with lifetimes in the μs regime in frozen solution at 77 K (Figure 1.12).^[134] Similar properties were observed in a number of tetrel(IV) porphyrin compounds, as well.^[135,136]

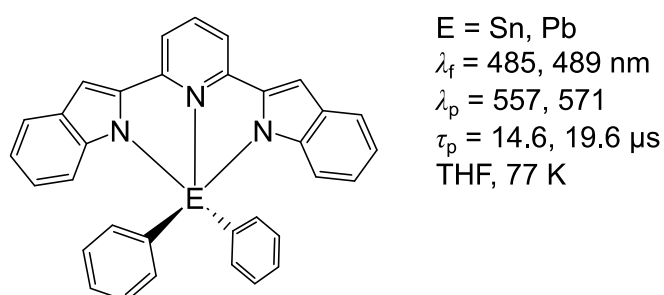


Figure 1.12: Molecular structure of cyclometalated bis(indolyl)pyridine tetrel(IV) complexes and their respective photophysical data.

Beside tetrel(IV) complexes showing TADF or phosphorescent properties, a large number of purely fluorescent emitters have been investigated and implemented in applications like biomedical molecular imaging.^[137–142]

In halogenated quinoline tin(IV) complexes $\text{Sn}(\text{QO})_2\text{X}_2$ ($\text{QOH} = 8\text{-hydroxyquinoline}$, $\text{X} = \text{Cl, F}$) the fluorescence at $\lambda_f = 531 \text{ nm}$ is considerably increased by exchange from chloride to fluoride with fluorescence quantum yields from $\Phi_{f,\text{Cl}} = 0.002$ to $\Phi_{f,\text{F}} = 0.01$, respectively (Figure 1.13).^[143] This enhancement is explained by the stronger donor properties of the fluoro ligand leading to a stronger rigidification of the system.

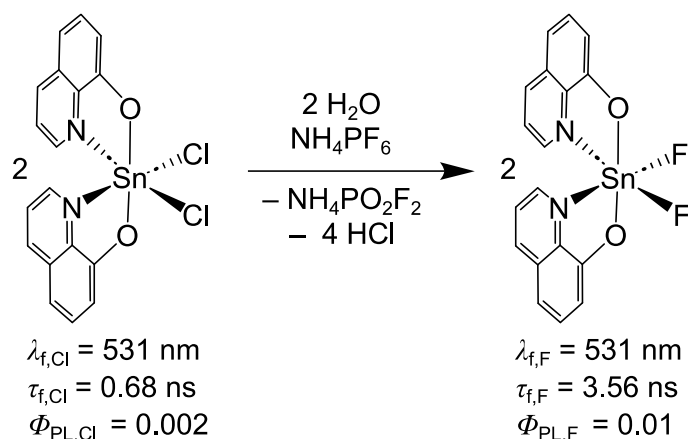


Figure 1.13: Molecular structure of $\text{Sn}(\text{QO})_2\text{X}_2$ with $\text{Cl}^- \rightarrow \text{F}^-$ substitution and the respective photophysical data in acetonitrile at room temperature.

Tetrel(IV) complexes present a variety of photophysical properties and despite a few examples, this field is still developing. However, all examples have one thing in common. The photoactive ESs are usually LL'CT or ILCT states. Distinct contributions from tetrel centered orbitals within the electronic transition are unusual.

One explanation is the σ^* -character of tetrel centered s- and p-type orbitals after complex formation, especially in cases of the typical fivefold or sixfold coordination. Consequently, excitation into a hypothetical LMCT state including σ^* -orbitals might lead to strong distortions in the ES. Hence, the variety of relevant electronic transitions in tetrel(IV) complexes is limited.

Thus, the change to electron richer tetrel centers would induce electronic transitions with metal centered contributions involving potential non-bonding tetrel centered orbitals and open up access to versatile ESs, comparable with the case of isoelectronic bismuth(III) complexes. Indeed, tetrel(II) complexes are potentially capable of showing a wide range of electronic transitions comparable with TMCs (section 1.5.3). Therefore, the attention of this work lies on tetrel(II) complexes with tin(II) and lead(II) as tetrel centers.

1.5 Tetrel(II) Complexes

1.5.1 Structural Properties

Tetrel(II) complexes are closely related to tetrylenes (EL_2), including carbenes (CL_2) and its heavier homologues silylenes (SiL_2), germylenes (GeL_2), stannylenes (SnL_2) and plumbylenes (PbL_2).^[144–149]

Over the last few decades, carbenes have become a major field in chemistry, largely owing to a solid understanding of their stability.^[144] Much attention has also been dedicated to the heavier analogs and approaches to stabilize as well as isolate these species have been established.^[145,146] These heavy tetrylenes show distinctive characteristics compared to the lighter carbenes and many advances concerning structural properties or reactivity have been achieved so far.^[147–150]

In contrast to carbon, the heavier group 14 elements (tetrels) provide a lower affinity toward hybridization. These elements prefer the $(ns)^2 (np)^2$ ($n > 2$) valence electron configuration.^[145] The reason for this lack of hybridization is due to the differences in valence orbital radii (Figure 1.14). Whereas the valence s- and p-orbitals of carbon have almost equal radii, the radii of the heavier elements are spatially more separated.^[150] This stems from the Pauli repulsion caused by the $(n-1)p$ -orbitals of the lower-lying shell which increase the radii of the valence np-orbitals ($n > 2$) at the heavier element (primogenic effect).^[151,152] In case of carbon the core consists only of the 1s-orbital leading to an expansion of the 2s-orbital radii to a value similar to the 2p-orbital.^[150] The similar values in carbon facilitate hybridization, whereas the large differences in the heavier homologues inhibit hybridization. The additional contraction of the 6s-orbital can be attributed to relativistic effects arising from the inner s shells.^[153]

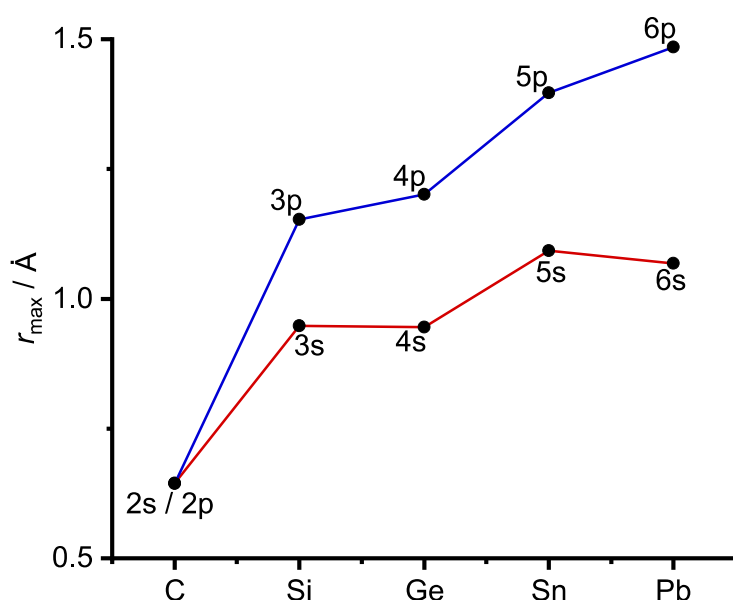


Figure 1.14: Variation in the radii of the ns and np valence orbitals. (adapted from ref.^[154], the values for $r_{\max}$ are taken from ref.^[155])

The radial separation of ns/np orbitals typically causes a singlet GS in a heavy tetrel(II) complex (Figure 1.15). The GS wavefunction is characterized by a tetrel centered fully occupied non-bonding (n_s) orbital and a vacant π -orbital (p_π) of mainly high s- and p-character, respectively.^[145] The energy of these orbitals can be influenced by several electronic and steric effects.

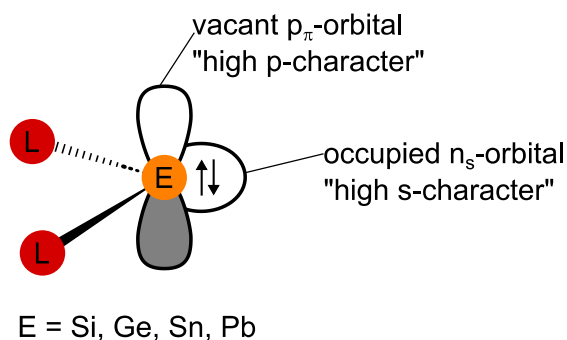


Figure 1.15: Schematic representation of the electronic structure of heavy tetrel(II) complexes EL_2 . The separation between the n_s - and p_π -orbital leads to a singlet GS.

The relative stability of a singlet GS in a tetrel(II) complex increases with descending element row, induced by the larger energy gap between the occupied n_s -orbital (HOMO) and the vacant p_π -orbital (LUMO).^[147,145] Certainly, this HOMO-LUMO gap (ΔE_{HL}) is a crucial feature that dictates the stability of the singlet GS and its reactivity, e.g. in oxidative addition reactions.^[156] Regardless of the tetrel center, ΔE_{HL} can be influenced by the electronegativity of the substituents, which are denoted as ligands in this work (inductive effect) (Figure 1.16).^[144,156,157]

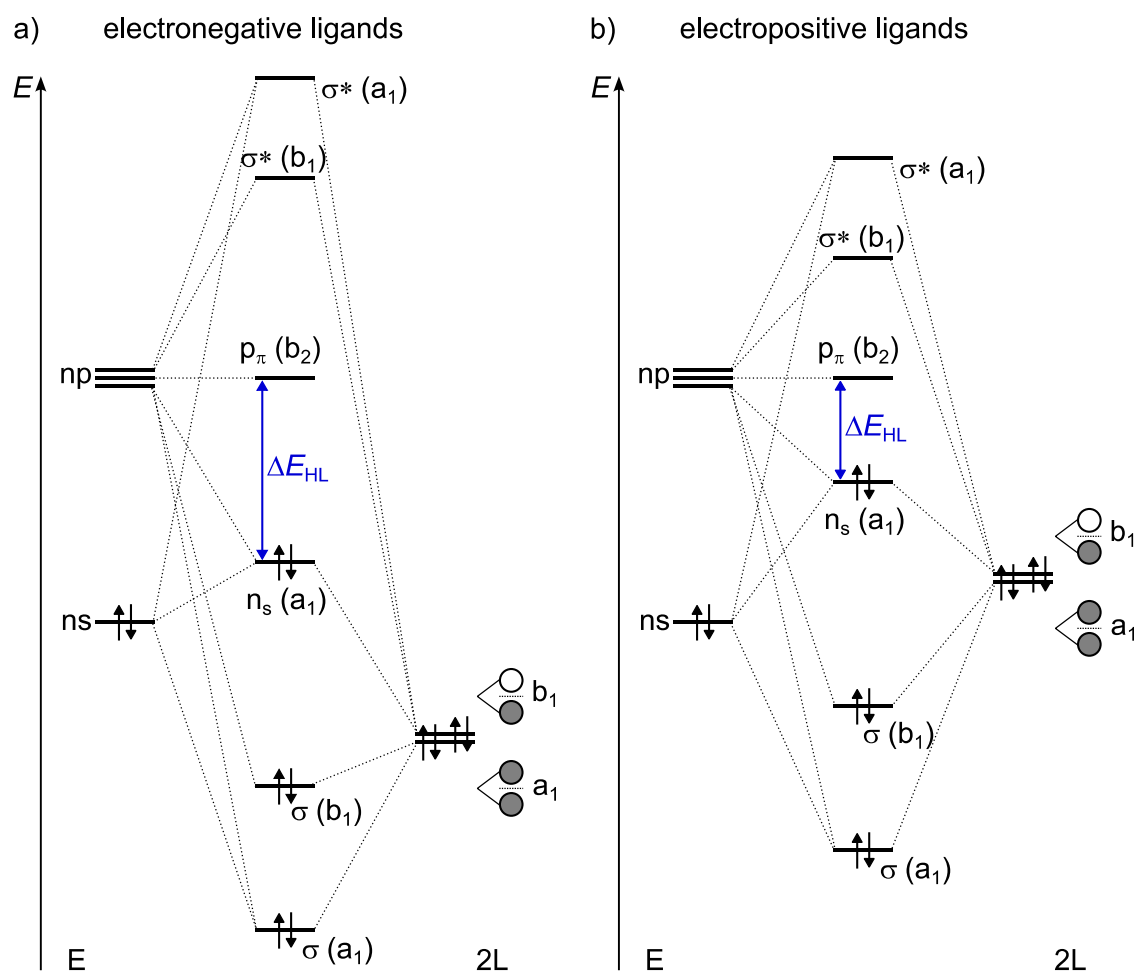


Figure 1.16: Molecular orbital diagram and electron population of a heavy tetrylene complex EL_2 in C_{2v} symmetry with a) electronegative ligands and b) electropositive ligands. The respective HOMO-LUMO gap ΔE_{HL} in blue.

This can be rationalized by a molecular diagram for a simple heavy tetrylene (EL_2) assuming C_{2v} symmetry: Electron-withdrawing ligands stabilize the n_s -orbital by enhancing its s-character, the p_π -orbital remains unchanged. Consequently, ΔE_{HL} increases with stabilization of the singlet GS (Figure 1.16a). On the contrary, electron-donating ligands induce more p-character in the n_s -orbital and lead to a smaller ΔE_{HL} (Figure 1.16b). This suggests that more p-character shifts the n_s -orbital to higher energies.

In general, heavy tetrylenes are considered highly reactive, since they provide only six valence electrons making them electron deficient relative to the octet rule. Therefore, the reactivity is mainly based on the vacant p_π -orbital.^[145] However, the reactivity of this orbital can be diminished by implementing π -donating ligands like halides, ^-OR or $^-NR_2$. The stabilization occurs by interacting of the additional lone pairs of the heteroatoms with the vacant p_π -orbital of the tetrel center, resulting in a more antibonding p_π^* -orbital as LUMO (mesomeric effect, Figure 1.17a).^[144,145] Thus, the HOMO-LUMO gap ΔE_{HL} increases and stabilizes the singlet GS of the tetrylene additionally (Figure 1.17b).

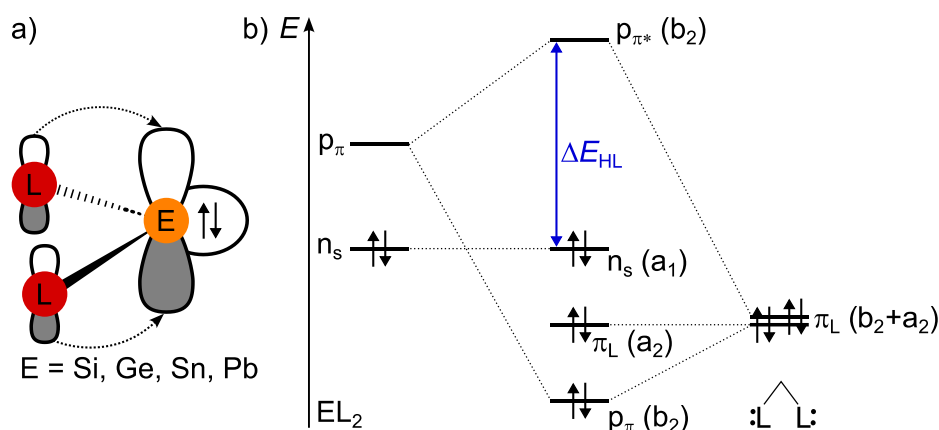


Figure 1.17: a) Schematic representation of the mesomeric effect between the vacant p_π -orbital of the tetrel center and the π -donating ligands L. b) Molecular orbital diagram and electron population describing the interaction of a heavy tetrel(II) complex EL_2 with the additional occupied π -orbitals of the ligands L. The resulting high HOMO-LUMO gap ΔE_{HL} is marked in blue.

A more effective stabilization strategy is the introduction of an additional inter- or intramolecular donor that increases the coordination number ($C > 2$) of the tetrel center (Figure 1.18a). This donor-stabilization of the vacant p_π -orbital decreases the reactivity tremendously and destabilizes the orbital by adding σ^* -character (p_{σ^*}) (Figure 1.18b).^[145,158–160] For example, in the stannylene $Sn(dpma)$ ($H_2dpma = N,N$ -(dipyrrolyl)-2-methyl)- N -methylamine) the two pyrrolate moieties establish the covalent bond and the amine operates as the additional donor (Figure 1.18c).^[160]

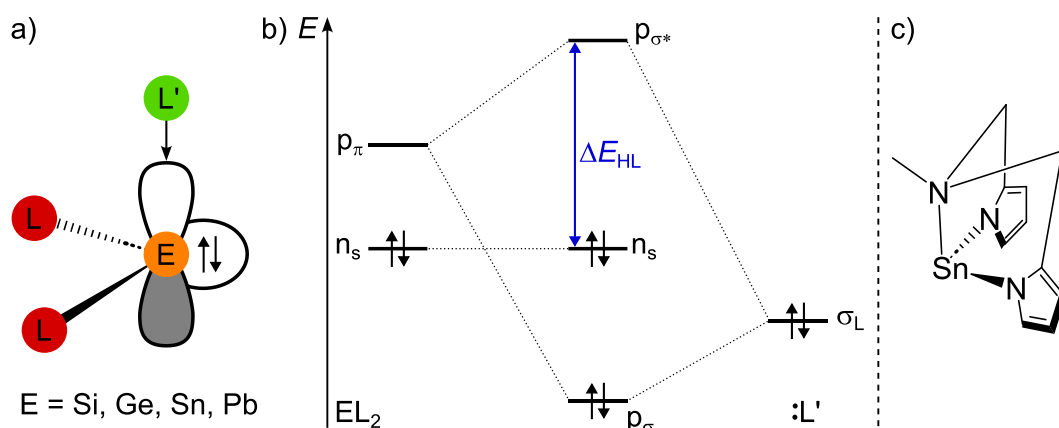


Figure 1.18: a) Schematic representation of an additional donor-stabilization in a tetrylene, due to the additional coordination of L' in green. b) Molecular orbital diagram and electron population describing the interaction of the additional donor L' with the p_π -orbital, resulting in a vacant p_{σ^*} -orbital. The HOMO-LUMO gap ΔE_{HL} is marked in blue. c) The structure of the stannylene $\text{Sn}(\text{dpma})$ as an example of donor-stabilization.^[160]

Beyond the electronic stabilization strategies, the introduction of bulky substituents can further reduce the reactivity due to the vacant p_π -orbital. In this case, the unoccupied p_π -orbital is sterically shielded which prevents inter- or intramolecular reactions such as nucleophilic attack or self-oligomerization/dimerization (Figure 1.19a).^[145] A strategy, that is particularly applied to aryl or alkyl substituted tetrylenes (ER_2).^[145,146]

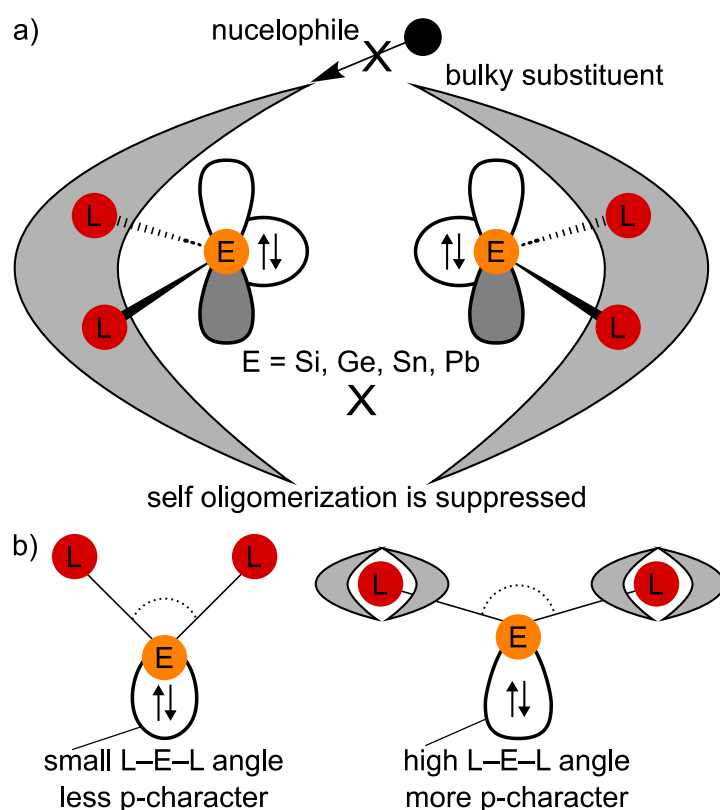


Figure 1.19: a) The role of bulky substituents for the stabilization of tetrylenes, adapted from ref.^[145] b) the influence of bulky substituents in the n_s -orbital: sterically less demanding substituents create a small $L-E-L$ angle and maintain less p -character in the n_s -orbital. On the other hand, bulky substituents provoke a large $L-E-L$ angle leading to higher p -character in the n_s -orbital.

Furthermore, bulky substituents do not solely affect molecular reactivity, involving the p_π -orbital. Moreover, the steric effects can also dictate the energy of the n_s -orbital and the resulting HOMO-LUMO gap ΔE_{HL} . In heavy tetrylenes, bulky substituents increase the L–E–L angle compared to smaller substituents (Figure 1.19b). A large L–E–L angle leads to an increase of p -character in the n_s -orbital, which shifts the orbital to higher energies and concomitantly diminishes the ΔE_{HL} .^[144,145,161]

Supposing the same ligand is applied, the L–E–L angle decreases as the element row descends and consequently, the ΔE_{HL} increases. This is due to the radial expansion of the tetrel s and p -orbitals on the one hand and to the longer tetrel ligand (E–L) bonds, provoking less steric repulsion, on the other hand. This aspect was discussed e.g. in a series of tetrylene hydrides (EH_2).^[162,163]

The listed stabilization strategies become relevant especially by comparing stannylenes and plumbylenes. Generally, insufficiently stabilized plumbylenes suffer from thermal lability and high sensitivity toward light, which dramatically hinders the handling and access to these compounds.^[147,148] On the contrary, stannylenes present less sensitivity toward light and high temperatures as well as better accessibility.

The unique electronic structure of heavy tetrylenes enables a large variety of reactions. In fact, a tetrylene can act as a Lewis base with its occupied n_s -orbital or as a Lewis acid with its electrophilic vacant p_π -orbital (Lewis-amphoteric character^[164]), leading to reactions like coordination to transition metal complexes^[165–168], cycloaddition^[169,170] or oxidative addition^[156,171–174] to σ -bonds like aryl/alkyl halides.

1.5.2 Dimerization

Tetrel(II) complexes are capable of dimerization and formation of alkene ($L_2C=CL_2$) analogs like disilenes ($L_2Si=SiL_2$), digermenes ($L_2Ge=GeL_2$), distannenes ($L_2Sn=SnL_2$) or diplumbenes ($L_2Pb=PbL_2$).^[175]

In 1973, Lappert and coworkers published the first stable stannylene $Sn[CH(SiMe_3)_2]_2$ which forms distannenes with a *trans*-bent structure in the solid state.^[176–179] This *trans*-pyramidalization was deduced from a double donor-acceptor interaction, describing an overlap between the filled n_s -orbital of one SnL_2 fragment with the vacant p_π -orbital of the second SnL_2 fragment (Figure 1.20a).^[177,179] Alternatively, the presence of a resonating nonbonded electron pair between the tin centers and a Sn–Sn single bond was also proposed, rationalizing the *trans*-pyramidalization (Figure 1.20b).^[179,180]

In fact, the *trans*-bent or *trans*-pyramidal geometry, along with a twisted arrangement of the EL_2 moieties, is a common structural characteristic of heavy ditetrenes, in contrast to the planar core in alkenes with a σ - and π -bond.^[181–184]

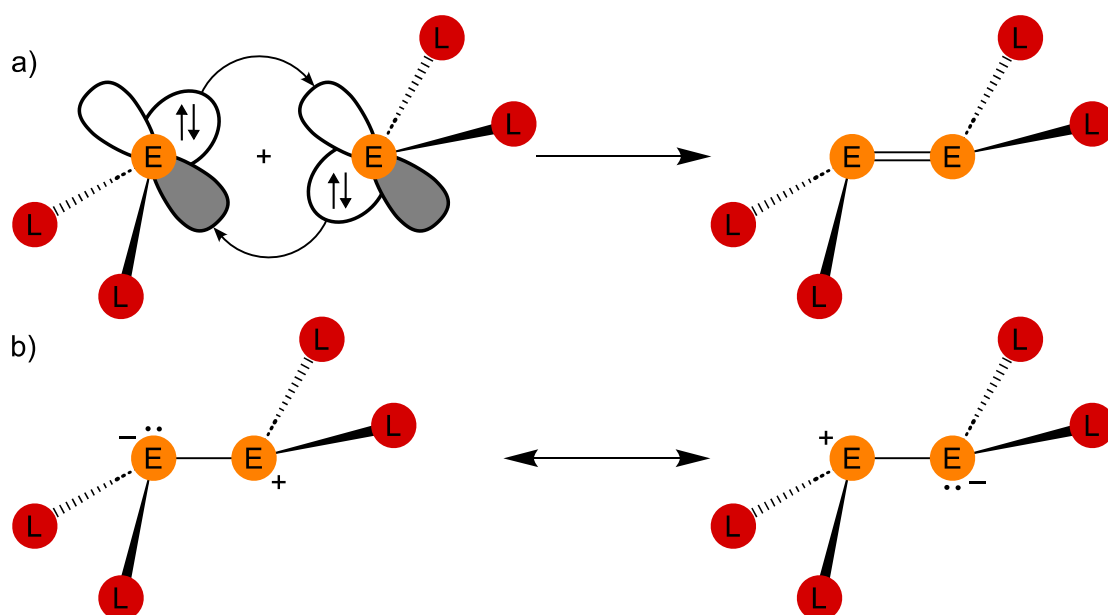


Figure 1.20: Schematic representation of a) the double donor-acceptor interaction and b) the resonating nonbonded electron pair in $L_2E=EL_2$ systems with E = heavier group 14 elements.

A criterion for the existence and for the structural change of $E=E$ double bonds provides the Carter-Goddard-Malrieu-Trinquier (CGMT) approach.^[185–188] The degree of distortion in a ditetrene ($L_2E=EL_2$) depends on the sum of the singlet-triplet energies $\Sigma\Delta E_{ST}$ of the respective single fragments EL_2 . Note, the singlet-triplet energy gap ΔE_{ST} is related to the aforementioned HOMO-LUMO gap ΔE_{HL} (Figure 1.16). This sum of the required singlet-triplet energies $\Sigma\Delta E_{ST}$ has been related to the energy from a σ - and π -bond formation $E_{\sigma+\pi}$ in a classical planar case (D_{2h}) and the following qualitative rules have been established:

- 1) If $\Sigma\Delta E_{ST} < 1/2 E_{\sigma+\pi}$ the resulting double bond is planar.
- 2) If $E_{\sigma+\pi} > \Sigma\Delta E_{ST} > 1/2 E_{\sigma+\pi}$ a *trans*-bent structure occurs.
- 3) If $\Sigma\Delta E_{ST} > E_{\sigma+\pi}$ there is no double bond formation.

Alternatively, $E_{\sigma+\pi}$ can be also assigned as the energy of breaking a planar double bond in two separate triplet fragments.^[189]

Overall, carbene fragments with triplet GS ($\Delta E_{ST} < 0$) create stable double bonds with planar structure. In contrast, heavy tetrylenes possess in most cases, with exceptions for silylenes^[190,191], a singlet GS ($\Delta E_{ST} > 0$) which leads to *trans*-pyramidal geometries. If the singlet GS is strongly stabilized ($\Delta E_{ST} \gg 0$), no dimerization occurs (Table 1.2).

In other words, the better the singlet GS is stabilized the less likely dimerization arises. Because of that, *Lappert's* diamino stannylene and plumbylene ($E[N(\text{SiMe}_3)_2]_2$, $E = \text{Sn, Pb}$) are monomeric in the solid state.^[192]

Table 1.2: Calculated sum of singlet-triplet gaps ($\Sigma\Delta E_{ST}$) in hydrides EH_2 ($E = \text{C-Pb}$) and double bond energies $E_{\sigma+\pi}$ of hypothetical planar geometries in kJ/mol, with the expected structure of the $\text{H}_2\text{E}=\text{EH}_2$ species.^[189]

EH_2	$\Sigma\Delta E_{ST}$	$1/2E_{\sigma+\pi}$	$E_{\sigma+\pi}$	Expected Structure
CH_2	-130	397	794	planar
SiH_2	148	214	427	planar
GeH_2	192	188	377	<i>trans</i> -bent
SnH_2	194	156	311	<i>trans</i> -bent
PbH_2	286	131	262	no dimer

A different approach to rationalize the *trans*-bent structure in heavy ditetrenes derives from MO theory and the symmetry-based interaction of the frontier orbitals in a second-order Jahn-Teller (SOJT^[193]) effect which leads to a change from D_{2h} (planar) to C_{2h} (*trans*-bent) symmetry (Figure 1.21).^[194,195]

In a planar $\text{L}_2\text{E}=\text{EL}_2$ system the π -orbital (HOMO) and the σ^* -orbital (LUMO+1) are orthogonal and cannot mix with each other. However, $D_{2h} \rightarrow C_{2h}$ symmetry lowering along the b_{1g} vibrational mode (*trans*-pyramidalization mode) enables the mixing of these orbitals. The same approach holds for the σ -orbital (HOMO-1) and π^* -orbital (LUMO) mixing. The prerequisite for a SOJT distortion in $\text{L}_2\text{E}=\text{EL}_2$ systems is an energetically close position of the relevant frontier orbitals which occurs with rising atomic number of E due to resulting weaker bonds.^[194] An equivalent discussion for *cis*-bent structures in $[\text{L}_2\text{E}=\text{EL}_2]^-$ anions has also been conducted in this context.^[195] In this case, $D_{2h} \rightarrow C_{2v}$ symmetry lowering occurs along the b_{2u} mode (*cis*-pyramidalization mode).

Additionally, quantum chemical investigations revealed that the dimerization of heavy tetrylenes is driven by significant contributions from strong electrostatic interactions and London dispersion forces.^[154,196,197]

Except of a few examples,^[198-202] the $\text{L}_2\text{E}=\text{EL}_2$ bonds in heavy ditetrenes are weak and dissociate in solution.^[145,182,183] Besides, the effects which influence the dimerization in the GS may play a role in the ES, as well.

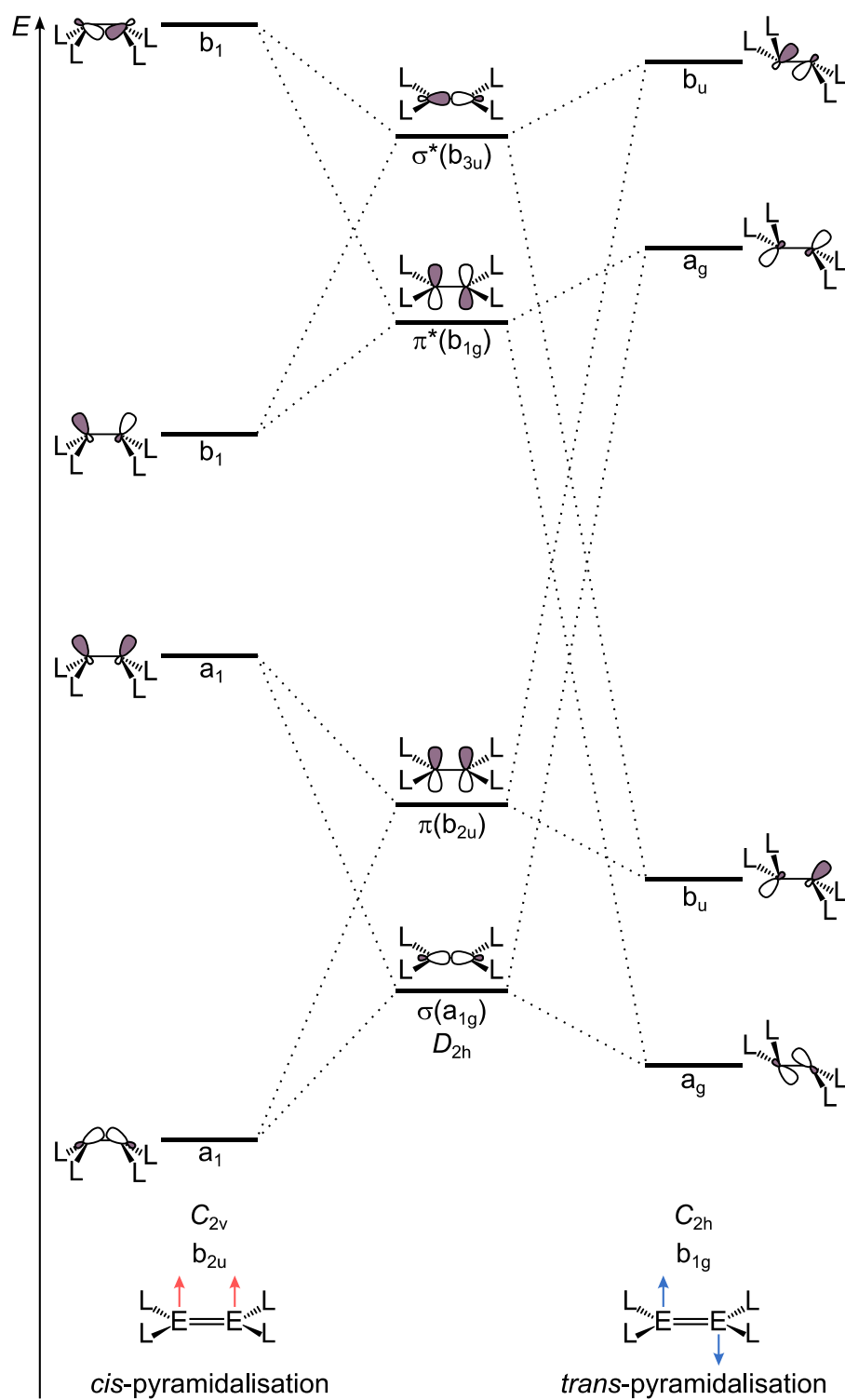


Figure 1.21: Correlation diagram for the changes in symmetry and energy of the frontier orbitals in $L_2E=EL_2$ from planar (D_{2h}) to cis -bent (C_{2v}) and $trans$ -bent (C_{2h}) geometry.

1.5.3 Photoactivity

In principle, the theory and knowledge developed for photoactive TMCs (section 1.3.1) can be transferred to heavy tetrel(II) complexes, as well. Owing to their unique electronic structure (section 1.5.1), a wide range of electronic transitions are possible. Consequently, MC, MLCT, LMCT, ILCT or LL'CT states must be considered and discussed when investigating the photophysical properties (Figure 1.22).

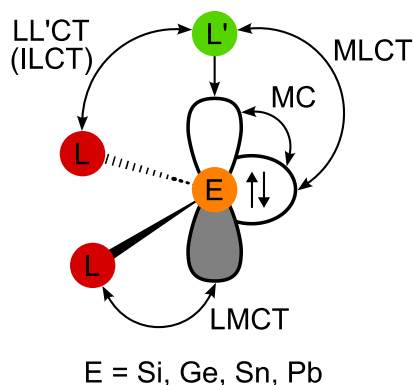


Figure 1.22: Schematic representation of selected electronic transitions in homoleptic tetrel(II) complexes EL_2 in case with additional Donor (L') stabilization, excluding LC and other possible LMCT ($L' \rightarrow E$) and MLCT ($E \rightarrow L$) transitions. In this nomenclature (MC, MLCT, LMCT), the group 14 element is considered a metal M throughout.

So far, examples of photoluminescent tetrel(II) complexes are very scarce. Mostly, the emission is either very weak or limited to frozen solutions and/or the solid state.^[53–55] This is surprising because since 1940 simple emissive tetrel(II) halido complexes have already been observed and reported.^[203]

Vogler and coworkers reevaluated this study on the basis of the halido complexes $[EX_3]^-$ ($E = \text{Ge–Pb}$; $X = \text{Cl}$; $E = \text{Sn, Pb}$; $X = \text{Br}$) and $[\text{PbX}_4]^{2-}$ ($X = \text{Cl, Br}$).^[204,205] All complexes display phosphorescence from ^3MC states at $\lambda_p = 510\text{–}604\text{ nm}$ after excitation with UV light in acetonitrile solution at room temperature.

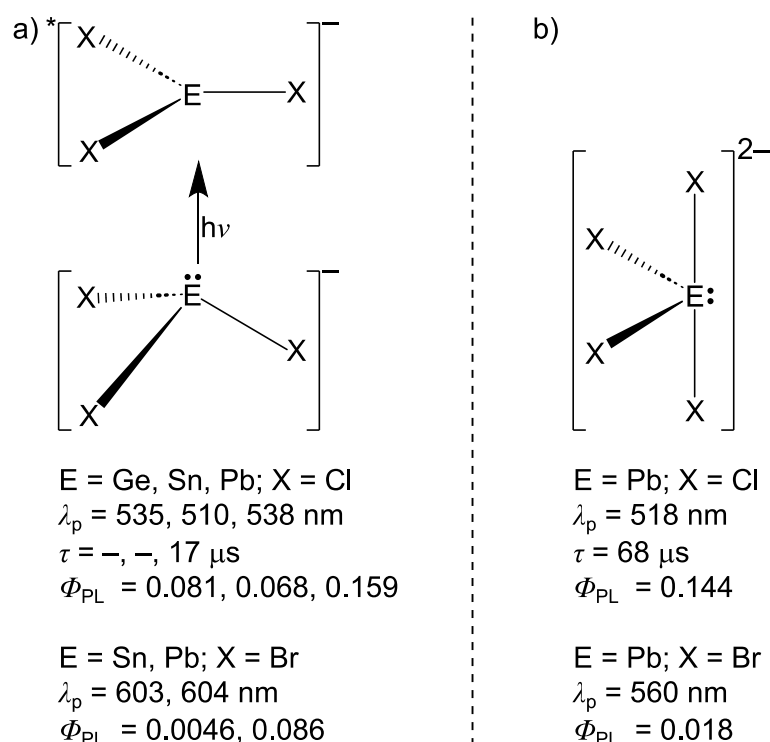


Figure 1.23: Molecular structure and photophysical data of tetrel(II) halido complexes a) $[\text{EX}_3]^-$ and b) $[\text{EX}_4]^{2-}$ in acetonitrile at room temperature.

For the $[\text{EX}_3]^-$ ions, the emissive ^3MC state is associated with a large structural reorganization from C_{3v} to D_{3h} symmetry which enables efficient non-radiative deactivation (Figure 1.23a).^[204] In this series, the tin(II) and germanium(II) complexes show short photoluminescence lifetimes τ below the detection limit as well as low photoluminescence quantum yields $\Phi_{PL} = 0.081$ (Ge, Cl); 0.068 (Sn, Cl); 0.0046 (Sn, Br) compared to $\tau = 17 \mu\text{s}$ for $[\text{PbCl}_3]^-$ and $\Phi_{PL} = 0.159$ (Pb, Cl); 0.086 (Pb, Br).^[204,205] However, $[\text{SnCl}_3]^-$ is still able to undergo bimolecular photooxidation to SnOCl_2 with oxygen upon excitation at $\lambda_{\text{exc}} = 254 \text{ nm}$ despite of its short lifetime τ .^[206] The tetra-coordinated $[\text{PbX}_4]^{2-}$ (X = Cl, Br) complexes display a butterfly (or seesaw) structure with C_{2v} symmetry. ^3MC phosphorescence was determined with quantum yields of $\Phi_{PL} = 0.144$ (Pb, Cl); 0.018 (Pb, Br) in acetonitrile at room temperature (Figure 1.23b).^[204,205]

Regarding emissive lead(II) compounds, a series of bis(β -diketonato) lead(II) complexes, reported by Vogler and coworkers, exhibits blue to green ILCT phosphorescence in the solid state at room temperature (Figure 1.24a).^[207] This weak emission is attributed to a large geometric reorganization leading to fast non-radiative relaxation. However, no photoluminescence lifetimes and quantum yields were reported. In the case of the lighter hexafluoroacetylacetonato tin(II) homologue no photoluminescence has been observed.^[208]

Scandola and coworkers reported the emission properties of the complex $\text{Pb}(\text{QO})_2$ (QOH = 8-hydroxyquinoline).^[209] This lead(II) compound shows a weak green fluorescence and a much weaker phosphorescence originating from $^3\text{ILCT}$ states in *N,N*-dimethylformamide (DMF) at room temperature ($\lambda_f = 550 \text{ nm}$, $\tau_f = 0.4 \text{ ns}$, $\Phi_f \approx 0.003$; $\lambda_p \approx 650 \text{ nm}$, $\tau_p = 3 \mu\text{s}$, $\Phi_p < 0.0001$) as well as glassy ethanol at 77 K ($\lambda_f = 510 \text{ nm}$, $\tau_f < 20 \text{ ns}$; $\lambda_p \approx 610 \text{ nm}$, $\tau_p = 180 \mu\text{s}$) (Figure 1.24b). The ILCT phosphorescence of $\text{Pb}(\text{QO})_2$ can be quenched by energy transfer in bimolecular reactions (section 1.3.2) with $[\text{Cr}(\text{CN})_6]^{3-}$ in DMF with a quenching rate constant of $k_q = 3.7 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$.^[209]

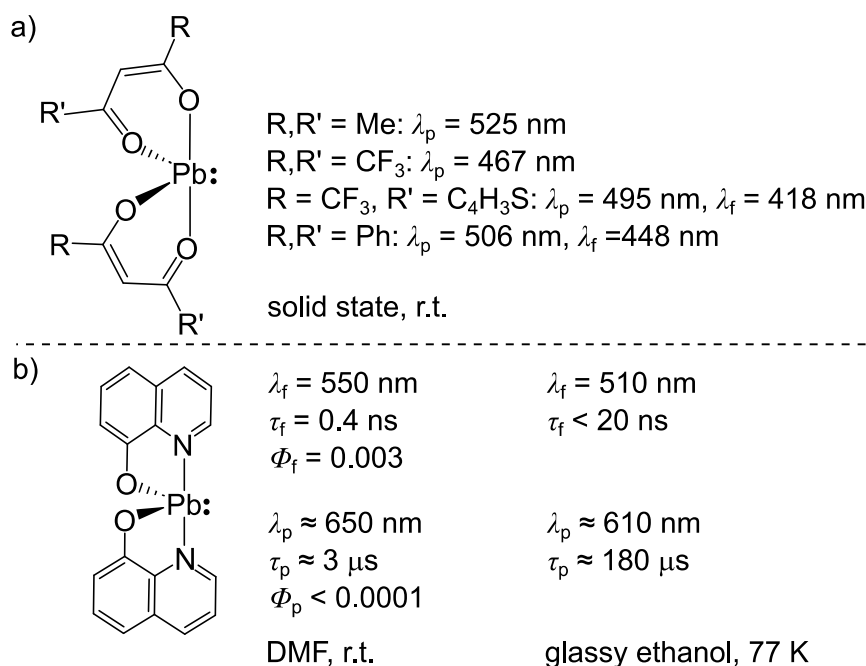


Figure 1.24. Molecular structure and photophysical data of a) β -diketonato lead(II) complexes in the solid state at room temperature and b) $\text{Pb}(\text{QO})_2$ in DMF at room temperature and glassy ethanol at 77 K, respectively.

Several coordination polymers of lead(II) with polydentate tetrazolato ligands show phosphorescence from $^3\text{ILCT}$, $^3\text{MLCT}$ and ^3MC states with contribution of $^3\text{XLCT}$ (halide-to-ligand CT). The highest photoluminescence lifetimes and quantum yields are up to $\tau_p = 1.55 \text{ ms}$ and $\Phi_{\text{PL}} = 0.165$ in the solid state.^[210] The molecular lead(II) complex with 6,6'-bis(1*H*-tetrazol-5-yl)-2,2'-bipyridine as proligand displays $^3\text{MLCT}$ phosphorescence with lower lifetimes and quantum yields compared to the polymers ($\lambda_p = 593 \text{ nm}$, $\tau_p = 347.5 \mu\text{s}$, $\Phi_{\text{PL}} = 0.02$).^[210] Also, various dipyrrynato carboxylate germanium(II) complexes emit photoluminescence at $\lambda_{\text{em}} = 589\text{--}598 \text{ nm}$ in toluene and $\lambda_{\text{em}} = 613\text{--}686 \text{ nm}$ in the solid state at room temperature.^[211]

In dipyrromethene tin(II) complexes, the substitution of a chlorido ligand with a weakly coordinating triflate (OTf^-) ligand increases the photoluminescence quantum yield from $\Phi_{\text{PL,Cl}} = 0.04$ to $\Phi_{\text{PL,OTf}} = 0.42$ with a small bathochromic shift of the observed fluorescence from $\lambda_{f,\text{Cl}} = 518 \text{ nm}$ to $\lambda_{f,\text{OTf}} = 524 \text{ nm}$ (Figure 1.25).^[212] This substantial increase in the quantum yield can be explained by an evaluation of the GS molecular orbitals using DFT calculations. The emissive $\pi\text{--}\pi^*$ transitions are quenched by close lying non-luminescent MLCT states, which are shifted to higher energies after Cl^-/OTf^- exchange.^[212]

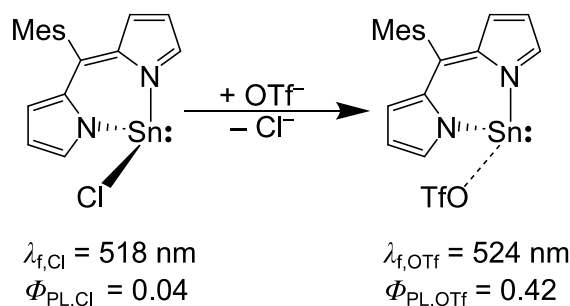


Figure 1.25: Molecular structure of the dipyrromethene tin(II) complex with Cl^-/OTf^- substitution and resulting photoluminescence quantum yield enhancement in benzene solution at room temperature.

Recently, works from Dodonov and coworkers of germanium(II) and tin(II) imide dimers bearing a planer E_2N_2 core ($E = \text{Ge}, \text{Sn}$) presented extraordinary photoluminescent properties.^[213,214] The emissive ESs are characterized as mixed ($n_s \rightarrow p_\pi$) ^3MC and ($N \rightarrow E$) $^3\text{LMCT}$ states by TD-DFT calculations (Figure 1.26).

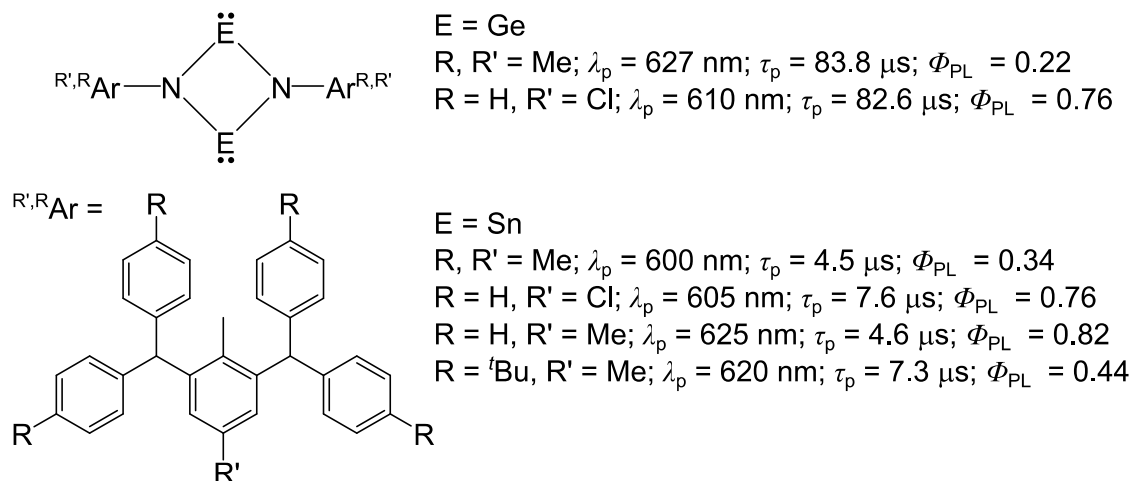


Figure 1.26: Molecular Structure and photophysical data of the E_2N_2 dimers in the solid state at 300 K.

Both germanium(II) compounds show phosphorescence upon $\lambda_p = 610\text{--}627 \text{ nm}$ with very high photoluminescence quantum yields of $\Phi_{\text{PL}} = 0.22\text{--}0.76$ in the solid state at 300 K. However, in toluene solution the quantum yields drop to $\Phi_{\text{PL}} = 0.085$ for both compounds.^[213] Similarly, four tin(II) dimers display phosphorescence at $\lambda_p = 600\text{--}625 \text{ nm}$ in the solid state at 300 K. The ES lifetimes and photoluminescence quantum yields of each compound are between $\tau_p = 4.5\text{--}7.6 \mu\text{s}$ and $\Phi_{\text{PL}} = 0.34\text{--}0.82$, respectively. Again, in toluene solution, the emissive properties decrease considerably, the lifetimes fall into the ns regime, and the photoluminescence quantum yields are diminished to $\Phi_{\text{PL}} = 0.003\text{--}0.016$.^[214]

In both studies, the dramatic differences of the photophysical properties between the solid state and solution indicate that non-radiative pathways dominate in the latter. However, no further investigations have been conducted to get deeper insights into the ES dynamics. Additionally, the photophysical differences among the aryl-substituents, for instance between the respective tin(II) dimers, have not been considered, as well.

Besides photoluminescence, tetrel(II) complexes demonstrate also photochemical reactivity. The well-known *Lappert's* diamino tetrylenes $E[\text{N}(\text{SiMe}_3)_2]_2$ ($E = \text{Ge}, \text{Sn}$) undergo disproportionation upon irradiation with UV light, forming persistent E^{III} radicals ($\bullet\text{EL}_3$).^[215–218] For the photochemical generation of the $\bullet\text{EL}_3$ radicals ($L = \text{alkyl}, \text{amino}$), Lappert und coworkers proposed two possible mechanisms, starting from the respective tetrylene (Figure 1.27).^[217]

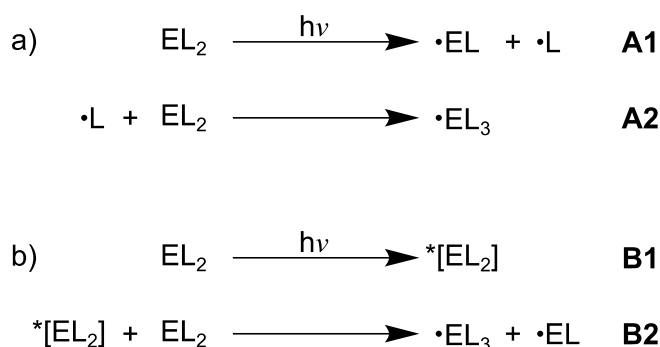


Figure 1.27: Discussed pathways for the formation of the E^{III} radicals $\bullet\text{EL}_3$ as proposed by Lappert and coworkers.^[217]

Mechanism **A** (Figure 1.27a) begins with the photoinduced homolysis of a E–L bond in the tetrylene EL_2 (**A1**). The free ligand radical $\bullet\text{L}$ is trapped subsequently by a further EL_2 in the GS forming the radical $\bullet\text{EL}_3$ (**A2**). Mechanism **B** (Figure 1.27b) is a bimolecular photoreaction between an photoexcited ${}^*\text{[EL}_2]$ (**B1**) and a second molecule EL_2 in the GS (**B2**) in a self-quenching reaction (section 1.3.2) with subsequent radical formation. Notably, the reaction in mechanism **B** would depend on the concentration of EL_2 , whereas the unimolecular reaction mechanism **A** would not show any influence on concentration of EL_2 . In both mechanisms, the E^I radical $\bullet\text{EL}$ is formed, but has never been detected either directly or via trapping.^[217,218]

However, chemical generation of $\bullet\text{Sn}[\text{CH}(\text{SiMe}_3)_2]$, resulting in a hexastannylprismane $\text{Sn}_6[\text{CH}(\text{SiMe}_3)_2]_6$, provides a clue to the fate of the E^I radical.^[219] Photolysis of tetrylenes with sterically demanding ligands like (EL_2 , $\text{L} = \text{N}(\text{SiEt}_3)_2$) did not lead to E^{III} radical formation, but enabled the detection of free aminyl radicals $\bullet\text{N}(\text{SiEt}_3)_2$.^[215] Further, tin(I) radical generation without tin(III) radical formation was observed after photolysis of the stannylene $\text{Sn}[\text{Ar}^{i\text{Pr}_4}]_2$ ($\text{Ar}^{i\text{Pr}_4} = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2)_2$).^[220] Both examples support mechanism **A**, but mechanism **B** cannot be ruled out in general for Lappert's diamino tetrylenes $\text{E}[\text{N}(\text{SiMe}_3)_2]_2$ ($\text{E} = \text{Ge, Sn}$) based on existing experimental results.

In contrast to the lighter homologues, irradiation of $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ does not lead to lead(III) radicals, instead photodecomposition to elemental lead occurs.^[217] However, lead formation could result from follow-up products of the respective radicals, which does not rule out the existence of both mechanisms for $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$.

Besides, the comparison of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ and $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ underlines the general issue that photolysis with subsequent elemental lead formation are common features in lead(II) chemistry, but much less common in tin(II) chemistry.^[147,148] Therefore, the focus in this work lies primarily on tin(II).

Persistent and/or isolable lead(III) radicals exist and can be obtained redox chemically.^[221–223] Furthermore, numerous examples of $\bullet\text{EL}_3$ radicals ($\text{E} = \text{Si–Sn}$) have been reported and investigated, as well.^[224–226]

Overall, few examples of photoluminescent tetrel(II) complexes are reported and demonstrate interesting features regarding phosphorescence and long-lived ESs. However, the nature of ESs and ES dynamics remained essentially unexplored. In many cases a tremendous drop of ES lifetime and phosphorescence intensity occurs by changing the environment from the solid state or frozen solutions to fluid solutions, which indicates dominant non-radiative ES deactivation pathways in fluid media. Though, the understanding of the deactivation pathways was either neglected or partially concluded from structural GS properties. Further issues are photodegradation processes like the

photoinduced radical formation in *Lappert's* diamino stannylene. The mechanism of this formation has not been elucidated experimentally, as well.

Understanding the ES dynamics and photo-induced chemical processes in heavy tetrel(II) complexes would help to develop concepts and establish highly emissive long-lived ESs. This could be achieved through spectroscopic measurements like temperature-dependent as well as time-resolved (transient) absorption and emission spectroscopy, augmented with (TD)-DFT calculations on the ES hypersurface i.e. consideration of nuclear motion in the ES.

Hence, understanding of the relevant ES dynamics is necessary to enhance the field of photoluminescent heavy tetrel(II) complexes to a similar level like in TMCs. This includes the ESs geometrical distortions and energetical positions as well as clarifying possible photochemical processes. Once this knowledge is acquired, concepts can be created as a foundation for future applications with photoactive and/or highly emissive tetrel(II) complexes.

2 Motivation and Aim

The photophysics of tetrel(II) complexes have remained mostly unexplored. However, the knowledge and understanding of the ES landscape and photophysics is a key prerequisite for developing rational design concepts on the way to photoactive materials, based on tetrels. The unique electronic structure of tetrel(II) complexes with a manifold of possible ESs, such as MC, MLCT, LMCT, ILCT or LL'CT states (Figure 1.22), opens a playground to gain deeper insight into the photophysics of main group complexes.

The principal aim is to shed more light on the underlying photophysical processes in tetrel(II) complexes and to get a tangible relationship between ligand design and resulting ES character. The major key points which are investigated in the frame of this thesis are as follows:

(i) As central ions, tin(II) and lead(II) are introduced. Both elements provide large and very large SOC constants ($\zeta(\text{Sn}) = 1855 \text{ cm}^{-1}$, $\zeta(\text{Pb}) = 5089 \text{ cm}^{-1}$, for comparison $\zeta(\text{Si}) = 130 \text{ cm}^{-1}$)^[85], which facilitate fast and effective ISC (section 1.2.2). However, due to its higher photo and thermal stability as well as less toxicity greater emphasis is placed on tin(II) compounds.

(ii) Targeting specific ES characters by the ligand topology in tripodal and meridional tin(II) complexes as well as by the coordination number ($C = 2, 3$).

(iii) The mechanism of the known photochemical radical formation of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_3$ is further elucidated by spectroscopic methods.

All experimental data are gathered and underpinned with (time-dependent) quantum chemical calculations to form a reasonable picture of the typical ES energy landscape. This includes the synthesis of novel compounds as well as the investigation of the well-known *Lappert's* diamino stannylene and plumbylene, which serve as prototypes, in the context of photophysics.

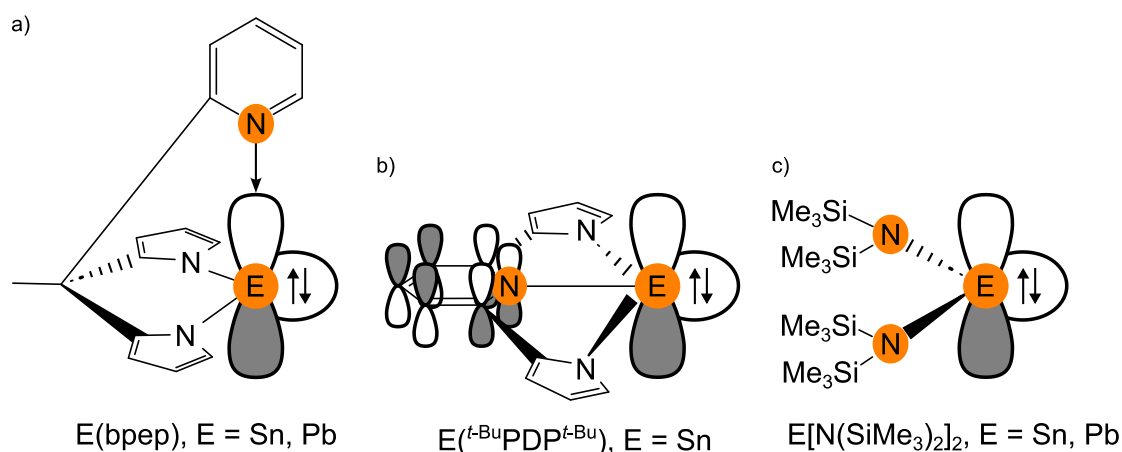


Figure 2.1: Illustration of the heavy tetrel(II) complexes in the focus of this work. *tert*-Butyl substituents in part b) are omitted for clarity.

The difference in the energy landscape between tin(II) and lead(II) complexes:

In the first project the tripodal ligand bpep^{2-} ($\text{H}_2\text{bpep} = 2\text{-[1,1-bis(1H-pyrrol-2-yl)ethyl]pyridine}$ with two electron-rich pyrrolato moieties and one electron-poor pyridine is combined with tin(II) ($\text{Sn}(\text{bpep})$) and lead(II) ($\text{Pb}(\text{bpep})$), respectively (Figure 2.1a).

The pyridine unit functions as an additional intramolecular donor to stabilize the vacant p_{π} -orbital by σ -interaction, resulting in a more antibonding and energetically higher p_{σ^*} -orbital (Figure 1.18). Therefore, both complexes ought to show high stability and provide convenient synthetic access. Further, the role of the additional donor is considered in the context of geometrical ES distortions and subsequent non-radiative ES decays. Emission spectroscopy at variable temperatures and DFT calculations on the ES hypersurface should support the assembling of an ES energy landscape for both complexes.

Addressing specific excited states by ligand topology:

The additional donor interaction, caused by the pyridine unit of the $bpep^{2-}$ ligand, has been removed by implementation of the dianionic meridional coordinating pyridine dipyrroliate pincer-type ligand $^{t-Bu}PDP^{t-Bu2-}$ ($H_2^{t-Bu}PDP^{t-Bu} = 2,6$ -bis(3,5-di-*tert*-butylpyrrol-2-yl)pyridine) in form of the $Sn(^{t-Bu}PDP^{t-Bu})$ complex (Figure 2.1b). Instead of a σ -interaction, the pyridine unit establishes a π -interaction with the vacant p_{π} -orbital. This topological modification should energetically decrease the tetrel centered p_{π} -orbital, leading to an ES with high LMCT character and concomitantly tune the emission energy.

Heavy carbene homologues – The typical tetrylenes:

In the previous projects, the HOMOs of the complexes are all dominated by the π_L -orbitals of the pyrrolate moieties, whereas the tetrel centered occupied n_s -orbital is energetically more separated and does not affect the ES dynamics. For the necessary adjustment one could say the key message is “keep it simple”.

Instead of creating complexes with large π -systems and high coordination numbers, the heavy carbene homologues with two simple ligands like amines $E(NR_2)_2$ might be sufficient, as well. In this case, the energetical position of the amine lone pairs could be at lower energy compared to the π_L -orbitals of the pyrrolates leading to a classic scenario with the occupied n_s -orbital as HOMO and the vacant p_{π} -orbital as LUMO. These tetrel-centered orbitals would result in an ES with MC character that could provide a strong phosphorescence.

Stable heavy carbene homologues with tin(II) and lead(II) as central atoms have been developed and extensively investigated with respect to the GS reactivity.^[145,146,149,150,147] However, their photophysical properties remained unexplored to date. Here, in two separated studies, the two well-known heavy tetrylenes, *Lappert's* diamino stannylene and plumbylene ($E[N(SiMe_3)_2]_2$, $E = Sn, Pb$), are considered and investigated (Figure 2.1c).^[215,227,228] Both tetrylenes provide a sufficient GS stability and are available in good yields even on large scale.^[229]

Besides, the tin(II) homologue undergoes formation to the tin(III) $\bullet Sn[N(SiMe_3)_2]_3$ and tin(I) $\bullet Sn[N(SiMe_3)_2]_2$ radical upon irradiation with UV light. Lappert and coworkers proposed two possible mechanisms for its formation (Figure 1.27).^[216,217] However, a clear experimental elucidation of the mechanism with the respective photophysics behind has never been conducted before. Notably, mechanism **A** would show unimolecular and mechanism **B** bimolecular behavior with respect to the concentration of the stannylene. In contrast, the plumbylene shows no detectable radical formation, instead precipitation of lead particles has been observed.^[217] This does not exclude the possibility, that both mechanisms could be intermediate stages until particle formation.

3 Results and Discussion

3.1 Overview

The results of the research accomplished in this work have been either published in or submitted to peer-reviewed journals or are available as preprint.^[230–232] These publications are reprinted in the following sections. The results of *Lappert's* diamino plumblylene are not published but described in section 3.5.

The first study “*Excited State Landscape of Phosphorescent Group 14 Complexes*” (section 3.2) deals with the complexes Sn(bpep) and Pb(bpep) (Figure 3.1) and covers their synthesis, structural characterization as well as ES dynamics, which were probed by steady-state and time-resolved emission spectroscopy. All experimental results are corroborated with detailed (TD)-DFT calculations.

The energetically lowest bands in the UV/Vis absorption spectrum of both complexes are of ILCT character, with charge transfers from the electron-rich pyrrolate to the electron-poor pyridine moieties, according to TD-DFT calculations. LMCT transitions at nearly higher energies are also observed.

Sn(bpep) exhibits green phosphorescence at $\lambda_{\text{em},293} = 535$ nm in the solid state at room temperature. This emission shifts to $\lambda_{\text{em},77} = 504$ nm upon cooling to 77 K. The lifetimes of the ESs and photoluminescence quantum yields are determined to $\tau_{293} = 14$ ns, $\Phi_{\text{PL},293} = 0.005$ and $\tau_{77} = 3.6$ ms, $\Phi_{\text{PL},77} = 0.58$, respectively. The strong temperature dependence of the ES lifetimes and photoluminescence quantum yields is ascribed to thermally activated non-radiative processes. Time-resolved emission spectroscopy at variable temperatures with the corresponding rate constants $k(T)$ enabled an Arrhenius plot with two activation barriers of $E_{a1} = 0.25$ eV and $E_{a2} = 0.10$ eV, dominating at high and low temperatures, respectively (section 1.2.3).

In contrast, the complex Pb(bpep) shows a weak phosphorescence at significantly lower energies with $\lambda_{\text{em},77} = 700$ nm at 77 K and no emission could be detected at room temperature. The photoluminescence lifetime and quantum yield are defined to $\tau_{77} = 92$ ns and $\Phi_{\text{PL},77} = 0.0024$.

According to DFT calculations, a nested $^3\text{ILCT}$ state could be located for both complexes. This state is connected to strongly distorted $^3\text{LMCT}$ states via E–N(Pyridine) bond or E–N(Pyrrolato) bond dissociation and a tilting of the respective heterocyclic pyridine or pyrrolate rings. This distortion occurs due to population of strongly antibonding σ^* -orbitals (Figure 1.18a).

The $^3\text{LMCT}$ state with the E–N(Pyridine) bond cleavage and tilted pyridine moiety possesses the lowest energy in both complexes. The calculated activation barriers between this $^3\text{LMCT}$ and the $^3\text{ILCT}$ state lie at 0.23 and 0.06 eV for Sn(bpep) and Pb(bpep), respectively. Experimentally, an activation barrier of $E_{a1} = 0.25$ eV is found for Sn(bpep).

Assuming the ES dynamics start at the $^3\text{ILCT}$ state, the complex Sn(bpep) shows non-Kasha phosphorescence from a $^3\text{ILCT}$ state which is thermally deactivated by the transfer to the strongly distorted $^3\text{LMCT}$ state. (Figure 3.1a).

In the case of the Pb(bpep) complex, DFT calculations indicate a smaller activation barrier between the nested $^3\text{ILCT}$ and the $^3\text{LMCT}$ state. This aspect suggests that rapid population to the $^3\text{LMCT}$ state occurs after excitation even at low temperatures. The strongly distorted $^3\text{LMCT}$ state at low energy decays back rapidly to the ^1GS , which fits

to the experimental results of a short-lived, weak low-energy emission. Therefore, the complex Pb(bpep) exhibits Kasha phosphorescence (Figure 3.1b).

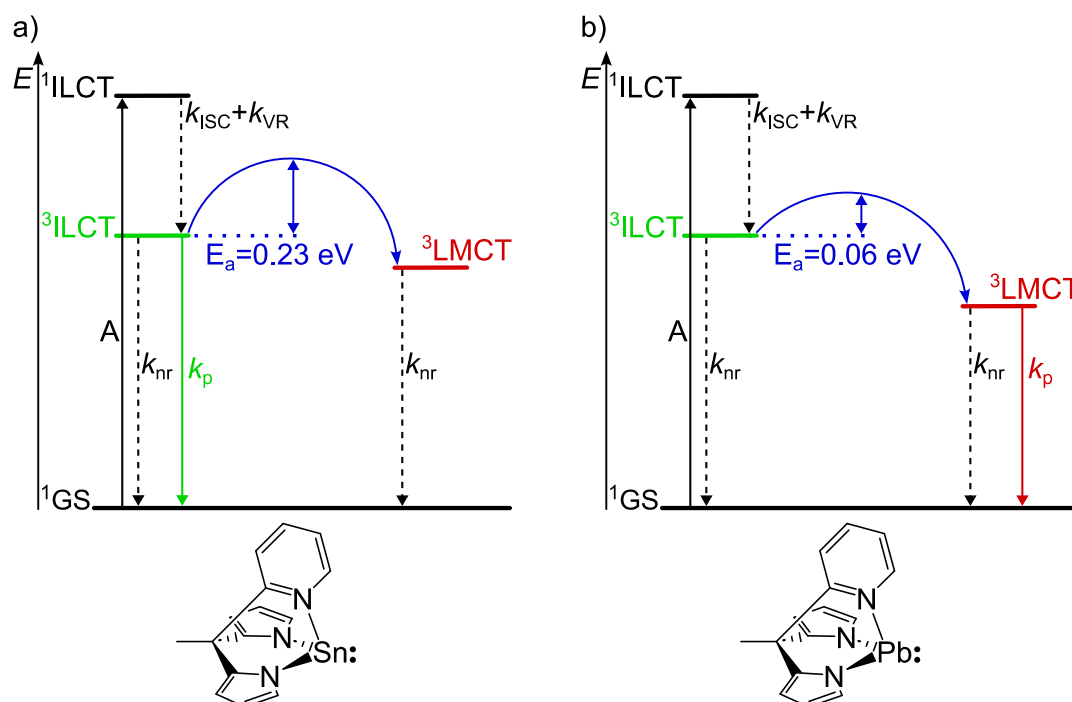


Figure 3.1: Schematic Jablonski diagrams with respective ES dynamics displaying activation barriers obtained from DFT calculations and the corresponding molecular structure of the E(bpep) (E = Sn, Pb) complexes.

In the Sn(bpep) complex, the strongly distorted $^3\text{LMCT}$ state defines the non-radiative deactivation pathway of the ES. The responsible p_{σ^*} -orbital stems from the additional donor interaction induced by the pyridine unit (Figure 1.18). To avoid this deactivation pathway the additional donor-stabilization must be removed e.g. by changing the ligand geometry.

In the second study “*Ligand Topology Tunes Energy and Character of Emissive Triplet States in Stannylenes*” (section 3.3), the tin(II) complex $\text{Sn}(\text{}^t\text{-BuPDP}^t\text{-Bu})$ fulfills the mentioned prerequisites due to its meridional geometry of the ligand (Figure 3.2a). The vacant p_{π} -orbital is introduced into the π -system of the pyridine moiety, which diminishes the orbital to lower energies compared to the case of Sn(bpep) as indicated by DFT calculations. However, $\text{Sn}(\text{}^t\text{-BuPDP}^t\text{-Bu})$ is reactive in its GS and undergoes a dimerization in non-coordinating solvents like benzene or adduct formation in coordinating solvents like THF which limits the investigation of the optical properties to the solid state.

According to TD-DFT calculations, the energetically lowest-lying states in $\text{Sn}(\text{}^t\text{-BuPDP}^t\text{-Bu})$ display high oscillator strengths in the visible region of mainly LMCT character. The charge transfer occurs from the electron-rich pyrrolate to the tetrel centered vacant p_{π} -orbital with pyridine π^*_L -orbital admixture. In turn, the ILCT and LMCT states of the Sn(bpep) complex were located at higher energies inducing green emission. Therefore, emission in $\text{Sn}(\text{}^t\text{-BuPDP}^t\text{-Bu})$ should be shifted to lower energies.

Indeed, $\text{Sn}(\text{}^t\text{-BuPDP}^t\text{-Bu})$ displays red emission at $\lambda_{\text{em},293} = 710 \text{ nm}$ at room temperature which shifts to $\lambda_{\text{em},77} = 690 \text{ nm}$ at 77 K in the solid state. The lifetimes and photoluminescence quantum yields are determined to $\tau_{293} = 221 \text{ ns}$, $\Phi_{\text{PL},293} = 0.0044$ and $\tau_{77} = 128 \text{ }\mu\text{s}$, $\Phi_{\text{PL},77} = 0.0116$, respectively. However, the emission intensity behaves

unusual based on a temperature dependent radiative rate constant k_r with $k_{r,77} = 100 \text{ s}^{-1}$ at 77 K and $k_{r,293} = 20000 \text{ s}^{-1}$ at room temperature. The intensity drops from 77 K to 125 K, rises again from 150 K to 175 K and drops once more until room temperature. The low value of $k_{r,77} = 100 \text{ s}^{-1}$ might originate from a ($\text{ES} \rightarrow \text{GS}$) transition which provides a small electric transition dipole moment (section 1.2.2). On the contrary, the ($\text{ES} \rightarrow \text{GS}$) transition at room temperature generates a high value of $k_{r,293} = 20000 \text{ s}^{-1}$ which may come from a different ES compared to the case at 77 K. This means that the observed phosphorescence in $\text{Sn}(\text{t-BuPDP}^{\text{t-Bu}})$ could stem from two different $^3\text{LMCT}$ states.

In the solid state, the unit cell consists of two $\text{Sn}(\text{t-BuPDP}^{\text{t-Bu}})$ molecules forming a slipped side by side orientated aggregate. TD-DFT calculations of this aggregate revealed a splitting of each state into two new states compared to the monomer. For example, the energetically lowest $^3\text{LMCT}$ state of the monomer splits up into a $^3\text{LMCT}_+$ state at high energy with large oscillator strength f and a $^3\text{LMCT}_-$ state at low energy with almost zero oscillator strength f (Figure 3.2b). Thus, at low temperatures only the $^3\text{LMCT}_-$ state is populated which is responsible for the low $k_{r,77}$ due to its low oscillator strength f (section 1.2.2). On the other hand, the $^3\text{LMCT}_+$ state is activated by increasing temperatures and shows a higher radiative rate (Figure 3.2b). Hence, the high $k_{r,293}$ is an average between the radiative rates of the $^3\text{LMCT}_+$ and $^3\text{LMCT}_-$ state following a Boltzmann distribution [Eq (11)]. The splitting of the $^3\text{LMCT}$ into states with large and small electric transition dipole moments μ might be induced by the aggregation of two $\text{Sn}(\text{t-BuPDP}^{\text{t-Bu}})$ molecules which can be traced back to excitonic interactions (section 1.2.4). In this case, the two $\text{Sn}(\text{t-BuPDP}^{\text{t-Bu}})$ molecules might form an H-aggregate with parallel aligned transition dipole moments. If the transition dipole moments are in phase the allowed $^3\text{LMCT}_+$ state is formed. If they are anti-phase, the $^3\text{LMCT}_-$ state is created (Figure 3.2c).

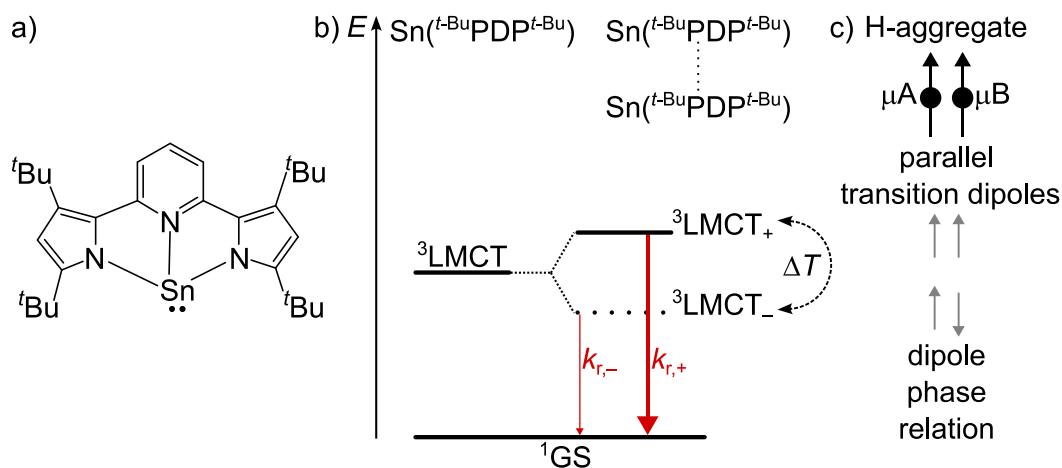


Figure 3.2: a) Molecular structure of $\text{Sn}(\text{t-BuPDP}^{\text{t-Bu}})$. b) The splitting of the $^3\text{LMCT}$ state into two new non-degenerate states due to aggregation. c) Excitonic interaction of an H-aggregate with the respective coupling of the transition dipole moments causing the splitting of the $^3\text{LMCT}$ state.

In summary, the change in ligand topology enabled ES targeting and the tuning of the emission energy. However, the meridional complex $\text{Sn}(\text{t-BuPDP}^{\text{t-Bu}})$ showed a higher GS reactivity compared to $\text{Sb}(\text{bpep})$. For this reason, investigations in solutions were hampered for instance by dimerization. On the other hand, aggregation in the solid state diminished the emission and the respective radiative rates.

The next study follows up with the stable and well-known *Lappert's* diamino stannylene, $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ and its photophysical properties (section 3.4). This stannylene shows a sufficient GS stability in solution and solid state. Furthermore, it is soluble in the most

organic solvents and shows no dimerization as determined by cryoscopy.^[227] This allows a detailed investigation of the known photoreactivity and photophysical processes in solution, as well.

Lappert's diamino stannylene furnishes a green strong long-lived phosphorescence peaking at $\lambda_{\text{em},77} = 555 \text{ nm}$ with a lifetime of $\tau_{77} = 25 \mu\text{s}$ in frozen 3-methylpentane solution at 77 K. With increasing temperature, a second orange emission band appears and remains until room temperature peaking at $\lambda_{\text{em},293} = 670 \text{ nm}$ whereas the green phosphorescence vanishes above 125 K. According to DFT calculations, the green emission stems from a triplet ES T_1 of mixed MC ($n_s \rightarrow p_\pi$) and LMCT ($N \rightarrow \text{Sn}$) character which is connected by a barrier with a second lower energy MC/LMCT state T_1' . The relaxed geometries differ only by the orientation of one trimethylsilyl group. Experimental data from time-resolved emission and ns-TA spectroscopy imply a thermal equilibrium between T_1 and T_1' at room temperature. Additional fs-TA measurements at variable excitation wavelengths show that after S_1 excitation at $\lambda_{\text{exc}} = 390 \text{ nm}$ a further triplet state T_2 is populated which converts to the T_1 state. In contrast, $S_0 \rightarrow T_1$ irradiation at $\lambda_{\text{exc}} = 490 \text{ nm}$ leads to direct population of the T_1 state (Figure 3.3a).

The lifetime of the T_1/T_1' state drops with increasing concentration of the stannylene at room temperature. This is a clear indication of dynamic self-quenching, assigned to triplet excimer formation (section 1.3.2). DFT geometry optimizations delivered two triplet excimers with twisted *cis*- and *trans*-bent geometries. The stronger stabilization of the *cis*-excimer in comparison to the *trans*-excimer can be rationalized by a second order Jahn-Teller (SOJT) effect (section 1.5.2). Both excimers possess very short lifetimes of $\tau_{\text{cis}} = 222 \text{ ps}$ and $\tau_{\text{trans}} = 2.2 \text{ ns}$, determined by fs-TA spectroscopy.

Furthermore, the study revealed that the excimer formation is a competing process to the radical formation of $\bullet\text{Sn}[\text{N}(\text{SiMe}_3)_2]_3$ which is created via a unimolecular process (Figure 3.3b). The experimental short ES lifetimes of both excimers and DFT calculated energies of the Gibbs free energies ΔG as well as high estimated barriers of ligand migration rather exclude mechanism **B**. Instead, the photodegradation quantum yield of $\Phi_{\text{deg}} = 0.002$ is independent on the concentration and depends only on the concentration of the excited molecules, supporting mechanism **A** (Figure 1.27a).

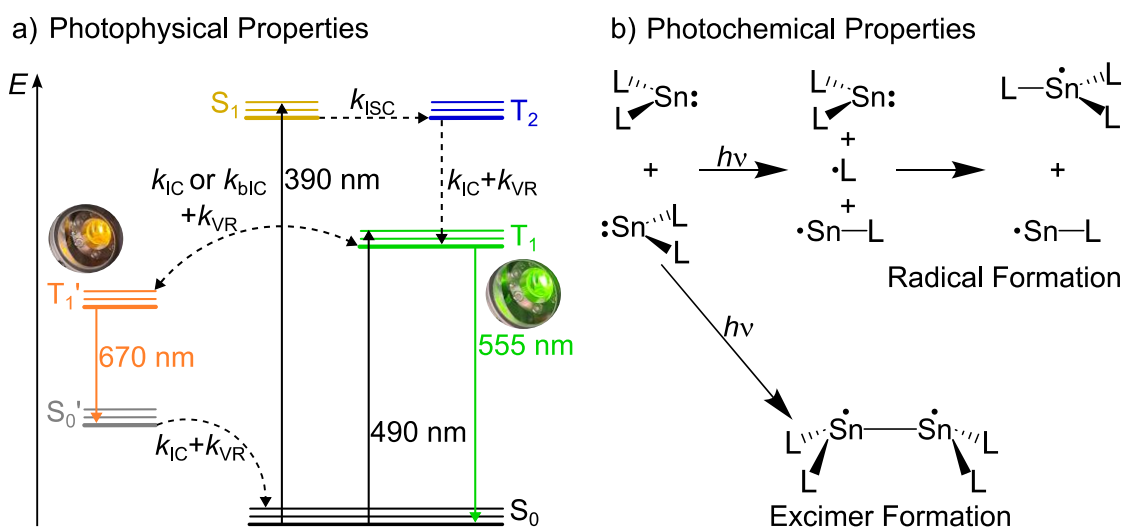


Figure 3.3: Schematic representation of the obtained photophysical a) and photochemical properties b) of *Lappert's* diamino stannylene. $L = \text{N}(\text{SiMe}_3)_2$.

The stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ demonstrates versatile photophysical and photochemical behavior. Building on the knowledge gained in this work, the heavier homologue *Lappert's* diamino plumbylene $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ was explored (section 3.5). In contrast to the stannylene the low-energy transitions in the plumbylene have a negligible amount of MC character and show mainly LMCT ($\text{N} \rightarrow \text{Pb}$) character according to TD-DFT calculations. This can be attributed to relativistic effects in lead, which lowers the energy of the n_s -orbital (Figure 1.14).^[150]

Lappert's diamino plumbylene exhibits a broad weak phosphorescence peaking at $\lambda_{\text{em},77} = 700 \text{ nm}$ in frozen 3-methylpentane solution at 77 K. The emission band disappears completely above 125 K. The phosphorescence originates from two almost degenerate triplet states, T_1 and T_2 , with lifetimes in the nanosecond regime. Direct $S_0 \rightarrow T_1$ excitation results the same emissive properties. Population of both states occurs via branching from the initial Franck-Condon state to the respective relaxed geometries, according to DFT calculations (Figure 3.4). The triplet states are strongly distorted, featuring elongated Pb–N bonds, which may explain the short-lived emission.

Furthermore, irradiation of $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ did not yield observable radicals as previously reported for $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$.^[215–218] Instead, precipitation of elemental lead was detected. The photodegradation quantum yield of $\Phi_{\text{deg}} = 0.05$ is also independent on the concentration. This supports the conclusion that the photolysis may start with the photoinduced homolysis of a Pb–L bond, which is step **A1** of mechanism **A**, and subsequent elemental lead formation from the radicals, starting from both ES T_1 and T_2 .

Since the ES lifetimes of $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ are in the ns regime at 77 K and no further emission at room temperature is detected, the T_1 and T_2 lifetimes at room temperature are assumed to be very short. On this basis, excimer formation is less likely than in the case of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$.

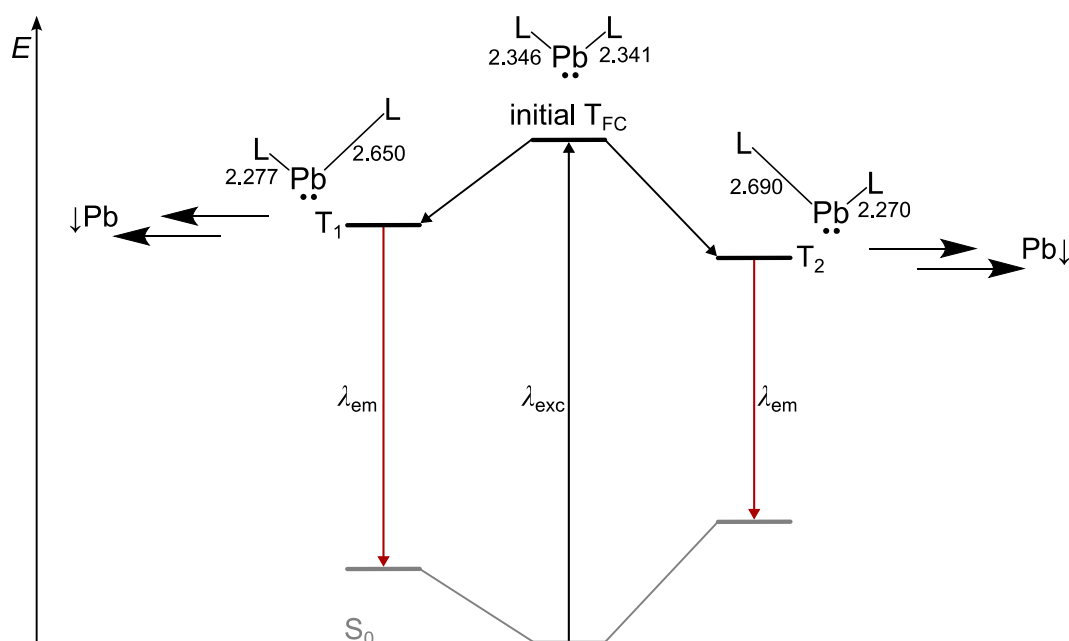


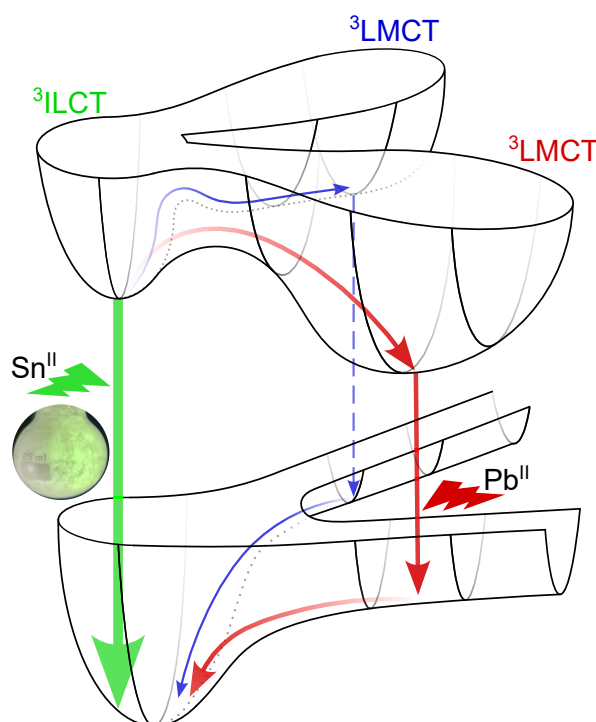
Figure 3.4: Schematic illustration of the obtained photophysical data of *Lappert's* diamino plumbylene with molecular structures of the respective ES geometries, including the Pb–L bond lengths in Å from DFT calculations. L = $\text{N}(\text{SiMe}_3)_2$. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Pb).

3.2 Excited State Energy Landscape of Phosphorescent Group 14 Complexes

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Two phosphorescent heavy tetrel(II) complexes (E(bpep), E = Sn, Pb) were synthesized and investigated toward their photophysical properties by absorption and temperature-dependent steady-state and time-resolved emission spectroscopy. Sn(bpep) shows green ILCT phosphorescence, whereas Pb(bpep) exhibits weak red LMCT phosphorescence in the solid state. Both complexes display a drastic change in the photophysical properties depending on variable temperatures. According to (TD)-DFT calculations, strong geometrical distortions of the LMCT states are responsible for the non-radiative pathways in Sn(bpep) and the weak emission in Pb(bpep).

Author Contributions

Philipp Sikora performed the synthesis, characterization, absorption experiments and (TD)-DFT calculations of the respective tetrel(II) complexes, as well as the visualization of the data. [REDACTED] and Philipp Sikora measured the steady-state and time-resolved emission experiments and interpreted the data. [REDACTED] solved and refined the crystal structures, conceived and designed the project, and prepared the manuscript with contributions from all authors. [REDACTED] supervised and [REDACTED] cosupervised this project.

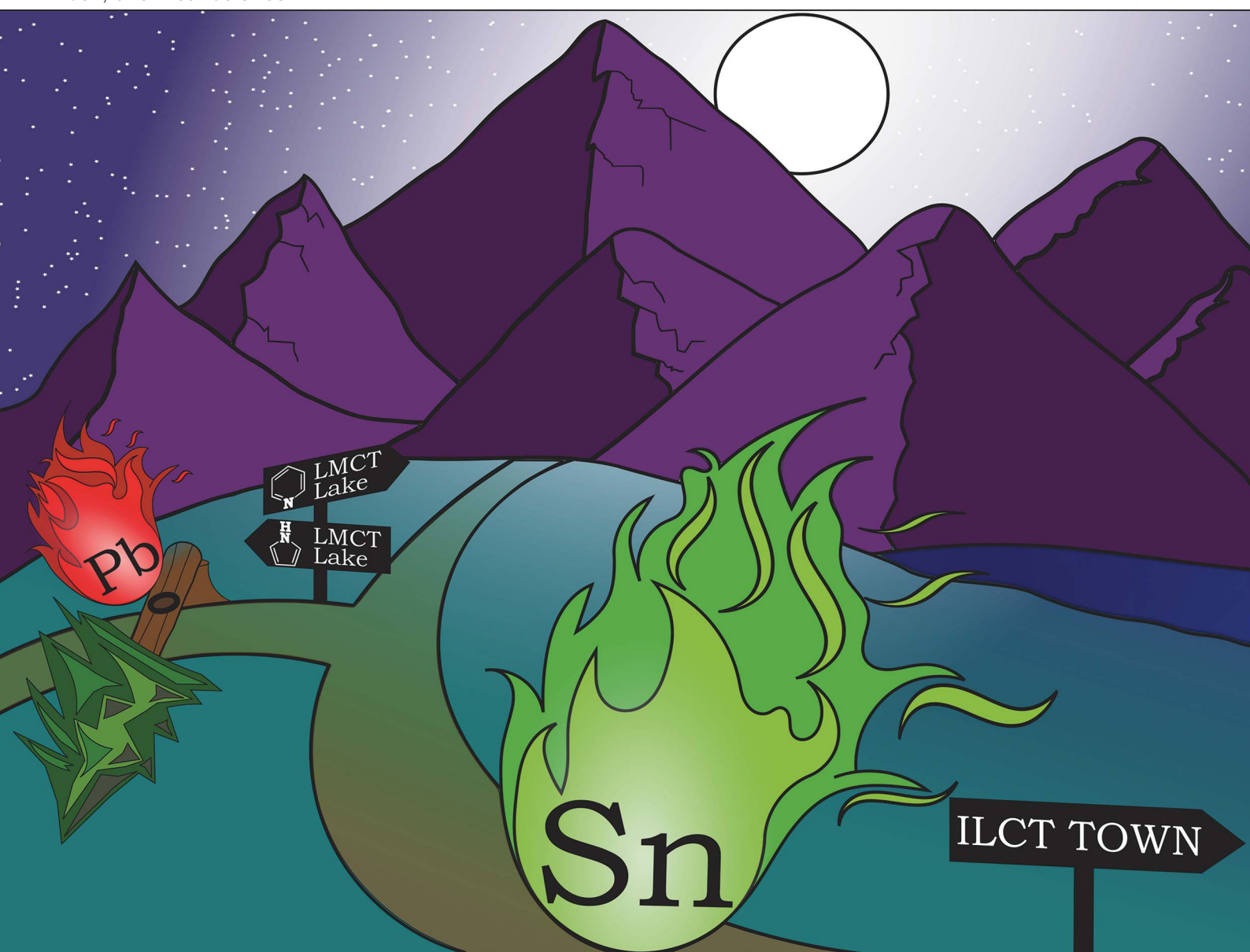
Supporting Information

for this article is found on page 138.

Cartesian coordinates of DFT optimized structures can be found online at: <https://pubs.rsc.org/en/content/articlelanding/2023/sc/d2sc06984a>. The article is licensed under CC BY-NC 3.0 (<https://creativecommons.org/licenses/by-nc/3.0/>) and was reproduced from ref.^[230]

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Excited state energy landscape of phosphorescent group 14 complexes†

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Great progress has been achieved on phosphorescent or photoactive complexes of the Earth-abundant transition metals, while examples for phosphorescent heavy main group element complexes are rare, in particular for group 14 complexes in the oxidation state +II. The known compounds often show only weak phosphorescence with fast non-radiative deactivation. The underlying photophysical processes and the nature of the phosphorescent electronic states have remained essentially unexplored. The present combined photophysical and theoretical study on tin(II) and lead(II) complexes E(bpep) with the dianionic tridentate ligand bpep²⁻ (E = Sn, Pb; H₂bpep = 2-[1,1-bis(1*H*-pyrrol-2-yl)ethyl]pyridine) provides unprecedented insight in the excited state energy landscape of tetrel(II) complexes. The tin complex shows green intraligand charge transfer (ILCT) phosphorescence both in solution and in the solid state. In spite of its larger heavy-atom effect, the lead complex only shows very weak red phosphorescence from a strongly distorted ligand-to-metal charge transfer (LMCT) state at low temperatures in the solid state. Detailed (TD-)DFT calculations explain these observations and delineate the major path of non-radiative deactivation via distorted LMCT states. These novel insights provide rational design principles for tetrel(II) complexes with long-lived phosphorescence.

1 Introduction

Photoluminescent, in particular phosphorescent and photoactive transition metal complexes (TMCs) of the Earth-abundant elements, mainly 3d elements, evolved to a potential alternative to the precious elements, *e.g.* ruthenium, iridium or platinum.^{1–5} The key prerequisite for applications in bimolecular photochemical reactions is a sufficiently long lifetime of the photoactive excited state (ES). This can be achieved for ESs with different spin multiplicities to the ground state (GS), rendering non-radiative and radiative processes between ES and GS spin-forbidden, thus extending the ES lifetime.⁶ In order to access ESs of different spin multiplicity to the GS and the initially populated Franck–Condon state, intersystem crossing (ISC) must be effective. ISC rates increase for ES's wavefunctions with high metal character invoking spin–orbit coupling (SOC) by a heavy-atom effect or by effective spin–vibronic coupling.⁷ The research on photoactive 3d or 4d TMCs envisaged mainly weakly distorted metal-to-ligand (MLCT) or ligand-to-metal charge transfer (LMCT) and intraconfigurational spin-flip states as potential photoactive states to invoke a high metal character for fast ISC.^{1–3} In pseudo-octahedral 3dⁿ

TMCs ($n = 1–9$) the high density of low-lying strongly distorted metal-centered (MC) states typically enables fast non-radiative deactivation of CT states.^{1–3} For photoactive pseudo-tetrahedral d¹⁰ copper(I) complexes, the flattening distortion of the photoluminescent ³MLCT states, can facilitate fast non-radiative deactivation.^{8–10} The photoluminescence lifetimes of pseudo-tetrahedral copper(I) complexes are also very sensitive to coordinating solvents and anions in the flattened ³MLCT states.^{9,11} This illustrates the interplay between ES ordering and ES distortion, which depends on the coordination geometry and rigidification of the complex. For 3d TMCs, the underlying photophysical processes are well understood and ground-breaking progress was achieved in the last few years.^{1–5}

Examples of heavy main group complexes, mainly group 14 and 15, showing beside conventional fluorescence,^{12,13} phosphorescence and/or thermally activated delayed fluorescence (TADF),^{10,14–16} are rare.^{17–19} Emission is often limited to frozen solutions or even to the solid state, precluding bimolecular reactivity.^{13,17–19} Complexes of group 15 elements, in particular bismuth(III) with 6s² electron configuration, can show phosphorescence.^{20–28} The oxidation state +IV dominates in tetrel group 14 complexes with potentially photoactive triplet states^{29–35} and fluorescent or photoluminescent states of yet unknown character.^{36–44} Photoluminescent tetrel(II) complexes are very scarce. Scandola and co-workers reported for Pb(QO)₂I (QOH = 8-hydroxyquinoline) a weak green fluorescence and an even weaker red phosphorescence from intraligand (IL) states in *N,N*-dimethylformamide (DMF, 298 K; λ_f = 550 nm, τ_f = 0.4 ns, Φ_f ≈ 0.003;

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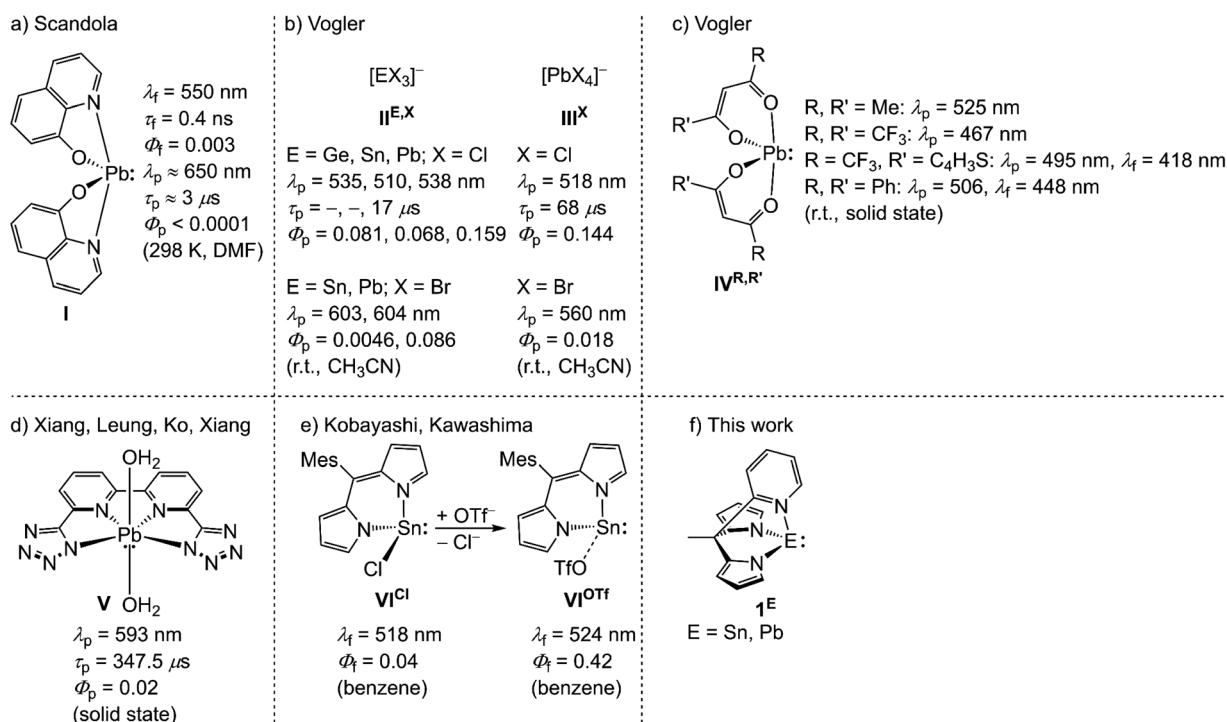
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$\lambda_p \approx 650$ nm, $\tau_p \approx 3$ μ s, $\Phi_p < 0.0001$) and glassy ethanol (77 K; $\lambda_f = 510$ nm, $\tau_f < 20$ ns; $\lambda_p \approx 610$ nm, $\tau_p = 180$ μ s), respectively (Scheme 1a).⁴⁵ The triplet state of the Pb complex **I** is efficiently quenched by energy transfer (EnT) in a bimolecular reaction with $[\text{Cr}(\text{CN})_6]^{3-}$ in DMF with a quenching rate constant of $k_q = 3.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.⁴⁵ Studies by Vogler and co-workers on photoluminescent halido germanium(II), tin(II) and lead(II) complexes $[\text{EX}_3]^- \text{II}^{\text{E},\text{X}}$ (E = Ge–Pb; X = Cl; E = Sn, Pb; X = Br) and $[\text{PbX}_4]^{2-} \text{III}^{\text{X}}$ (X = Cl, Br) revealed phosphorescence from MC states at 510–604 nm after excitation with UV light in fluid acetonitrile solution (Scheme 1b).^{46,47} The population of the emissive triplet state with a s^1p^1 electron configuration, is accompanied with large structural reorganization from C_{3v} to D_{3h} symmetry for $[\text{EX}_3]^-$ ions.⁴⁶ This distortion enables efficient non-radiative deactivation of the triplet state. In the series $[\text{EX}_3]^-$ (E = Ge–Pb, X = Cl, Br), the Sn complexes exhibit short photoluminescence lifetimes below the detection limit and the lowest quantum yields ($\Phi_p = 0.068$ (Cl); $\Phi_p = 0.0046$ (Br)) compared to Ge ($\Phi_p = 0.081$ (Cl)) and Pb ($\tau_p = 17$ μ s, $\Phi_p = 0.159$ (Cl); $\Phi_p = 0.086$ (Br)).^{46,47} Despite the short photoluminescence lifetime, $[\text{SnCl}_3]^-$ undergoes bimolecular photo-oxidation reactions to SnOCl_2 with oxygen after excitation with UV-C light ($\lambda_{\text{ex}} = 254$ nm).⁴⁸

Bis(β -diketonato) lead(II) complexes $\text{IV}^{\text{R,R'}}$ prepared by Vogler and co-workers show blue to green intraligand (IL) phosphorescence in the solid state. The phosphorescence is diminished in ethanol solution at r.t. The respective hexafluoroacetylacetonato tin(II) complex is not photoluminescent (Scheme 1c).^{27,49} The very weak phosphorescence of the β -diketonato lead(II) complexes is attributed to a large geometric reorganization leading to fast non-radiative relaxation.⁴⁹ Unfortunately, no photoluminescence

lifetimes and quantum yields were reported for these compounds. A series of coordination polymers of lead(II) with polydentate tetrazolato ligands are phosphorescent from ^3IL , ^3MC and $^3\text{MLCT}$ states with admixed $^3\text{XLCT}$ (halide-to-ligand CT) character. The photoluminescence lifetimes amount up to $\tau_p = 1.55$ ms and a maximum quantum yield of $\Phi_p = 0.165$ in the solid state.⁵⁰ The molecular congener **V** with 6,6'-bis(1H-tetrazol-5-yl)-2,2'-bipyridine as proligand shows $^3\text{MLCT}$ phosphorescence with significantly lower photoluminescence quantum yield in the solid state ($\lambda_p = 593$ nm, $\tau_p = 347.5$ μ s, $\Phi_p = 0.02$; Scheme 1d).⁵⁰ Substituting a chlorido ligand with a weakly coordinating triflate (OTf^-) ligand, increases the fluorescence quantum yield of a dipyrromethene tin(II) complex from 0.04 (**VI^{Cl}**) to 0.42 (**VI^{OTf}**) with a slight bathochromic shift of the fluorescence from $\lambda_f = 518$ nm to $\lambda_f = 524$ nm (Scheme 1e).⁵¹ The significant increase in quantum yield is ascribed on the basis of an inspection of the GS molecular orbitals from density functional theory (DFT) calculations to a shift of a non-photoluminescent MLCT state to higher energies upon stabilising the occupied non-bonding tin-centered orbital after Cl^-/OTf^- exchange.⁵¹

Heavy tetrel(II) complexes are related to tetrylenes, the heavier carbene homologues.^{52–56} The singlet ground state of heavier tetrylenes is described by a metal-centered occupied orbital with high s-character and a vacant or donor stabilised orbital with high p-character (Fig. 1).^{52–56} Clearly, MC, IL, LMCT, MLCT and ligand-to-ligand charge transfer (LL'CT) states with their respective ES distortions must be considered in exploring the energy landscape of electronic states with the focus on photoluminescent and in particular phosphorescent properties (Fig. 1).



Scheme 1 Photoluminescent tetrel(II) complexes with selected photophysical data.



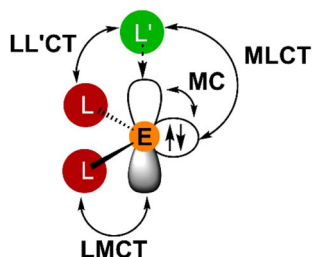


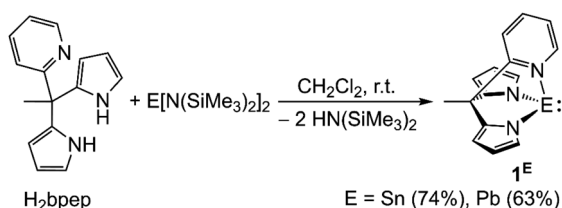
Fig. 1 Schematic representation of selected electronic transitions in donor (L') stabilised homoleptic tetrelenes EL_2 ($E = \text{Si, Ge, Sn, Pb}$), excluding IL and other possible LMCT ($L' \rightarrow E$) and MLCT ($E \rightarrow L$) transitions.

To the best of our knowledge, no combined experimental and quantum chemical studies are reported on the energy ordering and geometric distortions of excited states of photoluminescent tetrel(II) complexes. This study aims to shed more light on the underlying photophysical processes. The tripodal ligand $bpep^{2-}$ ($H_2bpep = 2-[1,1\text{-bis}(1H\text{-pyrrol-2-yl})\text{ethyl}]\text{pyridine}$)⁵⁷ with electron-rich pyrrolato and electron-poor pyridine donors in combination with the heaviest tetrels Sn and Pb for a large heavy-atom effect and fast ISC was chosen for this initial study (SOC constants: $\zeta(\text{Sn}) = 1855 \text{ cm}^{-1}$, $\zeta(\text{Pb}) = 5089 \text{ cm}^{-1}$).⁵⁸ $\text{Sn}^{\text{II}}(bpep)$ 1^{Sn} shows phosphorescence in the solid state and in solution, while the lead congener $\text{Pb}^{\text{II}}(bpep)$ 1^{Pb} with its larger heavy-atom effect is only very weakly photoluminescent. The elucidation of the different emission properties is supported by UV/vis absorption and variable-temperature steady-state and time-resolved emission spectroscopy as well as with detailed time-dependent (TD) DFT calculations.

2 Results and discussion

2.1. Synthesis, structural and spectroscopic properties

The tetrelenes $E^{\text{II}}(bpep)$ ($E = \text{Sn } 1^{\text{Sn}}$, $\text{Pb } 1^{\text{Pb}}$) are synthesised *via* a transamination of H_2bpep ⁵⁷ with bis[bis(trimethylsilyl)amido] tetrel(II) compounds $E^{\text{II}}[\text{N}(\text{SiMe}_3)_2]_2$ (ref. 59) in dichloromethane as colourless, moisture sensitive solids in 74% and 63% yields, respectively (Scheme 2). Complexes 1^E are poorly soluble in most organic solvents. 1^{Sn} is well soluble in tetrahydrofuran (THF) and sparsely in toluene, while 1^{Pb} is only soluble in dimethylsulfoxide (DMSO) among the tested solvents. 1^{Sn} and 1^{Pb} are fully characterised by elemental analysis, ESI⁺ mass spectrometry (ESI, Fig. S1 and S2†) and multinuclear (^1H , ^{13}C ,



Scheme 2 Syntheses of stannylene and plumbylene $E^{\text{II}}(bpep)$ ($E = \text{Sn } 1^{\text{Sn}}$, $\text{Pb } 1^{\text{Pb}}$) *via* transamination from $E[\text{N}(\text{SiMe}_3)_2]_2$ and H_2bpep , yields given in parentheses.

^{119}Sn , ^{207}Pb) NMR spectroscopy (ESI, Fig. S3–S14†). The ^{119}Sn resonance of 1^{Sn} appears in the similar chemical shift range of other donor stabilised dipyrrolato stannylenes (ESI, Fig. S5†).⁶⁰ The solids of 1^E are free of coordinating solvents, which could coordinate to the Sn or Pb atoms, as determined by ^1H NMR spectroscopy and elemental analyses. This speciation is important for the discussion of the photoluminescent properties in solution and in the solid state (ESI, Fig. S3 and S9†).

Crystals of 1^{Sn} , suitable for X-ray diffraction analyses were obtained from hot toluene. 1^{Sn} crystallises in the trigonal space group R_3 with two independent molecules $1^{\text{Sn,A}}$ and $1^{\text{Sn,B}}$ in the asymmetric unit (Fig. 2a; ESI, Fig. S15 and Table S1†). $1^{\text{Sn,B}}$ is disordered with a pyrrolato/pyridine site occupation, so that the more precise structural parameters of $1^{\text{Sn,A}}$ are discussed. Both molecules feature a distorted trigonal pyramidal coordination of the Sn atom. A further solid state structure of 1^{Sn} could be determined from crystals, obtained from slow diethylether diffusion to a solution of 1^{Sn} in a 1 : 1 mixture of 1,4-dioxane : tetrahydrofuran. Here, 1^{Sn} forms a centrosymmetric 1,4-dioxane (diox) bridged dimer $(1^{\text{Sn}})_2(\text{diox})$ (monoclinic space group $I2/a$) leading to a four-coordinate tin(II) ion (Fig. 2b; ESI, Table S1†). This solid state structure indicates that 1^{Sn} will likely form solvates in THF and THF/1,4-dioxane solutions. The 1,4-dioxane coordination with a Sn–O distance of $2.547(2) \text{ \AA}$ elongates the tin–nitrogen(pyridine) (Sn– N^{py}) bond from $2.317(5) \text{ \AA}$ (1^{Sn}) to $2.375(2) \text{ \AA}$ ($(1^{\text{Sn}})_2(\text{diox})$). This Sn– N^{py} bond weakening arises from the competing interactions of the pyridine and 1,4-dioxane donors with the tetrel p-type orbital (Fig. 1; ESI Table S1†). This will also influence the photophysical properties of 1^{Sn} (*vide infra*). The much lower solubility of 1^{Pb} in most organic solvents prohibited growing single crystals suitable for X-ray diffraction analysis, but the NMR spectroscopic, mass spectrometric and analytical data confirm the composition and purity.

The structures of 1^{Sn} , $1^{\text{Sn}}(\text{thf})$ and 1^{Pb} were optimised by DFT (CPCM-(THF)-RJCOSX-B3LYP-D3BJ-ZORA/def2-TZVPP/old-

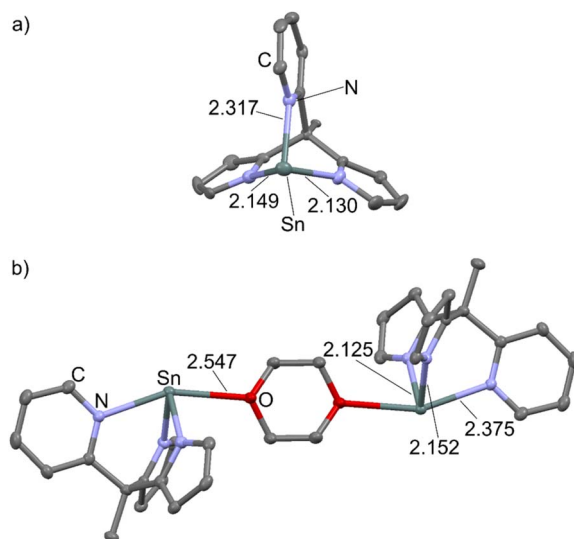


Fig. 2 Molecular structures of (a) 1^{Sn} and (b) of the 1,4-dioxane bridged dimer $(1^{\text{Sn}})_2(\text{diox})$ with selected structural parameters in $\text{\AA}$. H atoms omitted, thermal ellipsoids at 50% probability level.



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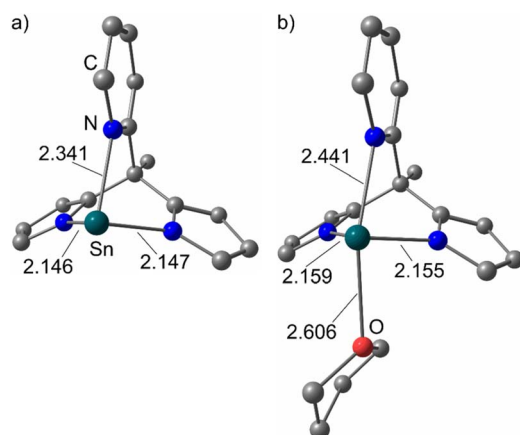


Fig. 3 DFT optimised structures of (a) 1^{Sn} and (b) $1^{\text{Sn}}(\text{thf})$ in the singlet ground state with selected structural parameters in Å (CPCM-(THF)-RIJCOSX-B3LYP-D3BJ-ZORA/def2-TZVPP/old-ZORA-TZVPP(Sn)).

ZORA-TZVPP(Sn)/SARC-ZORA-TZVPP(Pb)). The structural parameters are well reproduced by the DFT geometry optimised structures of 1^{Sn} (Sn-N^{pyr}: 2.341 Å) and $1^{\text{Sn}}(\text{thf})$ (Sn-O^{thf}: 2.606 Å, Sn-N^{pyr}: 2.441 Å) as a model for $(1^{\text{Sn}})_2(\text{diox})$ (Fig. 3; ESI, Table S1†). To probe the presence of different tetrahydrofuran adducts, DFT calculations on $1^{\text{Sn}}(\text{thf})_2$ were additionally performed. Two isomers *cis*- $1^{\text{Sn}}(\text{thf})_2$ and *trans*- $1^{\text{Sn}}(\text{thf})_2$ could be localised as local minima on the potential energy surface as van der Waals adducts between two and one THF molecules and 1^{Sn} (ESI, Fig. S16†). The THF dissociation is exergonic with Gibbs free energies at 298 K for *cis*-/*trans*- $1^{\text{Sn}}(\text{thf})_2$ (*cis*: $\Delta G_{298} = -38 \text{ kJ mol}^{-1}$, *trans*: $\Delta G_{298} = -47 \text{ kJ mol}^{-1}$) to $1^{\text{Sn}}(\text{thf})$ and THF and slightly exergonic for dissociation of $1^{\text{Sn}}(\text{thf})$ ($\Delta G_{298} = -11 \text{ kJ mol}^{-1}$). This indicates that the solvent-free complex 1^{Sn} is the dominant species in solution. An exergonic Gibbs free dissociation energy of $\Delta G_{298} = -31 \text{ kJ mol}^{-1}$ was experimentally determined for the THF dissociation of a cyclic dialkylstannylene THF adduct, supporting the present DFT results.⁶¹

The UV/vis absorption spectra of 1^{Sn} and 1^{Pb} in THF and dimethylsulfoxide (DMSO), respectively, show several intense, broad, overlapping absorptions in the UV region tailing into the visible region with extinction coefficients $\epsilon > 500 \text{ M}^{-1} \text{ cm}^{-1}$ with $\lambda < 350 \text{ nm}$ (Fig. 4). TD-DFT calculations reveal several spin-allowed low-energy $^1\text{ILCT}$ transitions (412–303 nm) with significant oscillator strength between the electron-rich pyrrolato and electron-poor pyridine moieties for 1^{Sn} (Fig. 4a; ESI, Fig. S17†). In addition, pyrrolato $\rightarrow$ Sn $^1\text{LMCT}$ (342, 288, 275 and 272 nm) transitions at similar energies are observed, which might play a role in the dynamics of 1^{Sn} (*vide infra*). Sn $\rightarrow$ pyridine $^1\text{MLCT}$ (271 and 234 nm) and mixed $^1(\text{ILCT/LMCT})$ (319 and 316 nm) transitions, as well as ^1MC (225 nm) transitions are found at higher energies at the Franck-Condon geometry. The TD-DFT spectrum of 1^{Pb} features $^1\text{ILCT}$ transitions (409–305 nm) at very similar energies as found for 1^{Sn} , indicating that the central ion does not significantly affect these ligand-centered ^1CT transitions. $^1\text{LMCT}$ and mixed $^1(\text{ILCT/LMCT})$ transitions of 1^{Pb} are found at lower energies with 367 and 342 nm, respectively, closer to the lowest $^1\text{ILCT}$ transitions (Fig. 4b; ESI, Fig. S18†, $^1\text{MLCT}$

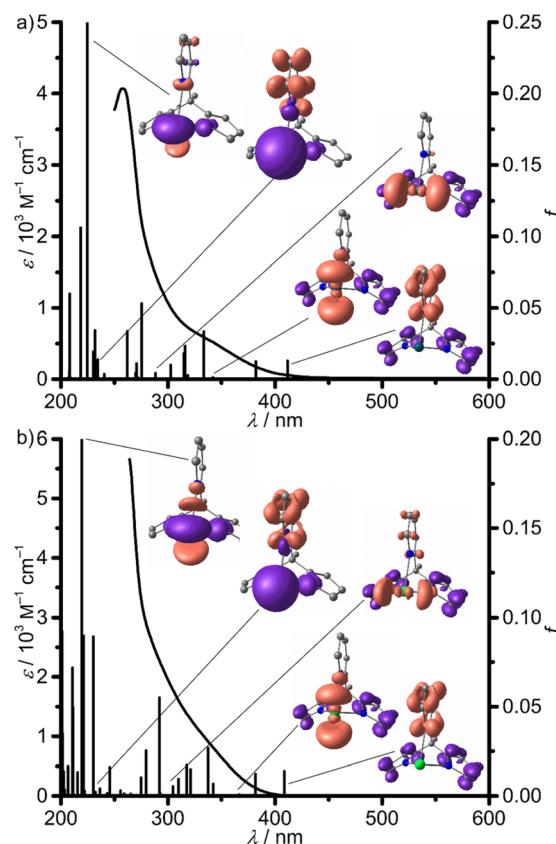


Fig. 4 UV/vis absorption spectra at 293 K of (a) 1^{Sn} in tetrahydrofuran and of (b) 1^{Pb} in dimethylsulfoxide with TD-DFT calculated oscillator strengths on 1^{E} and difference electron densities of selected characteristic spin-allowed transitions (isosurface value 0.005 a.u., purple = electron loss, orange = electron gain, CPCM-(THF)-RIJCOSX-B3LYP-D3BJ-ZORA/def2-TZVPP/old-ZORA-TZVPP(Sn)/SARC-ZORA-TZVPP(Pb)).

(237 nm), ^1MC (220 nm)). The lower $^1\text{LMCT}$ transition energies of 1^{Pb} are attributed to weaker Pb-N^{pyr} and lead-nitrogen(pyrrolato) bonds Pb-N^{pyr}, associated with a lowering of the vacant σ^* -orbitals (LUMO+1, LUMO+3) with high p(Pb)-character with respect to the derivative 1^{Sn} (LUMO+2, LUMO+3, Fig. 1; ESI, Fig. S19, S20 and Tables S1, S2†).

The investigation of the emission properties revealed a very weak photoluminescence of 1^{Sn} at $\lambda_{\text{em},293} = 611 \text{ nm}$ after excitation at $\lambda_{\text{exc}} = 325 \text{ nm}$ in 2-methyl-tetrahydrofuran (2-Me-THF) solution at 293 K (Fig. 5 and Table 1). Unfortunately, unidentified impurities in different batches of commercial spectroscopic grade 2-Me-THF and THF show photoluminescence in the UV with $\lambda_{\text{em}} < 400 \text{ nm}$ tailing into the weak emission of 1^{Sn} after excitation at the same wavelength (Fig. 5b; ESI, Fig. S21†). Variable-temperature emission spectra of 1^{Sn} in 2-Me-THF in a temperature range of 293–77 K show a significant increase in emission intensity and a blue-shift of the emission maximum from $\lambda_{\text{em},293} = 611 \text{ nm}$ in fluid solution at 293 K to $\lambda_{\text{em},77} = 523 \text{ nm}$ in frozen solution at 77 K (Fig. 5 and Table 1). This is probably a consequence of a rigidochromic effect.⁶² The excitation spectra at 293 and 77 K largely follow the absorption spectrum at the low energy part (Fig. 4; ESI, Fig. S22†). Due to the



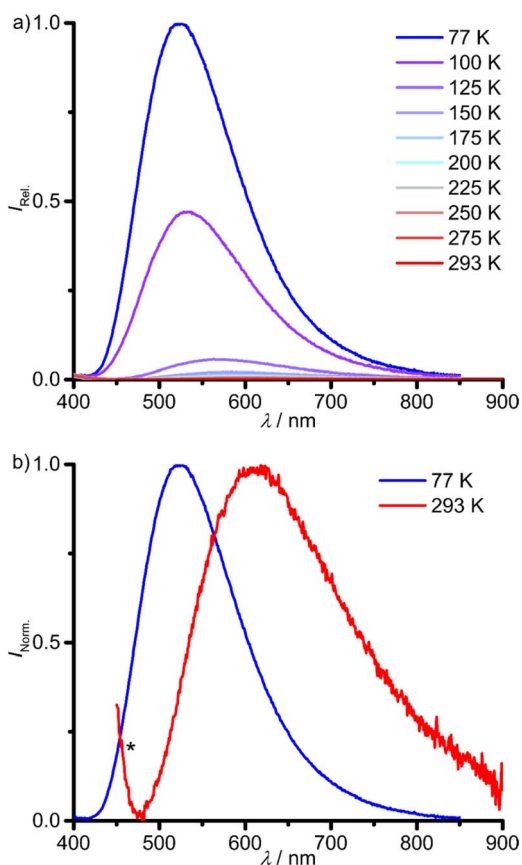


Fig. 5 (a) Temperature-dependent photoluminescence spectra of 1^{Sn} in deaerated 2-Me-THF between 77 K (blue) and 293 K (red) with $\lambda_{\text{exc}} = 325$ nm and (b) the normalised emission spectra at 77 K and 293 K. The asterisk denotes the emission of an unidentified impurity in 2-Me-THF.

Table 1 Emission properties of 1^{Sn} and 1^{Pb}

	$\lambda_{\text{p}}/\text{nm}$	τ_{p}	Φ_{p}
1^{Sn}			
293 K ^a	611	≤ 8 ns (n.d.)	n.d. ^c
77 K ^a	523	2.0 (37%), 0.5 (43%), 0.1 (20%) ms ^d	n.d. ^c
293 K ^b	535	14 ns	0.005
77 K ^b	504	3.6 ms	0.58
1^{Pb}			
77 K ^b	700	92 ns	0.0024

^a 2-Me-THF solution. ^b Solid state. ^c Not detectable. ^d Relative emission amplitudes in parentheses.

weak photoluminescence, high concentrations had to be used, which cause spectral distortion in the high energy range. The photoluminescence lifetime measurements of 1^{Sn} in fluid solution in the 125–293 K range gives ambiguous results due to the contribution of the photoluminescent impurity in 2-Me-THF. The determined lifetimes in the nanosecond range coincide with the emission of the unidentified impurity in 2-Me-THF ($\tau_{\text{em}} = 8$ ns at 125 K). Hence, the photoluminescence lifetime of 1^{Sn}

might be in a similar or smaller order of magnitude as rough estimate (ESI, Fig. S23†). The fluorescent impurity in 2-Me-THF, the very weak emission of 1^{Sn} at room temperature and the low solubility of 1^{Sn} in other solvents prevented the photoluminescence quantum yield determination in solution.

The photoluminescence lifetime of 1^{Sn} drastically increases to the millisecond range in frozen solution. The emission decay trace at 77 K is described with three lifetimes in the millisecond range ($\tau_1 = 2.0$ ms, $\tau_2 = 0.5$ ms, $\tau_3 = 0.1$ ms; Table 1). At 100 K, the lifetimes drop by one order of magnitude with τ_3 vanishing in the instrument response function (IRF, $\tau_1 = 0.1$ ms, $\tau_2 = 0.03$ ms; Table 1; ESI, Fig. S24†). The strong temperature dependence of the photoluminescence lifetimes is associated to thermally activated non-radiative deactivation processes, which become dominant at elevated temperatures, even in frozen solution. Competing photophysical processes of different $1^{\text{Sn}}(2\text{-Me-thf})_n$ adducts with varying number of coordinated 2-Me-THF molecules in (frozen) solution might account for a bi- or triexponential photoluminescence decay. The very long photoluminescence lifetime at 77 K assigns the emission to a phosphorescence process, *i.e.* emission from a triplet state. According to DFT calculations, phosphorescence occurs from a rather nested $^3\text{ILCT}$ state (*vide infra*).

Solid donor solvent-free 1^{Sn} emits at shorter wavelength $\lambda_{\text{p},293} = 535$ nm (293 K) and with a similar band shape as in solution (Fig. 5, 6a and Table 1). The emission blue-shifts to $\lambda_{\text{p},77} = 504$ nm upon cooling to 77 K (Fig. 6a and Table 1). The phosphorescence lifetimes from monoexponential fits and the photoluminescence quantum yields are determined to $\tau_{\text{p},293} = 14$ ns, $\Phi_{\text{p},293} = 0.005$ and $\tau_{\text{p},77} = 3.6$ ms, $\Phi_{\text{p},77} = 0.58$ at 293 and 77 K, respectively (Table 1; ESI, Fig. S25†).

The strong temperature dependence of the photoluminescence lifetime and yield is attributed to thermally activated non-radiative processes. According to the high phosphorescence quantum yield at 77 K, $^1\text{ES} \rightarrow ^3\text{ES}$ ISC should be very efficient. Hence, non-radiative ES deactivation occurs mainly from the triplet ES. An Arrhenius plot of the photoluminescence rate constants ($k(T) = 1/\tau_{\text{p}}(T)$) is fitted as a sum of three rate constants $k_0/k_1/k_2$ (eqn (1) and Fig. 6b).⁶³ k_0 includes non-thermally activated radiative and non-radiative processes, while $k_1(T)$ and $k_2(T)$ are temperature dependent, expressed as Arrhenius equations with frequency factors A_1/A_2 and activation energies E_{a1}/E_{a2} (eqn (1)).

$$\frac{1}{\tau_{\text{p}}(T)} = k(T) = k_0 + k_1(T) + k_2(T) = k_0 + A_1 e^{-\frac{E_{a1}}{RT}} + A_2 e^{-\frac{E_{a2}}{RT}} \quad (1)$$

The obtained fit parameters indicate two thermally activated processes depopulating the photoluminescent state with barriers of $E_{a1} = 0.25$ eV (2000 cm^{-1}), dominating the high temperature regime and $E_{a2} = 0.10$ eV (810 cm^{-1}), dominant in the low temperature regime (Fig. 6b and Table 2).

Thermally activated depopulation of the photoluminescent state *via* two non-emissive ESs at similar activation energies has been observed for Rh^{III} complexes.⁶³



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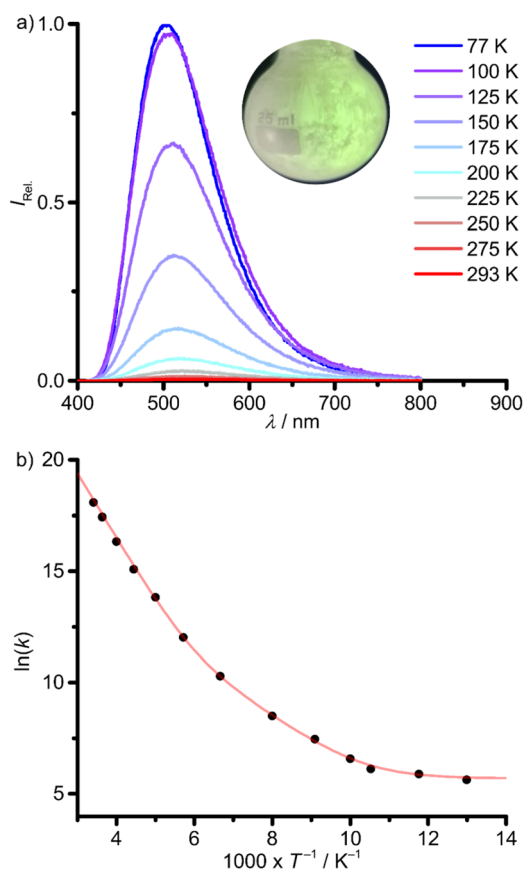


Fig. 6 (a) Temperature-dependent photoluminescence spectra of 1^{Sn} in the solid state between 77 K (blue) and 293 K (red) with $\lambda_{\text{exc}} = 350$ nm (inset: photograph of the green photoluminescence at ca. 77 K) and (b) Arrhenius plot of the photoluminescence rate constants ($k(T) = 1/\tau_p(T)$, $T = 77$ –293 K) with fit (red curve), according to eqn (1).

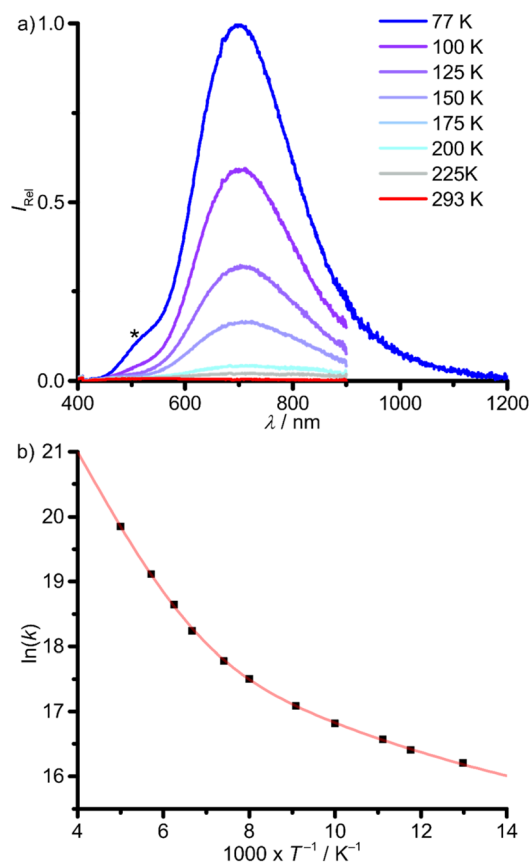


Fig. 7 (a) Temperature-dependent photoluminescence spectra of 1^{Pb} in the solid state between 77 K (blue) and 200 K (red) with $\lambda_{\text{exc}} = 350$ nm. The spectrum at 77 K is composed of two spectra, measured with different detectors. The asterisk denotes the photoluminescence of an unidentified minor impurity (oxidation or solvolysis product of 1^{Pb}). (b) Arrhenius plot of the photoluminescence rate constants ($k(T) = 1/\tau_p(T)$, $T = 77$ –200 K) with fit (red curve), according to eqn (1).

Table 2 Fit parameters for the emission decays of solid 1^{Sn} and 1^{Pb} , obtained from Arrhenius plots, according to eqn (1)

	1^{Sn}	1^{Pb}
k_0/s^{-1}	298	3.77×10^6
E_{a_1}/eV (cm^{-1})	0.25 (2000)	0.11 (890)
E_{a_2}/eV (cm^{-1})	0.10 (810)	0.02 (200)
A_1/s^{-1}	1.57×10^{12}	1.88×10^{11}
A_2/s^{-1}	6.14×10^7	2.62×10^8

In contrast, 1^{Pb} shows no photoluminescence in fluid DMSO solution at r.t. The low solubility of 1^{Pb} in glass forming solvents prevented the investigation of the photoluminescence properties in solution at low temperatures. Yet, 1^{Pb} shows a weak phosphorescence with $\lambda_{p,77} = 700$ nm in the solid state at 77 K. Raising the temperature shifts the emission to lower energies with a strong loss of intensity ($\lambda_{p,200} = 720$ nm, Fig. 7a). A minor impurity, below the NMR detection limit, with $\lambda_{\text{em}} = 500$ nm is ascribed to hydrolysis or oxidation products of 1^{Pb} , indicated by an asterisk in Fig. 7a. This assignment was verified by measuring the sample again after contact to air, showing

a decrease of the band at ≈ 700 nm and an increase of the band at ≈ 500 nm (ESI, Fig. S26†).

The photoluminescence lifetimes of 1^{Pb} determined from monoexponential fits drop from $\tau_{p,77} = 92$ ns to $\tau_{p,200} = 2.4$ ns upon warming from 77 to 200 K, respectively, with a very small photoluminescence quantum yield of $\Phi_{p,77} = 0.0024$ at 77 K (ESI, Fig. S27†). Two activation barriers $E_{a_1} = 0.11$ eV (890 cm^{-1}) and $E_{a_2} = 0.02$ eV (200 cm^{-1}) could be extracted from an Arrhenius plot of the photoluminescence rate constants ($k(T) = 1/\tau_p(T)$, eqn (1), Fig. 7b and Table 2). The much larger rate constant k_0 of 1^{Pb} (3.77×10^6 s^{-1}) vs. 1^{Sn} (298 s^{-1}) includes non-thermally activated radiative and non-radiative processes and will be discussed in the context of DFT calculations (*vide infra*). The phosphorescence of 1^{Pb} in the solid state at 77 K ($\lambda_{p,77} = 700$ nm, $14\,300$ cm^{-1}) occurs at significantly lower energy as that of 1^{Sn} ($\lambda_{p,77} = 504$ nm, $19\,800$ cm^{-1}), despite the very similar absorption spectra (Fig. 4, 6a and 7a). Hence, the emissive states must be of different nature. DFT calculations serve to assign the different emissive states (*vide infra*).



2.2. Quantum chemical investigations

From the TD-DFT analysis, it becomes clear that excitation with 325 and 350 nm as used in the experimental setups populates a number of singlet states with different character in the Franck-Condon region, including $^1\text{ILCT}$ and $^1\text{LMCT}$ states (Fig. 4). It is likely that ISC is very fast and efficient due to the primary heavy atom effect *via* very large SOC of Sn and Pb (SOC constants: $\zeta(\text{Sn}) = 1855 \text{ cm}^{-1}$, $\zeta(\text{Pb}) = 5089 \text{ cm}^{-1}$).⁵⁸ Consequently, we focus in the following discussion on the triplet states of ^1Sn and ^1Pb only. In order to shed light onto the divergent emission properties of the tin and lead complexes, DFT calculations were performed on the triplet states (CPCM-(THF)-RIJCOSX-UB3LYP-D3BJ-ZORA/def2-TZVPP/old-ZORA-TZVPP(Sn)/SARC-ZORA-TZVPP(Pb)). In both cases, three triplet states with distinct structural features could be located, namely $^3\text{ILCT}$, $^3\text{LMCT}_{\text{py}}$ and $^3\text{LMCT}_{\text{pyr}}$ states. The $^3\text{ILCT}$ state is essentially nested with the ^1GS . The major ^1GS

to $^3\text{ILCT}$ state geometric reorganization is an E-N^{py} bond contraction with a slight E-N^{pyr} elongation with parallel decrease of the angle between the pyrrolate mean-square planes from 130° to 106° (ESI, Tables S1 and S2[†]). The $^3\text{LMCT}_{\text{py}}$ and $^3\text{LMCT}_{\text{pyr}}$ states (py = pyridine and pyr = pyrrolato) are strongly distorted with broken E-N^{py} and E-N^{pyr} bonds, respectively, in addition to a tilting of the respective heterocyclic pyridine or pyrrolate rings (Fig. 8–10). The $^3\text{LMCT}_{\text{py}}$ state possesses the lowest energy in both complexes. The next higher state is $^3\text{ILCT}$ and $^3\text{LMCT}_{\text{pyr}}$ for the tin and lead derivatives, respectively (Table 3).

$^3\text{ILCT} \rightarrow ^3\text{LMCT}_{\text{py}}$ and $^3\text{ILCT} \rightarrow ^3\text{LMCT}_{\text{pyr}}$ DFT optimized transition states were located for ^1Sn giving activation barriers of 0.23 and 0.29 eV, respectively (Table 3 and Fig. 8). A much lower $^3\text{ILCT} \rightarrow ^3\text{LMCT}_{\text{py}}$ activation barrier of 0.06 eV was found for ^1Pb , while no $^3\text{ILCT} \rightarrow ^3\text{LMCT}_{\text{pyr}}$ transition state could be located in this case (Fig. 9a). 2D maps of the triplet surfaces projected along the E-N^{py} and E-N^{pyr} modes were calculated on a lower level of theory for ^1Sn and ^1Pb (Fig. 10). The map of ^1Sn

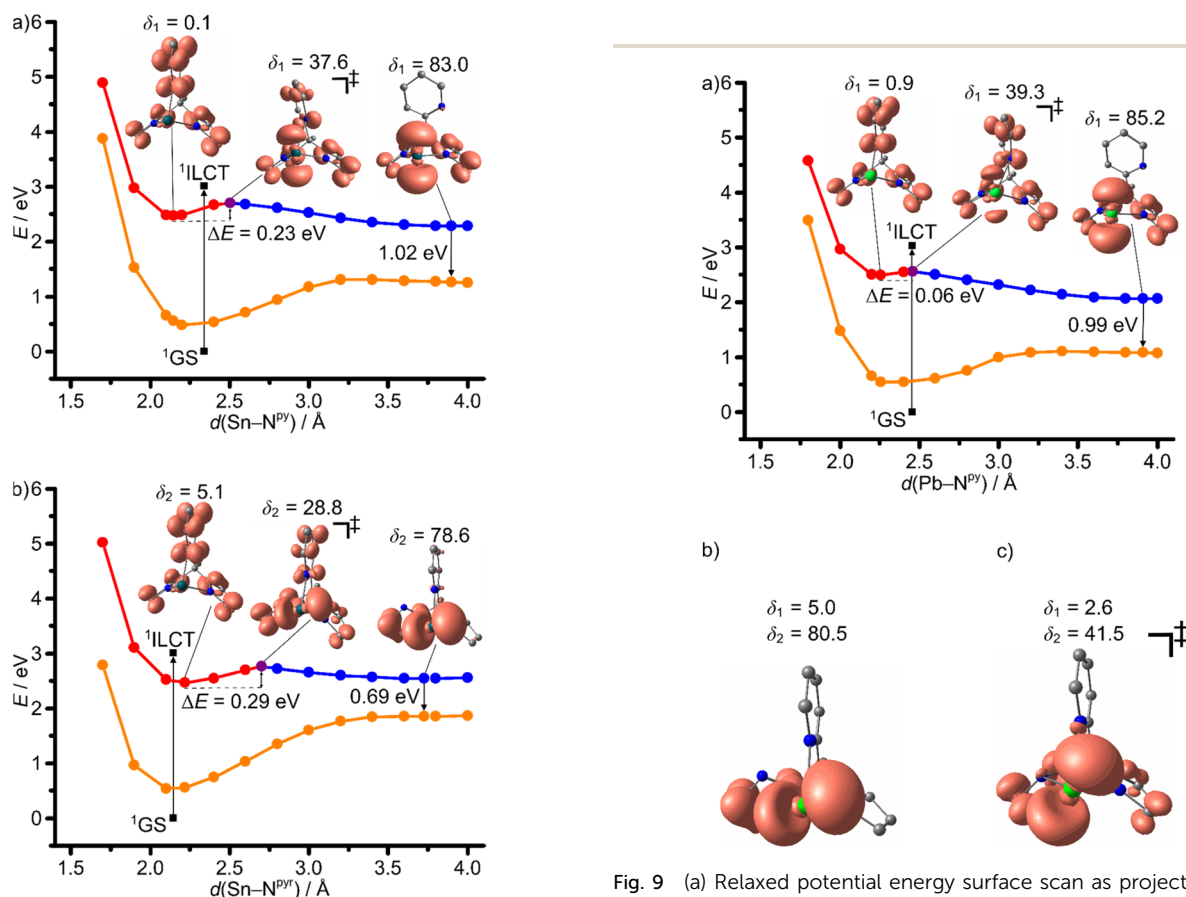


Fig. 8 Relaxed potential energy surface scans as projections along the (a) Sn-N^{py} and (b) Sn-N^{pyr} stretching modes on the triplet hypersurface $^3\text{1}^{\text{Sn}}$ with selected geometry optimised molecular structures with spin densities (isosurface value: 0.005 a.u.) and single point energies on singlet GS hypersurface $^1\text{1}^{\text{Sn}}$ at $^3\text{1}^{\text{Sn}}$ geometries (SCF energies). Selected Sn-N^{py/pyr}-C^{py/pyr}-C^{backbone} dihedral angles δ_1/δ_2 in deg. are indicated. $^3\text{ILCT}$ states in red, triplet transition states $^3\text{ILCT} \rightarrow ^3\text{LMCT}_{\text{py}}$ (a) and $^3\text{ILCT} \rightarrow ^3\text{LMCT}_{\text{pyr}}$ (b) in purple, $^3\text{LMCT}_{\text{py}}/^3\text{LMCT}_{\text{pyr}}$ states in blue and ^1GS in orange. Vertical transition from relaxed ^1GS to the $^1\text{ILCT}$ state from TD-DFT calculations (3.01 eV) indicated as black arrow. CPCM-(THF)-RIJCOSX-(U)B3LYP-D3BJ-ZORA/def2-TZVPP/old-ZORA-TZVPP(Sn).

Fig. 9 (a) Relaxed potential energy surface scan as projection along the Pb-N^{py} stretching mode on the triplet hypersurface $^3\text{1}^{\text{Pb}}$ with selected geometry optimised molecular structures with spin densities (isosurface value: 0.005 a.u.) and single point energies on singlet GS hypersurface $^1\text{1}^{\text{Pb}}$ at $^3\text{1}^{\text{Pb}}$ geometries (SCF energies). Selected Pb-N^{py}-C^{py}-C^{backbone} dihedral angles δ_1 in deg. are indicated. $^3\text{ILCT}$ state in red, triplet transition state $^3\text{ILCT} \rightarrow ^3\text{LMCT}_{\text{py}}$ in purple, $^3\text{LMCT}_{\text{py}}$ state in blue and ^1GS in orange. Vertical transition from relaxed ^1GS to the $^1\text{ILCT}$ state from TD-DFT calculations (3.03 eV) indicated as black arrow. Molecular structures with spin densities (isosurface value: 0.005 a.u.) and Pb-N^{py/pyr}-C^{py/pyr}-C^{backbone} dihedral angles δ_1/δ_2 in deg. of (b) the $^3\text{LMCT}_{\text{pyr}}$ state and of (c) the $^3\text{LMCT}_{\text{py}}/^3\text{LMCT}_{\text{pyr}}$ transition state, respectively. CPCM-(THF)-RIJCOSX-(U)B3LYP-D3BJ-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Pb).



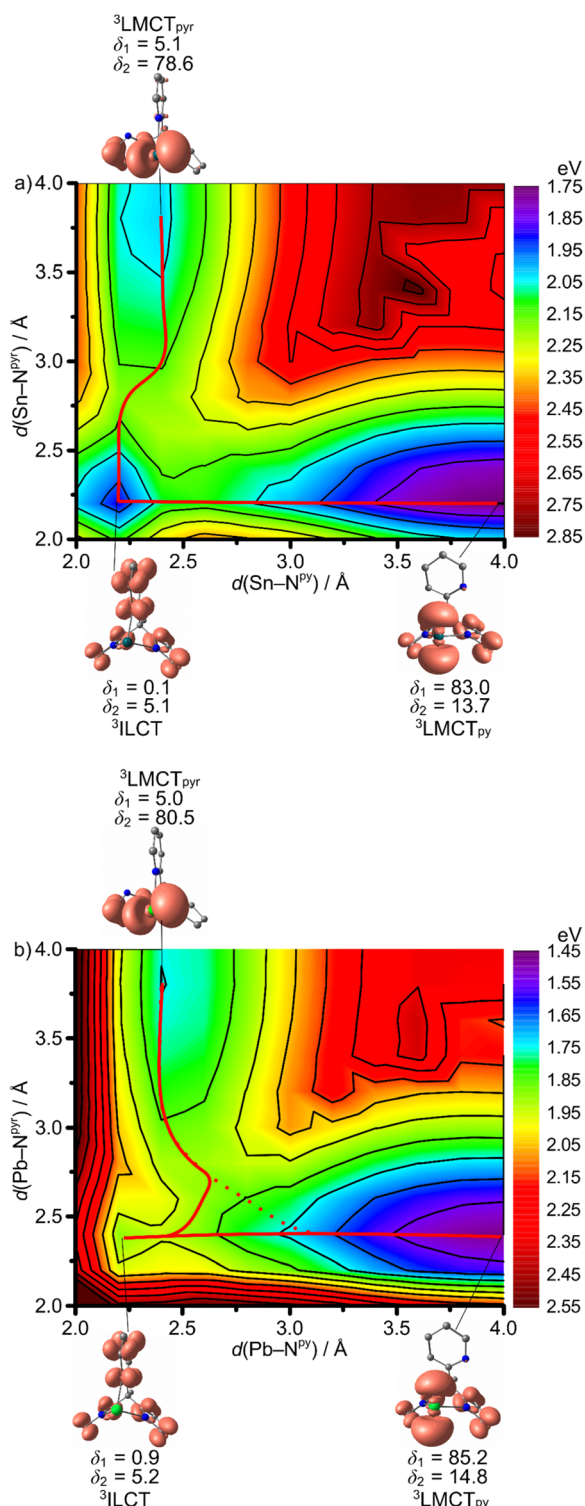


Fig. 10 Contour plots of 2D relaxed potential energy surface scans as projection along the E–N^{py} and E–N^{pyr} stretching modes on the triplet hypersurface ³E with selected geometry optimised molecular structures with spin densities (isosurface value: 0.005 a.u.) of (a) **1**^{Sn} and (b) **1**^{Pb}. Selected E–N^{py/pyr}–C^{py/pyr}–C^{backbone} dihedral angles δ_1/δ_2 in deg. are indicated and the graphically determined, estimated minimum energy paths for ³ILCT → ³LMCT_{py}/³LMCT_{pyr} (red lines) and ³LMCT_{py}/³LMCT_{pyr} internal conversion (dotted line). Energies are given vs. the ¹GS energy (ESI, Fig. S28†). CPCM–(THF)–RIJCOSX–UB3LYP–D3BJ–ZORA/def2-TZVPP/old-ZORA–TZVPP(Sn)/SARC–ZORA–TZVPP(Pb).

Table 3 Relative energies (SCF)^a of triplet states, ¹GS and transition states (TS) in eV, calculated by DFT for **1**^{Sn} and **1**^{Pb}

	1 ^{Sn}	1 ^{Pb}
³ ILCT	0	0
³ LMCT _{py}	−0.19	−0.43
³ LMCT _{pyr}	+0.08	−0.15
¹ GS _{relaxed}	−2.47	−2.49
¹ GS ³ ILCT-geom ^c	−1.91	−1.94
¹ GS ³ LMCT _{py} -geom ^c	−1.21	−1.42
¹ GS ³ LMCT _{pyr} -geom ^c	−0.61	−0.95
TS(³ ILCT → ³ LMCT _{py})	+0.23	+0.06
TS(³ ILCT → ³ LMCT _{pyr})	+0.29	—
TS(³ LMCT _{py} → ³ LMCT _{pyr}) ^d	—	+0.46

^a For Gibbs free energies, see: ESI, Table S3. ^b Relaxed geometry. ^c ¹GS at relaxed ³ILCT, ³LMCT_{py} and ³LMCT_{pyr} geometry, respectively. ^d Relative energy to the relaxed ³LMCT_{py} state.

clearly shows two trajectories from the ³ILCT state to the ³LMCT states along minimum energy paths (Fig. 10a). In contrast, the map of **1**^{Pb} discloses only a single minimum energy trajectory from the ³ILCT state towards the ³LMCT_{py} state, but suggests a (higher energy) path from the ³LMCT_{py} to the ³LMCT_{pyr} state (Fig. 10b). This excited state landscape explains the failure to locate a ³ILCT → ³LMCT_{pyr} transition state for **1**^{Pb}.

Assuming that the dynamics after ISC on the triplet surface start at the respective relaxed ³ILCT states, the different barriers to the ³LMCT states of 0.23/0.29 eV and 0.06 eV for **1**^{Sn} and **1**^{Pb}, respectively, will determine the following dynamics (Table 3). Without emphasising the calculated numbers too strongly, we note that for **1**^{Sn} an experimental barrier of $E_{a_1} = 0.25$ eV has been determined close the calculated values (Tables 2 and 3). As the ³LMCT_{pyr} state lies above the ³ILCT state, we assign the observed temperature-dependent emission of **1**^{Sn} at 535 nm to the ³ILCT state and the observed barrier to the ³ILCT → ³LMCT_{py} population transfer. Consequently, the emission of **1**^{Sn} is a non-Kasha emission due to a significant barrier to the lower energy triplet state (³LMCT_{py}).

On the other hand, the very small ³ILCT → ³LMCT_{py} barrier calculated for **1**^{Pb} suggests that rapid evolution to the ³LMCT_{py} state occurs along with Pb–N^{py} bond elongation and dissociation. This strongly distorted state at low energy can rapidly decay back to the ¹GS, which fits to the experimental observations of a weak, short-lived, low-energy emission of **1**^{Pb} (Table 1). The ³LMCT_{pyr} state of **1**^{Pb} lies above the ³LMCT_{py} state and the ³LMCT_{py} → ³LMCT_{pyr} barrier of 0.46 eV impedes its significant population leading to the assignment of the observed low-energy emission as originating from the ³LMCT_{py} state (Table 3 and Fig. 9b, c). The other small barriers of 0.02–0.11 eV observed in the photoluminescence decays of **1**^{Sn} and **1**^{Pb} might be associated to other modes that promote the ISC from the triplet states to the ¹GS (Table 2). These enabling modes are not covered in our calculations (Table 3).

It is to note, in the frame of these DFT calculations the rigid environment of a solid with constrained geometric reorganisation is not fully described and the barriers and ES energies might be higher due to externally forced rigidification. Yet,



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distinct geometric flexibility in the solid state has been discussed for photo-switches⁶⁴ and photoluminescent copper(I) complexes.⁶⁵ On the other hand, rigidification by aggregation significantly impacts the GS and ES potential energy surfaces, *e.g.* raising the energy of conical intersections and surface crossing points, which leads to aggregation-induced emission^{66,67} and in particular, aggregation-induced phosphorescence.^{18,68} The molecular flexibility in the solid state of **1**^{Sn} and in particular of **1**^{Pb} might be sufficient for thermally activated depopulation of the ³ILCT state *via* the lower-lying ³LMCT states. However, the lifetime and energy of the ³LMCT_{py} state are sufficiently high to observe the very weak phosphorescence of **1**^{Pb} at low temperatures (Fig. 7).

The experimental rate constant $k_0 = 298 \text{ s}^{-1}$ of **1**^{Sn} is much smaller than $k_0 = 3.77 \times 10^6 \text{ s}^{-1}$ of **1**^{Pb}. This finding might be associated with the different vertical energy gaps of 1.91 and 0.99 eV between the emissive states ³ILCT/³LMCT_{py} and the ¹GS (Fig. 8a, 9a and Table 3) and the different SOC contribution promoting ISC to the ¹GS in the ³ILCT (smaller SOC) and ³LMCT (higher SOC) states, respectively, together with the smaller heavy-atom effect for Sn, compared to Pb.

The excited state dynamics of **1**^{Sn} in frozen 2-Me-THF might additionally be affected by solvent coordination during freezing and hence the presence of different solvates in the frozen sample, *e.g.* **1**^{Sn}(2-Me-thf)_n, which might account for the multiple emission lifetimes. Consequently, TD-DFT calculations were performed on **1**^{Sn}(thf). Similar to **1**^{Sn}, the lowest Franck–Condon states are of ¹ILCT character, slightly shifted to higher energies (ESI, Fig. S29–31†).

The Sn–O^{thf} distance of 2.606 Å in the ¹GS increases to 2.925 Å in the ³ILCT state, while the Sn–N distances are essentially unchanged, according to DFT calculations (Fig. 3b and 11a; ESI, Table S1†). This suggests that the initially populated ³ILCT state of the adduct **1**^{Sn}(thf) is strongly distorted. The deactivation of the ³ILCT state occurs preferentially *via* the ³LMCT_{py} state suggested by a 2D relaxed triplet surface scan as a projection along the Sn–O^{thf} and Sn–N^{py} modes (Fig. 12). The trajectory for ³ILCT/³LMCT_{py} internal conversion follows the Sn–O^{thf} coordinate with THF dissociation, forming donor-free **1**^{Sn} within the ³ILCT state and then converts to the ³LMCT_{py} state along the Sn–N^{py} coordinate (Fig. 12). The ³LMCT_{py} state is slightly destabilised relative to the ³ILCT in the loose van-der-Waals adduct between THF and **1**^{Sn} in **1**^{Sn}(thf) (Tables 3 and 4; ESI, Tables S3 and S4†). A relaxed surface scan on the ³ILCT surface along the Sn–O^{thf} stretching mode shows that THF dissociation is essentially barrierless (Fig. 11a). Additionally, a ³MLCT and a ³LMCT_{pyr} state with dissociated pyrrolato moiety and THF, could be located as local minima for the THF adduct **1**^{Sn}(thf) at higher energies (Fig. 11; ESI, Table S1†). The geometries of the relaxed ³MLCT and ³ILCT states mainly differ by their Sn–O^{thf} distances and N^{py}–Sn–O^{thf} angles δ_3 , in accordance to the valence shell electron pair repulsion model as simplest explanation (Fig. 11a; ESI, Table S1†). Due to their comparably high energy, these ³MLCT and ³LMCT_{pyr} states should not play a significant role in the deactivation of the phosphorescent ³ILCT state (Table 4; ESI, Table S4†).

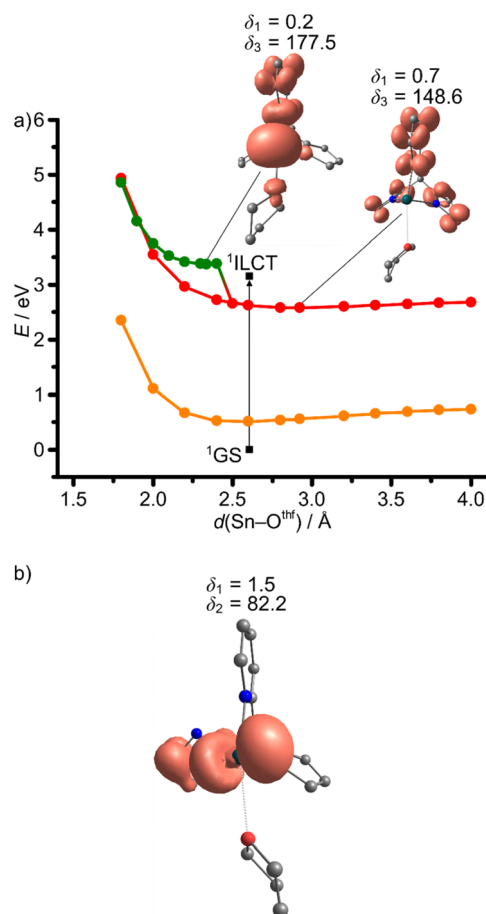


Fig. 11 (a) Relaxed potential energy surface scans as projections along the Sn–O^{thf} stretching mode on the triplet hypersurface ³**1**^{Sn}(thf) with selected geometry optimised molecular structures with spin densities and single point energies on singlet GS hypersurface ¹**1**^{Sn}(thf) at ³**1**^{Sn}(thf) geometries (SCF energies). ³ILCT state indicated in red, ³MLCT state in green and ¹GS in orange. Vertical transition from relaxed ¹GS to the ¹ILCT state from TD-DFT calculations (3.15 eV) indicated as black arrow. (b) Molecular structure of the ³LMCT_{pyr} state with spin density. Spin density isosurface values are at 0.005 a.u. Selected Sn–N^{pyr}–C^{pyr/pyr}–C^{backbone} dihedral angles δ_1/δ_2 and N^{pyr}–Sn–O^{thf} angles δ_3 in deg. are indicated. CPCM-(THF)-RIJCOSX-(U)B3LYP-D3BJ-ZORA/def2-TZVPP/old-ZORA-TZVPP(Sn).

In summary, the calculations suggest that donor-free **1**^{Sn} shows emission from a weakly distorted ³ILCT state (non-Kasha behavior) due to high enough barriers to the ³LMCT states, while **1**^{Pb} efficiently evolves from the initially populated nested ³ILCT state to the dissociative, low-energy, weakly emissive ³LMCT_{py} state. Compared to the often weakly distorted CT states of photoluminescent TMCs,^{1–3} the low-energy ³LMCT states observed here are highly distorted. Clearly, this arises from the rather non-bonding character of the involved transition metal d-orbitals, while ³LMCT states of **1**^{Sn} and **1**^{Pb} are characterised by the population of $\sigma^*(\text{E-X})$ orbitals leading to large distortions and even donor moiety dissociation (pyridine or pyrrolato). Excited states of ³MLCT nature involving the non-bonding tetrel-centered lone-pair of high s character would be



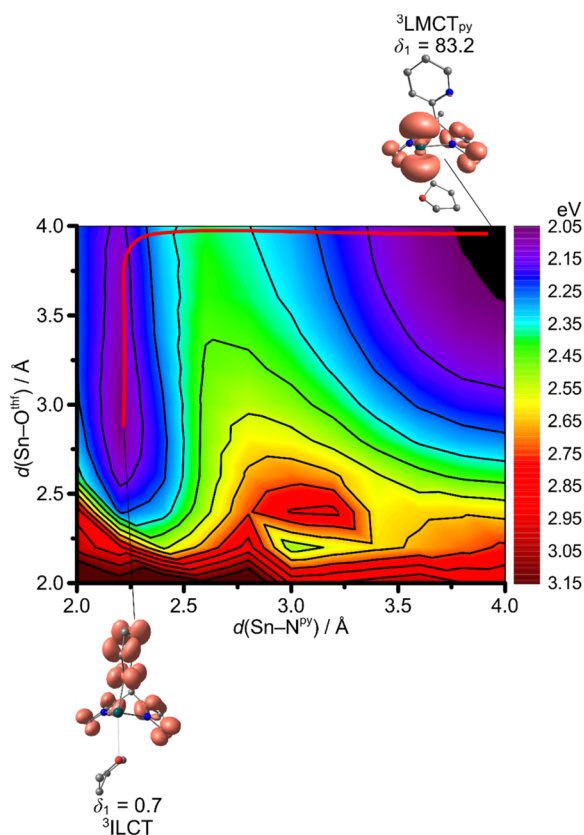


Fig. 12 Contour plot of a 2D relaxed potential energy surface scan as projection along the Sn–N^{py} and Sn–O^{thf} stretching modes on the triplet hypersurface ³1^{Sn}(thf) with selected geometry optimised molecular structures with spin densities (isosurface value: 0.005 a.u.). Selected E–N^{py}–C^{py}–C^{backbone} dihedral angles δ_1 in deg. are indicated and the graphically determined, estimated minimum energy path for ³ILCT → ³LMCT_{py} (red line) internal conversion. Energies are given vs. the ¹GS energy (ESI, Fig. S32†). CPCM-(THF)-RIJCOSX-UB3LYP-D3BJ-ZORA/def2-TZVPP/old-ZORA-TZVPP(Sn).

Table 4 Relative energies (SCF)^a of triplet states and ¹GS in eV, calculated by DFT for 1^{Sn}(thf)

³ ILCT	0
³ LMCT _{py}	−0.11
³ MLCT	+0.79
³ LMCT _{pyr}	+0.10
¹ GS _{relaxed} ^b	−2.58
¹ GS _{3ILCT-geom} ^c	−2.02
¹ GS _{3LMCT_{py}-geom} ^c	−1.15
¹ GS _{3MLCT-geom} ^c	−1.55
¹ GS _{3LMCT_{pyr}-geom} ^c	−0.73

^a For Gibbs free energies, see: ESI, Table S4. ^b Relaxed geometry. ^c ¹GS at relaxed ³ILCT, ³LMCT_{py}, ³MLCT and ³LMCT_{pyr} geometry, respectively.

less distorted. Such ³MLCT states indeed exist, yet at higher energies than the dissociative ³LMCT states in 1^{Sn} and 1^{Pb} (Fig. 1 and 4; ESI, Fig. S17 and S18†). ³LMCT states involving the empty p-type orbital in non-donor stabilised tetraenes might provide another weakly distorted and potentially emissive CT state in tetraenes.

3 Conclusions

Sn^{II}(bpep) 1^{Sn} shows phosphorescence from an ³ILCT state (non-Kasha behavior) in solution and in the solid state. The phosphorescence quantum yield and the photoluminescence lifetime drastically increase from $\tau_{p,293} = 14$ ns, $\Phi_{p,293} = 0.005$ to $\tau_{p,77} = 3.6$ ms, $\Phi_{p,77} = 0.58$ from 293 to 77 K in the solid state. In contrast, Pb^{II}(bpep) 1^{Pb} shows very weak short-lived phosphorescence at 77 K ($\tau_{p,77} = 92$ ns, $\Phi_{p,77} = 0.0024$) with strong decrease in lifetime to $\tau_{p,200} = 2.4$ ns at 200 K. This photoluminescence arises from a ³LMCT state, populated *via* IC from the initially populated ³ILCT state. The strong temperature dependence is attributed to two thermally activated processes with experimentally determined barriers of $E_{a1} = 0.25$ eV and $E_{a2} = 0.10$ eV for 1^{Sn} and $E_{a1} = 0.11$ eV and $E_{a2} = 0.02$ eV for 1^{Pb}. Two strongly distorted, dissociative ³LMCT states, according to (2D) relaxed potential energy surface scans by DFT calculations, open up pathways for fast (non-radiative) deactivation of the nested ³ILCT state. The corresponding barrier is significantly lower for 1^{Pb} (0.06/0.06 eV) than for 1^{Sn} (0.23/0.25 eV, DFT SCF/Gibbs free energies). ISC is fast despite the weak contribution of the Sn and Pb atoms to the excited state wavefunctions of the initially populated ¹ILCT state. The expectedly larger heavy-atom effect, leading to faster ISC of the lead compound 1^{Pb}, is compensated by the much faster deactivation due to the significantly smaller barriers, obtained from variable-temperature photoluminescence lifetime measurements and supported by DFT calculations. In solution, the population of the ³ILCT state of the THF adduct 1^{Sn}(thf) is accompanied with solvent decoordination and formation of 1^{Sn}.

In order to obtain phosphorescent tetrel(II) complexes, the focus should not be kept solely on the heavy-atom effect, invoking effective SOC to enable fast singlet-to-triplet ISC, but also on the ES ordering, enabling fast non-radiative deactivation of potential phosphorescent ESs. Geometric excited state reorganisation and solvent (de-)coordination seems to play a more pronounced role for tetraenes than for pseudo-octahedral TMCs, but seems comparable to pseudo-tetrahedral Cu^I complexes with their ES flattening distortion, prone to solvent or anion coordination.

With the energy landscape of 1^E (E = Sn, Pb), obtained from this initial study, a rational optimisation of the photoluminescent properties emerges. (1) The ³ILCT state should be pushed to energies below the ³LMCT states with electron-withdrawing substituents on the pyridine moieties. (2) The ³LMCT states could be pushed to higher energies with the lighter homologues germanium and silicon, probably with higher ³ILCT/³LMCT barriers by decreased molecular flexibility. (3) Rigidification of the pyridine moiety with bulky substituents could prevent the dissociation and torsional motion of the pyridine. (4) Lowering the energy of the tentatively weakly distorted ³MLCT states below the ³ILCT and ³LMCT states to obtain ³MLCT phosphorescence. (5) Mitigating the dissociative character of the ³LMCT states in non-donor stabilised tetraenes. Current investigations in these directions are in progress.



Data availability

All experimental and computational data are available in the ESI.† Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre under accession numbers CCDC 2211125 and 2211126.

Author contributions

[Redacted text]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

[Redacted text]

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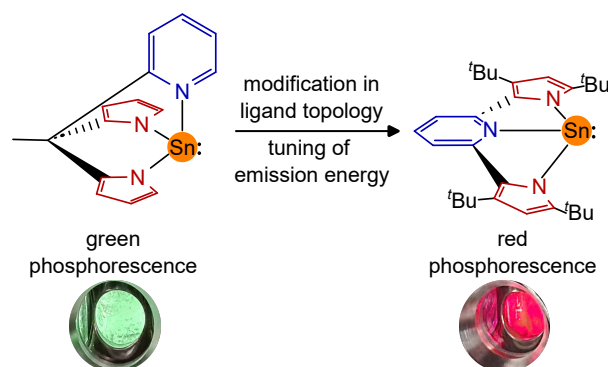


3.3 Ligand Topology Tunes Energy and Character of Emissive Triplet States in Stannylenes

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The tin(II) complex $\text{Sn}(\text{}^t\text{-BuPDP}^{\text{}^t\text{-Bu}})$ was synthesized and investigated toward the photophysical properties. The modification of the ligand topology should target ESs with LMCT character and tune the emission energy. Indeed, this complex shows red LMCT phosphorescence in the solid state. Emission spectroscopy at variable temperatures revealed an unusual temperature-dependent change of the radiative rate constant k_r . This issue was assigned to excitonic interactions due to aggregation in the solid state.

Author Contributions

Philipp Sikora performed the synthesis, characterization, analytical measurements and (TD)-DFT calculations as well as visualized the data and wrote the original draft. [REDACTED] and Philipp Sikora measured the steady-state and time-resolved emission experiments and interpreted the data. [REDACTED] solved and refined the crystal structures. [REDACTED] conceived and designed the project as well as finalized the manuscript with contributions from all authors. [REDACTED] supervised and [REDACTED] cosupervised this project.

Supporting Information

for this article is found on page 164.

Cartesian coordinates of DFT optimized structures can be found online at: <https://chemrxiv.org/doi/full/10.26434/chemrxiv.15000695/v1>

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8 March 2026

Ligand topology tunes energy and character of emissive triplet states in stannylenes

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Abstract

In the last decades, phosphorescent or photoactive complexes with earth abundant transition metals have gained huge attention. On the contrary, heavy main group elements with similar properties are rare, in particular group 14 complexes in the oxidation state +II, e.g. tetrylenes. The excited state properties remained mostly undiscussed and general design concepts for excited state properties-as established for transition metal complexes-are lacking. The present study offers a conceptional topological approach for understanding and addressing specific excited state properties of main group complexes, exemplary discussed by the Sn(t-Bu PDP t-Bu) complex 1 with 2 the dianionic pincer-type ligand t-Bu PDP t-Bu₂-(H₂ t-Bu PDP t-Bu = 2,6-bis(3,5-di-tert-butylpyrrol-2yl)pyridine). 1 shows red triplet ligand-to-metal charge transfer (3 LMCT) phosphorescence in the solid state. Emission intensities of solid 1 vary in an unusual manner with temperature. The obtained experimental results are underpinned and interpreted with detailed (SOC-TD)DFT calculations. The present results are put into context with the few reported studies on the photophysics of stannylenes to achieve a deeper general understanding of the photophysics of main group complexes.

Keywords

Main group complexes, group 14 elements, tetrel complexes, stannylenes, tin, phosphorescence, photoluminescence, photophysics

Ligand topology tunes energy and character of emissive triplet states in stannylenes

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KEYWORDS: Main group complexes, group 14 elements, tetrel complexes, stannylenes, tin, phosphorescence, photoluminescence, photophysics

ABSTRACT

In the last decades, phosphorescent or photoactive complexes with earth abundant transition metals have gained huge attention. On the contrary, heavy main group elements with similar properties are rare, in particular group 14 complexes in the oxidation state +II, e.g. tetrylenes. The excited state properties remained mostly undiscussed and general design concepts for excited state properties – as established for transition metal complexes – are lacking. The present study offers a conceptional topological approach for understanding and addressing specific excited state properties of main group complexes, exemplary discussed by the $\text{Sn}(\text{}^t\text{-BuPDP}^{\text{}^t\text{-Bu}})$ complex **1** with

the dianionic pincer-type ligand ${}^t\text{BuPDP}{}^t\text{Bu}^{2-}$ ($\text{H}_2{}^t\text{BuPDP}{}^t\text{Bu} = 2,6\text{-bis}(3,5\text{-di-}t\text{-butylpyrrol-2-yl})\text{pyridine}$). **1** shows red triplet ligand-to-metal charge transfer (${}^3\text{LMCT}$) phosphorescence in the solid state. Emission intensities of solid **1** vary in an unusual manner with temperature. The obtained experimental results are underpinned and interpreted with detailed (SOC-TD)DFT calculations. The present results are put into context with the few reported studies on the photophysics of stannylenes to achieve a deeper general understanding of the photophysics of main group complexes.

INTRODUCTION

Photoluminescence of transition metal complexes, in particular photoactive transition metal complexes (TMCs) of earth abundant elements, mainly 3d metal ions, developed into a considerable alternative to complexes with precious transition metals like ruthenium, iridium, platinum or gold.^{1–11} The prerequisite for photochemical applications is a sufficiently long lifetime of the excited states (ESs), which is often realized for ESs with different spin multiplicities than the ground state (GS), leading to spin-forbidden nonradiative and radiative processes between ES and GS, consequently extending the ES lifetime.¹² Alternatively, the ES of different spin multiplicity can serve as a reservoir for a fluorescent state which is repopulated in the thermally activated delayed fluorescence (TADF) cascade, thus extending the ES lifetimes, often observed for copper(I) complexes.^{13–17} In all cases, nonradiative processes need to be mitigated. Clear design concepts and structure property relationships were developed for TMCs: i) The emissive/photoactive ES should be rather undistorted, i.e. nested, either directly by the character of the ES, e.g. doublet spin-flip and triplet metal-to-ligand charge transfer (${}^3\text{MLCT}$) states in chromium(III) and iron(II) complexes, respectively,^{4,6,7,9} or by rigidification, e.g. in case of pseudo-tetrahedral copper(I) complexes preventing the flattening distortion.^{13–17} ii) Detrimental (distorted)

ESs opening pathways of nonradiative deactivation should be energetically separated from the emissive/photoactive states, e.g. the separation of the metal-centered (MC) states from the envisaged photoactive $^3\text{MLCT}$ states in iron(II) complexes by modulating ligand field strength and MLCT state energies.^{4,6,7,9} Additionally, efficient intersystem crossing (ISC) is required after initial population of the Franck-Condon (FC) state, which is driven by strong spin-orbit coupling (SOC).^{18–20} SOC can be invoked directly by orbital symmetry considerations as described by the El-Sayed rules,^{21,22} generalized by Marian,¹⁸ and by a heavy atom effect (that scales with Z_{eff}^4 for hydrogen-like atoms)²³ or indirectly by vibronic SOC and spin-vibronic SOC.^{18–20} Besides earth abundant TMCs, main group complexes of the abundant heavy elements might offer an alternative as photoluminescent compounds by contributing to the required SOC with the heavy atom effect.

Heavy main group complexes showing phosphorescence from triplet states and/or TADF from singlet states include mainly group 14 and 15 elements.^{24–27} For example, bismuth(III) complexes with $6s^2$ electron configuration can show phosphorescence.^{28–38} Photoluminescent, isoelectronic group 14 complexes in the oxidation state +II with s^2 electron configuration, are very rare. The S_0 ground state of heavy tetrylenes is characterized by an occupied and an unoccupied tetrel-centered orbital of high s and p character, respectively (Fig. 1).^{39–44} Several types of ES are conceivable. Early studies by Vogler and co-workers on anionic halido tetrel complexes, tetranides, $[\text{EX}_3]^- \text{I}^{\text{E,X}}$ (E = Ge–Pb: X = Cl; E = Sn, Pb: X = Br) and $[\text{PbX}_4]^{2-} \text{II}^{\text{X}}$ (X = Cl, Br) revealed phosphorescence from ^3MC states at 510–604 nm after UV light excitation (Chart 1a).^{45,46} This ^3MC state with s^1p^1 electron configuration is associated with a significant ES distortion from C_{3v} to D_{3h} symmetry in $[\text{EX}_3]^-$ complexes.⁴⁶ This distortion fosters efficient nonradiative deactivation of the ES. Scandola and co-workers reported a weak green fluorescence and an even weaker red phosphorescence from intraligand charge transfer (ILCT) states for $\text{Pb}(\text{QO})_2 \text{III}$ (QOH = 8-hydroxyquinoline) in fluid

and glassy solutions (Chart 1b).⁴⁷ Bis(β -diketonato)lead(II) complexes **IV^{R,R'}** reported by Vogler and co-workers exhibit blue to green ILCT phosphorescence in the solid state.

Chart 1. Tetrylene and tetrane complexes with selected photophysical data.

a) $[\text{EX}_3]^-$ I^{E,X} $\text{E} = \text{Ge, Sn, Pb}; \text{X} = \text{Cl}$ $\lambda_p = 535, 510, 538 \text{ nm}$ $\tau_p = -, -, 17 \mu\text{s}$ $\Phi_p = 0.081, 0.068, 0.159$ $\text{E} = \text{Sn, Pb}; \text{X} = \text{Br}$ $\lambda_p = 603, 604 \text{ nm}$ $\Phi_p = 0.0046, 0.086$ (r.t., CH_3CN)	b) III $\lambda_f = 550 \text{ nm}$ $\tau_f = 0.4 \text{ ns}$ $\Phi_f = 0.003$ $\lambda_p \approx 650 \text{ nm}$ $\tau_p \approx 3 \mu\text{s}$ $\Phi_p < 0.0001$ (298 K, DMF)	c) IV^{R,R'} $\text{R, R}' = \text{Me}: \lambda_p = 525 \text{ nm}$ $\text{R, R}' = \text{CF}_3: \lambda_p = 467 \text{ nm}$ $\text{R} = \text{CF}_3, \text{R}' = \text{C}_4\text{H}_9\text{S}: \lambda_p = 495 \text{ nm}, \lambda_f = 418 \text{ nm}$ $\text{R, R}' = \text{Ph}: \lambda_p = 506, \lambda_f = 448 \text{ nm}$ (r.t., solid state)	d) V $\lambda_p = 593 \text{ nm}$ $\tau_p = 347.5 \mu\text{s}$ $\Phi_p = 0.02$ (solid state)
e) VI^X $\text{X} = \text{Cl, OTf}$ $\lambda_f = 518, 524 \text{ nm}$ $\Phi_f = 0.04, 0.42$ (benzene)	f) VII $\text{R} = \text{alkyl/aryl}$ $\lambda = 589\text{--}598 \text{ nm}$ (r.t., toluene) $\lambda = 613\text{--}686 \text{ nm}$ (r.t., solid state)	g) VIII^{R,R'} $\text{R} = \text{H, R}' = \text{Me}, \lambda_p = 625 \text{ nm}$ $\tau_p = 4.6 \mu\text{s}, \Phi_p = 0.82$ $\text{R} = \text{Me, R}' = \text{Me}, \lambda_p = 600 \text{ nm}$ $\tau_p = 4.5 \mu\text{s}, \Phi_p = 0.34$ $\text{R} = \text{tBu, R}' = \text{Me}, \lambda_p = 620 \text{ nm}$ $\tau_p = 7.3 \mu\text{s}, \Phi_p = 0.44$ $\text{R} = \text{H, R}' = \text{Cl}, \lambda_p = 605 \text{ nm}$ $\tau_p = 7.6 \mu\text{s}, \Phi_p = 0.76$ (300 K, solid state)	h) IX $\lambda_p = 550 \text{ nm}, 605 \text{ nm}$ $\tau_p = 21 \mu\text{s}, 8.6 \mu\text{s}$ $\Phi_p = 0.8, 0.2$ (77 K, 293 K solid state)
i) X^E $\text{E} = \text{Sn, Pb}$ $\lambda_p = 504, 700 \text{ nm}$ $\tau_p = 3.6 \text{ ms}, 92 \text{ ns}$ $\Phi_p = 0.58, 0.0024$ (77 K, solid state)	j) XI^E $\text{E} = \text{Ge, Sn, Pb}; \text{R} = \text{Ph}$ $\text{E} = \text{Sn}; \text{R} = \text{tBu}$ This work 1	k) XII^E $\text{E} = \text{Si, Ge, Sn}$ $\lambda_{\text{TADF}} = 527, 519, 512 \text{ nm}$ $\tau_{\text{TADF}} = 0.9, 1.0, 2.0 \text{ ms}$ $\Phi_{\text{PL}} = 0.47, 0.49, 0.32$ THF, r.t.	l) XIII^E $\text{E} = \text{Si, Ge, Sn}$ $\lambda_{\text{TADF}} = 551, 536, 515 \text{ nm}$ $\tau_{\text{TADF}} = 4.1, 1.3, 1.4 \text{ ms}$ $\Phi_{\text{PL}} = 0.70, 0.75, 0.55$ THF, r.t.

The phosphorescence intensity is reduced in solution at room temperature. The weak phosphorescence of these bis(β -diketonato) plumbylenes was attributed to large amplitude motions in the ES leading to fast nonradiative relaxation.⁴⁸ The respective

hexafluoroacetylacetonato tin(II) complex is non-emissive, even in the solid state.^{48,49} A series of lead(II) coordination polymers with halido and polydentate tetrazolato ligands are phosphorescent from ^3IL , ^3MC and $^3\text{MLCT}$ states with contribution of $^3\text{XLCT}$ state character ($X = \text{halide}$). The photoluminescence lifetimes reach $\tau_p = 1.55$ ms with a maximum quantum yield of $\Phi_p = 0.165$ in the solid state. The monomolecular congener **V** with 6,6'-bis(1*H*-tetrazol-5-yl)-2,2'-bipyridine as proligand shows $^3\text{MLCT}$ phosphorescence with significantly lower photoluminescence quantum yield in the solid state as compared to the polymers ($\Phi_p = 0.02$; Chart 1d).⁵⁰ Substitution of a chlorido ligand with a weakly coordinating triflate (OTf^-) ligand tremendously rises the fluorescence quantum yield of a dipyrinato tin(II) complex from 0.04 (**VI^{Cl}**) to 0.42 (**VI^{OTf}**) and bathochromically shifts the fluorescence band maximum from $\lambda_f = 518$ to 524 nm (Chart 1e).⁵¹ A series of dipyrinato carboxylato germylenes **VII^R** fluoresce at $\lambda_f = 589\text{--}598$ and at $\lambda_f = 613\text{--}686$ nm in toluene and in the solid state at room temperature, respectively (Chart 1f).⁵² Dodonov and co-workers described low valent tin(II) imides possessing a planar Sn_2N_2 core. $[\text{H}^{\text{H,Me}}\text{ArNSn}]_2$ ($\text{H}^{\text{H,Me}}\text{ArNH} = 2,6\text{-Bis[di(phenyl)methyl]-4-methylalanine}$) **VIII^{H,Me}**, for example, shows phosphorescence from a mixed $^3(\text{MC/LMCT})$ state at $\lambda_p = 625$ nm with $\tau_p = 4.6$ μs and a high photoluminescence quantum yield of $\Phi_p = 0.82$ in the solid state at 300 K. The emission is strongly diminished in solution ($\Phi_p = 0.3\%$) (Chart 1g),⁵³ suggesting that nonradiative processes are significantly accelerated in solution.

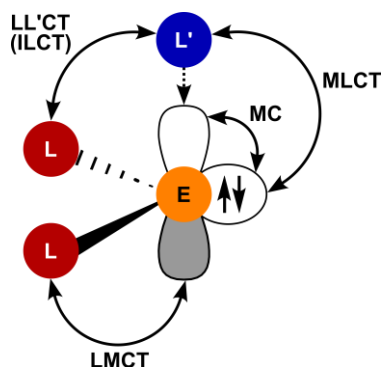


Figure 1. Schematic illustration of selected electronic transitions in donor (L') stabilized homoleptic tetrylenes EL_2 ($E = \text{Si, Ge, Sn, Pb}$), IL and other possible LMCT ($L' \rightarrow E$) and MLCT ($E \rightarrow L$) transitions omitted. Lone pair and p-orbital of E indicated.

Lappert's diamino stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ **IX**^{54,55} shows thermochromic green to orange phosphorescence and thermally activated delayed phosphorescence (TADP) between 77 and 293 K arising from mixed $^3[\text{MC}/\text{LMCT}]$ states ($\lambda_p = 550$ nm, $\tau_p = 21$ μs , $\Phi_p = 0.8$ in the solid state at 77 K, Chart 1h).⁵⁶ The intramolecular donor-stabilized stannylene $\text{Sn}(\text{bpep})$ **X^{Sn}** ($\text{H}_2\text{bpep} = 2$ -[1,1-bis(1*H*-pyrrol-2-yl)ethyl]pyridine) surpasses the lead congener $\text{Pb}(\text{bpep})$ **X^{Pb}** in terms of photophysical performance. **X^{Sn}** shows green non-Kasha phosphorescence from a pyrrolato-to-pyridine $^3\text{ILCT}$ state at $\lambda_p = 523$ and 504 nm at 77 K in solution and the solid state, respectively (Chart 1h, Figure 2a).⁵⁷ The emission lifetimes and photoluminescence quantum yields are strongly temperature dependent between 77 and 293 K both in solution ($\tau_{p,\text{av}} = 0.975$ $\mu\text{s}/<8$ ns) and in the solid state ($\tau_p = 3.6$ ms/14 ns, $\Phi_p = 0.58/0.005$). This indicates that thermally activated nonradiative processes become dominant at ambient temperatures. These were attributed to pyridine (or pyrrolato) donor dissociation with concomitant $^3\text{ILCT} \rightarrow ^3\text{LMCT}$ internal conversion (IC) and fast nonradiative ISC from the $^3\text{LMCT}$ state to the GS.⁵⁷ $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ and $\text{Sn}(\text{bpep})$ emit with similar emission wavelengths, yet from excited states with different character, namely $^3[\text{MC}/\text{LMCT}]$ and

$^3\text{ILCT}$, respectively. Pyridine donor coordination shifts the $^3\text{LMCT}$ state of $\text{Sn}(\text{bpep})$ to higher energy at the FC geometry and increases the formerly non-bonding p-type tetrel orbital in energy due to $\text{Sn}-\text{N}^{\text{py}} \sigma$ antibonding character. Large amplitude motion, corresponding to pyridine donor dissociation, lowers the energy of this $^3\text{ILCT}$ state significantly, enabling fast nonradiative decay via this mode.

The discussed tetrel(II) compounds clearly indicate that a diverse manifold of ESs can be considered emissive, such as ILCT, MC, MLCT, LMCT or XLCT states and combinations thereof. This is schematically depicted for selected transitions in Figure 1. Furthermore, fluorescence or TADF from singlet states or phosphorescence from triplet states are possible radiative pathways, depending on the excited state energies and ISC efficiencies. Design concepts in combination with structure property relationships, as discussed in the context of photoactive TMCs, to selectively modify the nature and energy of ESs are not well established for tetrel(II) compounds. Yet, a deeper understanding might give a rationale to design photoactive/photoluminescent tetrel(II) compounds.

Eliminating the tin p-type orbital donor interaction in $\text{Sn}(\text{bpep})$ can in principle prevent the pathway of nonradiative deactivation involving the EL' mode. This consideration led us to investigate a ligand system analogous to bpep^{2-} with similar pyrrolate/pyridine donor properties, yet with different coordination topology by changing the tripodal bpep^{2-} with the meridional coordinating pyridine dipyrrolide (PDP) pincer-type ligand $^t\text{-BuPDP}^{t\text{-Bu}2-}$ ($\text{H}_2^t\text{-BuPDP}^{t\text{-Bu}} = 2,6\text{-bis}(3,5\text{-di-}t\text{-butylpyrrol-2-yl})\text{pyridine}$, Chart 1j).⁵⁸ In the latter meridional coordination, the pyridine donor should switch from a σ to a π donor interaction with the vacant tin p-type orbital (Figure 2a, 2b). Switching the coordination topology from *facial* to *meridional* should lower the $^3\text{LMCT}$ state, but leave the $^3\text{ILCT}$ state energy essentially unaffected. This ligand coordination

mode should furthermore inhibit pyridine donor dissociation as nonradiative deactivation mode. The ground state reactivity of the tetrylene complexes $E(\text{PDP}^{\text{Ph}}) \text{XI}^E$ ($E = \text{Ge}, \text{Sn}, \text{Pb}$, $\text{H}_2^{\text{Ph}}\text{PDP}^{\text{Ph}} = 2,6\text{-bis}(3,5\text{-diphenyl-1H-pyrrol-2-yl})\text{pyridine}$) with a related ligand system has been studied previously (Chart 1j).^{59,60} However, the photophysics of these systems remained unexplored. In contrast, the photophysical properties of tetraene(IV) complexes with PDP-type ligands $E(\text{MePDP}^{\text{Ph}})_2 \text{XII}^E$ and $E(\text{Me})_2(\text{MePDP}^{\text{Ph}}) \text{XIII}^E$ ($\text{H}_2^{\text{Me}}\text{PDP}^{\text{Ph}} = 2,6\text{-bis}(5\text{-methyl-3-phenyl-1H-pyrrol-2-yl})\text{pyridine}$) have been reported. These tetraenes show prompt fluorescence and TADF with emission lifetimes in the millisecond range for the TADF process and high photoluminescence quantum yields (Chart 1k, 1l).^{61,62} Additionally, $\text{H}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$, $[\text{H}_3^{\text{Mes}}\text{PDP}^{\text{Ph}}]\text{Cl}$ and $\text{Li}_2^{\text{Mes}}\text{PDP}^{\text{Ph}}$ show intense fluorescence.⁶³

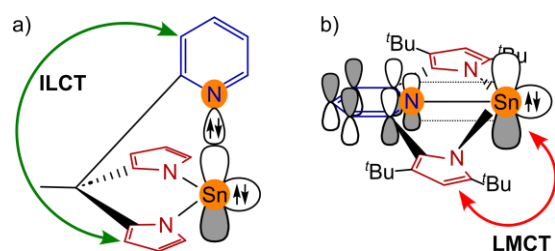
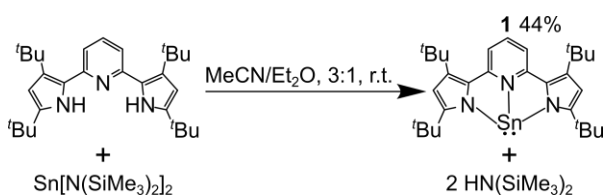


Figure 2. Conceptual approach to tune the character of the lowest-energy excited state of dipyrrolato/pyridine stannylenes by a) *facial* and b) *meridional* ligand topology.

This study sheds more light on the fundamental photophysical processes of tin(II) complexes and connects topological ligand design concepts with experimental photophysical results. We discuss the synthesis and structure as well as emission properties of the $\text{Sn}(\text{}^t\text{-BuPDP}^{\text{}^t\text{-Bu}})$ complex **1** (Chart 1j). The elucidation of these properties is supported by variable-temperature single crystal XRD analysis, variable-temperature steady-state and time-resolved emission spectroscopy as well as quantum chemistry calculations on the spin-orbit coupling (SOC) time-dependent (TD) density functional theory (DFT) level of theory.

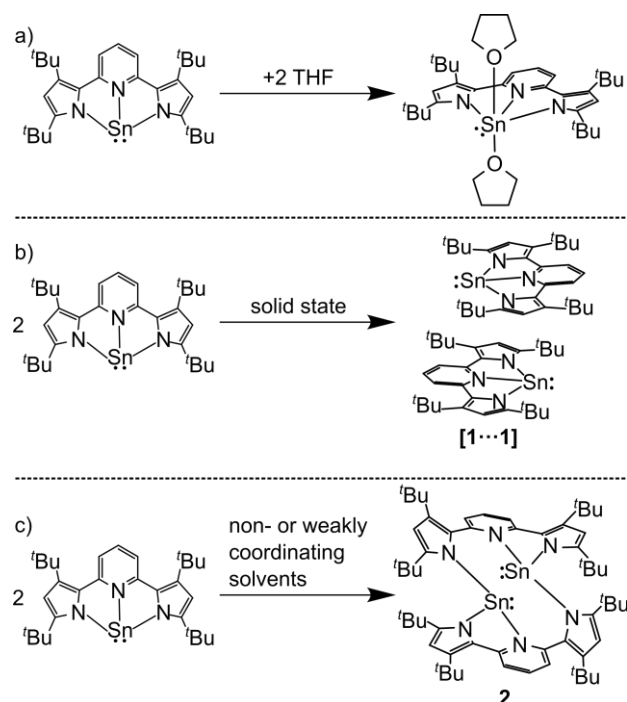
RESULTS AND DISCUSSION

Synthesis and Characterization of 1. The tetraylene complex $\text{Sn}(\text{}^t\text{BuPDP}^{\text{}^t\text{Bu}})$ **1** is synthesized by transamination of $\text{H}_2\text{}^t\text{BuPDP}^{\text{}^t\text{Bu}}$ ⁵⁸ with $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ ^{54,55} in a 3:1 mixture of acetonitrile and diethyl ether as an orange red, extremely moisture and air sensitive solid in 44% yield (Scheme 1).



Scheme 1. Synthesis of stannylene $\text{Sn}(\text{}^t\text{BuPDP}^{\text{}^t\text{Bu}})$ **1** via transamination from $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ and $\text{H}_2\text{}^t\text{BuPDP}^{\text{}^t\text{Bu}}$.

1 is well soluble in tetrahydrofuran (THF) but barely soluble in *n*-pentane or benzene despite the four *tert*-butyl substituents. The coordinating nature of THF might be responsible for the enhanced solubility in THF, most likely forming a THF adduct. THF coordination has been observed in a previous study with the related complex **XI^E** forming the bis(thf) adduct **XI^E(thf)₂**.⁵⁹ Donor-free **1** has been fully characterized by elemental analysis, APCI^+ mass spectrometry and multinuclear (^1H , ^{13}C , ^{119}Sn) NMR spectroscopy (Figures S1–S9). The ^{119}Sn NMR resonance of solid **1** appears at $\delta = -101.6$ ppm (Figure S9). The ^{119}Sn NMR resonance of **1** in THF appears with $\delta = -466.5$ ppm in the chemical shift range of analogous complexes (Figure S8),⁵⁹ indicative for thf adduct formation (Scheme 2a), analogous to the behavior of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$.⁶⁴ The adduct formation leads to a formal occupation of the p-type tetrel orbital with concomitant decreased paramagnetic (de)shielding.⁶⁵



Scheme 2. Formation of a) a thf adduct, b) a Van-der-Waals dimer $[\mathbf{1} \cdots \mathbf{1}]$ in the solid state and c) a dimer **2** in non- or weakly coordinating solvents from $\text{Sn}(\text{t-Bu})\text{PDP}(\text{t-Bu})$ **1**.

The absence of coordinating donors in the solid state is confirmed by single crystal X-ray diffraction (SC-XRD) analysis. Crystals of **1**, suitable for SC-XRD analyses were obtained from a saturated acetonitrile solution by slow evaporation of the solvent. **1** crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit (Figure 3a, Table S1). For the understanding of the photophysical properties (vide infra), a SC-XRD analysis was performed at variable temperatures (100–225 K). The stannylene features a T-type coordination of the nitrogen donors with slightly pyramidalized coordination of the Sn atom with a nitrogen(pyrrolate1)–tin–nitrogen(pyrrolate2) ($\text{N}^{\text{pyr1}}\text{--Sn--N}^{\text{pyr2}}$) angle of $117.07(6)^\circ$. The tin–nitrogen bond lengths of the pyridine (Sn--N^{py}) and pyrrolato donors ($\text{Sn--N}^{\text{pyr1}}/\text{Sn--N}^{\text{pyr2}}$) amount to 2.168(2) and 2.220(2)/2.197(2) Å at 120 K, respectively (Table S1). These bond parameters remain constant within the 3σ limit in the 100–225 K temperature range (Table S1). Two molecules **1** form a

centrosymmetric pair $[1 \cdots 1]$ with a slipped head-to-tail arrangement (Figure 3b, Scheme 2b). These pairs stack along the b axis (Figures S10–S12). In the $[1 \cdots 1]$ pair, the tin atoms have short intermolecular contacts to the pyridine carbon atoms (C17') of the partner molecule (Figures 3b, S13). Interestingly, the Sn–C17' distance within the $[1 \cdots 1]$ pair significantly increases from 3.694(2) to 3.747(2) Å between 100 and 225 K, but remains slightly below the sum of van-der-Waals radii of Sn and C (3.87 Å).⁶⁶ We denote this $[1 \cdots 1]$ pair a van-der-Waals dimer. The monomolecular structure of **1** has been optimized by DFT (CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-ZORA-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn)). These DFT calculations reproduce the experimental structural parameters obtained from SC-XRD analyses, including the pyramidalization of the tin atom ($N^{\text{pyr1}}\text{--Sn--}N^{\text{pyr2}}$: 117.04°) (Figure 3c, Table S1).

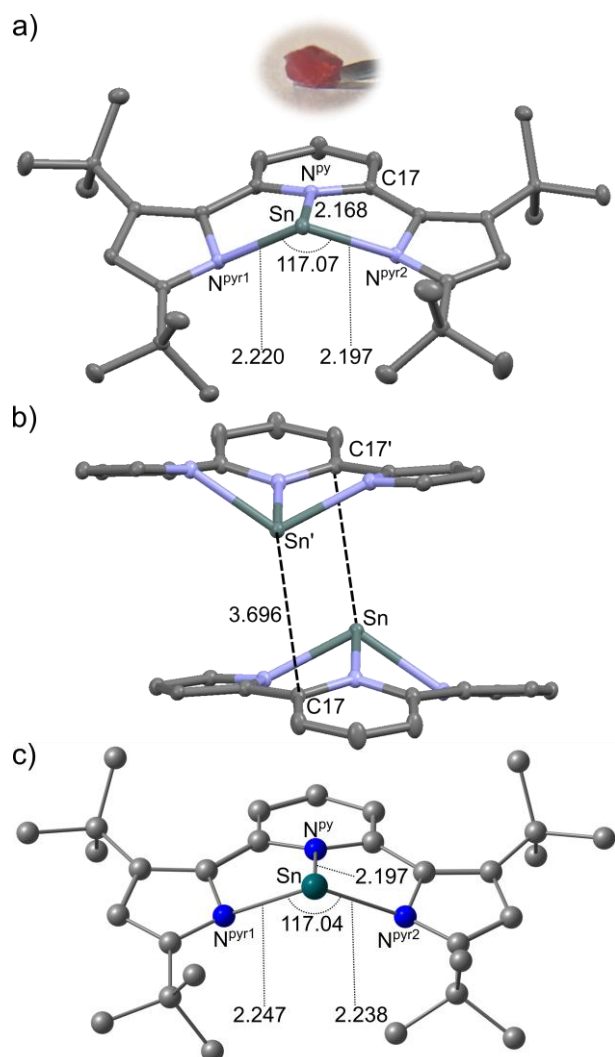


Figure 3. a) Molecular structure of **1** with selected structural parameters in Å and degrees [°] from SC-XRD analysis (photograph of a red crystal of **1** obtained by slow evaporation of an acetonitrile solution of **1**). b) Centrosymmetric pairs [**1**...**1**] with intermolecular Sn...C17' contacts at 120 K (thermal ellipsoids at 50% probability level). c) Molecular structure of **1** from DFT calculations (CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-ZORA-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn)). Hydrogen atoms omitted.

In non- or weakly coordinating solvents like benzene, **1** slowly rearranges to **2** with bridging PDP^{2-} ligands, as already observed for the phenyl-substituted derivative **XI^E** (Scheme 2c).⁵⁹ The slow

rearrangement can be followed by ^1H NMR and DOSY ^1H NMR spectroscopy (Figures S14–S19) showing a double set of ^1H NMR resonances for the ligand protons and a separate trace with a smaller diffusion coefficient for **2** in the DOSY spectra. A ratio for **1/2** of $\approx 1:0.08$ and $\approx 1:0.59$ is established in benzene 20 minutes and one day after sample preparation, respectively, as estimated by integration of the *tert*-butyl ^1H NMR resonances (Figure S17). An $\approx 1:0.40$ ratio of **1/2** is already obtained in 3-methylpentane 30 minutes after sample preparation, indicative for a faster monomer/dimer equilibration (Figure S19). The diffusion coefficients from DOSY NMR spectroscopy amount to $7.09 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ and $5.71 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ for **1** and **2**, respectively (Figure S18). As confirmed by SC-XRD analysis, the structure of the dimer **2** is similar to that of reported $[\text{X}^{\text{E}}]_2$ with $\mu\text{-}\kappa^1\text{N}^{\text{pyr1}}\text{:}\kappa^2\text{N}^{\text{pyr2}},\text{N}^{\text{py}} \text{R}^1\text{PDP}^{\text{R22-}}$ bridging ligands (Figure S20).⁵⁹

The UV/Vis absorption spectrum of a mixture of **1** with the dimer **2** in *n*-pentane is a superposition of the TDDFT calculated spectra of **1** and **2** shifted by $+3500 \text{ cm}^{-1}$ and -1650 cm^{-1} , respectively (Figure S21a–S21c), further confirming the dimerization in non-coordinating solvents. The spectrum at 77 K, 25 minutes after sample preparation, yields essentially the same pattern as at 293 K with a more structured low-energy band due to band narrowing at low temperatures (Figure S21d). This low-energy band could be fitted with three Voigt functions supporting the TDDFT calculations of **1** and **2** (Figure S21e).

The local coordination geometry of the tin ions in **2** resembles that of Sn(bpep) with σ -coordination of a pyridine to the p(Sn) orbital. According to the difference electron densities and charge transfer number analysis, the lowest energy electronic transition of **2** around 460 nm (shifted by -1650 cm^{-1}) possesses essentially pure ILCT character fully analogous to Sn(bpep) (Figures S22, S23).⁵⁷ In addition, the emission properties of **2** with its emission band peaking at $\lambda_{\text{p}} = 540$ at 293 K in solution are very similar to that of Sn(bpep) with $\lambda_{\text{p}} = 535$ nm at 293 K in the solid state (Figure

S24).⁵⁷ Due to the THF adduct formation in THF and the dimerization in aromatic and aliphatic solvents which result in p-type orbital occupation and hence to different excited state energies, a detailed comparative study of monomeric *meridional* $\text{Sn}(^t\text{BuPDP}^{t\text{Bu}})$ **1** and the monomeric *facial* stannylene $\text{Sn}(\text{bpep})$ (Figure 2) is not feasible in solution. Consequently, we focused on the investigation of solid **1** without any additional donors, i.e. coordinating solvent and without rearrangement to **2**.

Optical properties and excited state dynamics of solid 1. DFT calculations on **1** (Figures 4, S25) confirm the frontier molecular orbital order as envisaged in Scheme 2. The molecular orbital of high Sn p character in **1** is significantly stabilized by 0.74 eV (LUMO) through π conjugation with the pyridine, compared to $\text{Sn}(\text{bpep})$, with the p(Sn) orbital lying in the pyridine plane and interacting with the pyridine lone pair. The ligand-centered unoccupied molecular orbital of high pyridine character (LUMO+2) is destabilized by 0.81 eV (Figures 4, S25). These effects invert the LUMO characters as predicted by the qualitative model (LUMO inversion). The meridional coordination mode of $^t\text{BuPDP}^{t\text{Bu}2-}$ allows pyridine/pyrrolate π orbital conjugation resulting in HOMO–1, HOMO and LUMO+2 of mixed pyrrolate/pyridine character, as compared to related MOs in $\text{Sn}(\text{bpep})$ (Figure 4). Furthermore, the meridional coordination mode enables pyrrolate and pyridine π orbital admixtures to the tin s- and p-type orbitals, respectively.

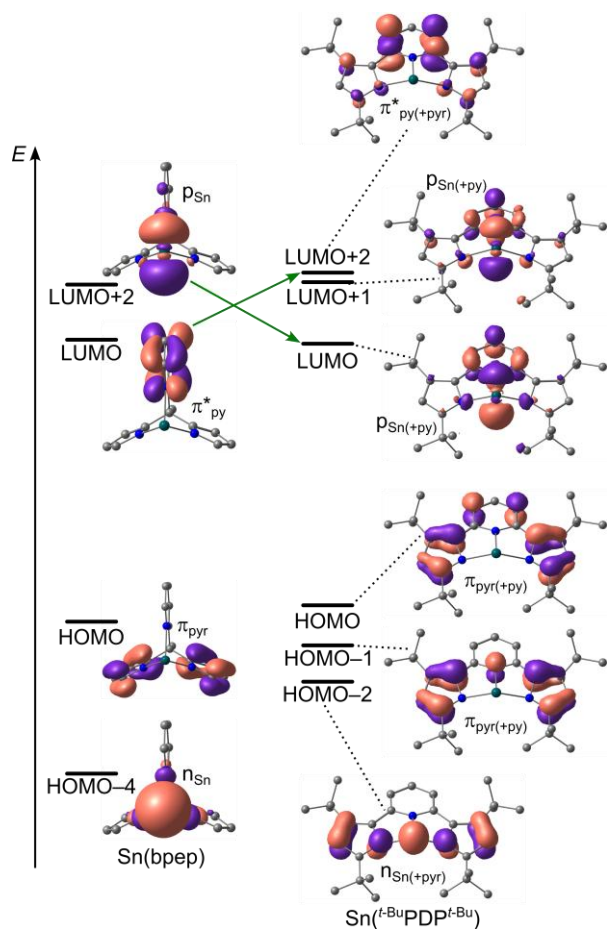


Figure 4. Calculated frontier orbitals of $\text{Sn}(\text{bpep})$ ⁵⁷ and $\text{Sn}(\text{}^t\text{-BuPDP}^t\text{-Bu})$ classified according to the dominant orbital character illustrating the LUMO inversion (isosurface value: 0.05 a.u.). CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-ZORA-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn).

TDDFT calculations of geometry optimized **1** deliver two spin-allowed transitions of high ¹LMCT character in the visible spectral region (all shifted by +3500 cm⁻¹), namely an intense $\text{S}_0 \rightarrow \text{S}_1$ (HOMO–LUMO) transition at 426 nm (blue), responsible for the orange red color and a weak $\text{S}_0 \rightarrow \text{S}_2$ (HOMO–1–LUMO) transition at 371 nm (Figures 5, S26, S27). The lowest-energy transition of dominant ¹ILCT (pyrrolate→pyridine) character is found at 335 nm ($\text{S}_0 \rightarrow \text{S}_3$, HOMO–

LUMO+1, Figures 5, S26, S27). In contrast, the lowest-energy ¹ILCT transition (HOMO–LUMO) of Sn(bpep) is calculated at lower energy (412 nm).

Spin-forbidden singlet-triplet transitions $S_0 \rightarrow T_n$ of varying LMCT/ILCT character are calculated in the visible spectral region (Figure 4). The $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_2$ transitions correspond to changes in the HOMO $\rightarrow$ LUMO and HOMO–1 $\rightarrow$ LUMO/HOMO $\rightarrow$ LUMO+2 occupations, respectively. At the FC geometry, the T_1 and T_2 states are of mainly ³LMCT and mixed ³[LMCT/ILCT] character, respectively. While the T_1 FC state is lower in energy than the S_1 state by 0.27 eV, the T_2 FC state is almost degenerate with the S_1 FC state. Unfortunately, recording solid-state absorption spectra for comparison with the calculated transitions was prohibited by the extreme air and moisture sensitivity of **1**. However, the UV/Vis absorption spectrum of **1** (+**2**) does show a maximum around 426 nm which (in part) corresponds to the $S_0 \rightarrow S_1$ transition of **1** (Figure S21).

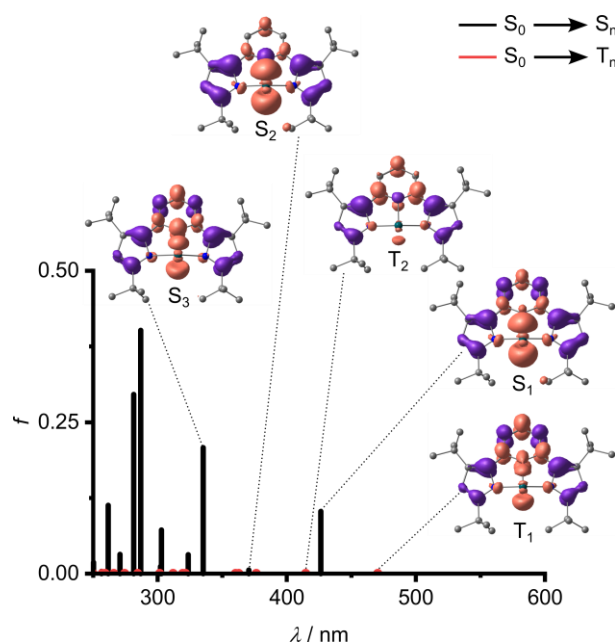


Figure 5. TDDFT calculated oscillator strengths of **1** for $S_0 \rightarrow S_n$ transitions, position of $S_0 \rightarrow T_n$ transitions marked by red points with difference electron densities of selected characteristic

transitions (isosurface value 0.003 a.u., purple = electron loss, orange = electron gain. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-ZORA-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn).

Excitation at $\lambda_{\text{exc}} = 450$ nm of **1** in the solid state results in a red emission peaking at 710 nm (Figure 6a). The emission lifetime amounts to $\tau_{\text{p},293} = 221$ ns with photoluminescence quantum yield of $\Phi_{\text{p},293} = 0.0044$ at 293 K, respectively (Figures S28, Table S3). The long lifetime suggests phosphorescence as emissive process. Upon cooling to 77 K, the maximum shifts hypsochromically to 690 nm by 408 cm^{-1} (Figures 6a, S29). Compared to Sn(bpep) with $\lambda_{\text{p},77} = 504$ nm, the emission of **1** at $\lambda_{\text{p},77} = 690$ nm is significantly red-shifted by 5350 cm^{-1} as expected from the frontier molecular orbital energies (Figure 4).⁵⁷ At 77 K, lifetime and quantum yield increase to $\tau_{\text{p},77} = 128 \text{ }\mu\text{s}$ and $\Phi_{\text{p},77} = 0.0116$, respectively (Figure S30, Table S3). The emission lifetime at 77 K $\tau_{\text{p},77}$ was fitted biexponentially, yet the second fraction amounts to only 3% ($\tau_{\text{p}2,77} = 313 \text{ }\mu\text{s}$), which can be caused by minor defects on the surface of the solid and is hence neglected in the following discussion (Figure S30). Excitation spectra ($\lambda_{\text{obs}} = 700$ nm), recorded between 293 and 77 K, are essentially superimposable (Figure S31). According to the TDDFT calculations, the absorption maximum at $\lambda_{\text{max}} = 426$ nm of the absorption spectrum at 77 K of a mixture of **1** and **2** in *n*-pentane is dominated by the $S_0 \rightarrow S_1$ absorption of monomeric **1** and this is reflected in the excitation spectrum of solid **1** with $\lambda_{\text{max}} = 420$ nm (Figures S20, S31). As absorption and filter effects distort the excitation spectra of solid **1** at higher energy, the excitation spectra diverge from the absorption spectra at $\lambda < 400$ nm.

Assuming a unity ISC quantum yield, the nonradiative and radiative rate constants k_{nr} and k_{r} were determined from the phosphorescence lifetimes and quantum yields at 77 and 293 K as $k_{\text{nr},77} = 7700$

s^{-1} , $k_{\text{nr},293} = 4.5 \times 10^6 \text{ s}^{-1}$ and $k_{\text{r},77} = 100 \text{ s}^{-1}$, $k_{\text{r},293} = 20000 \text{ s}^{-1}$. While the increased nonradiative decay at higher temperature is expected, the faster radiative decay at higher temperature suggests a thermally populated higher energy state with a higher radiative rate constant.

Detailed variable temperature studies reveal that the integrated emission intensity maximizes at 175 K and decreases above and below 175 K (Figure 6b). Below 125 K, the integrated emission intensity increases again which is expected behavior (Figure 6b). The peculiar effect with a maximum intensity is reproducible both for cooling and heating temperature ramps. Additionally, it is fully reversible persisting for several cooling/heating cycles (Figures S32, S33) and is independent from excitation wavelength ($\lambda_{\text{exc}} = 420, 480 \text{ nm}$) ruling out a temperature-dependent shift or narrowing of the absorption bands as underlying effects (Figures S34, S35).

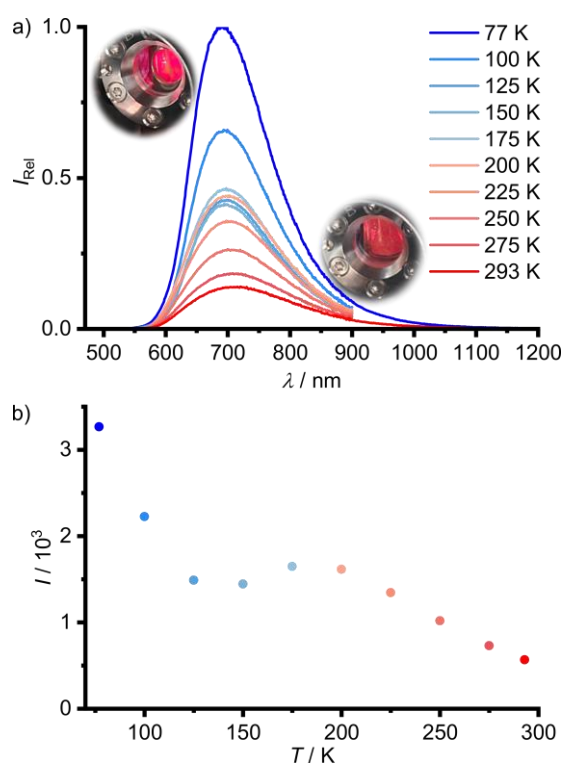


Figure 6. a) Temperature dependent phosphorescence spectra of **1** in the solid state between 77 K (blue) and 293 K (red) with $\lambda_{\text{exc}} = 450 \text{ nm}$. (Inset: Photographs of the red photoluminescence at 77

K, left and 293 K, right). b) Integrated phosphorescence emission intensity of **1** in the solid state between 77 and 293 K with $\lambda_{\text{exc}} = 450$ nm.

The phosphorescence rate constants $k_{\text{obs}}(T) = 1/\tau_{\text{p}}(T)$ were fitted with two independent thermally activated processes ($E_{\text{a},1}$; $E_{\text{a},2}$; A_1 ; A_2) according to an Arrhenius model (eq. 1, Figure 7a, Table S4). The first process is essentially temperature independent with a negligible activation barrier of $E_{\text{a},1} = 0.01$ eV and a small preexponential factor $A_1 = 4.40 \times 10^4 \text{ s}^{-1}$, while the second process has a barrier of $E_{\text{a},2} = 0.19$ eV with $A_2 = 7.86 \times 10^9 \text{ s}^{-1}$. To further elucidate the temperature dependence of the radiative and nonradiative processes with rate constants k_{nr} and k_{r} ($k_{\text{obs}} = k_{\text{nr}} + k_{\text{r}}$), individual Arrhenius analyses were performed for k_{nr} and k_{r} . To this end, the relative phosphorescence quantum yields were determined by integrating the emission bands over an energy scale from 11111 to 18900 cm^{-1} referenced to the phosphorescence quantum yield, which was determined absolutely at 293 K as $\Phi_{\text{p},293} = 0.0044$ (Table S5). The phosphorescence quantum yields at 77 K determined absolutely ($\Phi_{\text{p},77} = 0.0116$) and by the relative method ($\Phi_{\text{p,rel},77} = 0.024$) agree sufficiently well, considering the small absolute photoluminescence quantum yield, validating the procedure. The Arrhenius fit (eq. 1) for k_{nr} gives the same activation barriers $E_{\text{a},1}/E_{\text{a},2}$ and similar preexponential factors A_1/A_2 as the fit for k_{obs} (Figures 7a, S36, Tables S3, S4).

$$k_j = A_i \cdot e^{-\frac{E_{\text{a},i}}{k_{\text{B}}T}} \quad (\text{eq. 1})$$

With $j = r, \text{nr}$, A_i preexponential factor, $E_{\text{a},i}$ activation energy, k_{B} Boltzmann constant and T temperature.

This indicates that nonradiative processes dominate the excited state deactivation as already obvious from the low photoluminescence quantum yields. The energy barrier $E_{\text{a},2} = 0.19$ eV might

be tentatively ascribed to thermally activated $T_1 \rightarrow S_0$ ISC. Unexpectedly, k_r also shows a strong temperature dependence with $k_{r,77} = 100 \text{ s}^{-1}$ and $k_{r,293} = 20000 \text{ s}^{-1}$ at 77 and 293 K, respectively (Figure 7b, Tables S3, S4). Between 77 and 125 K, k_r is essentially temperature independent. Above 175 K, a thermally activated radiative process with a barrier $E_{a,r} = 0.11 \text{ eV}$ and a preexponential factor $A_r = 1.5 \times 10^6 \text{ s}^{-1}$ becomes dominant (Figure 7b, Tables S3, S4). In other words, a second emissive state at slightly higher energy, which has a significantly larger k_r , is populated at higher temperatures.

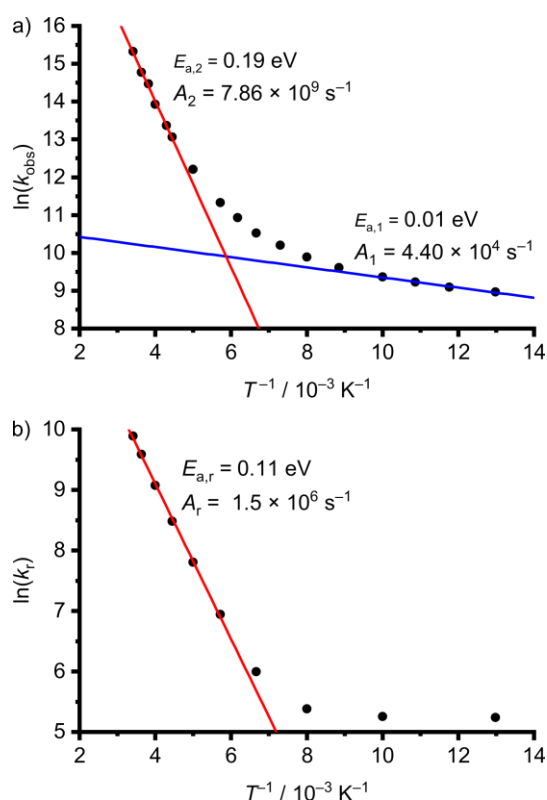
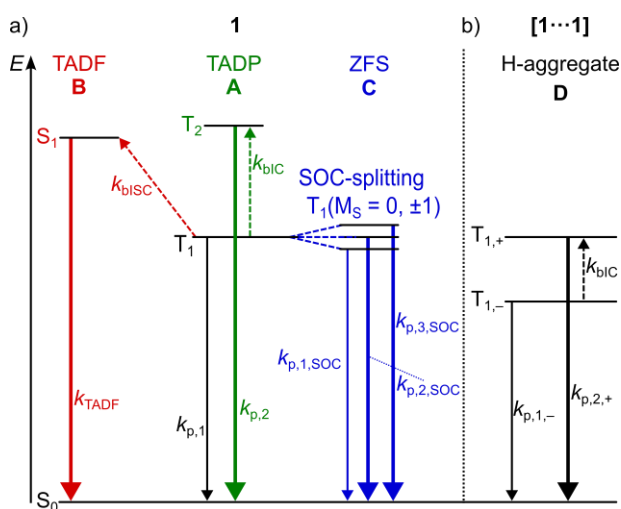


Figure 7. a) Arrhenius plot of the observed photoluminescence rate constants ($k_{\text{obs}}(T) = 1/\tau_p(T)$, $T = 77\text{--}293 \text{ K}$) with fits of the high and low temperature regimes in red and blue. b) Arrhenius plot of the radiative rate constants $k_r(T)$, $T = 77\text{--}293 \text{ K}$ with fit of the high temperature regime in red.

The emission band energy and band shape do not change significantly with temperature (Figure 6), indicating that the two emissive states have a similar energy gap to the S_0 state and a similar

electronic character. Several models can be invoked to describe the thermal population of a slightly higher-energy emissive state, yet with an appreciable activation barrier of $E_{a,r} = 0.11$ eV. Four conceivable models A – D are depicted in Scheme 3. In model A, the higher emissive state is the T_2 state, which is thermally populated by back-IC (TADP), while in model B, the higher emissive state is the S_1 state, which is populated by back-ISC (TADF). Model C accounts for the splitting of the T_1 triplet state into the $M_S = 0, \pm 1$ sublevels by SOC. This would be similar to the situation encountered by Ir(ppy)_3 with strong SOC enabled by Ir and a high-energy brighter M_S state with zero field splitting (ZFS) of 170 cm^{-1} .^{67,68} Model D includes excitonic coupling of the van-der-Waals dimer $[\mathbf{1}\cdots\mathbf{1}]$ (Scheme 3b).



Scheme 3. Conceivable models for the observed thermally activated photoluminescence in **1**: a) A $T_1 \rightarrow T_2$ back-IC with T_2 phosphorescence (green, TADP), B $T_1 \rightarrow S_1$ back-ISC with fluorescence from S_1 (red, TADF), C SOC-split T_1 state with thermal population of the $M_S = 0, \pm 1$ sublevels with different k_p (blue, ZFS) and b) D excitonic coupling in the van-der-Waals dimer $[\mathbf{1}\cdots\mathbf{1}]$.

To gain deeper insight into the nature of the emissive states and the pathway to these states, (SOC-TD)DFT calculations were performed on S_0 , T_1 and T_2 states of monomeric **1** and on excited states

of the van-der-Waals dimer $[1\cdots 1]$ that is present in the solid state. We start the discussion with the excited state landscape of monomeric **1**. At the FC geometry, S_1 and T_2 states of **1** are nearly degenerate (Figure 5), which could allow for fast $S_1 \rightarrow T_2$ ISC in the FC region after $S_0 \rightarrow S_1$ excitation. Compared to the calculated SOC constant for the S_1/T_1 state pair $\text{SOCC}(S_1/T_1) = 31 \text{ cm}^{-1}$, the corresponding constant for the S_1/T_2 state pair $\text{SOCC}(S_1/T_2) = 106 \text{ cm}^{-1}$ is much larger. This can drive $S_1 \rightarrow T_2$ ISC already in the FC region (Table S6). The ISC is then followed by $T_2 \rightarrow T_1$ internal conversion (IC) and vibrational relaxation (VR). The relaxed geometries of the T_1 and T_2 states were calculated by DFT (excited state) optimizations. The relaxed T_1 and T_2 states are characterized by a planar and a pyramidal T-type coordination geometry with interplanar angles of 0° and 20° between the $N^{\text{pyr1}}/\text{Sn}/N^{\text{py}}$ and $N^{\text{pyr1}}/\text{Sn}/N^{\text{py}}$ planes, respectively (Figure S37). Furthermore, the $N^{\text{pyr1}}\text{--Sn--}N^{\text{pyr2}}$ angles slightly differ in the T_1 and T_2 states with 141° and 136° , respectively. This places the T_2 state closer to the FC region, i.e. the S_0 geometry (Table S1, Figure S37). The energies of the T_1 and T_2 states vary similarly along the $N^{\text{pyr1}}\text{--Sn--}N^{\text{pyr2}}$ bending mode with T_1/T_2 energy gaps of $\approx 0.3\text{--}0.5 \text{ eV}$ according to a relaxed potential energy surface scan (Figure S38). These calculated T_1/T_2 energy gaps are too high to account for the experimentally observed thermally activated photoluminescence phenomenon with $E_{a,r} = 0.11 \text{ eV}$ (vide supra). With this argumentation, thermally activated $T_1 \rightarrow T_2$ back-IC does not appear feasible, and the high-temperature emission does not occur from the T_2 state (Scheme 3, model A). Additionally, the calculated T_1/S_0 gap of 0.86 eV at the relaxed flattened T_1 state geometry is way too small compared to the experimentally determined emission energy of 1.80 eV . This finding indicates that geometry relaxation (flattening and $N^{\text{pyr1}}\text{--Sn--}N^{\text{pyr2}}$ bending) and the concomitant energy gain is hampered by the rigid environment of the solid. Similarly, the S_1 state is higher in energy by $\approx 0.18\text{--}0.26 \text{ eV}$ than the T_1 state, so that TADF (Scheme 3, model B) appears unfeasible.

Concerning model C, the splitting of the T_1 state into its $M_s = 0, \pm 1$ sublevels by SOC has been calculated by SOC-DFT on the relaxed T_1 geometry as 1.1 cm^{-1} (Scheme 3, model C). This appears to be too small to account for the much larger experimentally determined barrier. As models A – C fail to explain the experimental data (small energy gap allowing for thermal population, but medium large barrier between the two emissive states), model D – excitonic coupling – is considered. In the solid state, **1** forms van-der-Waals dimers [**1**⋯**1**] of slipped head-to-tail arranged molecules of **1** with intermolecular Sn⋯C contacts around $3.7 \text{ \AA}$ (Figure S13, vide supra). In dimers or aggregates of dyes, the excitonic states can split into two levels through the interaction of electronic transition dipoles and such an excitonic coupling may be present in [**1**⋯**1**]. In an H aggregate of **1**, the transition dipoles of the T_1 state add in the upper $T_{1,+}$ state, but cancel in the lower $T_{1,-}$ state (Scheme 3).^{69–71} Hence, the upper and lower $T_{1,+}$ and $T_{1,-}$ states possess larger and smaller transition dipole moments, respectively. This would account for the experimentally observed high and low radiative rate constants at high and lower temperature of $k_{r,293} = 20000 \text{ cm}^{-1}$ and $k_{r,77} = 100 \text{ cm}^{-1}$, respectively. In this model D, we equate the experimentally determined activation barrier $\Delta E_{a,r} = 0.11 \text{ eV}$ of the radiative process (Figure 7b) to the barrier for $T_{1,-} \rightarrow T_{1,+}$ bIC, while the state splitting itself is comparably small. To support the proposed excitonic coupling, we performed SOC-TDDFT calculations on a truncated model dimer [**1**⋯**1**]^H based on the SC-XRD determined GS geometries (vide supra) with the *tert*-butyl substituents replaced by hydrogen atoms to reduce computational costs (Figure S39). TDDFT calculated transition densities of relevant $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_2$ transitions of **1** lack densities on the *tert*-butyl substituents validating the truncated dimer model (Figure S40). This dimer model at the FC geometry obtained from SC-XRD delivers split levels for each monomer transition $S_0 \rightarrow S_1$, $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_2$ with averaged energy gaps of 430 cm^{-1} , 22 cm^{-1} and 71 cm^{-1} for $S_{1,-}/S_{1,+}$, $T_{1,-}/T_{1,+}$ and

$T_{2,-}/T_{2,+}$ states, respectively (Table S7). The calculated oscillator strengths averaged over the respective three M_s triplet sublevels amount to zero and 3.2×10^{-6} for the $T_{1,-}$ and $T_{1,+}$ states, respectively, confirming the proposed H-aggregate excitonic coupling (Figure S41). The SOC-TDDFT calculated $T_{1,-}/T_{1,+}$ excitonic splitting of 0.003 eV (22 cm^{-1}) for $[\mathbf{1} \cdots \mathbf{1}]^H$ at the FC geometry is quite small accounting for the essentially constant emission band energy (Figure 6a). The experimental barrier $E_{a,r} = 0.11 \text{ eV}$ pertains to the barrier for the $T_{1,-}/T_{1,+}$ IC process in this model D, which is not covered by the DFT calculations at the FC geometry.

The phosphorescence of **1** with a pincer-type ligand is significantly red-shifted compared to the phosphorescence of Sn(bpep) with a tripodal ligand due to a change in electronic character from $^3\text{ILCT}$ of Sn(bpep) to $^3\text{LMCT}$ of **1** (LUMO inversion). The peculiar temperature-dependence of the emission intensity of **1** in the solid state arises from excitonic coupling in an H aggregate $[\mathbf{1} \cdots \mathbf{1}]$ and thermally activated phosphorescence from the higher-lying brighter triplet excitonic state.

SUMMARY AND CONCLUSION

Controlling the interaction of the tin(II) p(Sn) orbital in dipyrrolato stannylenes with a pyridine donor by the dipyrrolato/pyridine ligand topology (tripod/pincer) switches the σ -donor(pyridine) $\rightarrow$ p(Sn) interaction in Sn(bpep) to a π -donor(pyridine) $\rightarrow$ p(Sn) interaction in Sn($^{t\text{-Bu}}\text{PDP}^{t\text{-Bu}}$) **1**. The LUMO character of the stannylene changes from purely pyridine to (largely) p(Sn) and the LUMO energy is significantly lowered (LUMO inversion). Consequently, the nature of lowest energy emissive triplet state changes from $^3\text{ILCT}$ (pyrrolate $\rightarrow$ pyridine) to $^3\text{LMCT}$ (pyrrolate $\rightarrow$ p(Sn)). This topologically enabled lower $^3\text{LMCT}$ energy shifts the phosphorescence from the green emission color of Sn(bpep) to the red emission color of Sn($^{t\text{-Bu}}\text{PDP}^{t\text{-Bu}}$) **1**.

Apart from the in-plane pyridine-tin(II) π -interaction in **1**, the accessible p(Sn) orbital and the planarity of **1** enable coordination of donor solvents such as THF in solution and the formation of H aggregates in the solid state. The H dimer present in the solid state, leads to excitonic coupling with a brighter higher-energy and an almost dark lower-energy split level.

This study provides a concept to rational ligand design for photoluminescent tin(II) complexes by topological control of the frontier orbital energies and state characters. Future design concepts for phosphorescent stannylenes should additionally include steric shielding and rigidification to prevent σ -donor coordination to the Sn(p) orbital, to avoid excitonic coupling invoked by aggregation via van-der-Waals forces and to mitigate (dissociative) large-amplitude molecular motions in the excited states reducing nonradiative decay.

EXPERIMENTAL SECTION

General procedures. All reactions and measurements were performed under argon atmosphere unless otherwise noted. Gloveboxes (UniLab/MBraun – Ar 4.8, O₂ < 0.1 ppm, H₂O < 0.1 ppm) were used to store and weigh sensitive compounds for synthesis as well as to prepare samples that require absence of oxygen and water. The reagents were purchased from commercial suppliers (ABCR, Acros Organics, Alfa Aesar, Fischer Scientific and Sigma Aldrich). Acetonitrile was dried and distilled from CaH₂, diethyl ether and *n*-pentane from sodium and THF from potassium. Deuterated solvents were purchased from euriso-top and Deutero GmbH and were dried by the same procedures as above and stored over molecular sieve (3 Å). The compounds H₂^{*t*-Bu}PDP^{*t*-Bu} ⁵⁸ and Sn[N(SiMe₃)₂]^{72,55,54} were prepared according to literature procedures. Solution **NMR spectra** were recorded on a *Bruker* Avance DRX 400 spectrometer at 400.42 MHz (¹H), 100.70 MHz (¹³C{¹H}) and 149.23 MHz (¹¹⁹Sn). The ¹¹⁹Sn **cross-polarization (CP) solid state (ss) NMR experiment** was conducted on a *Bruker* DSX 400 MHz spectrometer at ¹H frequency of 399.87

MHz and ^{119}Sn frequency of 149.1 MHz using a 2.5 mm *Bruker* probe head at 20 kHz magic angle spinning (MAS). The initial 90° pulse was with a 4.0 μs length and a 4 s recycle delay was used. A ramped CP pulse (64 – 100%) with duration of 2 ms was used for recording the spectrum averaging 20 k transients. Two pulse phase modulation (TPPM) ^1H decoupling scheme was used while acquiring the ^{119}Sn NMR signal. The spectra were baseline-corrected, and a broadening of 200 Hz was applied. The ^{119}Sn NMR shift was referenced to external tetramethyltin (SnMe_4 , $\delta = 0$ ppm). All data were evaluated with the software *MestReNova* 12.0.4-22023. All resonances are reported in ppm versus the solvent signal as internal standard (^1H ; (^{13}C) NMR: THF- d_8 : $\delta = 1.72$, 3.58; (25.31, 67.21) ppm or external standards for ^{119}Sn NMR (SnMe_4 , $\delta = 0$ ppm). (s) = singlet, (d) = doublet, (t) = triplet. **Atmospheric pressure chemical ionization**, APCI $^+$ mass spectra were recorded on an *Agilent* 6545 QTOF-MS spectrometer by the central analytical facility of the Department of Chemistry of the Johannes Gutenberg University Mainz, Germany. The **elemental analysis** was performed by the *Mikroanalytisches Labor Kolbe*, c/o Fraunhofer Institut UMSICHT, Oberhausen, Germany. **UV/Vis absorption spectra** were recorded on a *Jasco* V-770 spectrometer or a *Cary-5000* spectrometer from *Agilent* using $d = 1.00$ cm quartz cuvettes with a Schott valve. **Steady-state emission spectra and photoluminescent decay curves** were measured with a *FLS1000* spectrometer from *Edinburgh Instruments* equipped with a cooled photomultiplier detector PMT-980 and a cooled NIR-sensitive photomultiplier detector N-G09 PMT-1700. A xenon arc lamp Xe2 (450 W) was used for excitation in steady-state measurements. Time-resolved luminescence experiments were recorded in the multi-channel scaling mode employing a pulsed diode laser VPL-450 ($\lambda_{\text{exc}} = 451.3$ nm) as excitation source. Single and biexponential lifetime decays were evaluated with the software *Fluoracle* provided by *Edinburgh Instruments*. Measurements at low temperature were carried out using a liquid nitrogen cooled

cryostat *Optistat DN* from *Oxford Instruments*. Absolute luminescence quantum yields Φ were determined using the *MicrostatN* from *Oxford Instruments* combined with the Cryosphere from *Edinburgh Instruments*. Relative uncertainty of Φ is estimated to be $\pm 20\%$. **Density functional theory calculations** were performed with the Orca 5.0.4. program package.^{73,74} Geometry optimizations were performed using (un)restricted Kohn-Sham orbitals DFT (RKS or UKS) and the B3LYP functional^{75–77} in combination with the ZORA-def2-TZVPP basis as recontracted *Ahlrich's* basis set def2-TZVPP⁷⁸ or the SARC-ZORA-TZVPP basis^{79–83} with the auxiliary basis SARC/J^{79–82} as decontracted def2/J⁸⁴ basis up to Kr to use the zeroth order regular approximation to describe relativistic effects in all calculations (keyword *ZORA*).^{85,86} Tight convergence criteria were chosen for (TD)DFT calculations (keywords *tightscf* and *tightopt*). The geometry optimization of the T₂ state was performed by TDDFT using the LibXC⁸⁷ library for the B3LYP functional⁸⁸ (keyword *LibXC(B3LYP)*) with the *followiroot true* keyword. All DFT calculations make use of the resolution of identity (Split-RI-J) approach for the Coulomb term in combination with the chain-of-spheres approximation for the exchange term (keyword *RIJCOSX*).^{89–92} To account for solvent effects, a conductor-like screening model (keyword *CPCM(hexane)*) modeling hexane was used in all calculations.^{93,94} Atom-pairwise dispersion correction was performed with the *Becke-Johnson* damping scheme (keyword *D3BJ*).^{95,96} A numerical frequency calculation confirmed that the optimized geometry corresponds to a minimum structure. Explicit solvent molecules were not taken into account. The charge transfer number analyses of the TDDFT calculated transitions were done using *TheoDORE*.^{97,98} Twenty spin-allowed and spin-forbidden and fifty spin-allowed transitions were calculated by TDDFT with and without the keyword *triplets true*. SOC-TDDFT calculations were performed using the additional keywords *DoSOC true*, *TDA false* and *RI-SOMF(IX)*.⁹⁹ All calculations were computed on the supercomputer Elwetritsch with

advisory services offered by the RPTU Kaiserslautern-Landau (<https://hpc.rz.rptu.de>), which is a member of the AHRP. All coordinates of the optimized structures are provided in an additional xyz file. Intensity data for **single crystal structure determinations** were collected with a STOE IPDS-2T or a STOE STADIVARI diffractometer from STOE & CIE GmbH with an Oxford cooling using Mo-K α radiation ($\lambda = 0.71073$ Å). The diffraction frames were integrated using the STOE X-Area¹⁰⁰ software package and were corrected for absorption with MULABS¹⁰¹ of the PLATON¹⁰² software package or with STOE X-Red¹⁰³ or STOE LANA^{104,105} of the STOE X-Area¹⁰⁰ software package. The structures were solved with SHELXT¹⁰⁶ and refined by the full-matrix method based on F^2 using SHELXL¹⁰⁷ of the SHELX¹⁰⁸ software package and the ShelXle¹⁰⁹ graphical interface. All non-hydrogen atoms were refined anisotropically while the positions of all hydrogen atoms were generated with appropriate geometric constraints and allowed to ride on their respective parent atoms with fixed isotropic thermal parameters. Crystallographic data for the structures reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2531627 (**1**@120 K), CCDC-2531628 (**1**@100 K), CCDC-2531629 (**1**@150 K), CCDC-2531630 (**1**@175 K), CCDC-2531631 (**1**@225 K), CCDC-2531632 (**2**). Crystallographic data is listed in the supporting information.

Synthesis of Sn(*t*-BuPDP*t*-Bu) 1: Sn[(N(SiMe₃)₂)₂] (419 mg, 0.95 mmol, 1.0 eq) in diethyl ether (4 mL) was added to a stirred solution of H₂^{*t*-Bu}PDP^{*t*-Bu} (413 mg, 0.95 mmol, 1.00 eq) in acetonitrile (12 mL). After stirring for 15 h at 293 K, the formed precipitate was separated from the solution with a centrifuge (3500 rounds min⁻¹, 15 min), washed with acetonitrile (3 × 3 mL) and dried under reduced pressure. **1** (235 mg, 44%) was obtained as a red powder. Crystals suitable for XRD analysis were obtained by slow evaporation of a concentrated acetonitrile solution of **1**. ¹H NMR (THF-*d*₈): δ = 7.51 (t, ³*J*_{HH} = 8.0, 1H, H¹), 7.29 (d, ³*J*_{HH} = 8.0, 2H, H²), 6.03 (s, 2H, H¹⁰), 1.44 (s,

18H, H¹³⁻¹⁴), 1.43 (s, 18H, H⁷⁻⁹) ppm. ¹³C{¹H} NMR (THF-*d*₈): δ = 153.3 (s, C⁹), 152.7 (s, C¹¹), 137.8 (s, C¹), 137.0 (s, C⁵), 130.5 (s, C⁴), 114.8 (s, C²), 109.3 (s, C¹⁰), 34.0 (s, C¹²), 33.2 (s, C¹³⁻¹⁵), 32.4 (s, C⁷⁻⁹), 32.2 (s, C⁶) ppm. ¹¹⁹Sn NMR (THF-*d*₈): δ = -466.5 ppm. ¹¹⁹Sn NMR (solid): δ = -101.6 ppm. MS (APCI⁺; CH₃CN): *m/z* (%) = 433.35 (100) [H₂^{*t*}-BuPDP^{*t*}-Bu + H]⁺, 552.24 (11) [1 + H]⁺, 1119.48 (20) [2 1 + H₂O + H]⁺. **Elemental analysis** calcd. for C₂₉H₄₁N₃Sn: C, 63.29; H, 7.51; N, 7.63. Found: C, 63.04; H, 7.46; N, 7.58.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at xx.

Analytical and spectroscopic data, results of quantum chemical calculations (PDF)

Cartesian coordinates of optimized geometries from quantum-chemical calculations (XYZ)

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Author Contributions

P.S. performed the synthesis, characterization, analytical measurements and (TD)DFT calculations, visualized the data and wrote the original draft. P.S. and [REDACTED] measured and interpreted the emission data. [REDACTED] solved the single crystal structures. [REDACTED]. conceived and designed the project. [REDACTED] finalized the manuscript with contributions from all authors. [REDACTED] supervised and [REDACTED] co-supervised the project.

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Notes

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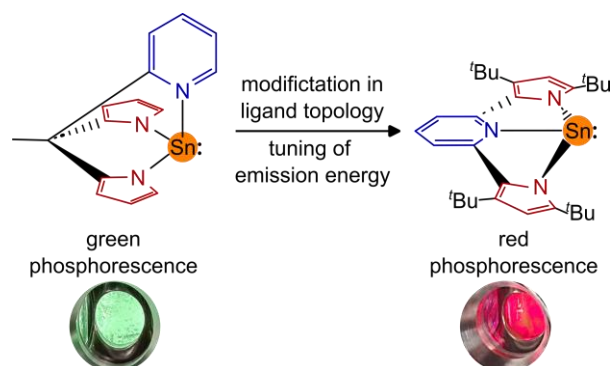
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Table of contents graphic

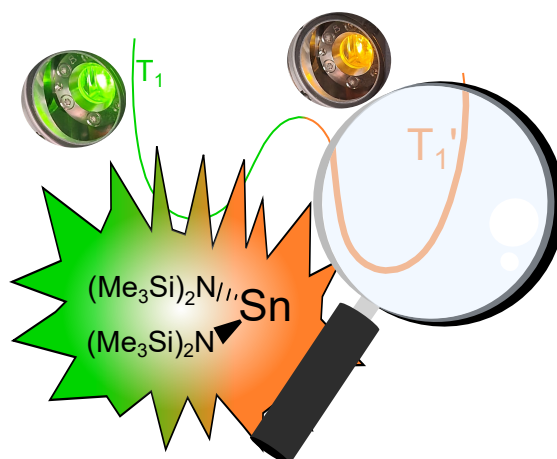


3.4 The Overlooked Dual Phosphorescence in *Lappert's* Diamino Stannylene

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The well-known *Lappert's* diamino stannylene was investigated toward its photophysical properties for the first time. This stannylene exhibits thermally activated green/orange dual phosphorescence from mixed MC/LMCT states. (TD)-DFT calculations indicate that small geometrical distortions along the trimethylsilyl group are responsible for the population of two emissive triplet states. Furthermore, the mechanism of radical formation was discussed, involving distannene excimers with second-order Jahn-Teller structures.

Author Contributions

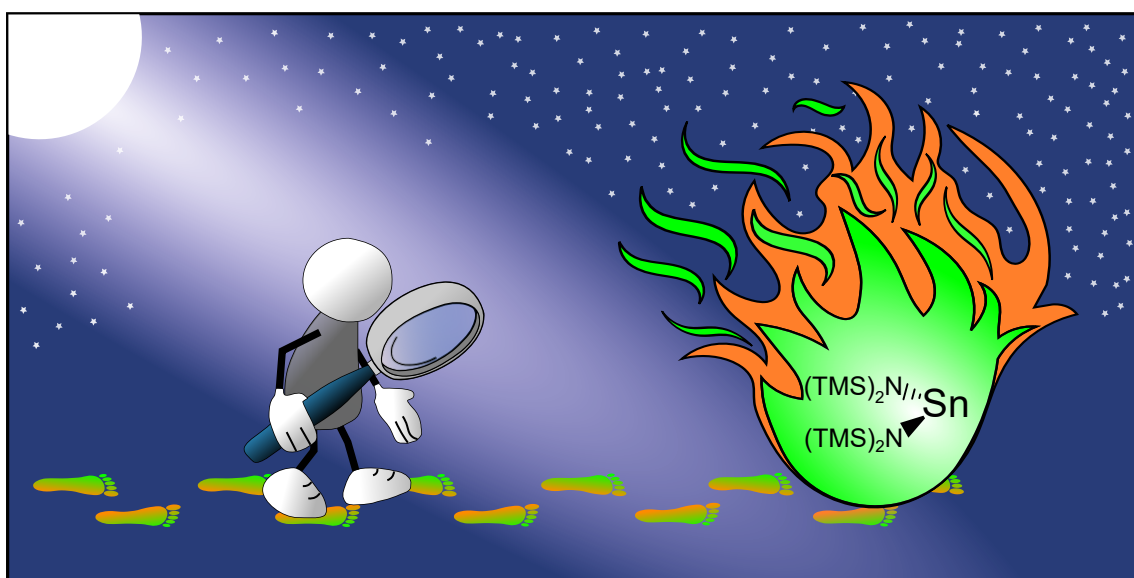
Philipp Sikora performed the synthesis of *Lappert's* diamino stannylene, conducted the absorption and emission spectroscopy experiments, accomplished the (TD)-DFT calculations, visualized the data and wrote the first draft of the manuscript. [REDACTED] measured the transient absorption experiments and helped with the interpretation of the data. [REDACTED] carried out the EPR experiments. [REDACTED] designed the project and finalized the manuscript with contributions from all authors. [REDACTED] supervised and [REDACTED] cosupervised this project.

Supporting Information

for this article is found on page 198.

Cartesian coordinates of DFT optimized structures can be found online at: <https://onlinelibrary.wiley.com/doi/10.1002/anie.202510044>.

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Phosphorescence of Stannylenes

The Overlooked Dual Phosphorescence of Lappert's Diamino Stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$

Philipp Sikora,

Abstract: The first stable heavy carbene homologues, the heavy tetrylenes, were reported in 1973 by Lappert and coworkers. These tetrylenes were extensively investigated with respect to ground state reactivity, such as small molecule activation, insertion into σ -bonds, coordination chemistry, materials chemistry, or catalysis. Their photophysical properties remained essentially unexplored. We report that the bright yellow-colored diamino stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ shows thermally activated dual orange/green phosphorescence with microsecond lifetime in fluid solution at room temperature, which has been overlooked for more than 50 years. These unique electronic and photophysical properties are studied in detail by temperature-dependent time-resolved emission and absorption spectroscopy and are corroborated by (time-dependent) density functional theory (DFT) calculations. The mechanism of photochemical radical formation has been disclosed, involving unprecedented stannylene excimers with second-order Jahn–Teller distorted structures. The present study provides new insights toward a rational design of tetrel(II) complexes with long-lived emissive excited states, with $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ being the prototype.

Introduction

Great progress has been achieved in the research of phosphorescent and photoactive transition metal complexes of the Earth-abundant elements, mainly 3d elements, and evolved to a potential alternative to complexes of the precious transition metals, e.g., ruthenium, iridium, or platinum.^[1–6] For photochemical applications, the prerequisite is a sufficiently long lifetime of the excited states (ESs), which is often fulfilled for ESs possessing different spin multiplicities than the ground state (GS). Radiative and nonradiative processes become spin-forbidden, extending the ES lifetime. Efficient intersystem crossing (ISC) after initial population of the Franck–Condon state provides access to ESs of different spin multiplicity. The ISC rate becomes large for strong spin-orbit coupling (SOC), often induced by a so-called heavy-atom effect, by direct SOC described by the qualitative El-Sayed rules,^[7,8] generalized by Marian,^[9] or by spin-vibronic coupling.^[9,10] According to the energy-gap law, the ESs should be rather nested, i.e., undistorted, for a long ES lifetime and not too low in energy.^[11] While suitable design concepts for strongly luminescent transition metal complexes have been developed, such as increasing the ligand field strength, rigidification for d^{10} complexes and prevention of self-quenching,^[2,3,5,12–19] analogous rules and structure–

property relationships are missing for phosphorescent heavy main group compounds.

Heavy main group complexes, especially with groups 14 and 15 elements showing phosphorescence and/or thermally activated delayed fluorescence (TADF), are rather rare.^[20–23] Phosphorescence has been reported for bismuth(III) complexes with $6s^2$ electron configuration,^[24–33] while photoluminescent isoelectronic group 14 complexes with the tetrel atom in the oxidation state +II are very scarce. The ESs are typically short-lived with only weak emission, often limited to frozen solution or to the solid state (**I–VIII**^E, Scheme 1).^[34–41] Our group investigated the ES landscape of pyrrolato tetrel(II) complexes **E(bpep)** (**VIII**^E, **E** = Sn, Pb, H_2bpep = 2-[1,1-bis(1*H*-pyrrol-2-yl)ethyl]pyridine) with the tin complex surpassing the lead congener in terms of photophysical performance. **VIII**^{Sn} shows non-Kasha phosphorescence from a triplet intraligand CT (³ILCT) state.^[41] Yet, this ³ILCT state deactivates very efficiently at room temperature in fluid solution and in the solid state via a lower-lying, strongly distorted ligand-to-metal CT (³LMCT) state leading to Sn–N^{py} bond cleavage.^[41]

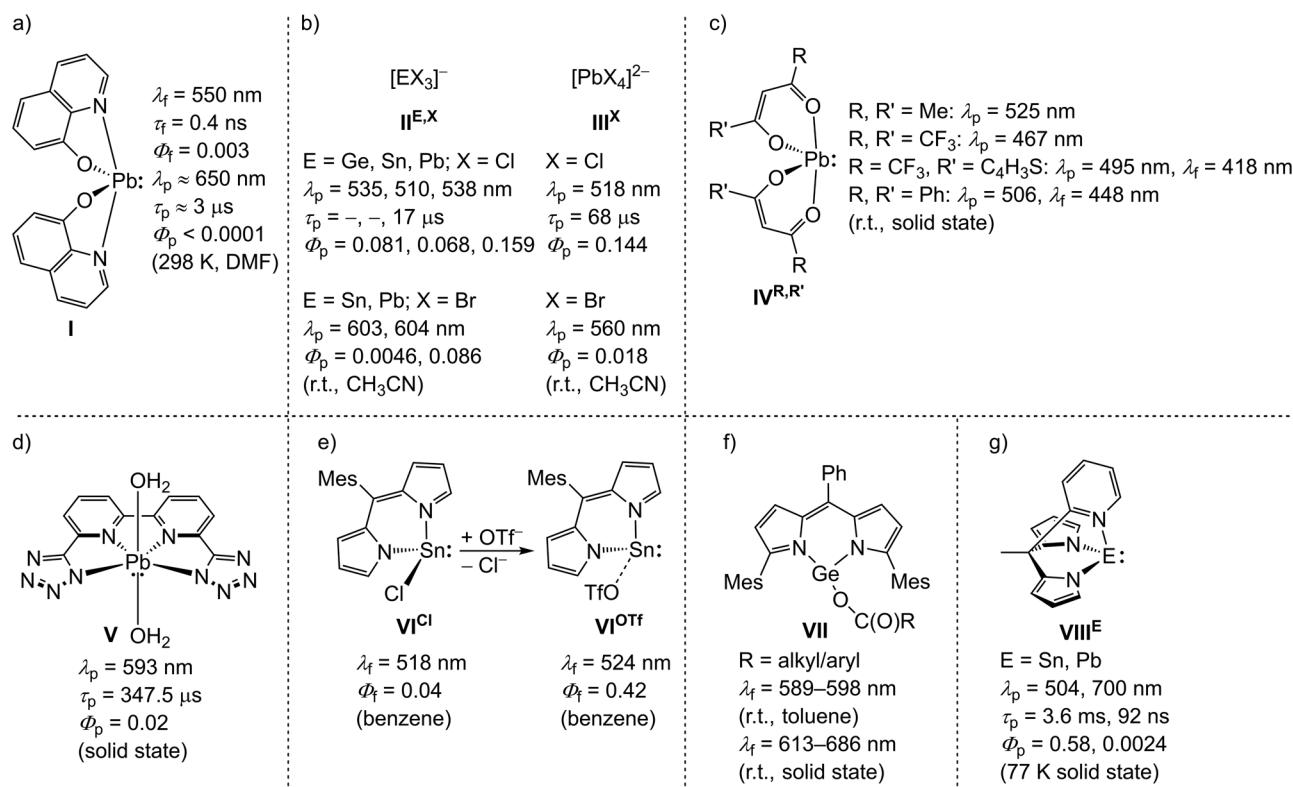
A deeper understanding of the structural, electronic, and reactivity properties of these tetrel +II compounds (heavy tetrylenes, i.e., heavy carbene homologues^[42–47]) might give a rationale for developing photoactive tetrel +II compounds.

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 Additional supporting information can be found online in the Supporting Information section

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Scheme 1. Photoluminescent tetrel(II) complexes with selected photophysical data: phosphorescent a) 8-quinolinolato plumblyene,^[34] b) halido tetranides,^[35,36] c) β -diketonato plumblyenes,^[37] d) diaqua tetrazolato lead(II) complex,^[38] fluorescent e) dipyrinatato chlorido/triflate stannylenes,^[39] f) dipyrinatato carboxylato germynes,^[40] and phosphorescent g) stannylyne and plumblyene with tridentate dipyrrolato-pyridine ligand.^[41]

Therefore, we set out to explore the undeveloped photo-physics and photochemistry of literature-known tetrylenes based on their well-explored GS properties.

Typically, the GS of heavy tetrylenes is a singlet state,^[42–48] based on the increasing radial and energetic separation of ns/np orbitals from C to Pb.^[49] The GS wavefunction of the heavier tetrylenes is characterized by a tetrel-centered fully occupied and a vacant orbital of high s- and p-character, respectively.^[43] Seminal reports of Lappert and coworkers on stable, isolable heavy tetrylenes started in 1973 with the report of $\text{E}[\text{CH}(\text{SiMe}_3)_2]_2$ ($\text{E} = \text{Sn, Pb}$),^[50] followed by $\text{E}[\text{N}(\text{SiMe}_3)_2]_2$ ($\text{E} = \text{Ge} - \text{Pb}$).^[51,52] $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ forms dimers (distannenes) with a *trans*-bent structure in the solid state.^[53,54] This *trans*-bent or *trans*-pyramidalized geometry together with a twisted arrangement of the SnR_2 moieties is a common structural feature of distannenes (Figure 1).^[55–57] In contrast to alkenes with a classical $\text{C}=\text{C}$ double bond (σ - and π -bond), the *trans*-pyramidalization of distannenes^[43,44,47,55,56] is ascribed to a double Lewis acid–base interaction of two singlet SnR_2 fragments.^[54] This binding motif originates in the increasing singlet-triplet energy difference from CR_2 to PbR_2 , due to the increasing ns/np-orbital separation^[49] with concomitant increase in Pauli repulsion.^[58] The tendency to dimerize decreases from CR_2 to PbR_2 .^[44,48,56,59,60]

The change from D_{2h} (planar) to C_{2h} (*trans*-bent) symmetry of the $\text{R}_2\text{E}=\text{ER}_2$ core arises from a second-order Jahn–Teller (SOJT) effect (Figure 1).^[44,48,61,62] Additionally,

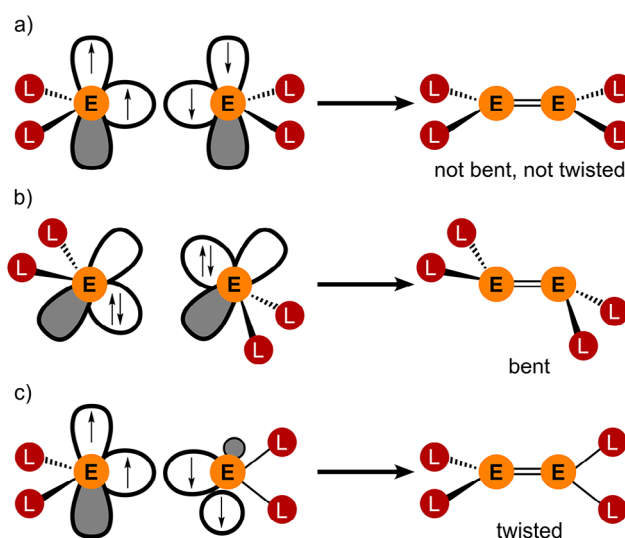
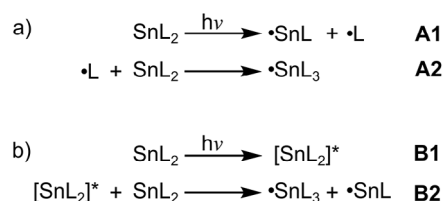


Figure 1. Geometries of ditetrenes from a) two triplet tetrylenes, b) two singlet tetrylenes, and c) two triplet tetrylenes with bulky ligands L (adapted from Ref. [57]).

the SnR_2 moieties of sterically congested systems, such as dihypersilyl stannylyne $\text{Sn}[\text{Si}(\text{SiMe}_3)_3]_2$ and systems with small singlet-triplet gaps are twisted.^[57,63–65] Quantum chemical investigations revealed that the dimerization is driven



Scheme 2. Possible routes for the formation of the tin(III) radical $\bullet\text{SnL}_3$ as proposed by Lappert and coworkers.^[93]

by significant contributions from strong electrostatic interactions and London dispersion forces.^[66–68] Apart from few examples,^[57,65,69–72] the $\text{Sn}=\text{Sn}$ bonds are weak and commonly the distannenes dissociate in solution.^[43,44,47,55,56] Clearly, photophysics will depend on the electronic structure of the tetrylenes and their possible dimerization in the GS and ESs, but their photophysics is basically unknown.

While the archetype diamino stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ (**Sn**) has been the focus of research for decades now, its photophysics is underexplored to date. Although this bright yellow-colored, thermally stable^[73] stannylene shows thermochromism (to dark orange color),^[52,73] it remains monomeric in solution as determined by cryoscopy^[52] and NMR spectroscopy.^[74] In contrast to the dialkyl stannylene $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$, the diamide **Sn** is also monomeric in the solid state.^[75] Nevertheless, the molecules are arranged as *trans*-bent centrosymmetric pairs with a 4.95 Å $\text{Sn}\cdots\text{Sn}$ distance (space group *Pccn*).^[76] The Lewis-amphoteric **Sn** acts as ligand in transition metal complexes with subsequent transformations^[77–80] and engages in addition and insertion reactions in the GS.^[81–87] Further, **Sn** is a valuable precursor to access new stannylenes in salt metathesis and transamination reactions.^[41,53,63,88–90] Thanks to its importance in small molecule activation, insertion into σ -bonds, coordination chemistry, materials chemistry, or catalysis, **Sn** is meanwhile available in good yields on a large scale.^[91]

Upon irradiation with UV light, **Sn** disproportionates, forming the persistent tin(III) radical $\bullet\text{Sn}[\text{N}(\text{SiMe}_3)_2]_3$.^[73,92,93] Similarly, $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ transforms to $\bullet\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_3$ by UV photolysis.^[92–94] While the lead congeners could not be generated photochemically,^[93] persistent/isolable lead(III) radicals can be obtained redox chemically.^[95–97] Numerous examples of $\bullet\text{EL}_3$ radicals ($\text{E} = \text{Si}–\text{Sn}$) have been reported.^[98–101] Lappert and coworkers proposed two possible pathways for the photochemical generation of $\bullet\text{SnL}_3$ radicals ($\text{L} = \text{alkyl, amino}$) from the respective stannylenes (Scheme 2).^[93] Mechanism A (Scheme 2a) starts with the photoinduced homolysis of a tin–ligand bond in SnL_2 (A1) and the free ligand radical $\bullet\text{L}$ is trapped by a further SnL_2 in the GS forming the tin(III) radical $\bullet\text{SnL}_3$ (A2). Mechanism B (Scheme 2b) is a bimolecular photoreaction between an electronically excited stannylene $[\text{SnL}_2]^*$ (B1), tentatively in the triplet state, which reacts with a second SnL_2 in the GS (B2). A tin(I) radical $\bullet\text{SnL}$, formed in both mechanisms, could not be detected either directly or via trapping.^[93,94] However, the fate of these elusive species could be elucidated

by chemical generation of $\bullet\text{Sn}[\text{CH}(\text{SiMe}_3)_2]$ with subsequent formation of a hexastannylprismane $\text{Sn}_6[\text{CH}(\text{SiMe}_3)_2]_6$.^[102]

Photolysis of stannylenes with sterically very demanding ligands, such as $\text{Sn}[\text{NR}_2]_2$ ($\text{R} = \text{SiEt}_3, \text{GePh}_3$), did not furnish the respective tin(III) radicals but allowed the detection of an aminyl radical for $\text{R} = \text{SiEt}_3$, supporting mechanism A (Scheme 2).^[73] Formation of tin(I) radicals without detection of tin(III) radicals after photolysis of the sterically congested $\text{Sn}[\text{Ar}^{i\text{Pr}4}]_2$ ($\text{Ar}^{i\text{Pr}4} = \text{C}_6\text{H}_3-2,6-(\text{C}_6\text{H}_3-2,6-i\text{Pr}_2)_2$)^[103] was reported in addition, supporting mechanism A as well (Scheme 2). On the other hand, mechanism B cannot be ruled out a priori for **Sn** on the basis of existing experimental results.

Importantly, the occurrence of a possible bimolecular photoreaction would be a clear indication that ESs of these prototypical monomeric stannylenes must be long-lived—at least in the nanosecond regime for a diffusion-controlled bimolecular reaction. For this reason, we chose the thermally stable diamino stannylene **Sn** for deep photophysical investigations. New insights into the photophysical/chemical properties are presented in this detailed experimental and computational study, revealing a so far overlooked strong dual photoluminescence, excimer formation, and ES SOJT effects. The mechanism of the photochemical $\bullet\text{Sn}[\text{N}(\text{SiMe}_3)_2]_3$ radical formation is further underpinned. The present work includes UV–vis absorption, time-resolved emission, and ns/fs-transient absorption (TA) spectroscopy at variable temperatures and excitation energies, supported by detailed (time-dependent) density functional theory ((TD)DFT) calculations.

Results and Discussion

Photophysical Properties

The UV–vis absorption spectrum of **Sn** in *n*-pentane at room temperature shows two intense bands at 287 and 389 nm ($\epsilon = 3080$ and $1830 \text{ M}^{-1} \text{ cm}^{-1}$) and a much weaker band at 490 nm ($\epsilon = 31 \text{ M}^{-1} \text{ cm}^{-1}$; Figure 2 and Table 1), in accordance to an earlier report.^[52] All absorption bands sharpen and slightly shift hypsochromically upon cooling to 77 K (Table 1 and Figure S3). The band at 389 nm was assigned to a metal-centered (MC) transition from the metal lone-pair to the metal p-type orbital by Lappert and coworkers.^[73] However, our TDDFT calculations on the geometry relaxed structure of **Sn** give a more differentiated picture. Both strong bands at 287 and 389 nm belong to spin-allowed electronic transitions ($\text{S}_0 \rightarrow \text{S}_n$), characterized by mainly LMCT($\text{N} \rightarrow \text{Sn}$)/MC contributions as determined from charge transfer number analysis (Figures 2 and S4; Table 1). The weak band at 490 nm is assigned to a spin-forbidden $\text{S}_0 \rightarrow \text{T}_1$ transition of mixed MC/LMCT character. The presence of a spin-forbidden $\text{S}_0 \rightarrow \text{T}_1$ absorption band with appreciable intensity suggests that SOC must be very effective in **Sn**. SOC is induced by the heavy-atom effect with a significant metal character in the T_1 state (Figure 2, SOC constant $\zeta(\text{Sn}) = 1855 \text{ cm}^{-1}$).^[104] For comparison, the SOC constants for platinum and osmium, showing appreciable

Table 1: Optical properties of **Sn**.

<i>T</i> (K)	λ_{abs} (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ_{em} (nm)	τ_p	Φ
293 ^{a)}	287, 389, 490	3080, 1830, 31	650	1.2 μs ^{b)} , 16 ns ^{c)}	0.018 ^{b)}
77 ^{d)}	283, 310 (sh), 381, 480	n.d.	555	25 μs	n.d.
293 ^{e)}	n.d.	n.d.	605	8.6 μs	0.2 ^{f)}
77 ^{e)}	n.d.	n.d.	550	21 μs	0.8 ^{f)}

n.d.: not detectable. ^{a)} In *n*-pentane. ^{b)} $c = 0.32$ mM ($\lambda_{\text{exc}} = 375/390$ nm). ^{c)} $c = 25$ mM ($\lambda_{\text{exc}} = 450$ nm). ^{d)} In 3-methylpentane. ^{e)} In the solid state. ^{f)} $\lambda_{\text{exc}} = 480$ nm.

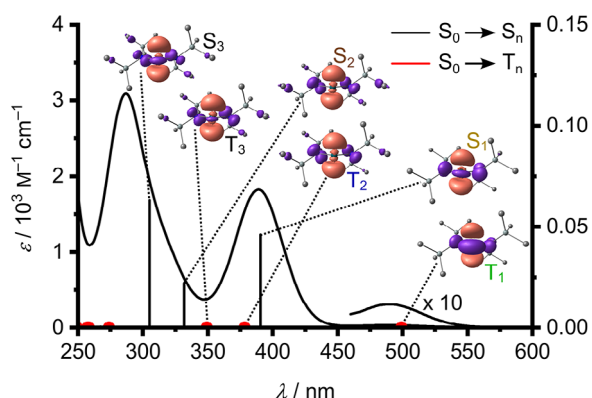


Figure 2. Absorption spectrum at 293 K of **Sn** in *n*-pentane ($c = 0.61$ mM) at 293 K with TDDFT calculated oscillator strengths for $S_0 \rightarrow S_n$ transitions, position of $S_0 \rightarrow T_n$ transitions marked by red points and difference electron densities of selected transitions (isosurface value 0.005 a.u., purple = electron loss, orange = electron gain. CPCM(hexane)-RIJ/COSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

$S_0 \rightarrow T_1$ absorption bands in their prototypical complexes amount to 4481 and 3381 cm⁻¹, respectively.^[104–107]

Assuming an idealized C_{2v} geometry of the N–Sn–N core, the $S_0 \rightarrow S_1/T_1$, $S_0 \rightarrow S_2/T_2$ and $S_0 \rightarrow S_3/T_3$ transitions are mainly of HOMO(a_1)/HOMO–1(b_2)/HOMO–2(a_2) → LUMO(b_2) character, respectively (Table S1). Group theoretical considerations identify S_1/T_1 , S_2/T_2 , and S_3/T_3 as states with $^{1/3}B_2$, $^{1/3}A_1$, and $^{1/3}B_1$ term symbols, respectively. As SOC is expected between states, which are connected via rotations,^[108] namely $S_0(^1A_1) \leftrightarrow T_1(^3B_2)/T_3(^3B_1)$, $S_1(^1B_2) \leftrightarrow T_2(^3A_1)/T_3(^3B_1)$, $S_2(^1A_1) \leftrightarrow T_1(^3B_2)/T_3(^3B_1)$. These considerations together with the experimental observation of the $S_0 \rightarrow T_1$ transition are supported by SOC-TDDFT calculations with non-negligible SOC constants and with significant oscillator strengths for the $S_0 \leftrightarrow T_1$ transitions at the Franck–Condon geometry (Tables S2 and S3).

Spin-allowed $S_0 \rightarrow S_1$ excitation of **Sn** at $\lambda_{\text{exc}} = 390$ nm furnishes green strong and long-lived $T_1 \rightarrow S_0$ phosphorescence peaking at 555 nm with $\tau = 25$ μs lifetime in frozen 3-methylpentane solution at 77 K (Figure 3, green spectrum). The $S_0 \rightarrow T_1$ (480 nm)/ $T_1 \rightarrow S_0$ (555 nm) Stokes shift amounts to 2820 cm⁻¹ (Figures 3 and S5; Table 1).

At 95 K, the green emission band shifts to 560 nm and a second, orange phosphorescence band ($T_1' \rightarrow S_0'$) appears peaking at 640 nm (Figure 3). The exact nature of the involved singlet and triplet states will be discussed below. Upon raising the temperature 95 K → 100 K → 125 K, where the sample

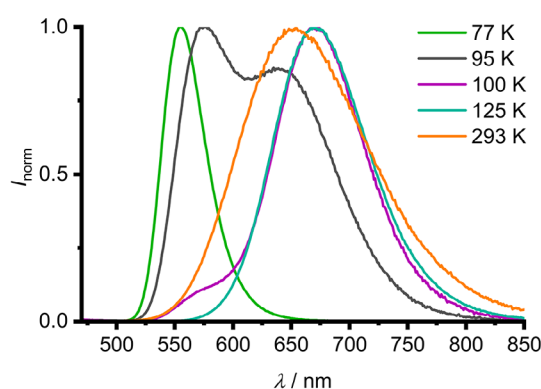


Figure 3. Normalized temperature-dependent photoluminescence spectra of **Sn** in 3-methylpentane between 77 K (green) and 293 K (orange) with $\lambda_{\text{exc}} = 390$ nm.

solution is fluid for the latter, the green emission band vanishes and the orange emission band bathochromically shifts to 670 nm (Figure 3). This behavior is fully reversible. At 293 K in fluid solution, **Sn** is still emissive with a broad band peaking at 650 nm. The excitation spectrum follows the absorption spectrum confirming that the emission stems from **Sn** (Figure S6). Band shape analysis with Voigt functions delivers two underlying bands with maxima at 643 and 679 nm, resembling the (rigidochromically shifted) $T_1 \rightarrow S_0$ and $T_1' \rightarrow S_0'$ bands (Figures 3 and S6–S9). This suggests that the emissive T_1 and T_1' states thermally equilibrate via (back) internal conversion (IC/bIC) at 293 K.

With increasing concentration from 0.32 to 25 mM at 293 K, the photoluminescence lifetime drastically drops from 1.2 μs to 16 ns (Table 1). This is a clear indication of dynamic self-quenching, tentatively assigned to excimer formation, similar to the aggregation of square-planar platinum(II) complexes.^[16–18] Stern–Volmer analysis from photoluminescence lifetime measurements yields a quenching rate constant of $k_q = 2.3 \cdot 10^9$ M⁻¹ s⁻¹ close to the diffusion limit. Additional static quenching (pre-association of ground state molecules),^[109] as observed for platinum(II) and gold(III) complexes,^[16–19] can be ruled out as steady-state emission measurements show a linear concentration dependence as well. This suggests exclusive dynamic quenching in this concentration range (Figures S10 and S11). The absence of static luminescence quenching by dimer formation is in full accordance to earlier reports on the monomeric nature of **Sn** in solution (cryoscopy, NMR spectroscopy).^[52,74]

The natural photoluminescence lifetime in the absence of self-quenching at the $c \rightarrow 0$ M limit is estimated as $\tau_0 = 9.5$ μs ($k_0 = 105\,000$ s⁻¹, y axis intercept) at 293 K (Figure S10).

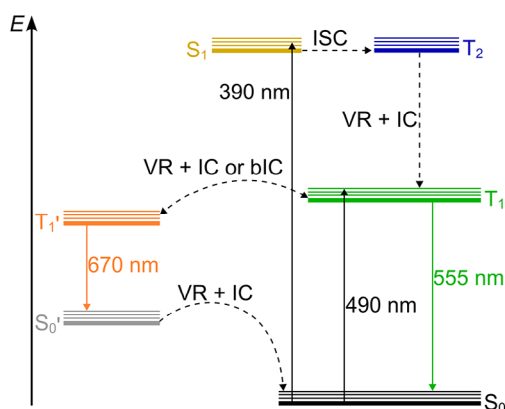


Figure 4. Jablonski diagram of **Sn** with relevant photophysical processes.

The photoluminescence quantum yield determined at low concentration of 0.32 mM amounts to $\Phi = 0.018$ at 293 K (Table 1). The intrinsic quantum yield in the absence of self-quenching for $c \rightarrow 0$ M is determined as $\Phi_0 = 0.14$. The respective nonradiative rate constant is obtained as $k_{nr,0} = k_0 - k_r = 90\,000\text{ s}^{-1}$ from the radiative rate constant of $k_r = \Phi/\tau = 15\,000\text{ s}^{-1}$. The radiative rate constant k_r of **Sn** ranges in between that of phosphorescent chromium(III) complexes ($k_r \approx 100\text{ s}^{-1}$, Laporte-forbidden MC transition, weak SOC) and prototypical $[\text{Ru}(\text{bpy})_3]^{2+}$ ($k_r \approx 110\,000\text{ s}^{-1}$, $^3\text{MLCT}$ emission, strong SOC),^[110] indicating that SOC operates significantly in **Sn**.

The combined data on the temperature-dependent population of the T_1/T_1' states indicate that T_1 and the slightly lower-energy T_1' state are connected by a barrier so that at 293 K both states are accessible by IC and bIC. The combined data allow to assemble a Jablonski-type diagram including relevant photophysical processes (Figure 4). After $S_0 \rightarrow S_1$ excitation, $S_1 \rightarrow T_2$ ISC occurs with high probability according to the similar S_1/T_2 energies and the calculated large SOC constant (Table S2). After subsequent $T_2 \rightarrow T_1$ IC and vibrational relaxation (VR), green non-Kasha $T_1 \rightarrow S_0$ phosphorescence is observed at 77 K. At elevated temperatures, thermally activated $T_1 \rightarrow T_1'$ IC becomes operative with subsequent orange $T_1' \rightarrow S_0'$ phosphorescence. At 293 K, dual $T_1' \rightarrow S_0'/T_1 \rightarrow S_0$ phosphorescence is observed via thermally activated $T_1' \rightarrow T_1$ bIC, with T_1 and T_1' states being in thermal equilibrium.

To gain deeper insight into the dynamics of the photophysical processes between T_1 and T_1' , time-resolved emission spectroscopy (TRES) was performed at 95 K, where both emission bands are similar in intensity with well-resolved band maxima (Figures 3 and 5). The TRES scan with direct $S_0 \rightarrow T_1$ excitation ($\lambda_{\text{exc}} = 450\text{ nm}$) reveals that the green T_1 emission appears solely within the first 5 μs and further evolves to the orange T_1' emission (Figures S12 and S13).

Global analysis yields four time constants $\tau_1 - \tau_4$. Several conformers might be local minima on the 3N–6 dimensional hypersurface, slightly differing from the minimum geometry of the S_0 state. Such slightly distorted geometries might be present in the frozen solution. According to the evolution-associated spectra, we tentatively assign $\tau_1 = 1$ and $\tau_2 = 5\text{ }\mu\text{s}$

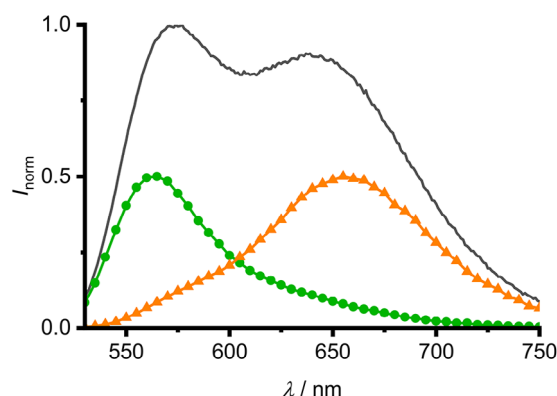


Figure 5. Normalized emission spectrum of **Sn** at 95 K in 3-methylpentane in grey, normalized time-resolved emission spectra from time-averaged spectra between 1–2 μs (green) and 47–60 μs (orange) ($\lambda_{\text{exc}} = 450\text{ nm}$, $S_0 \rightarrow T_1$).

to decays of states with similar T_1 character, but with small geometry differences (Figure S13). $\tau_3 = 13\text{ }\mu\text{s}$ might originate from an intermediate conformer during the $T_1 \rightarrow T_1'$ conversion and $\tau_4 = 26\text{ }\mu\text{s}$ is ascribed to the T_1' state decay. The steady-state emission spectrum at 95 K with direct $S_0 \rightarrow T_1$ excitation at the high energy tail ($\lambda_{\text{exc}} = 450\text{ nm}$) coincides with that obtained from $S_0 \rightarrow S_1$ excitation ($\lambda_{\text{exc}} = 390\text{ nm}$; Figures 3, 5, and S3). These data indicate that the T_1/T_1' population transfer starts in the T_1 state (as shown in Figure 4) and is not a result of branching in higher-energy singlet or triplet states. The steady-state emission spectrum consists of the time-averaged spectra within the 1–2 (T_1 emission) and 47–60 μs (T_1' emission) ranges. This clearly demonstrates the initial T_1 population with subsequent $T_1 \rightarrow T_1'$ IC (Figures 3–5).

To gain insight into the distinct nature of the T_1 and T_1' states, relaxed potential energy surface scans on the triplet hypersurface were conducted using DFT. Two local minima were localized. The relaxed geometries differ merely by the orientation of one SiMe_3 group described by the dihedral angle $\alpha(\text{Sn}-\text{N}-\text{Si}-\text{C})$ (Figure 6), while the electronic structure of the two conformers T_1 and T_1' remains unperturbed with nearly identical spin density distributions (Figure S14). The DFT energies for the vertical $T_1 \rightarrow S_0/T_1' \rightarrow S_0'$ transitions (2.11 eV (587 nm)/1.94 eV (639 nm) fit very well to the experimental observed emission energies at 95 K (2.21 eV (560 nm)/1.91 eV (650 nm); Figures 5 and 6). A transition state connects the T_1 and T_1' state minima via a small $T_1 \rightarrow T_1'$ barrier of 0.02 eV as obtained from DFT calculations (Figure S14). The sufficiently small $T_1' \rightarrow T_1$ barrier of 0.05 eV allows bIC at 293 K (Figure 6). S_0 is stabilized with respect to S_0' by $\Delta G = -5.8\text{ kJ mol}^{-1}$ (−0.06 eV), suggesting a negligible thermal population of the S_0' state.

To further substantiate the proposed assignments and dynamics, we employed nanosecond and femtosecond transient absorption (ns/fs-TA) spectroscopy at different temperatures and with different excitation wavelengths in conjunction with TDDFT calculations. The time-averaged ns-TA spectrum at 95 K at early times (0.3–2 μs) features one broad ES absorption (ESA) in the visible and two sharper ESAs

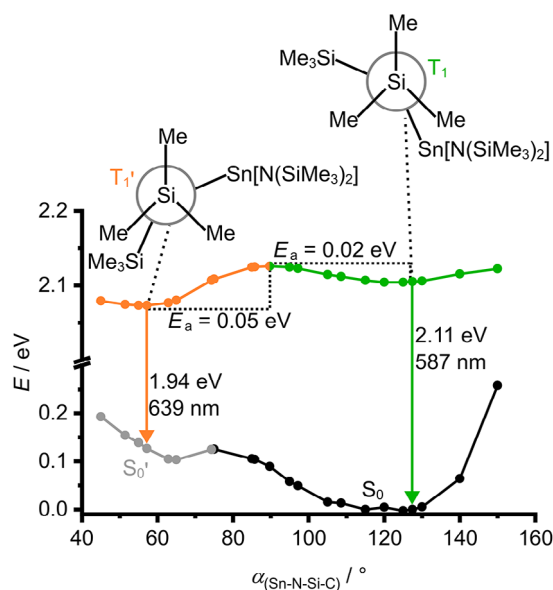


Figure 6. Relaxed potential energy surface scan of **Sn** as projection along the rotation of a trimethylsilyl group, described by the dihedral angle α (Sn–N–S–C) with selected Newman projections of the T_1 state ($\alpha = 127^\circ$) in green and T_1' state ($\alpha = 57^\circ$) in orange with single point energies on singlet GS hypersurface at triplet geometries. CPCM(hexane)-RIJ/COSX-B3LYP-D3BJ-SARC/JJ-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn).

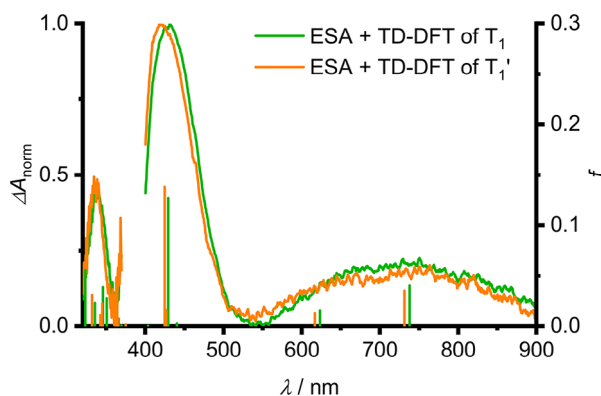


Figure 7. Normalized, time-averaged ns-TA spectra of **Sn** at 95 K in 3-methylpentane of T_1 (0.3–2 μ s) and T_1' (8–20 μ s) after $S_0 \rightarrow S_1$ excitation at $\lambda_{\text{pump}} = 390$ nm with TDDFT calculated oscillator strengths, shifted by 0.5 eV to higher energies, at the relaxed triplet geometries in green and orange, respectively.

in the UV spectral region. Within 8–20 μ s, the ESA bands shift hypsochromically while retaining the ESA band pattern (Figure 7). Assigning the spectra at early and late times to the T_1 and T_1' states, their electronic nature must be essentially identical, as noted above. TDDFT calculations of geometry relaxed T_1 and T_1' states essentially reproduce the ns-TA spectra and describe the observed hypsochromic shift of the ESA bands very well. This agreement further supports the assignment of T_1 and T_1' to different conformers (Figure 7). The photophysical dynamics obtained from ns-TA measurements match to those from TRES (Figures S12, S13, S15, and S16). The time-averaged ns-TA spectrum at 293 K is

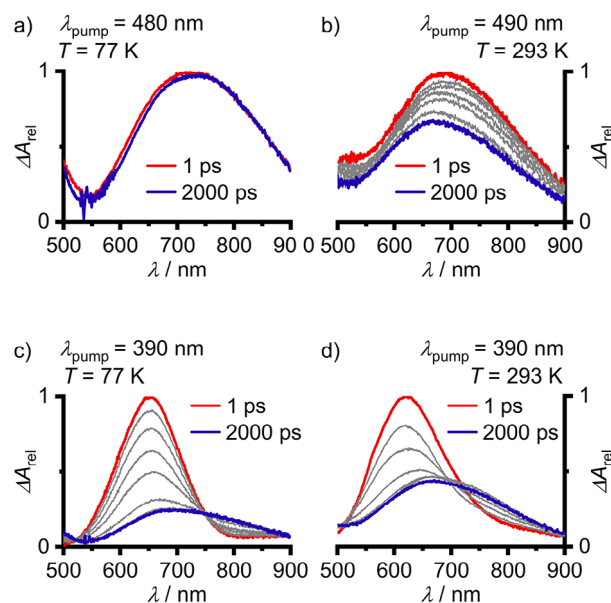


Figure 8. fs-TA spectra of **Sn** in 3-methylpentane after $S_0 \rightarrow T_1$ excitation with $c = 22$ mM at a) 77 K ($\lambda_{\text{pump}} = 480$ nm), b) 293 K ($\lambda_{\text{pump}} = 490$ nm, time delays of grey spectra 3, 5, 10, 20, and 1000 ps) and after $S_0 \rightarrow S_1$ excitation ($\lambda_{\text{pump}} = 390$ nm) with $c = 4.8$ mM at c) 77 K (time delays of grey spectra 20, 50, 100, 200, 500, and 1000 ps), and at d) 293 K (time delays of grey spectra 3, 5, 10, 20, and 100 ps).

hence composed of the ESAs of the T_1 and T_1' states in full agreement with the thermally activated dual $T_1 \rightarrow S_0/T_1' \rightarrow S_0'$ phosphorescence at 293 K (Figures 3 and S17).

To investigate the photophysical processes on ultrashort time scales, fs-TA spectroscopy was performed. Pumping the spin-forbidden $S_0 \rightarrow T_1$ transition required a higher concentration as for $S_0 \rightarrow S_1$ excitation (Figure 8). The TA spectrum of the T_1 state is immediately observed after $S_0 \rightarrow T_1$ excitation at 77 K (Figure 8a). The observed ESA matches with the weak broad ESA from ns-TA measurements at 95 K (Figure 7). The ESA narrows with $\tau_1 = 2.2$ ps, which is assigned to VR of the vibrationally hot T_1 state. The second nondecaying component within the ns regime of the experimental setup obtained from global analysis is ascribed to the vibrationally relaxed T_1 state. At 293 K, the T_1 state formed by direct excitation evolves with $\tau_1 = 14$ ps via IC and VR to T_1' (Figure 8b). Finally, the equilibrated T_1/T_1' states deactivate to the GS in the ns regime in good agreement to the emission measurements (Figures S18–S21 and Table 1).

The fs dynamics are further investigated probing the spin-allowed $S_0 \rightarrow S_1$ excitation at 77 K. After fast ISC (≤ 200 fs instrumental time resolution limit), the ESA of the T_2 state is observed peaking at ca. 650 nm. The T_2 ESA then converts to the ESA of T_1 showing an isosbestic point at 750 nm (Figure 8c). A triexponential fit delivers three time constants with $\tau_1 = 76$ ps, $\tau_2 = 262$ ps and τ_3 for the nondecaying T_1 state component. τ_1 and τ_2 may be tentatively ascribed to VR and $T_2 \rightarrow T_1$ IC. All these photophysical processes are significantly accelerated in fluid solution at 293 K with $\tau_1 = 2.6$ ps, $\tau_2 = 5.4$ ps and a third nondecaying component for the equilibrated T_1/T_1' states (Figures 8d and S22–S25). The concentration dependence of the T_1/T_1' states' lifetime is

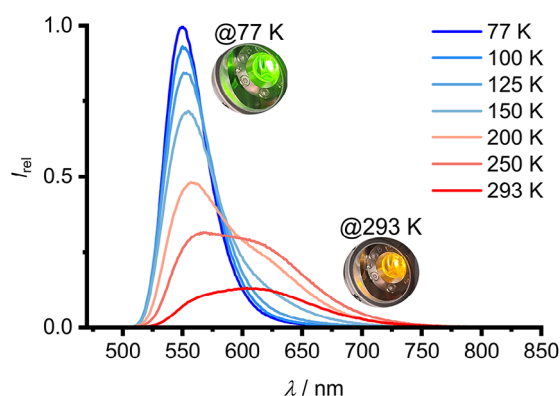


Figure 9. Temperature-dependent photoluminescence spectra of **Sn** in the solid state between 77 K (blue) and 293 K (red) with $\lambda_{\text{exc}} = 450$ nm (inset: photographs of the green and orange photoluminescence at ca. 77 and 293 K, respectively).

in accordance with the observation of dynamic self-quenching as discussed above.

The emission properties of **Sn** in the solid state are very similar to those in solution (Figure 9 and Table 1). The green $T_1 \rightarrow S_0$ phosphorescence is observed over the entire temperature range. The relative intensity of the orange $T_1' \rightarrow S_0'$ phosphorescence band rises with increasing temperature until 293 K (Figures S26–S29). Interestingly, self-quenching is effectively prevented in the solid state, leading to very high photoluminescence quantum yields of $\Phi = 0.2$ and 0.8 with emission lifetimes $\tau = 8.6$ and $21 \mu\text{s}$ at 293 and 77 K, respectively (Table 1). These numbers outcompete several optimized emitting copper(I) complexes based on thermally activated delayed fluorescence mechanisms.^[12–15] The radiative rate constant $k_{r,77} = 38\,000 \text{ s}^{-1}$ at 77 K is ascribed to the T_1 state with a nonradiative rate constant $k_{nr,77} = 9500 \text{ s}^{-1}$. The radiative rate constant $k_{r,293} = 23\,000 \text{ s}^{-1}$ at 293 K is smaller with contributions of both triplet states (T_1 and T_1'). Therefore, k_r of the T_1' state is smaller than k_r of the T_1 state in the solid state. This is also supported by the smaller $k_r = 15\,000 \text{ s}^{-1}$ determined in solution with dominating T_1' state emission. At 293 K in the solid state, thermally activated nonradiative decay is significantly accelerated by one order of magnitude with $k_{nr,293} = 93\,000 \text{ s}^{-1}$, which coincides with $k_{nr,0} = 90\,000 \text{ s}^{-1}$ obtained from Stern–Volmer analysis in solution. This confirms further, that self-quenching is negligible in the solid state. The strong and temperature-dependent green-orange emission of **Sn** in the solid state (Figure 9) recommends **Sn** as luminescent, time-gated ratiometric temperature sensor, operating in 150–293 K range by using a single compound and blue light excitation (Boltzmann thermometer; Figure S29).^[111,112]

Photochemical Properties

Beyond the unique photophysical properties of the unquenched monomeric **Sn** in the solid state and in dilute solution, we studied the self-quenching of **Sn** and the photoinduced radical formation in solution. With increasing

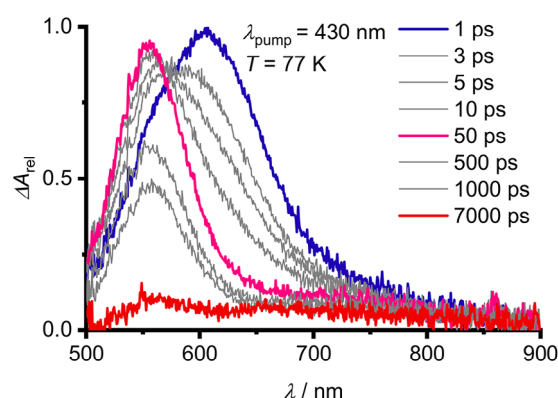


Figure 10. fs-Transient absorption spectra of **Sn** in 3-methylpentane at 77 K after excitation at $\lambda_{\text{pump}} = 430$ nm at $c = 22$ mM.

concentration ($c = 5 - 43$ mM, 3-methylpentane, 77 K), a new weak absorption band appears in the UV–vis absorption spectrum (Figure S30). Hence, we ascribe this band to $S_0^{\text{dim}} \rightarrow S_1^{\text{dim}}$ transitions of loose Van der Waals (VdW) dimers with singlet ground states in the nonpolar hydrocarbon solvent. DFT calculations find two local minima for such loose VdW dimers, namely *cis*- $^1[\text{Sn} \cdots \text{Sn}]$ and *trans*- $^1[\text{Sn} \cdots \text{Sn}]$ (Figures S31 and S32). The nature of these VdW dimers and their excimer counterparts will be discussed in more detail below.

The bathochromic shift of the $S_0^{\text{dim}} \rightarrow S_1^{\text{dim}}$ transitions in comparison to the $S_0 \rightarrow S_1$ transition of **Sn** is supported by TDDFT calculations (Figures 2 and S30–S32). The $S_0^{\text{dim}} \rightarrow S_1^{\text{dim}}$ absorption feature of the VdW dimer is not visible at 293 K, either due to band broadening of the $S_0 \rightarrow S_1$ transition of **Sn** or due to entropy-driven dissociation of the VdW dimer at higher temperatures (Figure S33). Without emphasizing the TDDFT calculated oscillator strengths too strong, the monomer appears to outnumber the VdW dimers (Figures 2, S3, and S30–S33). To probe the ES dynamics of the VdW dimer, we employed fs-TA spectroscopy with quite selective $S_0^{\text{dim}} \rightarrow S_1^{\text{dim}}$ excitation ($\lambda_{\text{pump}} = 430$ nm) at 77 K. An ESA at 605 nm is observed (1 ps, Figure 10). With the very similar band position and shape of the T_2 state ESA of **Sn** (Figures 8c, 10, S34, and S35), we assign this ESA of the VdW dimer to triplet states T_2^{ex} of the vibrationally hot excimers *cis/trans*- $^3[\text{Sn} \cdots \text{Sn}]$ (1 ps, 605 nm). Consecutive geometry relaxation/cooling by formation of the geometry relaxed excimers *cis/trans*- $^3[\text{Sn}_2]$ in the T_2^{ex} state occurs with $\tau_1 = 2.2$ ps (Figures 10, S34, and S35). The $T_2^{\text{ex}} \rightarrow T_1^{\text{ex}}$ IC ($\tau_2 = 11$ ps) follows with the ESA of the T_1^{ex} state peaking at 550 nm. The assignment to T_1^{ex} states is supported by TDDFT calculations (Figures 10 and S35–S37). Even at 77 K, the thus formed excimers *cis/trans*- $^3[\text{Sn}_2]$ are short-lived and finally decay with $\tau_3 = 222$ ps and $\tau_4 = 2.2$ ns, respectively (Figures 10 and S34, S35). Under the given excitation conditions, a nondecaying component remains. This corresponds to the long-lived T_1 state of the monomeric **Sn**, generated by the direct $S_0 \rightarrow T_1$ excitation via the high-energy absorption band tail at 430 nm (Figures S38 and S39). Due to broadening of the $S_0 \rightarrow T_1$ absorption band of **Sn** and/or the accelerated excimer deactivation, fs-TA spectroscopic detection of *cis/trans*- $^3[\text{Sn}_2]$

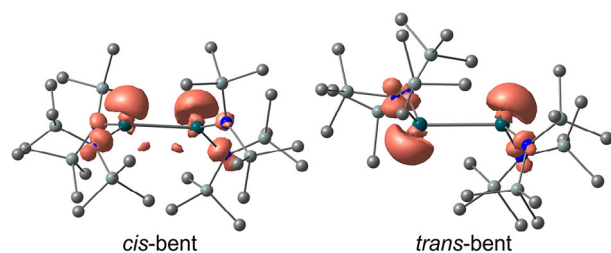


Figure 11. DFT-calculated optimized geometries of the *cis*-bent and *trans*-bent excimers with spin densities (isosurface value: 0.01). CPCM-(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn).

was impeded at 293 K in fluid solution (Figure S40). Yet, *cis/trans*- $^3[\text{Sn}_2]$ excimer formation is also likely responsible for the dynamic self-quenching of **Sn** at higher temperature.

DFT geometry optimizations delivered two GS adducts *cis*- $^1[\text{Sn}\cdots\text{Sn}]$ and *trans*- $^1[\text{Sn}\cdots\text{Sn}]$ and their respective triplet excimers *cis*- $^3[\text{Sn}_2]$ and *trans*- $^3[\text{Sn}_2]$ as local minima with twisted *cis*- and *trans*-bent geometries, respectively (Figures 11 and S41). The spin density in both excimers is mainly located at the tin atoms. The DFT-derived Sn $\cdots$ Sn distances in the GS adducts *cis/trans*- $^1[\text{Sn}\cdots\text{Sn}]$ (3.81 and 3.78 Å) are shorter than those in the XRD structure (4.95 Å)^[76] with *trans*-bent geometry (Figure S41). The excimers possess significantly shorter distances of 2.92 and 3.06 Å for *cis*- $^3[\text{Sn}_2]$ and *trans*- $^3[\text{Sn}_2]$, respectively. The *cis* isomers are thermodynamically preferred over their *trans*-isomer counterparts by $\Delta G = -17 \text{ kJ mol}^{-1}$ (-0.18 eV) for *cis/trans*- $^1[\text{Sn}\cdots\text{Sn}]$ and $\Delta G = -27 \text{ kJ mol}^{-1}$ (-0.28 eV) for *cis/trans*- $^3[\text{Sn}_2]$, respectively.

The very small vertical *cis*- $^3[\text{Sn}_2] \rightarrow$ *cis*- $^1[\text{Sn}_2]$ energy gap of only 0.53 eV (2340 nm) enables very fast nonradiative deactivation ($\tau_3 = 222 \text{ ps}$, Figure S35) in agreement with the energy-gap law.^[11] Thus, excimer formation is responsible for efficient dynamic self-quenching of the **Sn** phosphorescence in fluid solution by the preferred formation of *cis*- $^3[\text{Sn}_2]$. The *trans*- $^3[\text{Sn}_2] \rightarrow$ *trans*- $^1[\text{Sn}_2]$ vertical energy gap was calculated to 1.33 eV (932 nm), leading to a much slower ES decay ($\tau_4 = 2.2 \text{ ns}$; Figure S35).

Orbital symmetry considerations help to understand the preferred pyramidalization in the triplet excimers (Figure 12). The *trans*-bent structure (C_{2h}) of distannenes in the singlet GS was ascribed to SOJT coupling.^[44,48,61,62] Analogous *cis*- and *trans*-bent structures for $[\text{E}_2\text{L}_4]^-$ radical anions were also discussed in this context.^[62] Indeed, $D_{2h} \rightarrow C_{2h}$ symmetry lowering along the b_{1g} vibrational mode mixes the fully occupied $\sigma(a_g)$ and $\pi(b_{2u})$ orbitals with the unoccupied $\pi^*(b_{1g})$ and $\sigma^*(b_{3u})$ orbitals in distannenes in the GS, respectively. The same symmetry argument holds for the triplet state with doubly occupied $\sigma(a_g)$ and singly occupied $\pi(b_{2u})$ orbitals, which mix with singly- and unoccupied $\pi^*(b_{1g})$ and $\sigma^*(b_{3u})$ orbitals, respectively, upon $D_{2h} \rightarrow C_{2h}$ symmetry-lowering (*trans*- $^3[\text{Sn}_2]$; Figure 12 and Table S4). On the other hand, the $D_{2h} \rightarrow C_{2v}$ symmetry change along the b_{2u} vibrational mode mixes orbitals, which are closer in energy ($\sigma(a_g) \leftrightarrow \pi(b_{2u})$ and $\pi^*(b_{1g}) \leftrightarrow \sigma^*(b_{3u})$). The resulting smaller orbital energy gap makes the SOJT coupling more

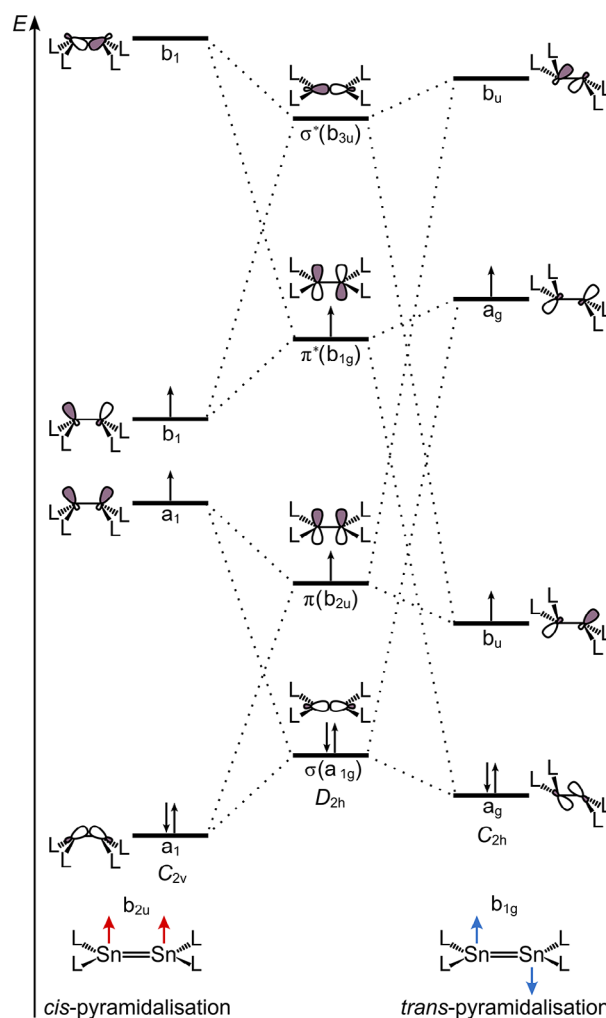


Figure 12. Correlation diagram for the changes in symmetry and energy of frontier orbitals of $\text{L}_2\text{Sn} = \text{SnL}_2$ from planar (D_{2h}) to *cis*-bent (C_{2v}) and *trans*-bent (C_{2h}) geometry.

effective and hence stabilizes *cis*- $^3[\text{Sn}_2]$ over *trans*- $^3[\text{Sn}_2]$. The b_{2u} mode is exclusively SOJT active in the ES, while the b_{1g} mode is SOJT active in the GS and ES of distannenes and ethylene homologues in general.

The formation of triplet excimers with concomitant ligand migration might be a step in the photochemical generation of the tin(III) radical $\cdot\text{Sn}[\text{N}(\text{SiMe}_3)_2]_3$ (mechanism B; Scheme 2b).^[93] In the bimolecular mechanism B, the rate-determining step of the radical formation would be the bimolecular excimer formation followed by ligand migration. UV-vis spectroscopic tracking of the photolysis reaction with excitation wavelength $\lambda_{\text{exc}} = 412 \text{ nm}$ and excitation power $P = 0.55 \text{ W}$, reveals that the color of the solution changes from yellow to brown, without formation of precipitates (Figure 13). During a 15 min period of irradiation, the absorptions of **Sn** almost vanished.

An X-band EPR spectrum of the resulting brown solution shows the resonance of the expected $\cdot\text{Sn}[\text{N}(\text{SiMe}_3)_2]_3$ radical (Figure S42).^[73,92,93] Photolysis experiments at variable concentrations to probe the molecularity of the rate-determining

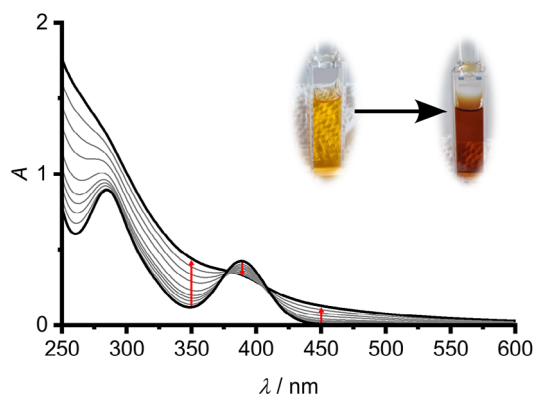


Figure 13. UV-vis absorption spectra (0–15 min) during photolysis of **Sn** at $c = 0.23$ mM in *n*-pentane irradiated at $\lambda_{\text{exc}} = 412$ nm ($P = 0.55$ W). The photographs show the solution before and after irradiation.

step reveal a quasi-linear dependence of absorption versus time within the first 2 min at $\lambda = 350$ nm (product absorption; Figure S43).

Assuming the concentration of **Sn** as constant (method of initial rates), the photodecomposition yield of $\Phi_{\text{deg}} = 0.002$ is independent on the concentration and merely depends on the concentration of excited molecules within experimental uncertainty (Figure S43). This clearly supports, as suggested earlier,^[73] that the $\bullet\text{Sn}[\text{N}(\text{SiMe}_3)_2]_3$ radical forms following mechanism A via unimolecular tin–ligand bond homolysis of **Sn** (A1) with subsequent $\bullet\text{N}(\text{SiMe}_3)_2$ radical trapping of **Sn** in the GS (A2) (Scheme 2a). The rate of radical formation is concentration independent, while excimer formation is. This indicates that Sn–N bond homolysis must occur from a short-lived higher-lying (hot) ES.

Mechanism A is also preferred based on thermodynamic considerations, with the excimer *cis*- $^3[\text{Sn}_2]$ being stabilized by 0.11 eV relative to the formation of the radicals $\bullet\text{Sn}[\text{N}(\text{SiMe}_3)_2]_3$ and $\bullet\text{Sn}[\text{N}(\text{SiMe}_3)_2]$ according to Gibbs free energies from DFT calculations (Scheme 2 and Figure S44). Additionally, the estimated barriers and dissociation limits from 1D and 2D relaxed potential energy surface scans are slightly higher for ligand migration in mechanism B, as compared to ligand dissociation and association in mechanism A (Scheme 2 and Figures S45–S50). Finally, the most striking (kinetic) argument is the very short lifetime of the excimers *cis*/*trans*- $^3[\text{Sn}_2]$, preventing any ligand migration before relaxation to the GS.

Conclusion

The stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ **Sn** shows unreported temperature-dependent dual green/orange phosphorescence with microsecond lifetime from two conformers (T_1 and T_1' states) in solution. At high concentrations, the emission is strongly quenched by triplet excimer formation *cis*- and *trans*- $^3[\text{Sn}_2]$. The *cis*-excimer is thermodynamically preferred by a second-order Jahn–Teller effect and provides the fastest decay path.

In the solid state, excimer formation is effectively mitigated and very high photoluminescence quantum yields of

0.2 and 0.8 with long microsecond excited state lifetimes are achieved at 293 and 77 K, respectively. These numbers clearly compete with photoluminescent transition metal complexes.

The bimolecular mechanism of the photochemical $\bullet\text{Sn}[\text{N}(\text{SiMe}_3)_2]_3$ radical generation in solution was ruled out, while the unimolecular Sn–N bond homolysis of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ is confirmed as initial rate-determining step with subsequent aminyl radical trapping by $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$.

The long-known diamino stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ possesses promising photophysical properties—luminescence and long excited state lifetimes. Suppressing excimer and radical formation in suitably designed stannylens might even pave the way for optical materials and photocatalysis applications. Investigations along these lines are currently in progress.

Supporting Information

The Supporting Information contains synthesis and separation procedures, experimental spectroscopic data, and quantum chemical data (pdf), including Cartesian coordinates (xyz). The authors have cited additional references within the Supporting Information.^[52,54,73,113–138]

Acknowledgements

[Redacted text]

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Excimer • Phosphorescence • Radicals • Stannylene • Transient absorption spectroscopy

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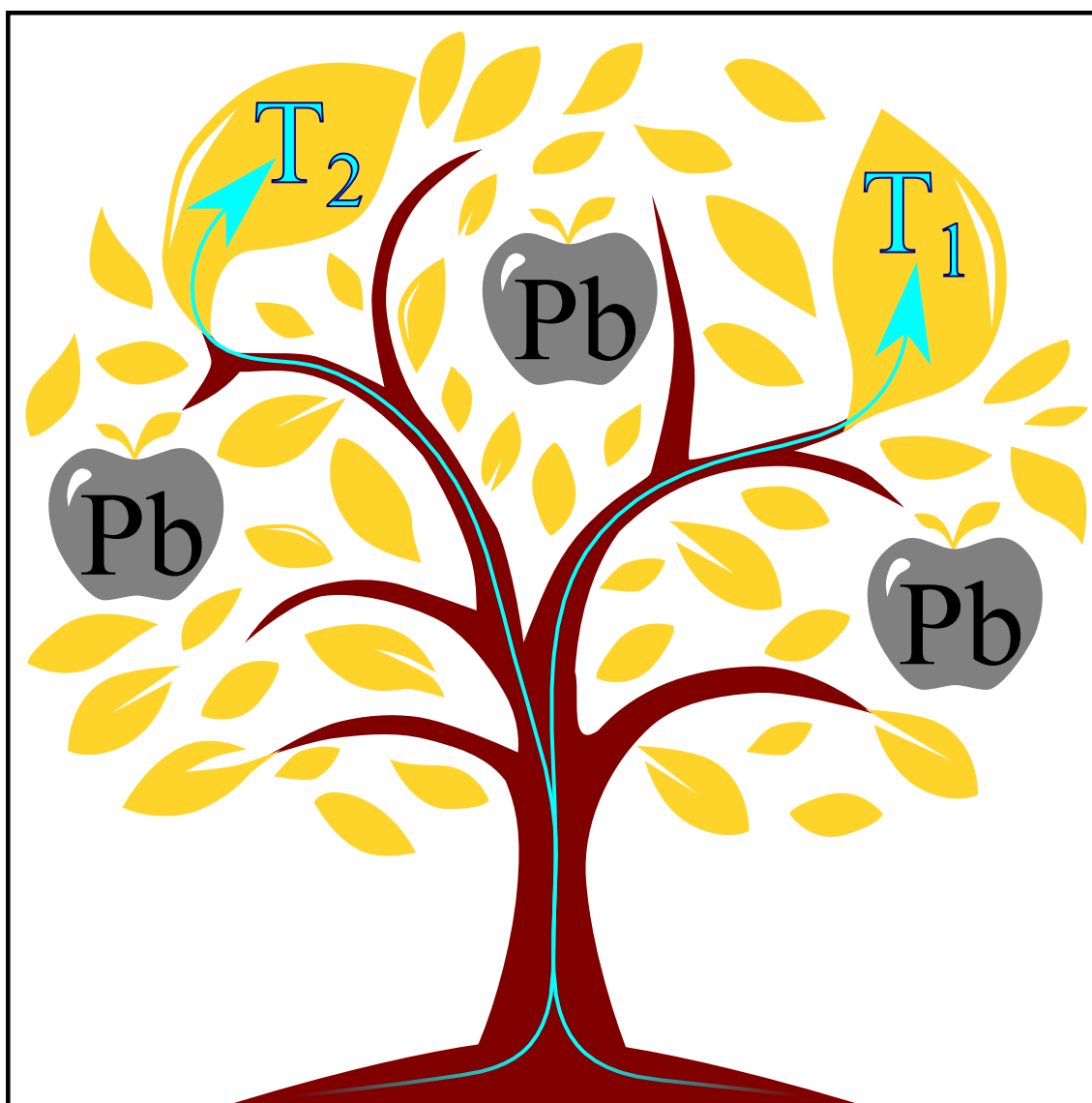
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3.5 The Photophysics of *Lappert's* Diamino Plumbylene



3.5.1 Results and Discussion

The UV/Vis absorption spectrum of $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ (**PbH**) in *n*-pentane at room temperature shows two intense bands at 315 and 410 nm ($\epsilon = 2000$ and $1500 \text{ M}^{-1} \text{ cm}^{-1}$, Figure S 3) as well as a shoulder at 350 nm (Figure 3.5a, Table 3.1). All absorption bands sharpen and slightly shift hypsochromically upon cooling at 77 K and an additional shoulder at 440 nm appears (Table 3.1, Figure S 4 – Figure S 5). TD-DFT calculations reveal that both strong bands at 315 and 410 nm belong to spin-allowed electronic transitions ($S_0 \rightarrow S_n$) which are mainly characterized either by LMCT($\text{N} \rightarrow \text{Pb}$) contributions for the band at 410 nm or by mixed MC/LMCT contributions for the band at 315 nm, as determined by charge transfer number analysis (Figure 3.5, Figure S 6). The additional shoulder at 440 nm at 77 K is assigned to a spin-forbidden $S_0 \rightarrow T_1$ transition of mainly LMCT character (Table 3.1). The presence of a spin-forbidden $S_0 \rightarrow T_1$ transition indicates that SOC is strong in **PbH**. The significantly high orbital coefficient at the lead center in the T_1 state induces SOC by the heavy-atom effect. The lighter homologue Lappert's stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ displays also a spin-forbidden $S_0 \rightarrow T_1$ transition at larger wavelengths with higher MC contributions.^[232] The absence of the MC contribution in **PbH** can be rationalized by stronger relativistic effects, which stabilize and hence energetically separate the n_s -orbital from the frontier ligand orbitals.^[150,153]

TD-DFT calculations show also a further spin forbidden $S_0 \rightarrow T_2$ transition, energetically close to the $S_0 \rightarrow S_1$ transition. Interestingly, the respective T_1 and T_2 states vary in the different sizes of the orbital coefficients at the $\text{N}(\text{SiMe}_3)_2^-$ moieties (Figure 3.5b). Whereas the T_1 state shows a huge orbital coefficient on the “right” ligand moiety (N^1) compared to the “left” ligand moiety (N^2), the T_2 state displays the opposite (Figure 3.5b, respective nitrogen atoms marked in blue).

Supposing an idealized C_{2v} geometry of the N–Pb–N core, the $S_0 \rightarrow S_1/T_1$, $S_0 \rightarrow S_2/T_2$ and $S_0 \rightarrow S_3/T_3$ transitions are particularly of HOMO(a_1)/HOMO–1(b_1)/HOMO–2(a_1) $\rightarrow$ LUMO(b_2) character (Table S 1). According to group theoretical considerations the states S_1/T_1 , S_2/T_2 and S_3/T_3 can be classified with the term symbols $^1/3B_2$, $^1/3A_2$ and $^1/3B_2$. The SOC is strong between states, which are connected by rotations.^[58] In this case, $S_0(^1A_1) \leftrightarrow T_1(^3B_2)/T_2(^3A_2)/T_3(^3B_2)$, $S_1(^1B_2) \leftrightarrow T_2(^3A_2)$ and $S_2(^1A_2) \leftrightarrow T_1(^3B_2)/T_3(^3B_2)$ transitions should be favored by SOC. SOC-TD-DFT calculations support these considerations by revealing non-negligible SOC constants and high oscillator strength for the $S_0 \rightarrow T_n$ transitions at the Franck-Condon geometry (Table S 2, Figure S 7). These aspects additionally confirm the experimentally observed $S_0 \rightarrow T_1$ transition.

Table 3.1: Optical properties of **PbH**.

T / K	$\lambda_{\text{abs}} / \text{nm}$	$\epsilon / \text{M}^{-1} \text{cm}^{-1}$	$\lambda_{\text{em}} / \text{nm}$	τ_p / ns
293 ^{a)}	410, 350 (sh), 315, 250	1500, 2000, 4700	n.d.	n.d.
77 ^{b)}	440 (sh), 395, 345 (sh), 306	n.d.	700	295, 912 ^{c)}

n.d. = not detectable, ^{a)} in *n*-pentane, ^{b)} in 3-methylpentane. ^{c)} $\lambda_{\text{exc}} = 450 \text{ nm}$

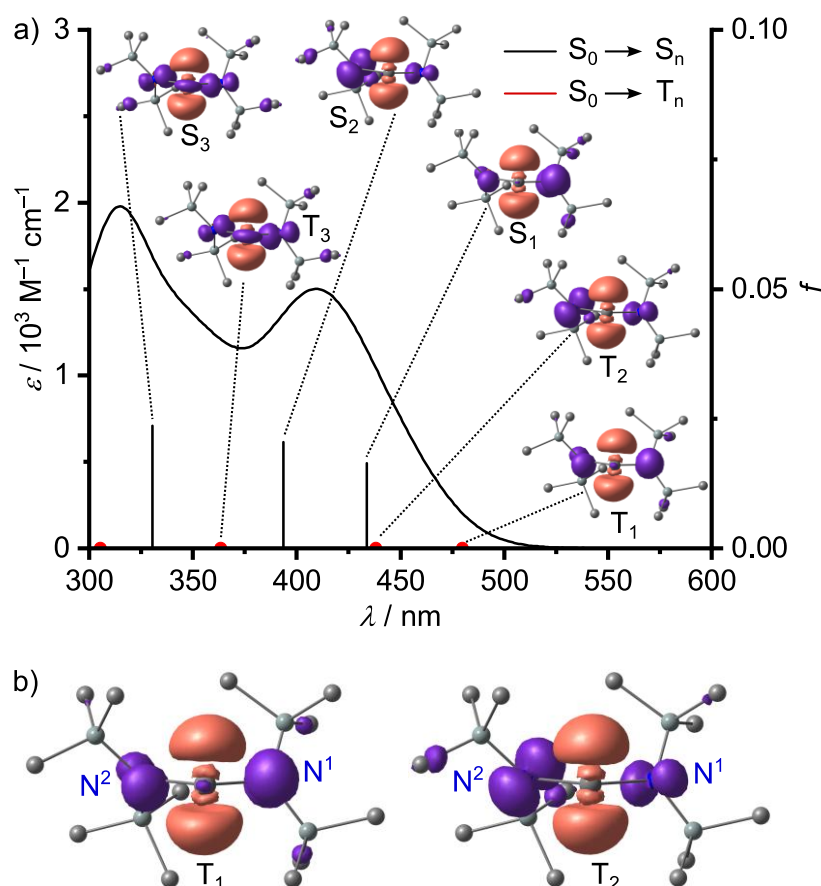


Figure 3.5: a) UV/Vis absorption spectrum of **PbH** in *n*-pentane at room temperature with TD-DFT calculated oscillator strengths for $S_0 \rightarrow S_n$ transitions, position of $S_0 \rightarrow T_n$ transitions marked by red points and difference electron densities of selected transitions (isosurface value 0.005 a.u., purple = electron loss, orange = electron gain). b) Zoom of difference electron densities of the T_1 and T_2 state with the respective ligand moieties marked in blue. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Pb).

Spin-forbidden $S_0 \rightarrow T_1$ at $\lambda_{\text{exc}} = 450$ nm as well as spin-allowed $S_0 \rightarrow S_1$ excitation at $\lambda_{\text{exc}} = 410$ nm of **PbH** furnishes a weak broad phosphorescence peaking at $\lambda_{\text{em},77} = 700$ nm in frozen 3-methylpentane solution at 77 K (Figure 3.6). The excitation spectrum follows the absorption spectrum confirming that this emission originates from **PbH** (Figure S 8). The phosphorescence is not detectable above 125 K.

A fluorescent trace impurity, below the NMR detection limit (Figure S1), with $\lambda_{\text{em},77} = 550$ nm is ascribed to photolysis or hydrolysis products of **PbH**, indicated by an asterisk in Figure 3.6. This assignment was verified by comparing two different batches of **PbH**, one freshly distilled batch which was used for the presented measurements and a second one which was stored over a longer time at -15°C (Figure S 9).

The photoluminescence lifetimes of **PbH** determined from a biexponential fit at $\lambda_{\text{em}} = 850$ nm amount to $\tau_{1,77} = 295$ ns and $\tau_{2,77} = 912$ ns with 70 and 30%, respectively. (Figure S 10). Hence, the broad phosphorescence of **PbH** at $\lambda_{\text{em},77} = 700$ nm seems to stem from two emissive states that are not in a thermal equilibrium. This indicates a high barrier between these states and an efficient relaxation back into the GS either through high radiative k_r or non-radiative rate constants k_{nr} . Since the emission at 77 K is weak and rather short-lived, k_{nr} must be high which hints at a strongly distorted geometry in the ES.

The intensity of the band for the spin-forbidden $S_0 \rightarrow T_1$ transition indicates significant SOC. Consequently, all ISC processes are likely efficient and all related ES dynamics in

PbH should take place on the triplet hypersurface. In addition, TD-DFT calculations show the presence of two triplet states in the visible region namely T_1 and T_2 .

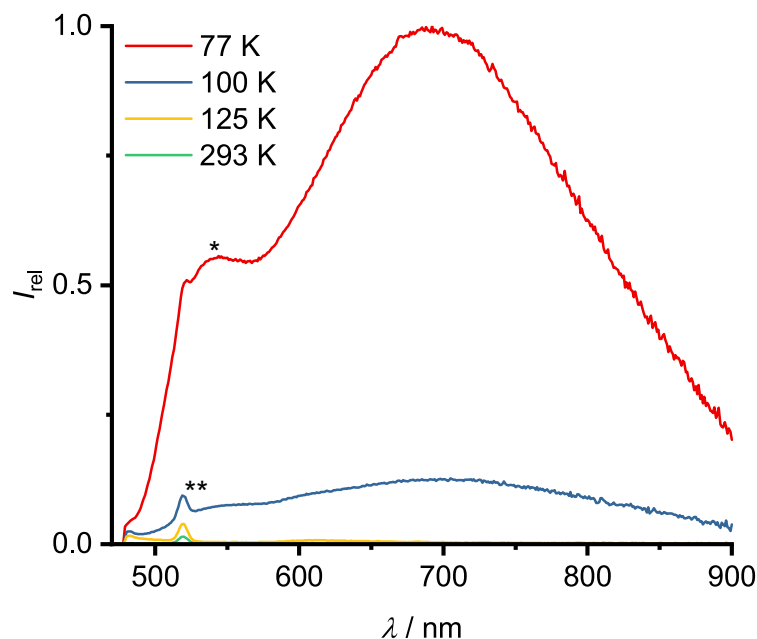


Figure 3.6: Temperature-dependent photoluminescence spectra of **PbH** in 3-methylpentane between 77 K (red) and 293 K (green) with $\lambda_{\text{exc}} = 450$ nm. One asterisk denotes the photoluminescence of an unidentified trace impurity (photolysis or solvolysis product of **PbH**), two asterisks mark a Raman band.

Two triplet states with distinct structural features could be located by DFT calculations. These states, namely T_1 and T_2 , possess mainly LMCT character, with ligand to metal transfer from the “right” ligand moiety $N^1 \rightarrow \text{Pb}$ for T_1 and from the “left” ligand moiety $N^2 \rightarrow \text{Pb}$ for T_2 , respectively (Figure 3.7). Both sides are inequivalent due to the different conformations of the respective ligand moieties, which lift the degeneracy and stabilizes T_2 over T_1 .

In comparison with the molecular orbitals of the ^1GS (Table S 1), The T_1 state can be obtained from a $\text{HOMO} \rightarrow \text{LUMO}$ and T_2 as $\text{HOMO}-1 \rightarrow \text{LUMO}$ transition. The major ^1GS to T_1 and T_2 geometric reorganization is a considerable elongation of the respective $\text{Pb}-\text{N}^1$ or $\text{Pb}-\text{N}^2$ bond (Table S 3). A DFT optimized transition state between T_1 and T_2 connects both states with an activation barrier of 0.30 eV and 0.31 eV, respectively.

DFT energies for the vertical $T_1 \rightarrow S_0$ and $T_2 \rightarrow S_0$ transitions amount to 1.57 eV (790 nm) and 1.42 (873 nm), with T_2 being slightly stabilized to T_1 . The experimental observed broad emission at $\lambda_{\text{em},77} = 700$ nm corresponds to 1.77 eV.

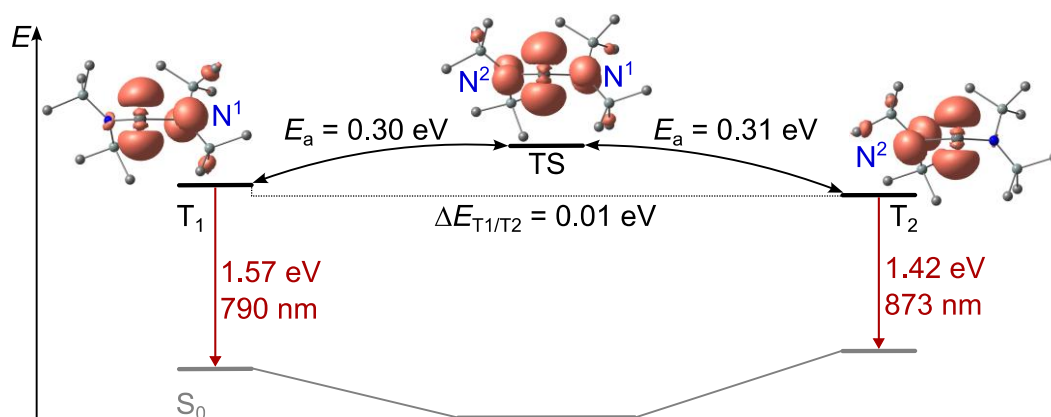


Figure 3.7: Spin densities of the geometry optimized triplet states T_1 and T_2 with the optimized transition state, the activation barrier E_a and vertical transitions in red. The respective ligand moieties are marked in blue. Isosurface value: 0.005 a.u.. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Pb).

A 2D map of the **PbH** triplet hypersurface projected along the Pb–N¹ and Pb–N² elongation modes was calculated on a lower level of theory (Figure 3.8). The map reveals two minima corresponding to the triplet states T_1 and T_2 . In contrast, the map of the relating singlet hypersurface displays one minimum (Figure S 11). Comparison of the two surfaces indicates that, following photoexcitation of **PbH**, the initial Franck-Condon state lies on the edge between the two triplet minima and close to the transition state. If ISC occurs immediately after photoexcitation, the dynamics start from the Franck-Condon state geometry on the triplet hypersurface.

Assuming again an idealized C_{2v} symmetry of the N–Pb–N core, the Franck-Condon state to transition state transfer can be described along the symmetric stretching mode a_1 for both triplet states. Beginning at the transition state, the degeneracy of T_1 and T_2 is removed by the asymmetric stretching mode b_1 along the respective Pb–N bonds, provoking a branching. Finally, population of the relaxed T_1 and T_2 states goes along a further uncoupled elongation of the respective Pb–N bond.

Since both states are low-lying and strongly distorted, rapid relaxation back to the 1GS is likely. In the experiment, two lifetimes of $\tau_{1,77} = 295$ ns and $\tau_{2,77} = 912$ ns could be detected.

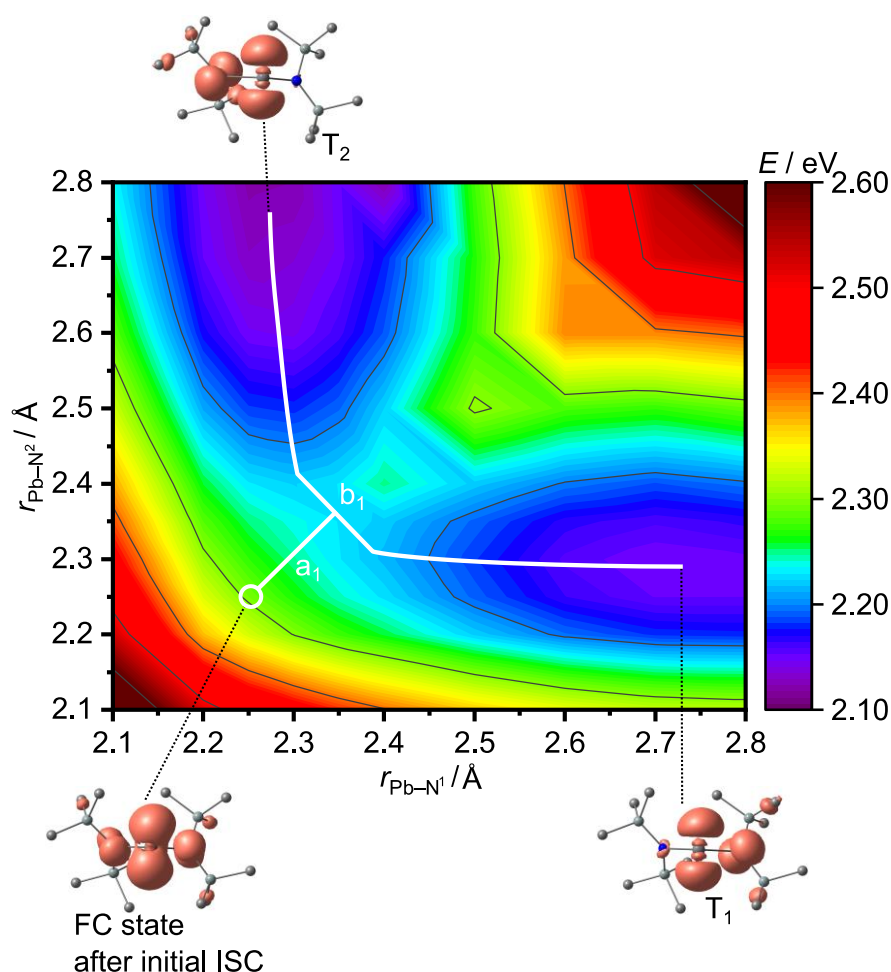


Figure 3.8: Contour plot of 2D relaxed potential energy surface scan as projection along the Pb–N¹ and Pb–N² stretching mode on the triplet hypersurface of **PbH** with the respective stretching mode a₁ and b₁ for C_{2v} symmetry and selected geometry optimized structures of T₁ and T₂ as well as the initial Franck-Condon state after photoexcitation with spin densities (isosurface value: 0.005 a.u.). The white line visualizes the branching and population of both triplet states. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Pb).

Experimentally, **PbH** exhibits a weak emission peaking at $\lambda_{\text{em},77} = 700$ nm and two ES lifetimes in the ns regime are found at 77 K (Figure 3.6, Table 3.1, Figure S 10). Thermal equilibration via the barrier of 0.30 eV between T₁ and T₂ is too slow, due to the short ES lifetimes, to compete with fast ES→GS decay. Combined with the results from DFT analysis, the observed emission and detected lifetimes can be assigned to the T₁ and T₂ states. Both states have short lifetimes as a result of strong geometric distortions and their low-lying ES energies.

At 77 K, **PbH** displays lifetimes in the ns regime. At room temperature, there is no emission detectable, which indicates short-lived ESs. Further, UV/Vis absorption spectroscopy has not revealed any aggregation of **PbH** in concentration dependent experiments (Figure S 12, Figure S 13). Based on that, a triplet excimer formation in **PbH**, like in the case of Sn[N(SiMe₃)₂]₂,^[232] is rather unlikely, but cannot be ruled out.

Irradiation of **PbH** does not lead to radical formation as in case of the stannylenes Sn[N(SiMe₃)₂]₂.^[217] Instead, elemental lead is formed. However, the mechanisms of the radical formation (section 1.5.3) may represent the initial step, followed by further reduction and ligand loss leading to elemental lead formation. Like in Sn[N(SiMe₃)₂]₂, the photoinduced Pb–N bond cleavage could be the first step of the photolysis mechanism.

UV/Vis spectroscopic tracking of the photolysis reaction upon $\lambda_{\text{exc}} = 455$ nm irradiation and excitation power of $P = 0.03$ W shows formation of lead particles. Scattering contributions from these particles in the absorption spectra are corrected using fit functions based on Mie light scattering (Figure S 15 – Figure S 20).^[233] The resulting corrected absorption spectra show a decrease of the signal at $\lambda_{\text{abs}} = 410$ nm during a 480 s period of irradiation (Figure 3.9). In order to elucidate the molecularity of the rate-determining step, photolysis experiments at variable concentrations reveal a quasi-linear dependence of absorption at $\lambda_{\text{abs}} = 410$ nm versus the respective considered time (Figure S 21).

Assuming the concentration of **PbH** remains unchanged during the measurement (method of initial rates), the photodegradation quantum yield of $\Phi_{\text{deg}} = 0.05$ is not affected by the **PbH** concentration and solely depends on the number of ES molecules within experimental uncertainty, similar to $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$. This implies that the lead particle formation may begin with the unimolecular Pb–L bond homolysis from one or both triplet states T_1 and T_2 (step **A1** of mechanism **A**) with following lead particle formation. For comparison, the photodegradation quantum yield of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ amounts to $\Phi_{\text{deg}} = 0.002$.^[232] Further, dissociation limits from relaxed potential energy surface scans are higher for $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ (0.66 eV) than for **PbH** (0.49 eV), indicating a greater tendency for Pb–N bond cleavage (Figure S 22).

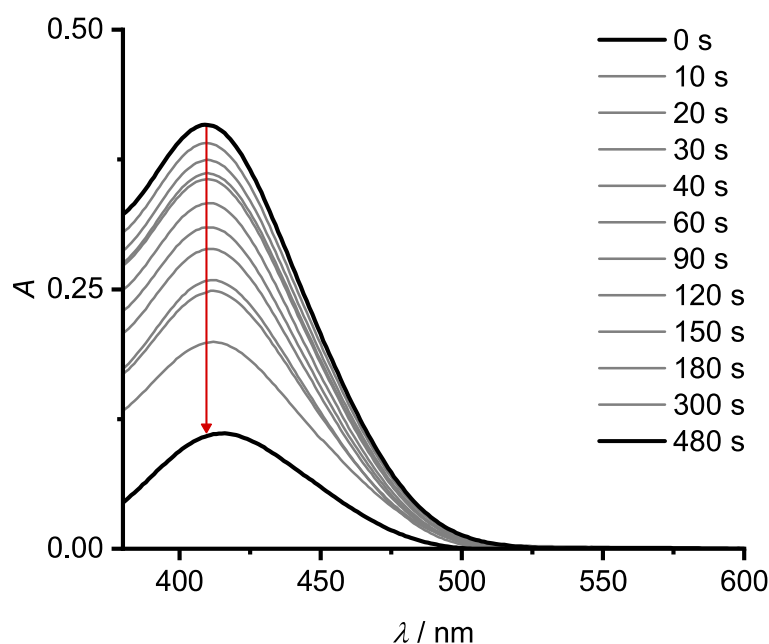


Figure 3.9: UV/Vis absorption spectra during photolysis of **PbH** at $c = 0.27$ m in *n*-pentane irradiated at $\lambda_{\text{exc}} = 455$ nm ($P = 0.03$ W) at room temperature. Scattering contributions, caused by solid lead particles, were corrected by assuming Mie light scattering. The slight shift in the latter absorption band maxima arises from distortions induced by solid lead particles.

3.5.2 Conclusion

The plumbylene $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ **PbH** shows phosphorescence at $\lambda_{\text{em}} = 700$ nm with nanosecond lifetimes from two triplet states T_1 and T_2 in frozen 3-methylpentane solution at 77 K. According to DFT, both states are strongly distorted along the $\text{Pb}-\text{N}^1$ and $\text{Pb}-\text{N}^2$ bond, respectively. An optimized transition state connects both states with an activation barrier of around 0.3 eV. Due to the effective ES deactivation the establishment of a thermal equilibrium between T_1 and T_2 is prevented. The population of both triplet states occurs through a branching from the initial Franck-Condon state. These aspects may explain the short-lived biexponential lifetime and low energy emission.

Irradiation experiments of **PbH** support the assumption that lead formation may start with a photoinduced $\text{Pb}-\text{L}$ bond homolysis from the respective triplet states according to the unimolecular step **A1** of mechanism **A**.

In terms of photophysical performance, the lighter stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ surpasses the plumbylene **PbH** tremendously. Especially, the ES lifetimes differ by three orders of magnitude ($\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ microsecond regime, **PbH** nanosecond regime) which can be traced back to the larger geometric distortions in the ES of **PbH** compared to $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$.

A reason for that could lie in the different MC contributions in the respective lowest ES. Whereas the n_s -orbital contribution in the HOMO of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ is high leading to a MC/LMCT state, in the HOMO of **PbH** the n_s contribution is almost vanished resulting in a rather pure LMCT character (Figure S 23). These LMCT states weaken the $\text{Pb}-\text{N}$ bonds. In $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$, MC state admixture diminishes ES distortion, which is in stark contrast to interconfigurational MC states in TMC.

As estimated from relaxed surface scans by DFT, the bond dissociation energy for $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ is higher than in **PbH** with 0.66 eV and 0.49 eV, respectively (Figure S 22). Therefore, it seems that the more MC character the electronic transition keeps, the less distorted and more stable the relaxing geometry of the ES is.

Future approaches to obtaining highly luminescent lead(II) complexes should target the energetical increase of the n_s -orbital to create pivotal ESs with MC character. This could be realized for example by introducing electropositive ligands with bulky substituents which increase the p-character in the n_s -orbital due to electronic and steric effects (Figure 1.19).

4 Summary and Outlook

Since the first report of the stable stannylene $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ by Lappert and coworkers, numerous studies on the ground state properties of heavy tetrel(II) complexes have been reported.^[145,146,149,150,147,148] On the other hand, the photophysics and the photochemistry of these complexes have not been probed and discussed in detail. Despite a few examples in the literature, correlation between ligand design and excited state character as well as relevant excited state dynamics had not been considered. These aspects were elucidated in this work. Tetrel(II) complexes with tripodal, meridional and basic-tetrylene structures were analyzed, inter alia, with temperature-, concentration-, excitation-wavelength-dependent and time-resolved spectroscopic methods. The results revealed considerable effects, defining the first step into rational ligand design for particularly phosphorescent materials with long-lived excited states.

Tin(II) vs. Lead(II):

In the series of investigated complexes, the tin(II) complexes demonstrate a better performance regarding photophysical properties than the respective lead(II) complexes. In the first project the excited state lifetimes and photoluminescence quantum yields for $\text{Sn}(\text{bpep})$ are higher ($\tau_{77} = 3.6 \text{ ms}$, $\Phi_{\text{PL},77} = 0.58$) than for $\text{Pb}(\text{bpep})$ ($\tau_{77} = 92 \text{ ns}$, $\Phi_{\text{PL},77} = 0.0024$). The respective radiative and non-radiative rate constants amount to $k_{\text{r},77} = 160 \text{ s}^{-1}$ and $k_{\text{nr},77} = 120 \text{ s}^{-1}$ for $\text{Sn}(\text{bpep})$ or $k_{\text{r},77} = 26000 \text{ s}^{-1}$ and $k_{\text{nr},77} = 10800000 \text{ s}^{-1}$ for $\text{Pb}(\text{bpep})$, respectively. The lead(II) center with its strong SOC significantly promotes radiative and non-radiative processes. However, in the present case, non-radiative processes dominate via small activation barriers E_{a} the excited state dynamics considerably.

Comparison between $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ and $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ regarding the photodegradation quantum yields ($\Phi_{\text{deg}}(\text{Sn}) = 0.002$ vs. $\Phi_{\text{deg}}(\text{Pb}) = 0.05$) underlines the general stability issue in lead(II) complexes, as well.

On the other hand, tin(II) complexes provide significant SOC with efficient ISC, generating intense phosphorescence. In the case of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ even $\text{S}_0 \rightarrow \text{T}_1$ transition is easily observable. Its intrinsic photoluminescence quantum yield without self-quenching and respective radiative rate constant amount to $\Phi_{\text{PL}} = 0.14$ and $k_{\text{r},293} = 15000 \text{ s}^{-1}$ in solution at room temperature.

Hence, tin(II) clearly outcompetes lead(II) as tetrel center and should be preferred in tetrel(II) materials with similar ligand topology as the systems investigated within this work.

The role of the excited state:

The ligand topology of the tin(II) complexes determines the excited state character. The tripodal $\text{Sn}(\text{bpep})$ complex exhibits ILCT phosphorescence, which involves the relevant π_{L} - and π_{L}^* -orbitals from the ligand system (Figure 4.1a). Considering the relevant frontier orbitals, the tetrel centered n_{s} -orbital is energetically separated from the occupied π_{L} -orbitals of the ligand. Further, additional donor sigma coordination destabilizes the resulting p_{σ^*} -orbital shifting above the π_{L}^* -orbitals (Figure 1.18). However, occupation of the antibonding p_{σ^*} -orbital in the excited state provokes strongly distorted LMCT states, which are connected to the emissive ILCT state and responsible for non-radiative deactivation. This leads to dramatic temperature dependence regarding the

photophysical properties. For instance, the excited state lifetimes drop from $\tau_{77} = 3.6$ ms at 77 K to $\tau_{293} = 14$ ns at room temperature.

To avoid this deactivation a rigid environment, hampering the donor dissociation can be established or alternatively the additional donor must be removed. This was achieved by switching from the tripodal geometry to a meridional as realized in the $\text{Sn}(\text{}^t\text{-BuPDP}^{\text{}^t\text{-Bu}})$ complex. Here, the vacant p_{π} -orbital mixes with the pyridine π_{L} -orbitals and is diminished to lower energies, resulting in an emissive excited state with mainly LMCT character (Figure 4.1b). Hence, addressing specific excited states by specific ligand design was successful. However, in non-coordinating solvents $\text{Sn}(\text{}^t\text{-BuPDP}^{\text{}^t\text{-Bu}})$ undergoes dimerization and ligand rearrangement. In the resulting dimer, the local coordination of the tin(II) centers resembles that of $\text{Sn}(\text{bpep})$. The monomeric $\text{Sn}(\text{}^t\text{-BuPDP}^{\text{}^t\text{-Bu}})$ complex seems to be a reactive species with an unfavored geometry for this system, which limited the investigation of its optical properties to the solid state. Aggregation in the solid state leads to a temperature-dependent change of the radiative rate constants k_{r} with $k_{\text{r},77} = 100 \text{ s}^{-1}$ at 77 K and $k_{\text{r},293} = 20000 \text{ s}^{-1}$ at room temperature, which is attributed to excitonic interactions.

In both previous studies, pyridine dipyrrolide ligands with a coordination number of $C = 3$ were implemented to the tin(II) center. The results are undesired effects like the dimerization in the case of $\text{Sn}(\text{}^t\text{-BuPDP}^{\text{}^t\text{-Bu}})$ or strong excited state distortions due to the additional donor in the case of $\text{Sn}(\text{bpep})$. Both issues were avoided by reducing the coordination number to $C = 2$, leading to two stable bonds and establishing typical structures of heavier carbene homologues (section 1.5.1). In the mentioned complexes $\text{Sn}(\text{bpep})$ and $\text{Sn}(\text{}^t\text{-BuPDP}^{\text{}^t\text{-Bu}})$, the π_{L} -orbitals of the pyrrolate units are energetically higher than the tetrel centered n_{s} -orbitals. Thus, the later ones are not relevant in the respective excited state dynamics, for example in form of MLCT or MC transitions (Figure 4.1a and b). To achieve this, the pyrrolate units and their large π -systems can be replaced for instance by simple amine ligands.

A compound which fulfills these attributes is the well-known *Lappert's* diamino stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$. Since its first report, this stannylene has been investigated in detail concerning the ground state properties.^[215,227,228] This thesis discloses its excited state properties. The emissive excited state provides mixed MC/LMCT character. In this case, the frontier orbitals are the n_{s} -orbital with amine π_{L} -orbital admixture as HOMO and the vacant p_{π} -orbital as LUMO (Figure 4.1c). With a photoluminescence quantum yield of $\Phi_{\text{PL},293} = 0.2$ in the solid state at room temperature, which has been overlooked for over fifty years, and the intrinsic quantum yield of $\Phi_{\text{PL}} = 0.14$ in solution, *Lappert's* diamino stannylene surpasses the other complexes in terms of photophysical performance. This is based on the less distorted excited states with significant MC character. However, self-quenching and excimer formation opens a new deactivation pathway, which diminishes its photoluminescence in solution. Other issues are the photodegradation and subsequent radical formation, which prohibit long irradiation times. Nevertheless, the quenching process indicates that stannylenes are potential candidates for photocatalysis.

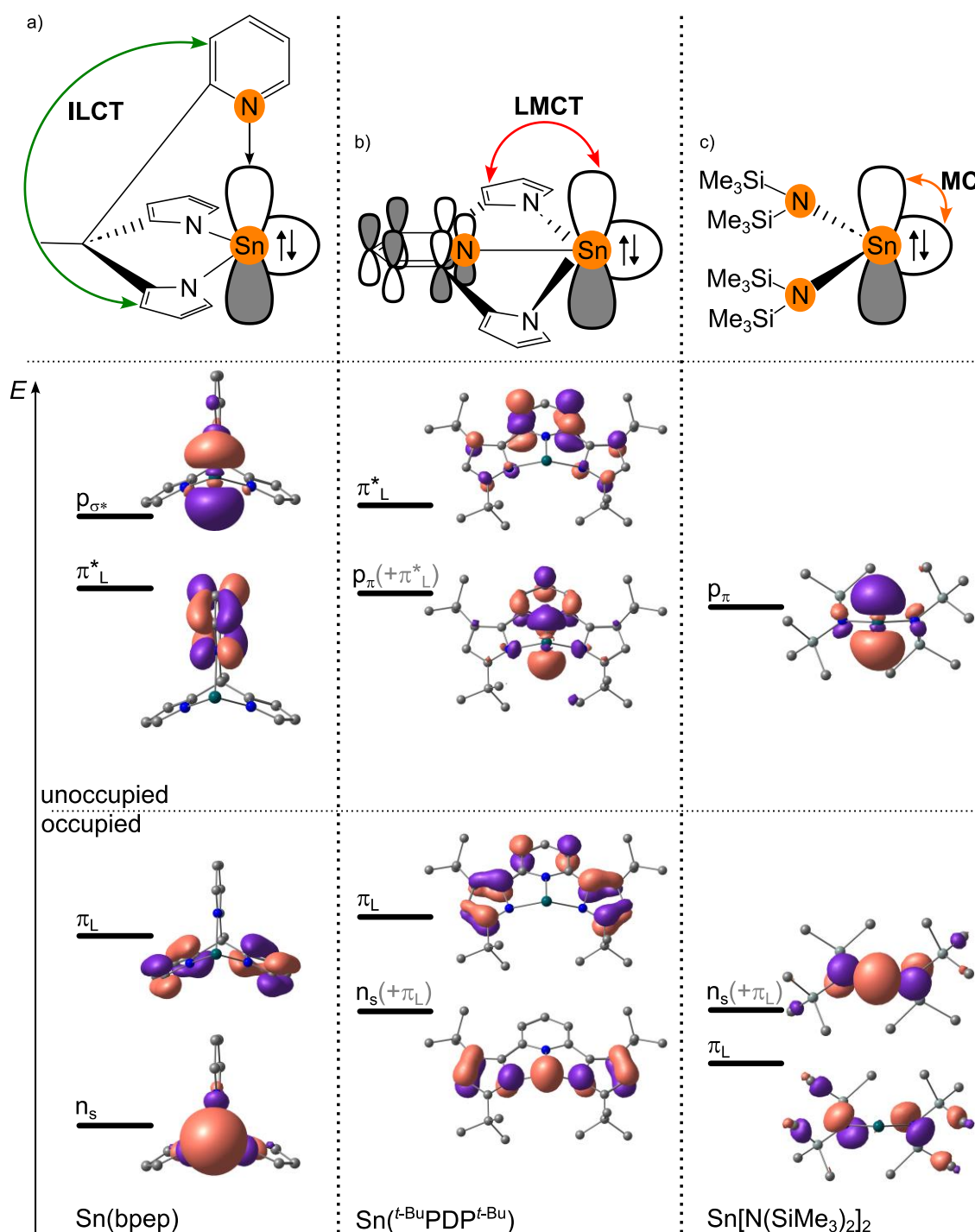


Figure 4.1: Illustration of the investigated tin(II) complexes in this work with their relevant electronic transitions and respective frontier orbitals acquired from DFT calculations: CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn) hydrogen atoms omitted.

Considering the results of the present studies and examples of tetrel(II) complexes reported in the literature, some aspects may be generalized.

Additional donor stabilization like in Sn(bpep) as well as in the reported lead(II) compounds (Figure 1.24)^[207–209] result in rather weak emissions from ILCT states. Deactivation through strongly distorted LMCT states as in Sn(bpep) might be responsible for this issue.

Changing the ligand topology from tripodal to meridional geometry, like in $\text{Sn}(\text{}^t\text{BuPDP}^{\text{}^t\text{Bu}})$, reduced the energy of the p_π orbital, shifted the emission to lower energies and provoked an excited state with mainly LMCT character. However, the LMCT state splits to two states with small and large electric transition dipole moments μ due to excitonic interactions caused by H-aggregate formation in the solid state.

Finally, *Lappert's* diamino stannylene $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ and literature examples with similar structural properties display high excited state lifetimes and quantum yields (Figure 1.26).^[213,214] This behavior is primarily attributed to high radiative rate constants e.g. $k_{\text{r},293} = 23000 \text{ s}^{-1}$ for $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ in the solid state, which is based on strong SOC induced from less distorted excited states with a significant MC contribution.

Based on the results from this work, highly phosphorescent tetrel(II) complexes can be achieved by establishing a typical tetrylene structure (section 1.5.1) and most importantly the excited state should consist of significant MC character. The later point becomes decisive if one compares the excited states of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ and $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$. The triplet excited state in the plumbylene is of almost pure LMCT character with strong distortion and resulting weak emission, whereas the stannylene with additional MC character is only weakly distorted in the emissive triplet excited state with better photophysical performance.

On the contrary, interconfigurational MC states play a deactivating role in TMCs with inversion symmetry, causing distorted excited states, whereas less distorted MLCT states are responsible for high photoluminescent rates (section 1.3.1). Electronic transitions like the MLCT in pseudo-octahedral $[\text{Ru}(\text{bpy})_3]^{2+}$ start in the non-bonding t_{2g} orbitals, their depopulation affects the geometry and the respective M–L bonds marginally. An analogous scenario holds for MC transitions in tetrel(II) complexes. The transition from the non-bonding n_s -orbital to the p_π -orbital results in a less distorted excited state like in *Lappert's* diamino stannylene. On the other hand, LMCT transitions of the present tetrel(II) complexes, which involved orbitals with high antibonding character as in the case of the E(bpep) complexes, caused distorted excited states with short lifetimes and small quantum yields.

Lessons for the future:

Based on the results of this work, several key factors for designing highly photoluminescent tetrel(II) complexes can be delineated (Figure 4.2).

High coordination numbers ($C > 2$) at the tetrel center should be avoided. On the one hand, the additional donor coordination opens access to strong distortions in the excited state and impedes high photoluminescence quantum yields. On the other hand, regardless of whether donor stabilization occurs, high coordination numbers enable various geometries and formation of various species in solution, for instance the dimerization of $\text{Sn}(\text{}^t\text{BuPDP}^{\text{}^t\text{Bu}})$, which hamper the spectroscopic interpretation. Therefore, the most promising solution for these issues is the change to simple basic-tetrylene structures with two ligands ($C = 2$).

However, simple tetrylenes can undergo dimerization if the singlet ground state is not sufficiently stabilized (section 1.5.2). Stable single ground states are guaranteed mainly by a high singlet-triplet energy gap ΔE_{ST} which is proportional to the HOMO-LUMO gap ΔE_{HL} . Thus, the chosen ligands must induce high energy gaps, for example by mesomeric or inductive effects (section 1.5.1). Even if dimerization is suppressed in the ground state, excimer formation on the excited state hypersurface can occur, as in the case of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$. Here, additional introduction of bulky substituents at the ligand

is necessary to prevent excimer formation as a deactivation pathway. In addition, bulky substituents may prohibit undesired ground state aggregation which occurred in the case of $\text{Sn}(^t\text{-BuPDP}^t\text{-Bu})$.

The excited states with the highest radiative rate and least distortions provide significant MC contributions. This depends on the energetical position of the tetrel centered orbitals n_s and p_π . Yet the more stabilized the tetrylene becomes, the more unlikely the tetrel centered orbitals are involved in the relevant electronic transitions. Hence, a compromise between singlet ground state stabilization and excited state with MC contribution must be accomplished. To keep ligands that still provide the mentioned stabilization effects, the L–E–L angle becomes a tunable parameter. Larger angles lead to energetically higher n_s -orbitals, which might favor MC transitions. Additionally, the probability of observing MC transitions increases with ascending element row, which favors tin(II) over lead(II) as tetrel center.

The photodegradation mechanisms for the tetrylenes $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ and $\text{Pb}[\text{N}(\text{SiMe}_3)_2]_2$ follow a unimolecular behavior, which is initiated by a homolytic E–L bond cleavage. Therefore, implementation of rigid backbones might impede the bond homolysis by fast recombination and lead to higher stability toward light.

C = 2; two ligands are sufficient

E = Sn is recommended for higher stability

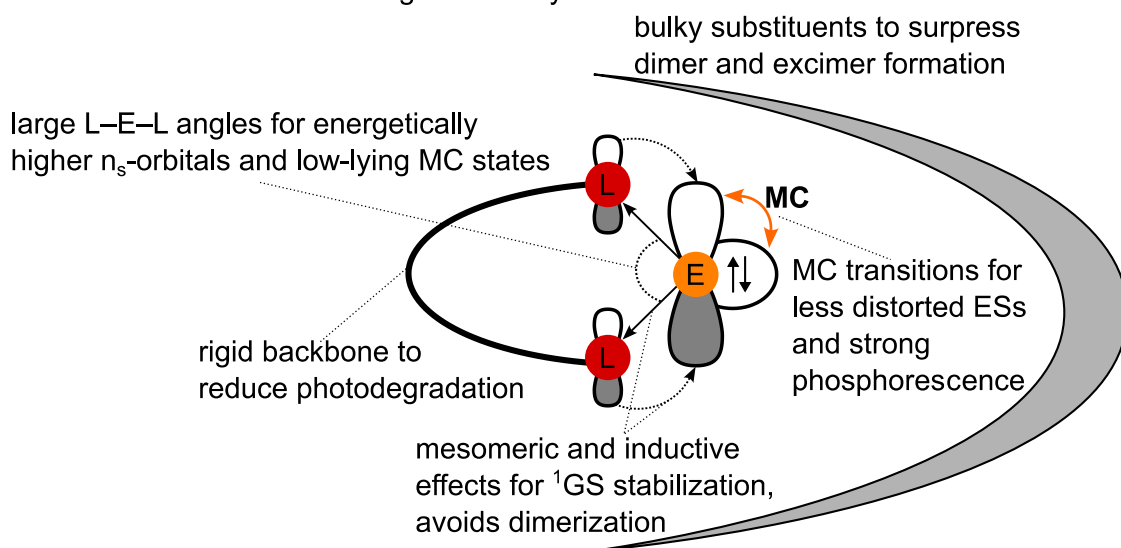


Figure 4.2: Schematic illustration of a concept for obtaining highly photoluminescent tetrel(II) complexes based on the results of this work.

In summary, tetrel(II) complexes with different geometries were analyzed by sophisticated spectroscopic measurements and underpinned with detailed (TD)-DFT calculations. The results enabled excited state energy ordering and drawing a clearer picture of the relevant excited state dynamics. Especially, the simple *Lappert's* diamino stannylene displays a wide range of photophysical and photochemical effects, which have been overlooked over the last few decades. This underlines the fact that the research of tetrel(II) complexes in the context of photophysics is still in its infancy and much potential is still hiding. The results of this work set up the first step and pave the way for concepts to obtain highly photoluminescent tetrel(II) complexes.

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6 Appendix

6.1 Supporting Information: Excited State Energy Landscape of Phosphorescent Group 14 Complexes

Supplementary Information File

Excited State Energy Landscape of Phosphorescent Group 14 Complexes

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General Procedures

All reactions and measurements were performed under argon atmosphere unless otherwise noted. Gloveboxes (UniLab/MBraun – Ar 4.8, O₂ < 1 ppm, H₂O < 0.1 ppm) were used to store and weight sensitive compounds for synthesis as well as to prepare samples that require absence of oxygen and water. The reagents were purchased from commercial suppliers (ABCR, Acros Organics, Alfa Aesar, Fischer Scientific and Sigma Aldrich). Dichloromethane was dried and distilled from CaH₂, 1,4-dioxane from sodium, THF and 2-methyl-tetrahydrofuran from potassium. Deuterated solvents were purchased from euriso-top and Deutero GmbH and were dried by the same procedure as above and stored over molecular sieve (3 Å). The compounds H₂bpep¹ and M[N(SiMe₃)₂]₂² were prepared according to literature procedures.

All NMR Spectra were recorded on a Bruker Avance DRX 400 spectrometer at 400.42 MHz (¹H), 100.70 MHz (¹³C{¹H}), 149.23 MHz (¹¹⁹Sn) and 83.79 MHz (²⁰⁷Pb). All data were evaluated with the software *MestReNova 12.0.4-22023*. All resonances are reported in ppm versus the solvent signal as internal standard (¹H; (¹³C) NMR: THF-*d*₈: δ = 1.72, 3.58; (25.31, 67.21) ppm; DMSO-*d*₆: δ = 2.50; (29.84, 206.26) ppm)³ or external standards for ¹¹⁹NMR (SnMe₄, δ = 0 ppm) and ²⁰⁷Pb (PbMe₄, δ = 0 ppm). (s) = singlet, (d) = doublet, (t) = triplet.

Electrospray ionization ESI(+) mass spectra were recorded on an *Agilent 6545 QTOF-MS* spectrometer.

Elemental analyses were performed by the central analytic service of the Department of Chemistry of the University of Mainz using an *Elementar vario EL Cube* or by the Mikroanalytisches Labor Kolbe, c/o Fraunhofer Institut UMSICHT, Oberhausen, Germany.

UV/VIS/NIR spectra were recorded on a *Jasco V-770* spectrometer using gastight 1.00 cm quartz cells with a Schott valve. Measurements in THF were carried out in special UVasol®-THF for spectroscopy from Sigma Aldrich. The extinction coefficients are given at maximum absorption and for shoulders, highlighted as sh.

Steady-state emission spectra and photoluminescent decay curves (solution and solid-state samples) were measured with a *FLS1000 spectrometer* from *Edinburgh Instruments* equipped with a cooled photomultiplier detector PMT-980 and a Lifetime HSPMT-920. A xenon arc lamp Xe2 (450 W) was used for excitation in steady-state measurements. Time-resolved luminescence experiments were conducted using the μ s-xenon-flashlamp μ F2 (pulse width ca. 2 μ s) and a picosecond pulsed diode laser EPL-375 as excitation source. Measurements at low temperature were carried out using a liquid nitrogen cooled cryostat *Optistat DN* from *Oxford Instruments*. Absolute luminescence quantum yields Φ were determined using the MicrostatN from Oxford Instruments combined with the Cryosphere from Edinburgh Instruments. Relative uncertainty of Φ is estimated to be $\pm 20\%$. The Arrhenius fits were performed on basis of eq. 1 (Fig. 6b and 7b; Table 2, main text).⁴ A global fit of the data of **1^{Sn}** did not give satisfactory results due to the large range of $k(T)$. Therefore, E_{a1} , dominant in the high temperature region, was obtained from a linear Arrhenius fit by including four data points between 293 and 225 K. E_{a1} was kept constant, while the remaining parameters k_0 , A_1 , E_{a2} and A_2 were optimised, including the eight data points from 77 to 175 K. In case of **1^{Pb}**, a global fit in the range 200 to 77 K gave satisfactory results. An alternative, more sophisticated approach with the assumption of excited states in thermal equilibrium during decay, following a Boltzmann distribution,⁵ gave identical fit results within error, indicating that the fit, according to eq. 1 is sufficiently precise.

DFT Calculations

All calculations were performed using the quantum computing suite 5.0.2.^{6,7} Geometry optimization was performed using (un-)restricted Kohn-Sham orbitals DFT (UKS/RKS) and the B3LYP functional^{8–10} in combination with Ahlrich's split valance triple-zeta basis set def2-TZVPP,¹¹ old-ZORA-TZVPP (Sn) and SARC-ZORA-TZVPP (Pb) with the auxiliary basis SARC/J.^{12–16} Tight convergence criteria were chosen for DFT calculations (keywords *tightscf* and *tightopt*). All DFT calculations make use of the resolution of identity (Split-RI-J) approach for the Coulomb term in combination with the chain-of-spheres approximation for the exchange term (keyword *RIJCOSX*).^{17,18} The zeroth order regular approximation was used to describe relativistic effects in all calculations (keyword *ZORA*).^{12–16,19,20} To account for solvent effects, a conductor-like screening model (keyword *CPCM(thf)*) modeling thf was used in all calculations.^{21,22} Atom-pairwise dispersion correction was performed with the Becke-Johnson damping scheme (keyword *D3BJ*).^{23,24} A numerical frequency calculation confirmed that the optimized geometry corresponds to a minimum structure or a transition state structure, respectively. Explicit counter ions and/or solvent molecules were not taken into account, if not explicitly noted. The 2D relaxed potential energy surface scans with 121 points were performed on the CPCM-(THF)-RIJCOSX-UB3LYP-D3BJ-ZORA/def2-SVP/old-ZORA-TZVPP(Sn)/SARC-ZORA-TZVPP(Pb) level with subsequent single-point calculations at higher level (CPCM-(THF)-RIJCOSX-(U)B3LYP-D3BJ-ZORA/def2-TZVPP/old-ZORA-TZVPP(Sn)/SARC-ZORA-TZVPP(Pb)). Transition states were localised, using the *optts* keyword and assigned with a subsequent calculation of the internal reaction coordinate (keyword *IRC*). Fifty vertical spin-allowed transitions were calculated by TD-DFT. The charge transfer number analyses of the TD-DFT calculated transitions were done using TheoDORE 2.4.²⁵ All calculations were computed on the Elwetritsch supercomputer at the Technical University of Kaiserslautern (elwe.rhrk.uni-kl.de). This is a member of the AHRP (Alliance for High Performance Computing Rhineland-Palatinate).

Crystal Structure Determination

Intensity data for crystal structure determination were collected with a STOE IPDS-2T diffractometer from STOE & CIE GmbH with an Oxford cooling using Mo-K α radiation ($\lambda = 0.71073$ Å). The diffraction frames were integrated using the STOE X-Area²⁶ software package and were corrected for absorption with STOE X-Red of the X-Area²⁶ software package. The structures were solved with SHELXT²⁷ and refined by the full-matrix method based on F^2 using SHELXL²⁸ of the SHELX²⁹ software package and the ShelXle³⁰ graphical interface. All non-hydrogen atoms were refined anisotropically while the positions of all hydrogen atoms were generated with appropriate geometric constraints and allowed to ride on their respective parent atoms with fixed isotropic thermal parameters. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2211126 for **1^{Sn}** and no. CCDC-2211125 for **(1^{Sn})₂(diox)**.

Crystallographic Data of **1^{Sn}**

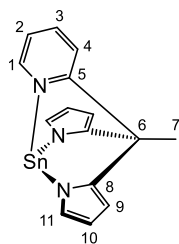
C₁₅H₁₃N₃Sn (353.97); trigonal; $R3$; $a = 28.972(4)$ Å, $b = 28.972(4)$ Å, $c = 8.1427(16)$ Å; $\alpha = 90^\circ$; $\beta = 90^\circ$; $\gamma = 120^\circ$; $V = 5919(2)$ Å³; $Z = 18$; density, calcd. = 1.787 g cm⁻³, $T = 120(2)$ K, $\mu = 1.931$ mm⁻¹; $F(000) = 3132$; crystal size $0.220 \times 0.180 \times 0.100$ mm³; $\theta = 2.435$ to 27.944 deg.; $-37 \leq h \leq 38$, $-37 \leq k \leq 38$, $-10 \leq l \leq 10$; rfln collected = 38896; rfln unique = 6268 [$R(\text{int}) = 0.0603$]; completeness to $\theta = 25.242$ deg.: 100.0%; absorption correction: integration; max. and min. transmission 0.8301 and 0.6389; data 6268; restraints 161, parameters 455; goodness-of-fit on $F^2 = 1.133$; final indices [$I > 2\sigma(I)$] $R_1 = 0.0370$, $wR_2 = 0.0952$; R indices (all data) $R_1 = 0.0378$, $wR_2 = 0.0958$; largest diff. peak and hole 1.565 and -0.495 e.Å⁻³.

Crystallographic Data of **(1^{Sn})₂(diox)**

C₃₄H₃₄N₆O₂Sn₂ (796.05); monoclinic; $I2/a$; $a = 15.389(3)$ Å, $b = 8.8015(18)$ Å, $c = 23.005(9)$ Å; $\alpha = 90^\circ$; $\beta = 101.75(3)^\circ$; $\gamma = 90^\circ$; $V = 3050.6(15)$ Å³; $Z = 4$; density, calcd. = 1.733 g cm⁻³, $T = 120(2)$ K, $\mu = 1.680$ mm⁻¹; $F(000) = 1584$; crystal size $0.800 \times 0.343 \times 0.040$ mm³; $\theta = 2.484$ to 27.902 deg.; $-20 \leq h \leq 20$, $-11 \leq k \leq 9$, $-30 \leq l \leq 30$; rfln collected = 13572; rfln unique = 3638 [$R(\text{int}) = 0.0177$]; completeness to $\theta = 25.242$ deg.: 99.9%; absorption correction: integration; max. and min. transmission 0.9292 and 0.5064; data 3638; restraints 0, parameters 200; goodness-of-fit on $F^2 = 1.110$; final indices [$I > 2\sigma(I)$] $R_1 = 0.0293$, $wR_2 = 0.0719$; R indices (all data) $R_1 = 0.0309$, $wR_2 = 0.0730$; largest diff. peak and hole 2.919 and -0.787 e.Å⁻³.

Synthesis of Sn(bpep) 1^{Sn}

Sn[(N(SiMe₃)₂)₂] (556 mg, 1.27 mmol, 1.01 eq) in dichloromethane (5 mL) was added to a stirred solution of H₂bpep (300 mg, 1.26 mmol, 1.00 eq) in dichloromethane (5 mL). After stirring for 15 h at ambient temperature, the precipitate was separated from the solution and washed with dichloromethane (3 × 3 mL) and dried under reduced pressure. **1^{Sn}** (330 mg, 74%) was obtained as a colourless solid.



¹H NMR (THF-*d*₈): δ = 8.38–8.36 (m, 1H, H¹), 7.68 (ddd, ³J_{HH} = 8.1, 7.4, ⁴J_{HH} = 1.8 Hz, 1H, H³), 7.60 (dt, ³J_{HH} = 8.1, ⁴J_{HH} = 1.2 Hz, 1H, H⁴), 7.06 (ddd, ³J_{HH} = 7.4, 5.2, ⁴J_{HH} = 1.2 Hz, 1H, H²), 6.77 (dd, ³J_{HH} = 2.3, ⁴J_{HH} = 1.4 Hz, 2H, H¹¹), 6.01 (dd, ³J_{HH} = 3.1, ⁴J_{HH} = 1.4 Hz, 2H, H⁹), 5.84 (dd, ³J_{HH} = 3.1, 2.4 Hz, 2H, H¹⁰), 2.28 (s, 3H, H⁷) ppm.

¹³C NMR (THF-*d*₈): δ = 165.9 (s, C⁵), 147.7 (s, C¹), 141.6 (s, C³), 139.0 (s, C⁸), 124.0 (s, C¹¹), 122.4 (s, C²), 120.2 (s, C⁴), 107.2 (s, C¹⁰), 103.2 (s, C⁹), 46.9 (s, C⁶), 20.9 (s, C⁷) ppm.

¹¹⁹Sn NMR (THF-*d*₈): δ = –401.2 ppm.

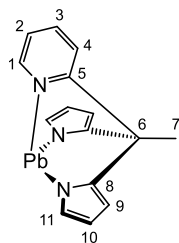
MS (ESI⁺; CH₃CN): *m/z* (%) = 378.00 (7) [**1^{Sn}**+Na⁺], 393.98 (64) [**1^{Sn}**+K⁺], 731.02 (20) [2 **1^{Sn}**+Na⁺], 746.99 (100) [2 **1^{Sn}**+K⁺].

Elemental analysis calcd. for C₁₅H₁₃N₃Sn: C, 50.89; H, 3.70; N, 11.87. Found: C, 50.50; H, 3.67; N, 11.74.

UV/Vis (THF): λ_{max} (ϵ) = 340 (534, sh), 258 (4070), 236 (4380) nm (M^{–1} cm^{–1}).

Synthesis of Pb(bpep) 1^{Pb}

Pb[(N(SiMe₃)₂)₂] (1120 mg, 2.13 mmol, 1.01 eq) in dichloromethane (8 mL) was added to a stirred solution of H₂bpep (500 mg, 2.11 mmol, 1.00 eq) in dichloromethane (8 mL). A colourless precipitate was formed immediately. After stirring for 15 h at ambient temperature, the precipitate was separated from the solution and washed with dichloromethane (3 × 5 mL) and dried under reduced pressure. **1^{Pb}** (556 mg, 63%) was obtained as a colourless solid.



¹H NMR (DMSO-*d*₆): δ = 8.57 (dd, ³J_{HH} = 5.2, ⁴J_{HH} = 1.7 Hz, 1H, H¹), 7.83 (td, ³J_{HH} = 8.0, ⁴J_{HH} = 1.7 Hz, 1H, H³), 7.76 (dt, ³J_{HH} = 8.0, ⁴J_{HH} = 1.5 Hz, 1H, H⁴), 7.30 (ddd, ³J_{HH} = 8.0, 5.2, ⁴J_{HH} = 1.5 Hz, 1H, H²), 6.86–6.83 (m, 2H, H¹¹), 6.17 (dd, ³J_{HH} = 3.0, ⁴J_{HH} = 1.5 Hz, 2H, H⁹), 5.96 (dd, ³J_{HH} = 3.0, 2.2 Hz, 2H, H¹⁰), 2.27 (s, 3H, H⁷) ppm.

¹³C NMR (DMSO-*d*₆): δ = 165.0 (s, C⁵), 147.6 (s, C¹), 140.1 (s, C⁸), 139.8 (s, C³), 124.0 (s, C¹¹), 121.3 (s, C²), 119.2 (s, C⁴), 105.9 (s, C¹⁰), 102.3 (s, C⁹), 50.2 (s, C⁶), 22.0 (s, C⁷) ppm.

²⁰⁷Pb NMR (DMSO-*d*₆): δ = 388.3 ppm.

MS (ESI⁺; DMSO/CH₃CN): *m/z* (%) = 482.05 (19) [**1^{Pb}**+K⁺], 893.19 (10) [2 **1^{Pb}**+Li⁺], 909.16 (20) [2 **1^{Pb}**+Na⁺], 925.14 (25) [2 **1^{Pb}**+K⁺].

Elemental analysis calcd. for C₁₅H₁₃N₃Pb: C, 40.72; H, 2.96; N, 9.50. Found: C, 40.15; H, 3.02; N, 9.29.

UV/Vis (DMSO): λ_{max} (ϵ) = 312 (1540, sh), 278 (3010), 264 (5660) nm (M^{–1} cm^{–1}).

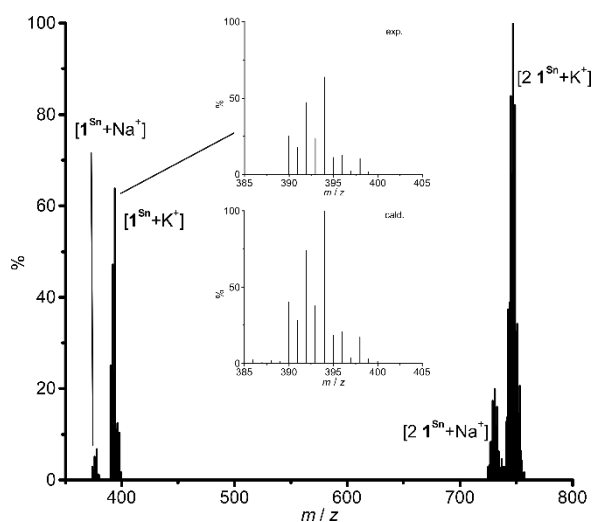


Fig. S1 ESI⁺ mass spectrum of **1^{Sn}** in tetrahydrofuran with insets of the experimentally found and calculated isotope pattern for [**1^{Sn}**+K⁺].

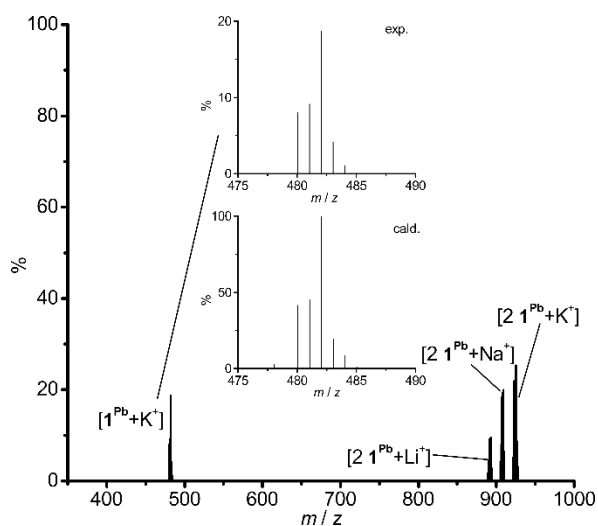


Fig. S2 ESI⁺ mass spectrum of **1^{Pb}** in dimethylsulfoxide with insets of the experimentally found and calculated isotope pattern for [**1^{Pb}**+K⁺].

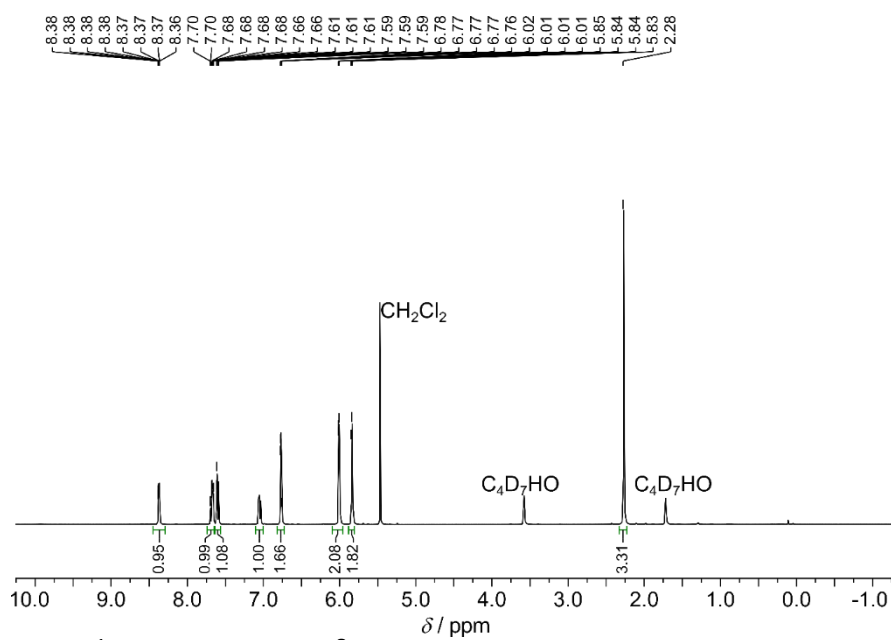


Fig. S3 ¹H NMR spectrum of **1**^{Sn} in tetrahydrofuran-*d*₈.

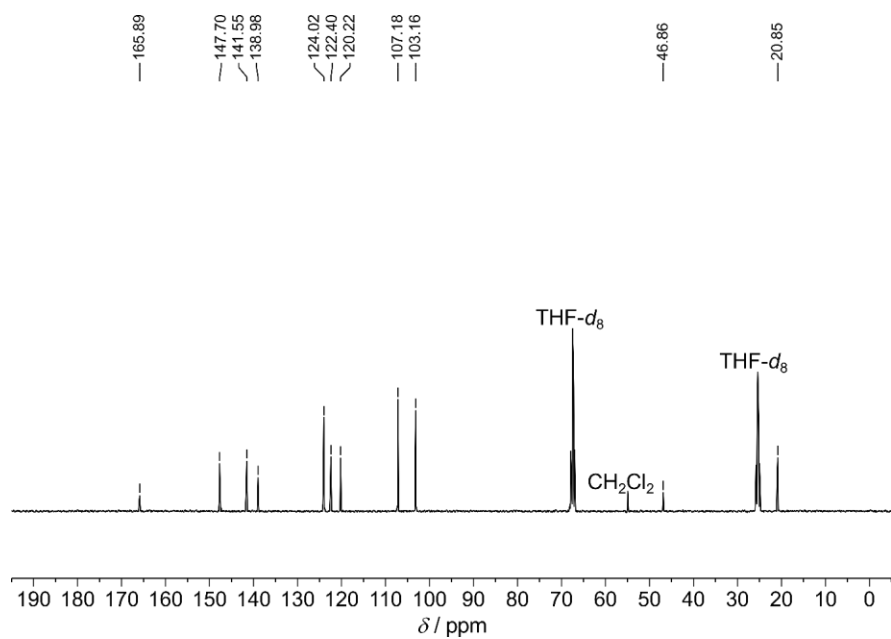


Fig. S4 ¹³C{¹H} NMR spectrum of **1**^{Sn} in tetrahydrofuran-*d*₈.

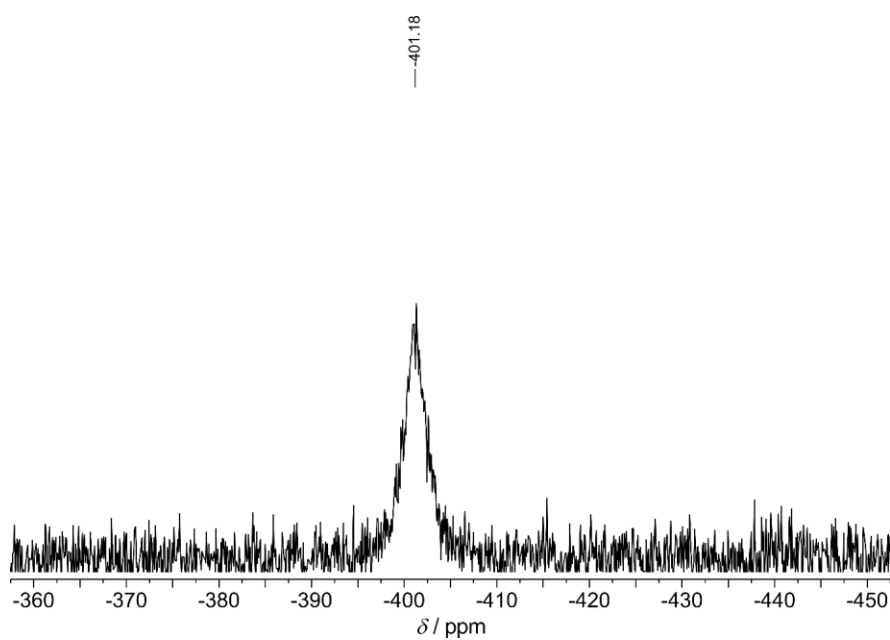


Fig. S5 ^{119}Sn NMR spectrum of 1^{Sn} in tetrahydrofuran- d_8 .

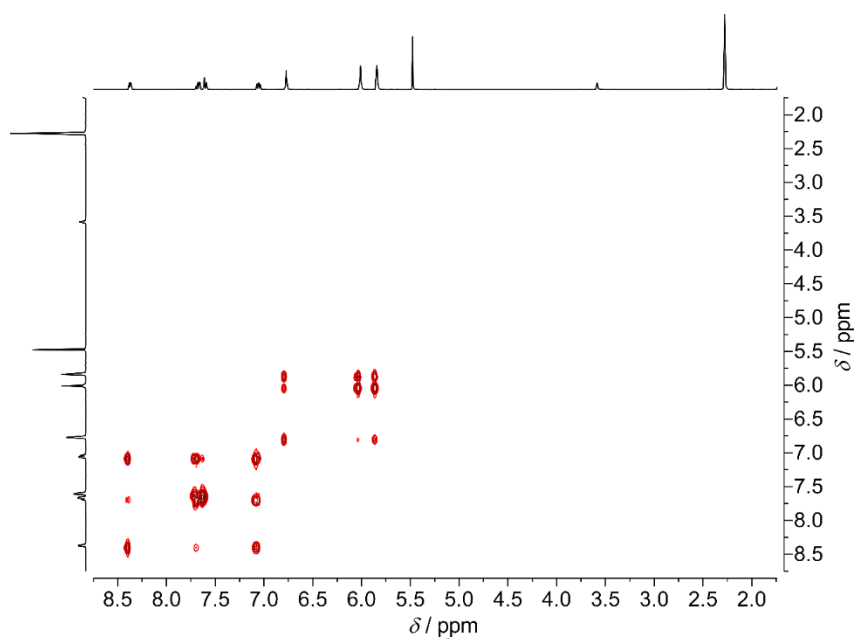


Fig. S6 ^1H , ^1H COSY NMR spectrum of 1^{Sn} in tetrahydrofuran- d_8 .

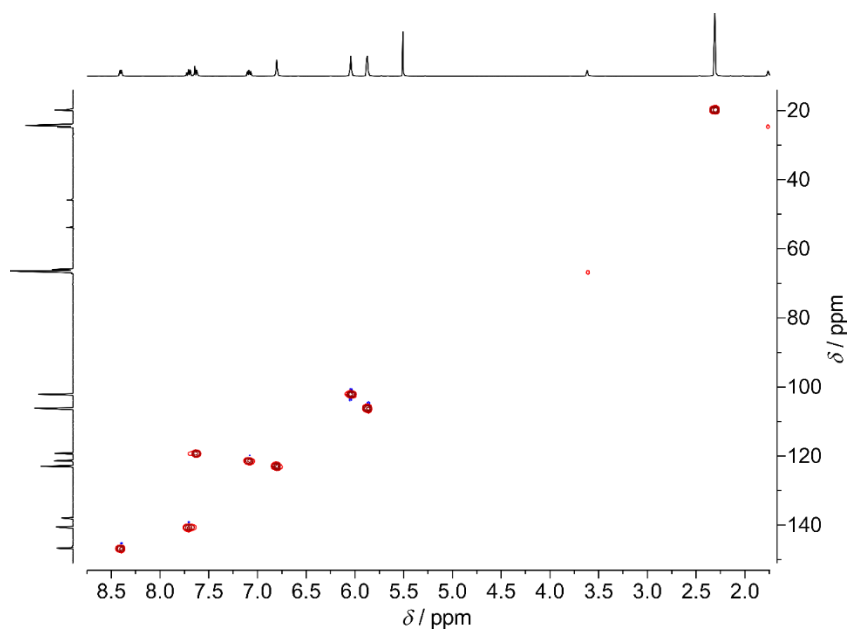


Fig. S7 $^{13}\text{C}, ^1\text{H}$ HSQC NMR spectrum of 1^{Sn} in tetrahydrofuran- d_8 .

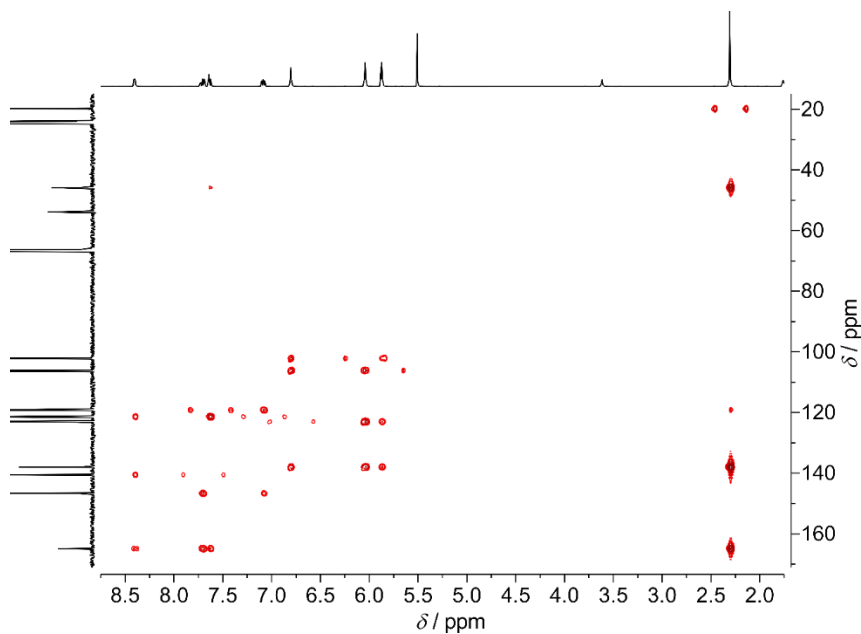


Fig. S8 $^{13}\text{C}, ^1\text{H}$ HMBC NMR spectrum of 1^{Sn} in tetrahydrofuran- d_8 .

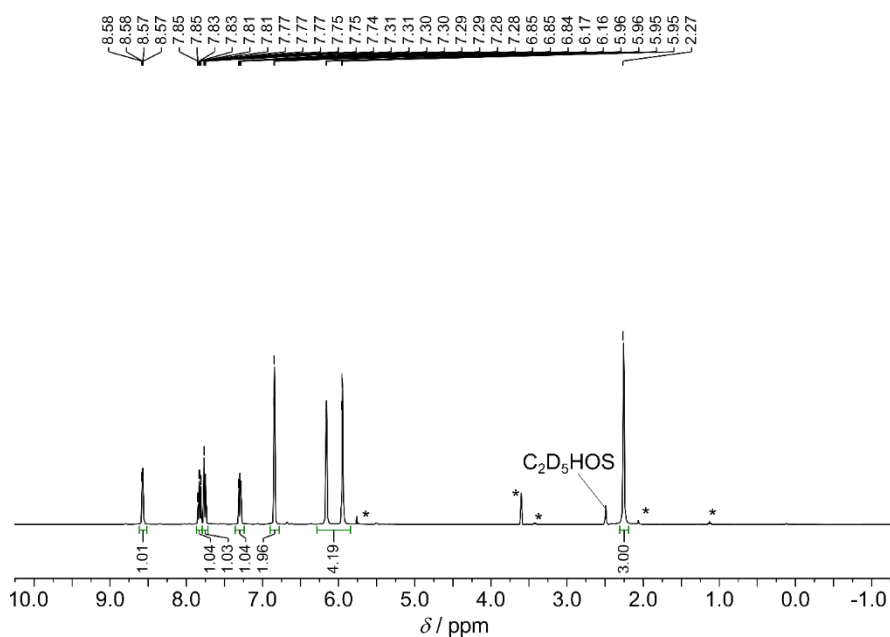


Fig. S9 ^1H NMR spectrum of 1^{Pb} in dimethylsulfoxide- d_6 . The asterisks denote solvent impurities.

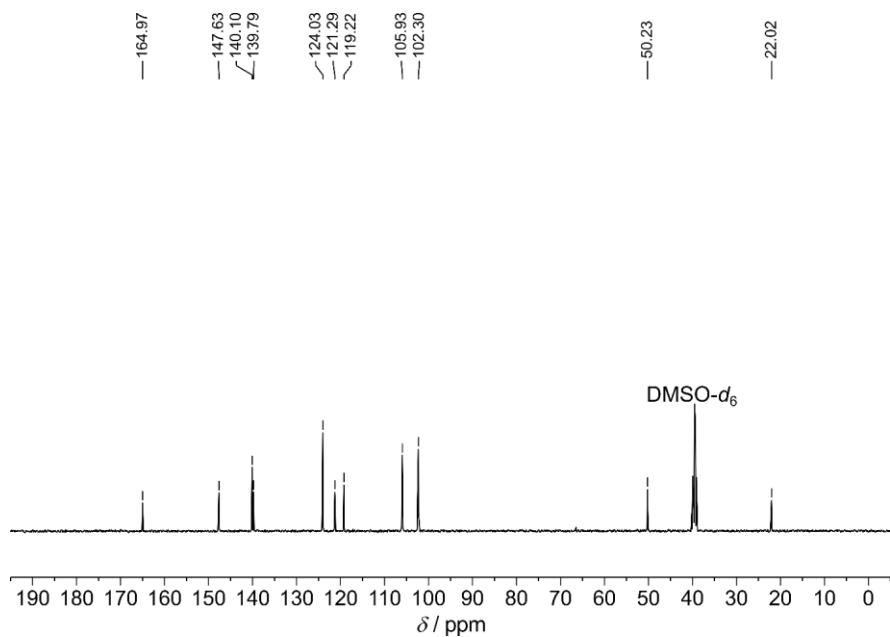


Fig. S10 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1^{Pb} in dimethylsulfoxide- d_6 .

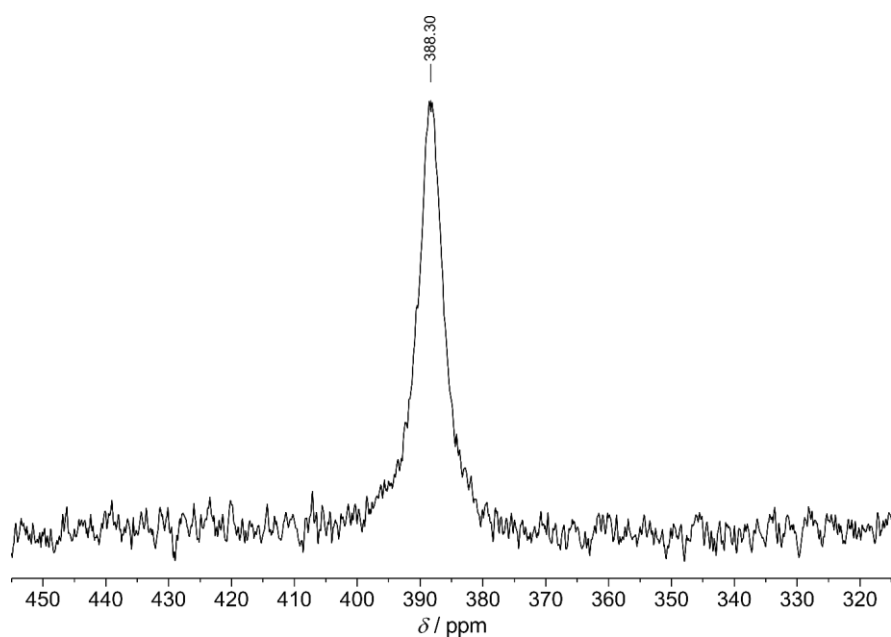


Fig. S11 ^{207}Pb NMR spectrum of **1^{Pb}** in dimethylsulfoxide- d_6 .

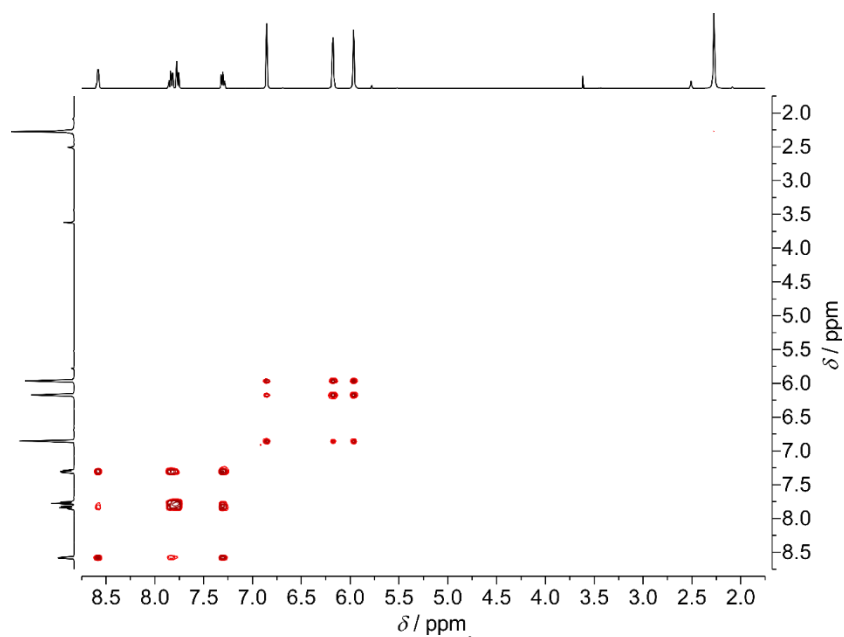


Fig. S12 $^1\text{H}, ^1\text{H}$ COSY NMR spectrum of **1^{Pb}** in dimethylsulfoxide- d_6 .

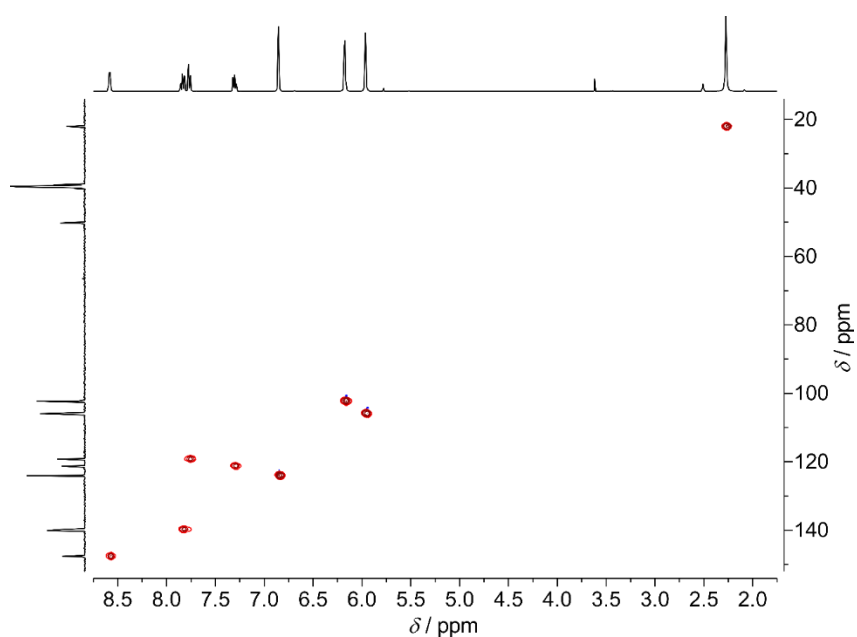


Fig. S13 $^{13}\text{C}, ^1\text{H}$ HSQC NMR spectrum of **1^{Pb}** in dimethylsulfoxide- d_6 .

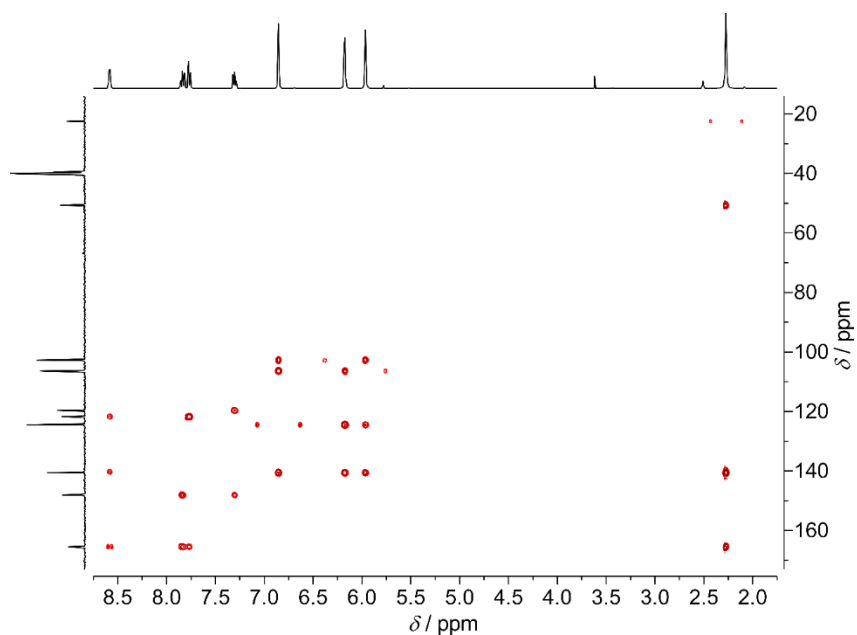


Fig. S14 $^{13}\text{C}, ^1\text{H}$ HMBC NMR spectrum of **1^{Pb}** in dimethylsulfoxide- d_6 .

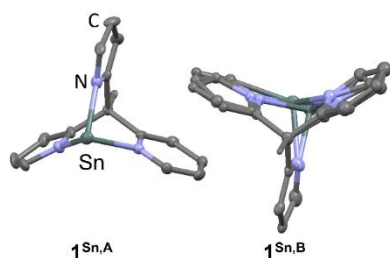


Fig. S15 Molecular structure of **1^{Sn}** in the solid state (trigonal space group R_3) with two molecules **1^{Sn,A}** and disordered **1^{Sn,B}** in the asymmetric unit. H atoms omitted, thermal ellipsoids at 50% probability level.

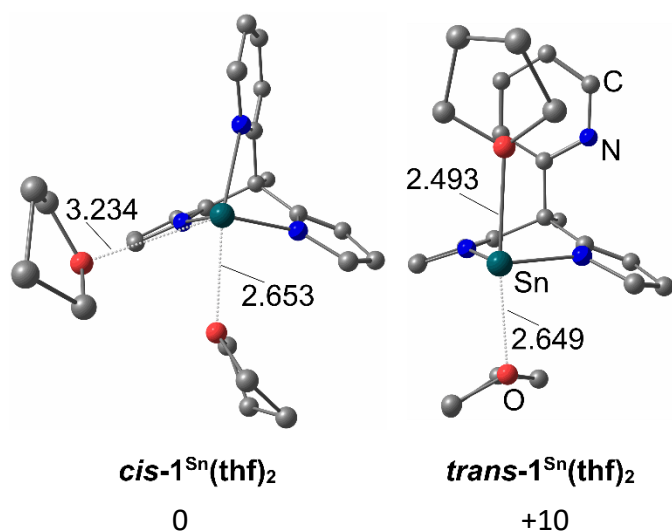


Fig. S16 DFT optimised geometries of *cis-trans*-1^{Sn}(thf)₂ with relative Gibbs free energies ΔG_{298} at 298 K in kJ mol⁻¹ and distances in Å.

Table S1 Selected structural parameters in Å and deg. of solid state structures of 1^{Sn} (molecule A, 1^{Sn,A}) and (1^{Sn})₂(diox) from XRD analyses and of DFT calculated geometry optimised structures of 1^{Sn} and 1^{Sn}(thf) in the ¹GS and ³ILCT/³LMCT/³MLCT states.

	1 ^{Sn,A} (XRD)	(1 ^{Sn}) ₂ (diox) (XRD)	1 ^{Sn} (DFT)	3ILCT1 ^{Sn} (DFT)	3LMCTpy1 ^{Sn} (DFT)	3LMCTpyr1 ^{Sn} (DFT)
Sn-N ^{py}	2.317(5)	2.375(2)	2.341	2.147	3.897	2.323
Sn-N ^{pyr}	2.130(5) 2.149(7)	2.125(2) 2.152(2)	2.146 2.147	2.218 2.220	2.248 2.240	3.726 2.176
Sn-O		2.547(2)				
N ^{pyr} -Sn-N ^{pyr}	84.1(2)	84.08(9)	85.1	79.4	79.3	81.5
N ^{py} -Sn-N ^{pyr}	80.24(18) 79.0(2)	77.93(8) 79.93(8)	80.3 80.3	83.2 83.3	54.9 80.1	81.3 56.5
O-Sn-N ^{py}		155.98(7)				
O-Sn-N ^{pyr}		80.94(8) 87.07(8)				
Sn-N ^{py} -C ^{py} - C ^{backbone}	2.1	2.4	0.3	0.1	83.0	5.1
Sn-N ^{pyr} - C ^{pyr} -C ^{backbone}	5.5	3.7	0.2	5.1	13.7	78.6

	1 ^{Sn} (thf) (DFT)	3ILCT1 ^{Sn} (thf) (DFT)	3LMCTpy1 ^{Sn} (thf) (DFT)	3LMCTpyr1 ^{Sn} (thf) (DFT)	3MLCT1 ^{Sn} (thf) (DFT)
Sn-N ^{py}	2.441	2.182	3.917	2.451	2.127
Sn-N ^{pyr}	2.155 2.159	2.221 2.225	2.245 2.242	2.202 3.800	2.087 2.083
Sn-O	2.606	2.925	4.378	2.726	2.338
N ^{pyr} -Sn-N ^{pyr}	85.6	80.6	79.3	80.4	88.4
N ^{py} -Sn-N ^{pyr}	77.2 77.6	81.6 81.5	54.7 79.9	55.9 77.8	88.9 89.1
O-Sn-N ^{py}	149.7	148.6	121.5	158.2	177.5
O-Sn-N ^{pyr}	81.6 79.4	76.1 73.3	74.7 62.2	81.5 113.8	90.9 88.4
Sn-N ^{py} -C ^{py} - C ^{backbone}	0.5	0.7	83.2	1.5	0.2
Sn-N ^{pyr} - C ^{pyr} -C ^{backbone}	5.4	8.7	14.4	82.2	3.7
N ^{py} -Sn-O	149.7	148.6	121.5	158.2	177.5

Table S2 Selected structural parameters in Å and deg. of DFT calculated geometry optimised structures of **1^{Pb}** and **1^{Pb}(thf)** in the in the ¹GS and ³ILCT/³LMCT states.

	1^{Pb} (DFT)	³ILCT1^{Pb} (DFT)	³LMCTpy1^{Pb} (DFT)	³LMCTpyr1^{Pb} (DFT)	1^{Pb}(thf) (DFT)	³ILCT1^{Pb}(thf) (DFT)
Pb-N ^{py}	2.455	2.256	3.908	2.459	2.577	2.301
Pb-N ^{pyr}	2.260 2.260	2.344 2.344	2.378 2.373	3.703 2.303	2.276 2.270	2.352 2.351
Pb-O					2.700	2.912
N ^{pyr} -Pb-N ^{pyr}	82.4	76.9	76.8	80.1	83.5	78.2
N ^{py} -Pb-N ^{pyr}	77.9 77.9	80.5 80.5	54.3 78.4	78.1 55.9	74.6 74.5	78.7 78.5
O-Pb-N ^{py}					146.4	146.0
O-Pb-N ^{pyr}					81.4 79.7	76.4 74.1
Pb-N ^{py} -C ^{py} - C _{backbone}	0.2	0.9	85.2	5.0	0.7	1.5
Pb-N ^{pyr} - C ^{pyr} -C _{backbone}	1.2	5.2	14.8	80.5	3.6	11.1

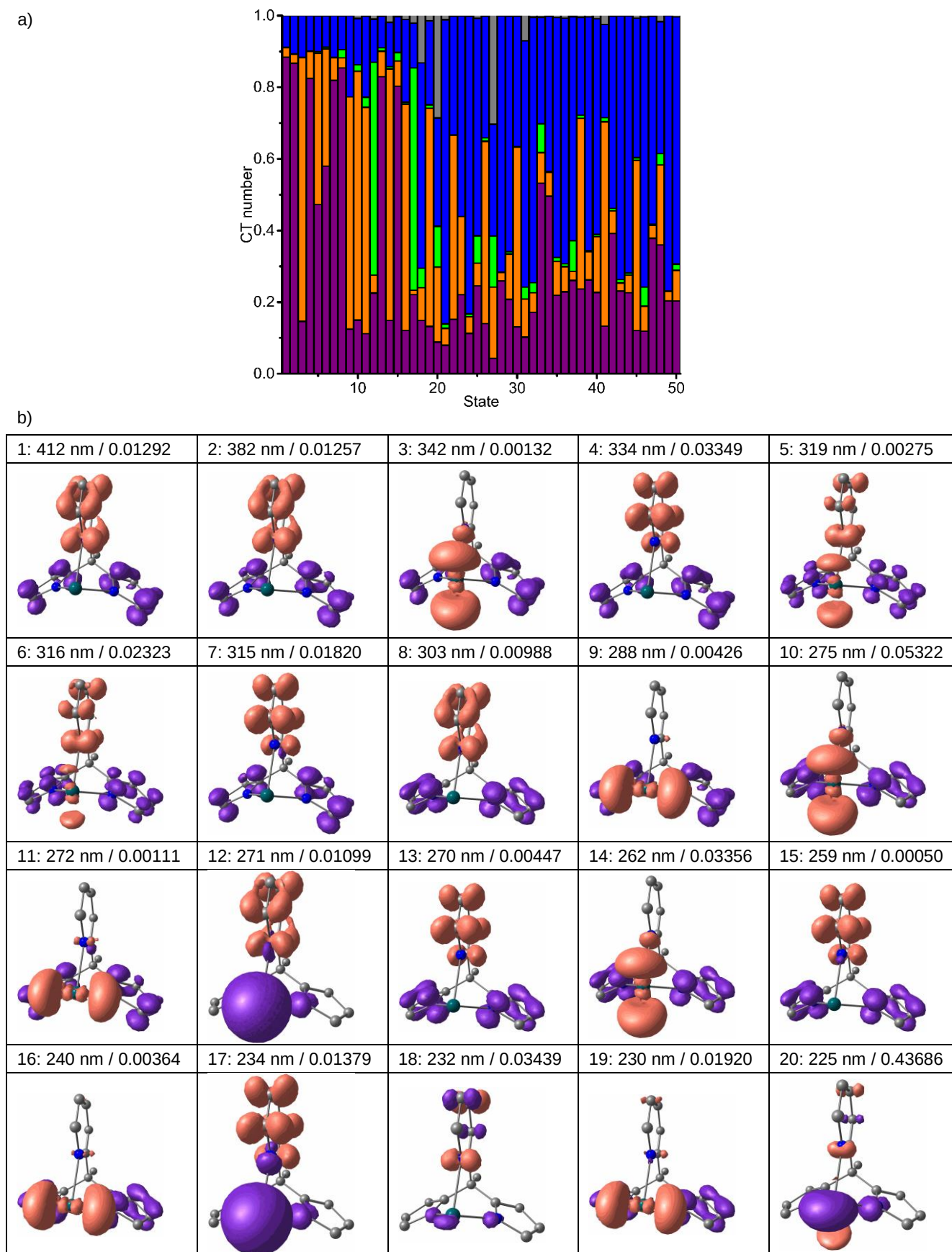


Fig. S17 a) Charge transfer analysis of the 50 lowest spin-allowed transitions of 1^{Sn} (purple: ILCT, orange: LMCT, green: MLCT; blue: LC, grey: MC) and b) difference electron densities of the 20 lowest spin-allowed transitions of 1^{Sn} with the respective wavelength and oscillator strength (purple = electron loss; orange = electron gain) displayed at an isosurface value of 0.005 a.u..

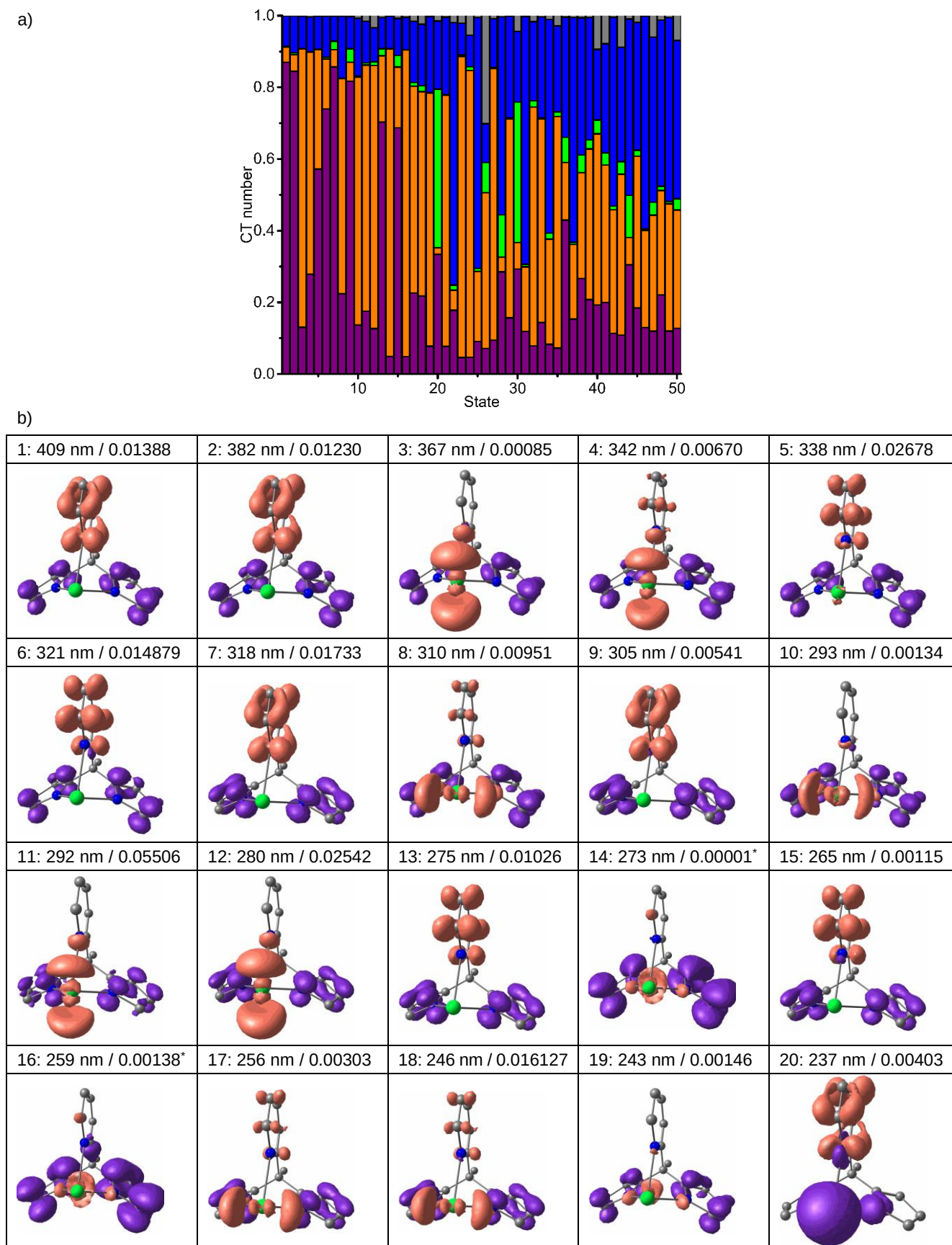


Fig. S18 a) Charge transfer analysis of the 50 lowest spin-allowed transitions of **1^{Pb}** (purple: ILCT, orange: LMCT, green: MLCT; blue: LC, grey: MC) and b) difference electron densities of the 20 lowest spin-allowed transitions of **1^{Pb}** with the respective wavelength and oscillator strength (purple = electron loss; orange = electron gain) displayed at an isosurface value of 0.005 a.u. and 0.0017 a.u. highlighted with an asterisk.

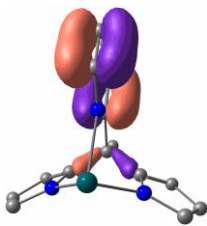
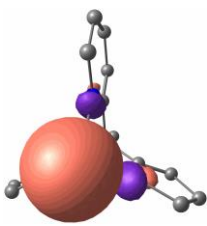
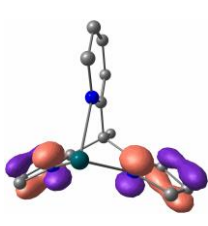
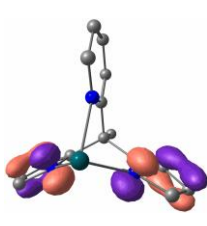
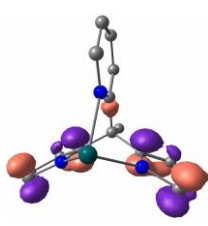
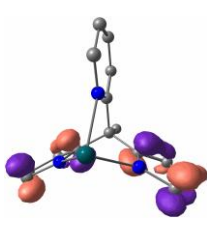
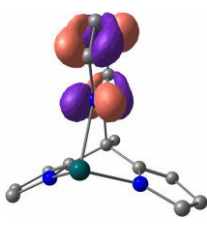
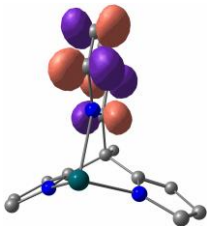
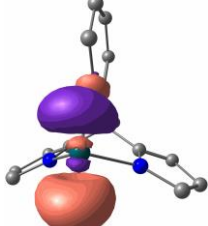
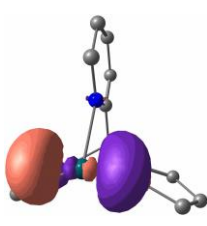
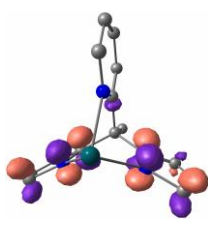
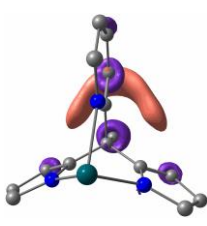
HOMO-5 / -7.6520	HOMO-4 / -7.0270	HOMO-3 / -6.4278	HOMO-2 / -6.2177	HOMO-1 / -5.6078	HOMO / -5.3316
					
LUMO / -1.6815	LUMO+1 / -0.9956	LUMO+2 / -0.9773	LUMO+3 / -0.2726	LUMO+4 / 0.9456	LUMO+5 / 1.2967
					

Fig. S19 Selected molecular orbitals of 1^{Sn} with energies given in eV, displayed at an isosurface value of 0.06 a.u..

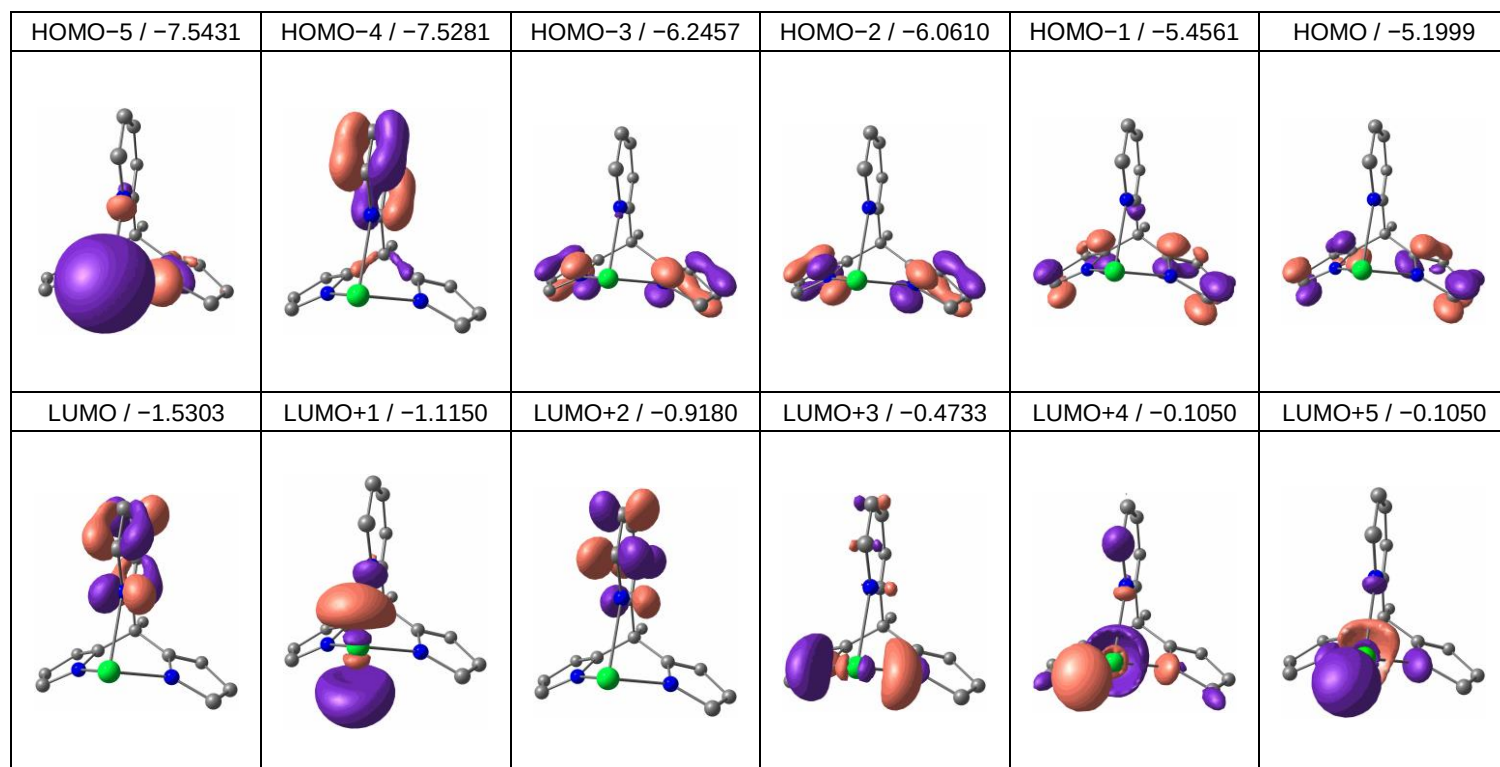


Fig. S20 Selected molecular orbitals of **1^{Pb}** with energies given in eV, displayed at an isosurface value of 0.06 a.u..

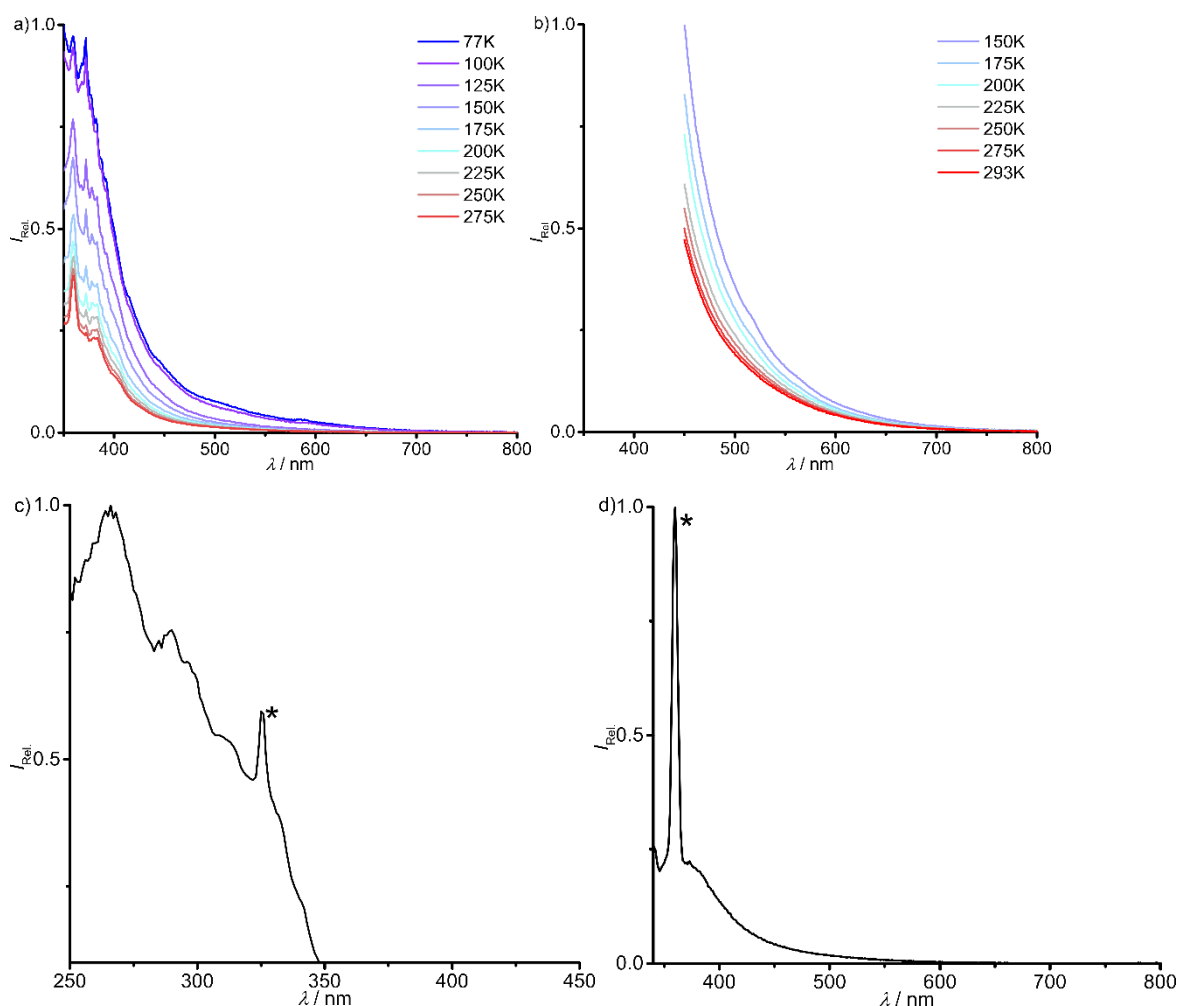


Fig. S21 Variable-temperature emission spectra a) between 77 and 275 K, b) between 150 K and 293 K, c) excitation spectrum ($\lambda_{\text{em}} = 380$ nm) at 77 K of the unidentified luminescent impurity in 2-methyl-tetrahydrofuran with $\lambda_{\text{exc}} = 325$ nm and d) emission spectrum of the unidentified impurity in tetrahydrofuran with $\lambda_{\text{exc}} = 325$ nm at 293 K in the absence of $\mathbf{1}^{\text{E}}$. The asterisks denote Raman bands of the solvent.

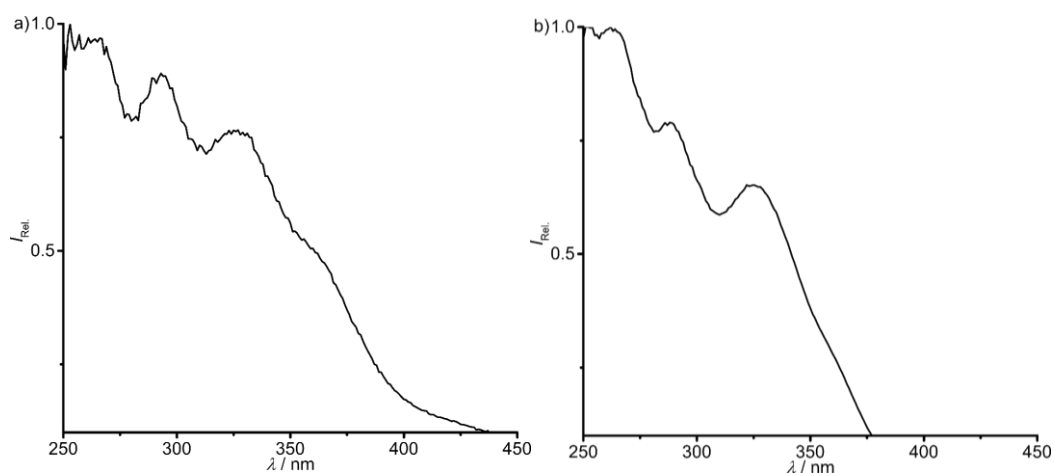


Fig. S22 Excitation spectra of $\mathbf{1}^{\text{Sn}}$ in 2-methyl-tetrahydrofuran at a) 293 ($\lambda_{\text{em}} = 580$ nm) and b) 77 K ($\lambda_{\text{em}} = 530$ nm). The high absorbance of the sample at $\lambda < \approx 325$ nm causes filter effects, yielding distorted excitation spectra.

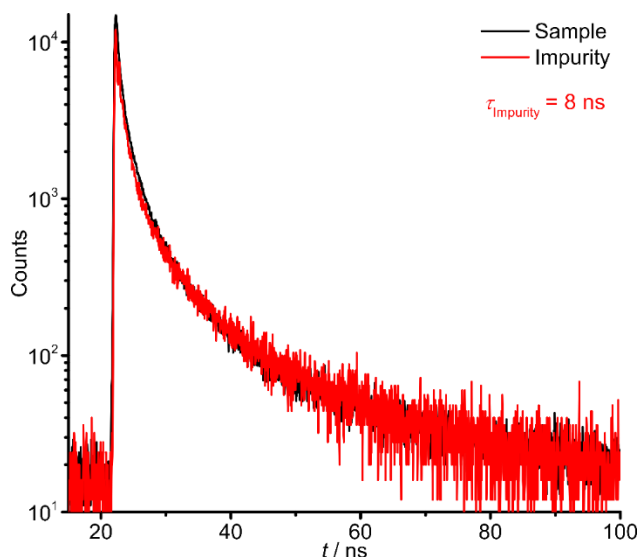


Fig. S23 Emission decay curves of 1^{Sn} in 2-methyl-tetrahydrofuran after excitation at $\lambda_{\text{exc}} = 375 \text{ nm}$ with $\lambda_{\text{em}} = 575 \text{ nm}$ (black curve) and of the unidentified luminescent impurity in 2-methyl-tetrahydrofuran at $\lambda_{\text{exc}} = 375 \text{ nm}$ with $\lambda_{\text{em}} = 400 \text{ nm}$ at 150 K (red curve) with luminescence lifetime from monoexponential fit.

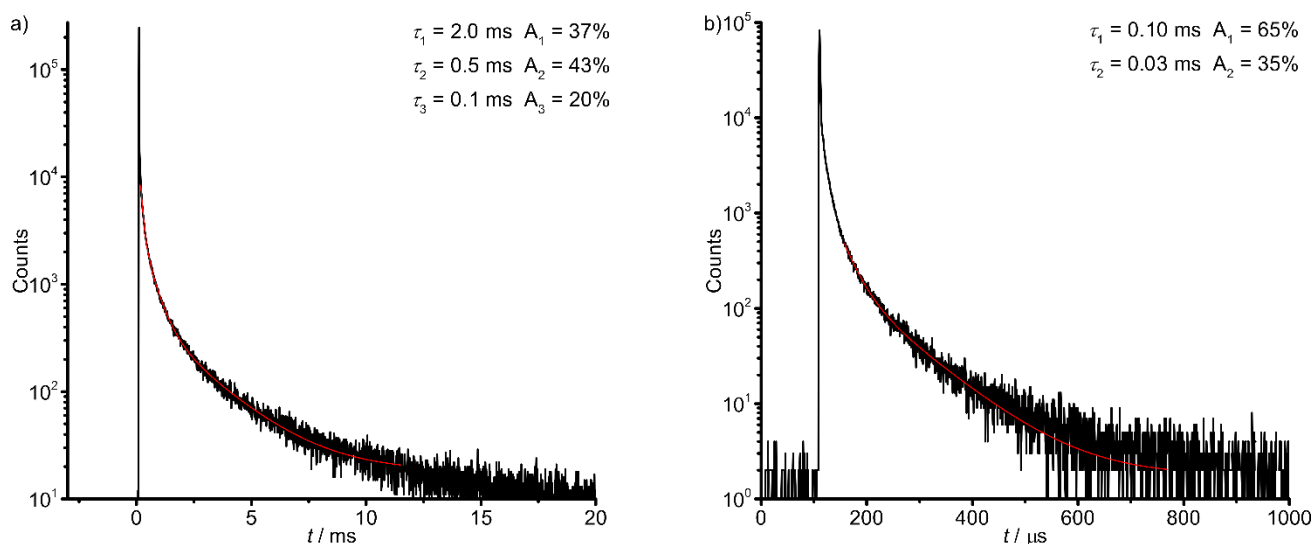


Fig. S24 Emission decay curves of 1^{Sn} in 2-methyl-tetrahydrofuran at $\lambda_{\text{exc}} = 325 \text{ nm}$ with $\lambda_{\text{em}} = 530 \text{ nm}$ and a) 77 K and b) 100 K (black curves), respectively, with luminescence lifetimes with relative emission amplitudes, from tri and biexponential fits (red curves), respectively.

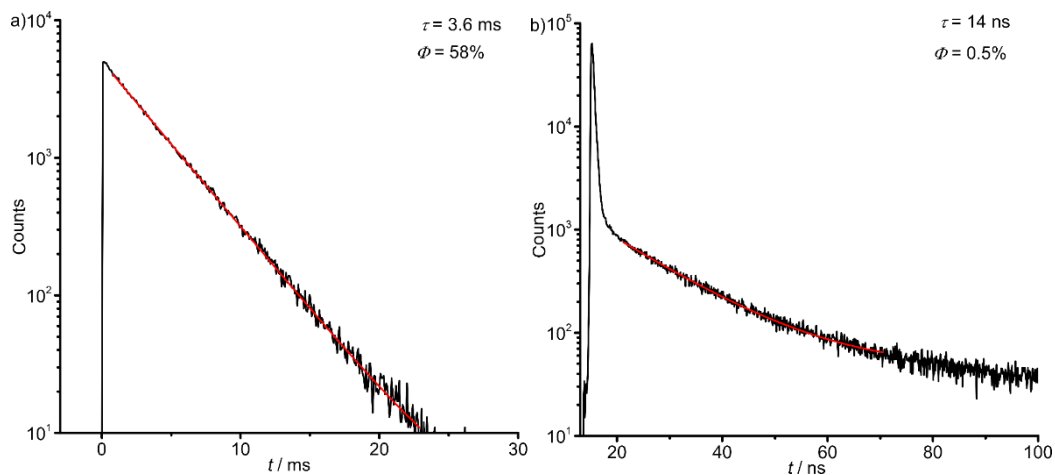


Fig. S25 Emission decay curves of **1^{Sn}** at a) $\lambda_{\text{exc}} = 350$ nm with $\lambda_{\text{em}} = 505$ nm and b) at $\lambda_{\text{exc}} = 375$ nm with $\lambda_{\text{em}} = 505$ nm at 77 K and 293 K (black curves) in the solid state, respectively, with luminescence lifetimes from monoexponential fits (red curves) and luminescence quantum yields.

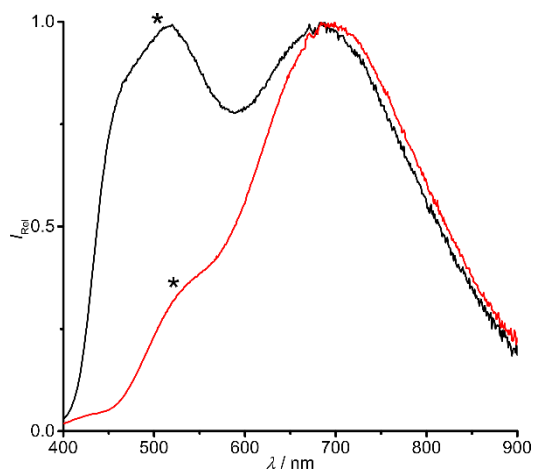


Fig. S26 Normalised emission spectra of a solid sample of **1^{Pb}** with an unidentified minor impurity (oxidation or solvolysis product of **1^{Pb}**), denoted with an asterisk, before (red curve) and after contact to air (black curve) at 77 K with $\lambda_{\text{exc}} = 375$ nm.

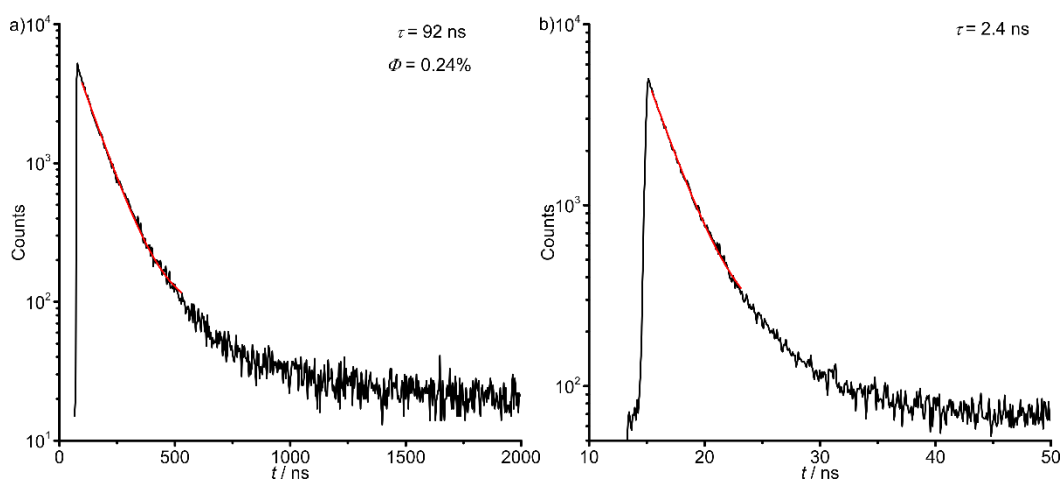


Fig. S27 Emission decay curves of **1^{Pb}** at $\lambda_{\text{exc}} = 375$ nm with $\lambda_{\text{em}} = 700$ nm at a) 77 K and b) 200 (black curves), respectively, with luminescence lifetimes from monoexponential fits (red curves) and luminescence quantum yield at 77 K.

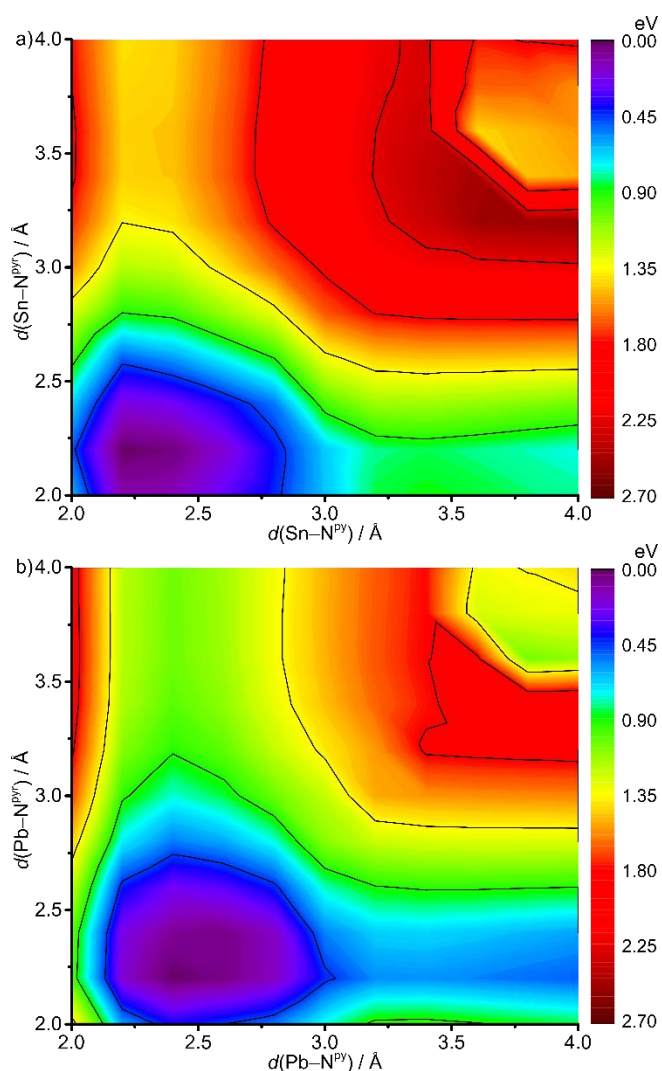


Fig. S28 Contour plot of the ${}^3\mathbf{1}^E$ potential energy surfaces, according to single-point energies of a 2D relaxed potential energy surface scan as projection along the E–N^{py} and E–N^{pyr} stretching modes on the triplet hypersurface ${}^3\mathbf{1}^E$ of a) $\mathbf{1}^{\text{Sn}}$ and b) $\mathbf{1}^{\text{Pb}}$ (CPCM-(THF)-RIJCOSX-B3LYP-D3BJ-ZORA/def2-TZVPP/old-ZORA-TZVPP(Sn)/SARC-ZORA-TZVPP(Pb)).

Table S3 Relative Gibbs free energies ΔG_{298} at 298 K of triplet states, ${}^1\text{GS}$ and transition states (TS) in eV, calculated by DFT for $\mathbf{1}^{\text{Sn}}$ and $\mathbf{1}^{\text{Pb}}$.

	$\mathbf{1}^{\text{Sn}}$	$\mathbf{1}^{\text{Pb}}$
${}^3\text{ILCT}$	0	0
${}^3\text{LMCT}_{\text{py}}$	−0.16	−0.38
${}^3\text{LMCT}_{\text{pyr}}$	+0.10	−0.11
${}^1\text{GS}$	−2.31	−2.33
$\text{TS}({}^3\text{ILCT} \rightarrow {}^3\text{LMCT}_{\text{py}})$	+0.25	+0.06
$\text{TS}({}^3\text{ILCT} \rightarrow {}^3\text{LMCT}_{\text{pyr}})$	+0.36	–
$\text{TS}({}^3\text{LMCT}_{\text{py}} \rightarrow {}^3\text{LMCT}_{\text{pyr}})$	–	+0.48

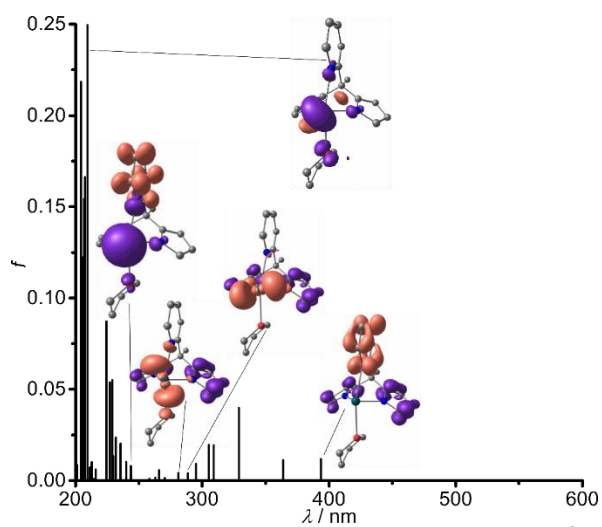
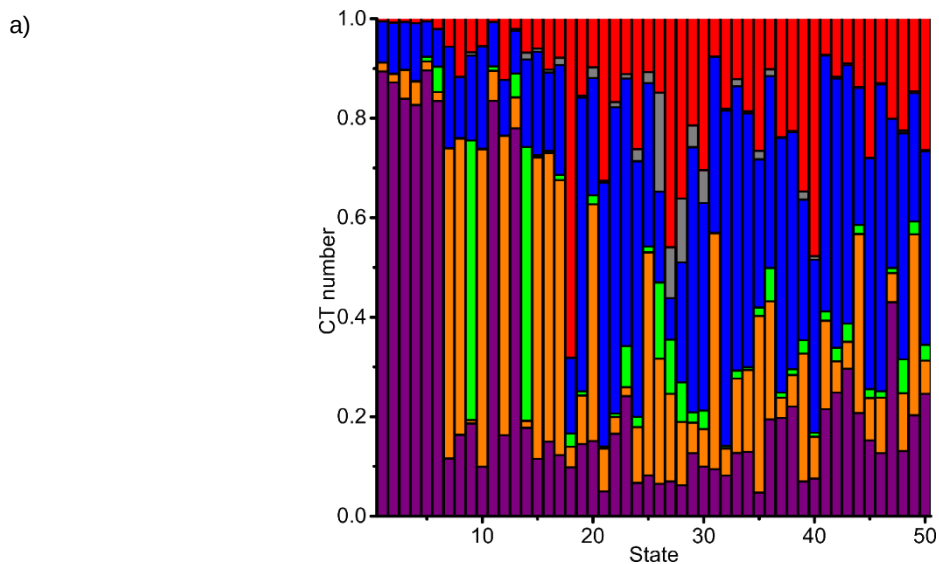


Fig. S29 TD-DFT calculated oscillator strengths on $1^{\text{Sn}}(\text{thf})$ and difference electron densities of selected characteristic spin-allowed transitions (isosurface value 0.005 a.u., purple = electron loss, orange = electron gain, CPCM-(THF)-RIJCOSX-B3LYP-D3BJ-ZORA/def2-TZVPP/old-ZORA-TZVPP(Sn)).



b)

1: 394 nm / 0.0118	2: 364 nm / 0.0113	3: 329 nm / 0.0396	4: 309 nm / 0.0192	5: 305 nm / 0.0194
6: 295 nm / 0.00921	7: 289 nm / 0.00404	8: 281 nm / 0.00413	9: 277 nm / 0.000155	10: 271 nm / 0.00149
11: 266 nm / 0.00575	12: 263 nm / 0.00156	13: 258 nm / 0.000949	14: 244 nm / 0.00789	15: 240 nm / 0.0104
16: 235 nm / 0.0201	17: 232 nm / 0.0236	18: 230 nm / 0.0133	19: 229 nm / 0.0549	20: 227 nm / 0.0540

Fig. S30 a) Charge transfer analysis of the 50 lowest spin-allowed transitions of $1^{Sn}(thf)$ (green: MLCT, purple: ILCT, orange: LMCT, blue: IL, grey: MC) and b) difference electron densities of the 20 lowest spin-allowed transitions of $1^{Sn}(thf)$ with the respective wavelength and oscillator strength (purple = electron loss; orange = electron gain) displayed at an isosurface value of 0.005 a.u..

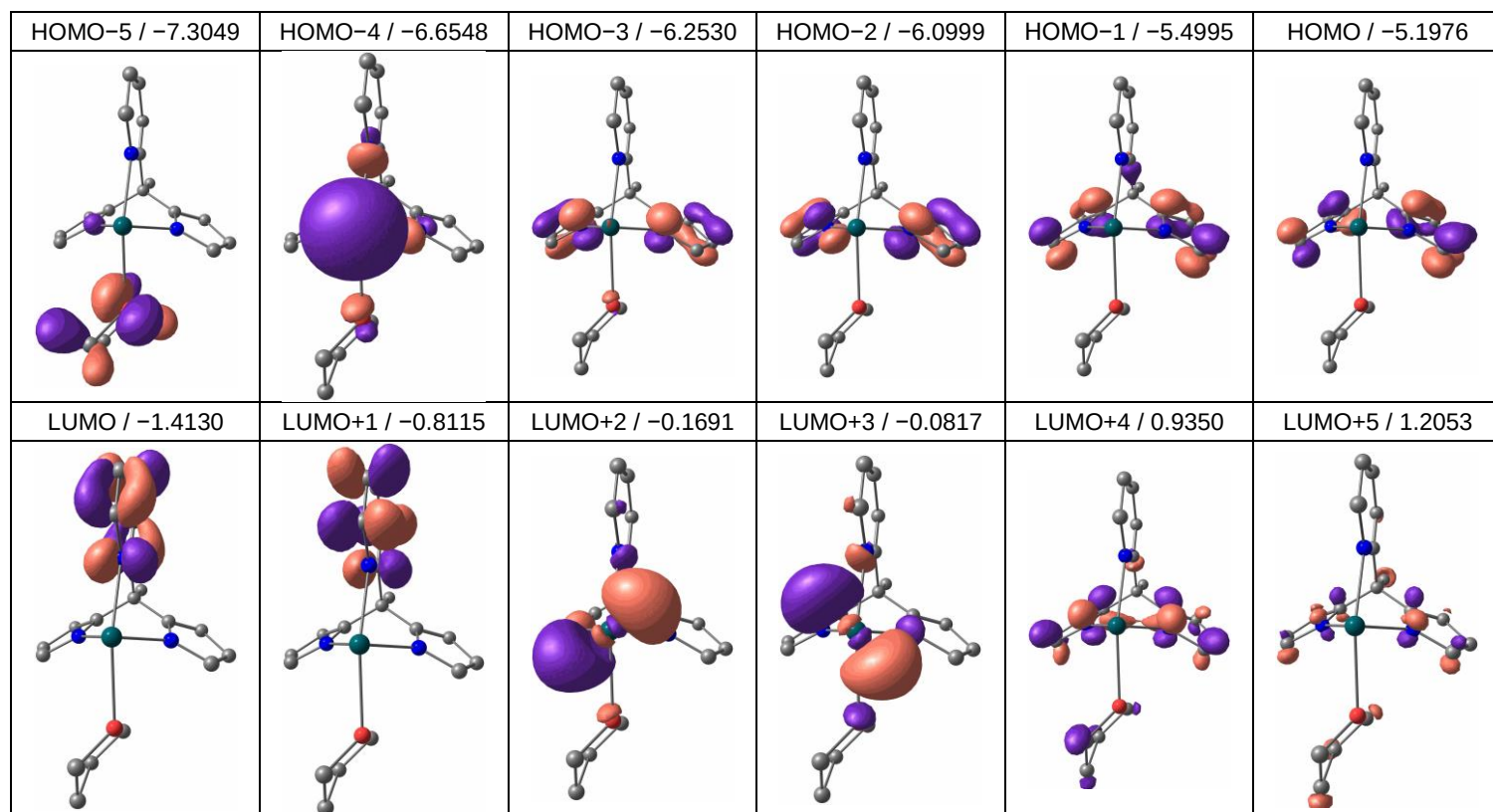


Fig. S31 Selected molecular orbitals of $1^{\text{Sn}}(\text{thf})$ with energies given in eV, displayed at an isosurface value of 0.07 a.u..

Table S4 Relative Gibbs free energies ΔG_{298} at 298 K of triplet states, ^1GS and transition states (TS) in eV, calculated by DFT for $1^{\text{Sn}}(\text{thf})$.

$^3\text{ILCT}$	0
$^3\text{LMCT}_{\text{py}}$	-0.09
$^3\text{MLCT}$	+0.85
$^3\text{LMCT}_{\text{pyr}}$	+0.12
^1GS	-2.43

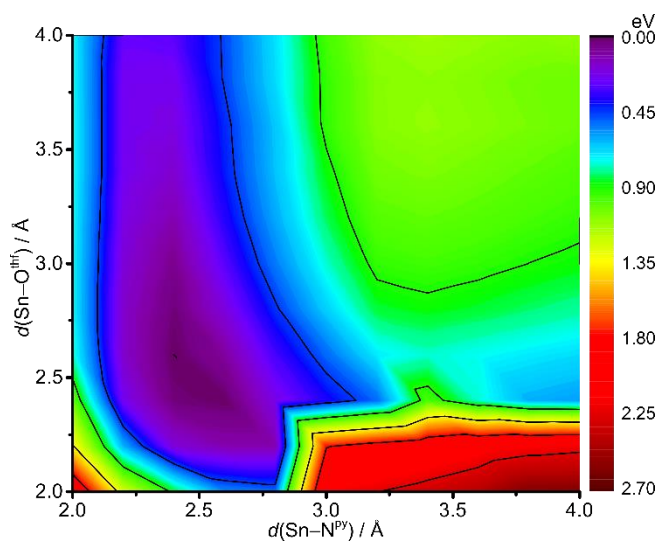


Fig. S32 Contour plot of the $1^{\text{Sn}}(\text{thf})$ potential energy surface, according to single-point energies of a 2D relaxed potential energy surface scan as projection along the $\text{Sn}-\text{N}^{\text{py}}$ and $\text{Sn}-\text{O}^{\text{thf}}$ stretching modes on the triplet hypersurface $^31^{\text{Sn}}$ of $1^{\text{Sn}}(\text{thf})$ (CPCM-(THF)-RIJCOSX-B3LYP-D3BJ-ZORA/def2-TZVPP/old-ZORA-TZVPP(Sn)).

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6.2 Supporting Information: Ligand Topology Tunes Energy and Character of Emissive Triplet States in Stannylenes

Supplementary Information File:
Ligand topology tunes energy and character of emissive triplet states in stannylenes

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Crystallographic Data of Sn(^t-BuPDP^t-Bu) **1**

C₂₉H₄₁N₃Sn (550.34); triclinic; $P\bar{1}$; $a = 10.347(2)$ Å, $b = 10.991(2)$ Å, $c = 13.383(3)$ Å; $\alpha = 71.82(3)^\circ$; $\beta = 88.06(3)^\circ$; $\gamma = 67.08(3)^\circ$; $V = 1325.2(6)$ Å³; $Z = 2$; density, calcd. = 1.379 g cm⁻³, $T = 120(2)$ K, $\mu = 0.985$ mm⁻¹; $F(000) = 572$; crystal size $0.640 \times 0.550 \times 0.430$ mm³; $\theta = 2.811$ to 27.863 deg.; $-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $-16 \leq l \leq 17$; rfln collected = 11914; rfln unique = 6284 [$R(\text{int}) = 0.0200$]; completeness to $\theta = 25.242$ deg.: 99.6%; absorption correction: Semi-empirical from equivalents; max. and min. transmission 0.4841 and 0.3993; data 6284; restraints 0, parameters 310; goodness-of-fit on $F^2 = 1.127$; final indices [$I > 2\sigma(I)$] $R_1 = 0.0231$, $wR_2 = 0.0564$; R indices (all data) $R_1 = 0.0254$, $wR_2 = 0.0575$; largest diff. peak and hole 0.519 and -0.296 e Å⁻³.

Crystallographic Data of Sn(^t-BuPDP^t-Bu) **1** from variable-temperature measurements

100 K: C₂₉H₄₁N₃Sn (550.34); triclinic; $P\bar{1}$; $a = 10.3515(6)$ Å, $b = 10.9903(6)$ Å, $c = 13.3717(7)$ Å; $\alpha = 71.796(4)^\circ$; $\beta = 88.045(4)^\circ$; $\gamma = 67.127(4)^\circ$; $V = 1324.84(13)$ Å³; $Z = 2$; density, calcd. = 1.380 g cm⁻³, $T = 100(2)$ K, $\mu = 0.985$ mm⁻¹; $F(000) = 572$; crystal size $0.390 \times 0.310 \times 0.210$ mm³; $\theta = 2.127$ to 32.940 deg.; $-15 \leq h \leq 15$, $-15 \leq k \leq 16$, $-18 \leq l \leq 20$; rfln collected = 22540; rfln unique = 8386 [$R(\text{int}) = 0.0289$]; completeness to $\theta = 25.242$ deg.: 99.0%; absorption correction: integration; max. and min. transmission 0.9054 and 0.6744; data 8386; restraints 0, parameters 310; goodness-of-fit on $F^2 = 1.034$; final indices [$I > 2\sigma(I)$] $R_1 = 0.0315$, $wR_2 = 0.0746$; R indices (all data) $R_1 = 0.0368$, $wR_2 = 0.0753$; largest diff. peak and hole 1.308 and -1.497 e Å⁻³.

150 K: C₂₉H₄₁N₃Sn (550.34); triclinic; $P\bar{1}$; $a = 10.3590(7)$ Å, $b = 11.0232(7)$ Å, $c = 13.4186(8)$ Å; $\alpha = 71.581(5)^\circ$; $\beta = 87.946(5)^\circ$; $\gamma = 67.106(5)^\circ$; $V = 1332.58(16)$ Å³; $Z = 2$; density, calcd. = 1.372 g cm⁻³, $T = 150(2)$ K, $\mu = 0.980$ mm⁻¹; $F(000) = 572$; crystal size $0.390 \times 0.310 \times 0.210$ mm³; $\theta = 2.123$ to 32.954 deg.; $-15 \leq h \leq 15$, $-15 \leq k \leq 16$, $-19 \leq l \leq 20$; rfln collected = 22791; rfln unique = 8434 [$R(\text{int}) = 0.0304$]; completeness to $\theta = 25.242$ deg.: 99.2%; absorption correction: integration; max. and min. transmission 0.9062 and 0.6797; data 8434; restraints 0, parameters 310; goodness-of-fit on $F^2 = 1.027$; final indices [$I > 2\sigma(I)$] $R_1 = 0.0319$, $wR_2 = 0.0737$; R indices (all data) $R_1 = 0.0379$, $wR_2 = 0.0744$; largest diff. peak and hole 0.981 and -1.382 e Å⁻³.

175 K: C₂₉H₄₁N₃Sn (550.34); triclinic; $P\bar{1}$; $a = 10.3695(6)$ Å, $b = 11.0407(6)$ Å, $c = 13.4415(8)$ Å; $\alpha = 71.443(4)^\circ$; $\beta = 87.935(5)^\circ$; $\gamma = 67.100(4)^\circ$; $V = 1337.07(14)$ Å³; $Z = 2$; density, calcd. = 1.367 g cm⁻³, $T = 175(2)$ K, $\mu = 0.976$ mm⁻¹; $F(000) = 572$; crystal size $0.390 \times 0.310 \times 0.210$ mm³; $\theta = 2.122$ to 32.916 deg.; $-15 \leq h \leq 15$, $-15 \leq k \leq 16$, $-19 \leq l \leq 20$; rfln collected = 22992; rfln unique = 8458 [$R(\text{int}) = 0.0296$]; completeness to $\theta = 25.242$ deg.: 99.0%; absorption correction: integration; max. and min. transmission 0.9061 and 0.6789; data 8458; restraints 0, parameters 310; goodness-of-fit on $F^2 = 1.017$; final indices [$I > 2\sigma(I)$] $R_1 = 0.0311$, $wR_2 = 0.0708$; R indices (all data) $R_1 = 0.0381$, $wR_2 = 0.0715$; largest diff. peak and hole 0.998 and -1.238 e Å⁻³.

225 K: C₂₉H₄₁N₃Sn (550.34); triclinic; $P\bar{1}$; $a = 10.3748(3)$ Å, $b = 11.0785(3)$ Å, $c = 13.4980(4)$ Å; $\alpha = 71.213(2)^\circ$; $\beta = 88.013(2)^\circ$; $\gamma = 67.048(2)^\circ$; $V = 1345.11(7)$ Å³; $Z = 2$; density, calcd. = 1.359 g cm⁻³, $T = 225(2)$ K, $\mu = 0.971$ mm⁻¹; $F(000) = 572$; crystal size $0.390 \times 0.310 \times 0.210$ mm³; $\theta = 2.119$ to 33.843 deg.; $-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-19 \leq l \leq 21$; rfln collected = 28066; rfln unique = 9321 [$R(\text{int}) = 0.0287$]; completeness to $\theta = 25.242$ deg.: 99.8%; absorption correction: integration; max. and min. transmission 0.9073 and 0.6798; data 9321; restraints 0, parameters 310; goodness-of-fit on $F^2 = 1.013$; final indices [$I > 2\sigma(I)$] $R_1 = 0.0313$, $wR_2 = 0.0767$; R indices (all data) $R_1 = 0.0372$, $wR_2 = 0.0783$; largest diff. peak and hole 1.076 and -1.157 e Å⁻³.

Crystallographic Data of $\text{Sn}_2(\text{t-BuPDP}^{\text{t-Bu}})_2$ **2**

Crystals for XRD analysis were obtained from a solution of a mixture of **1** and **2** in diethyl ether after storing at $-30\text{ }^\circ\text{C}$ for six weeks.

$\text{C}_{62}\text{H}_{92}\text{N}_6\text{OSn}_2$ (1174.79); triclinic; $P\bar{1}$; $a = 14.254(3)\text{ \AA}$, $b = 14.370(3)\text{ \AA}$, $c = 15.023(3)\text{ \AA}$; $\alpha = 82.07(3)^\circ$; $\beta = 87.03(3)^\circ$; $\gamma = 83.87(3)^\circ$; $V = 3028.0(11)\text{ \AA}^3$; $Z = 2$; density, calcd. = 1.288 g cm^{-3} , $T = 120(2)\text{ K}$, $\mu = 0.868\text{ mm}^{-1}$; $F(000) = 1228$; crystal size $0.170 \times 0.083 \times 0.020\text{ mm}^3$; $\theta = 2.504$ to 27.966 deg. ; $-18 \leq h \leq 17$, $-18 \leq k \leq 18$, $-19 \leq l \leq 19$; rfln collected = 52878; rfln unique = 14423 [$R(\text{int}) = 0.1600$]; completeness to $\theta = 25.242\text{ deg.}$: 99.9%; absorption correction: semi-empirical from equivalents; max. and min. transmission 1.19353 and 0.82302; data 14423; restraints 0, parameters 666; goodness-of-fit on $F^2 = 1.089$; final indices [$I > 2\sigma(I)$] $R_1 = 0.0627$, $wR_2 = 0.1055$; R indices (all data) $R_1 = 0.1182$, $wR_2 = 0.1263$; largest diff. peak and hole 0.795 and $-1.068\text{ e.\AA}^{-3}$.

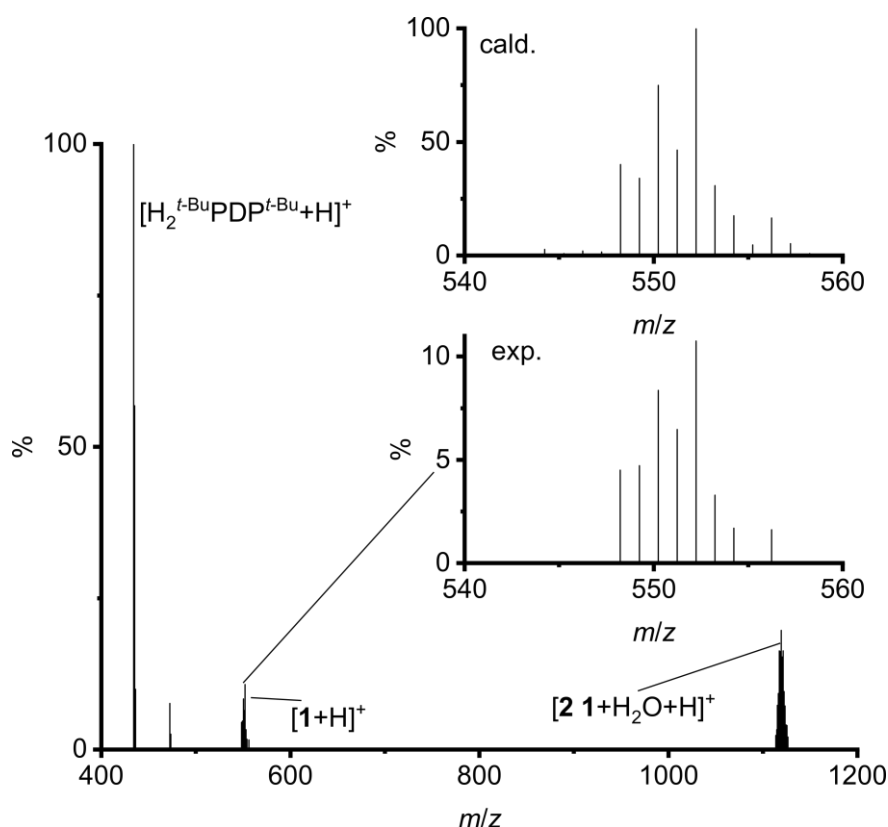


Figure S1. APCI⁺ mass spectrum of **1** in acetonitrile with insets of the experimentally found and calculated isotope pattern for **[1+H]⁺**.

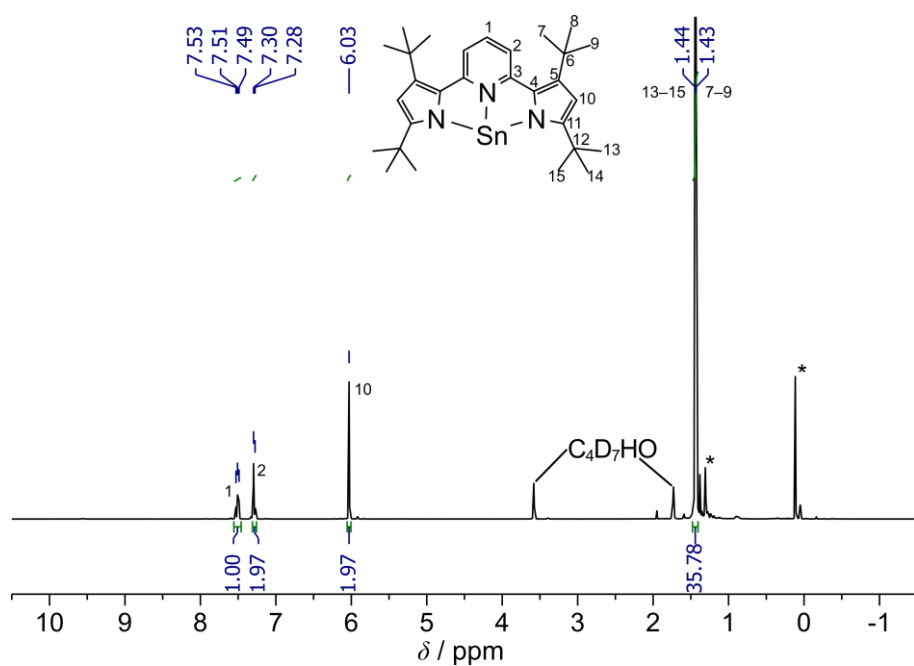


Figure S2. ¹H NMR spectrum of **1** in tetrahydrofuran-*d*₈ with atom numbering for the assignment. The asterisks denote resonances of silicon grease and small amounts of hydrolysis products.

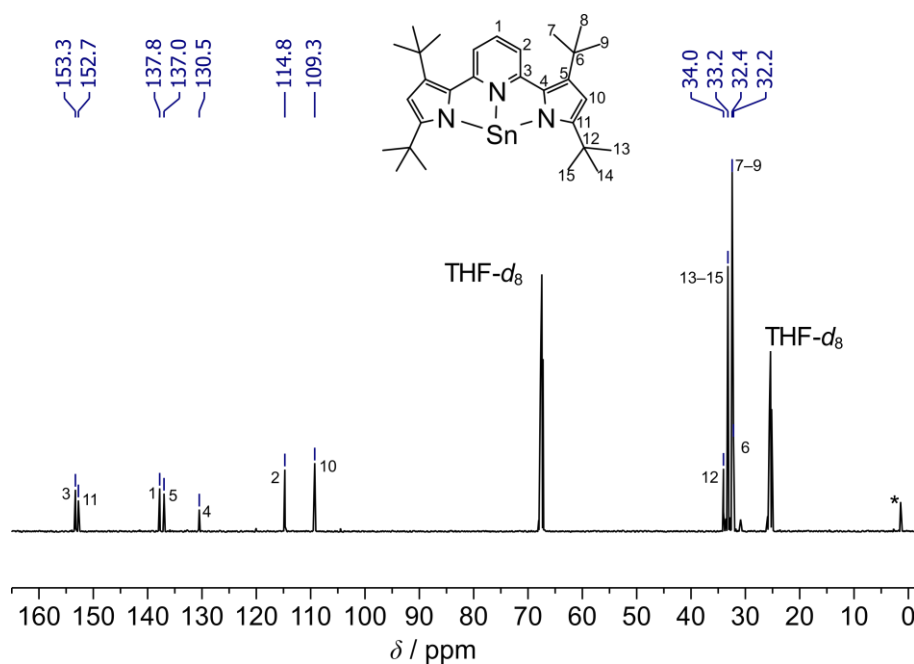


Figure S3. ¹³C{¹H} NMR spectrum of **1** in tetrahydrofuran-*d*₈ with atom numbering for the assignment. The asterisk denotes resonance of silicon grease.

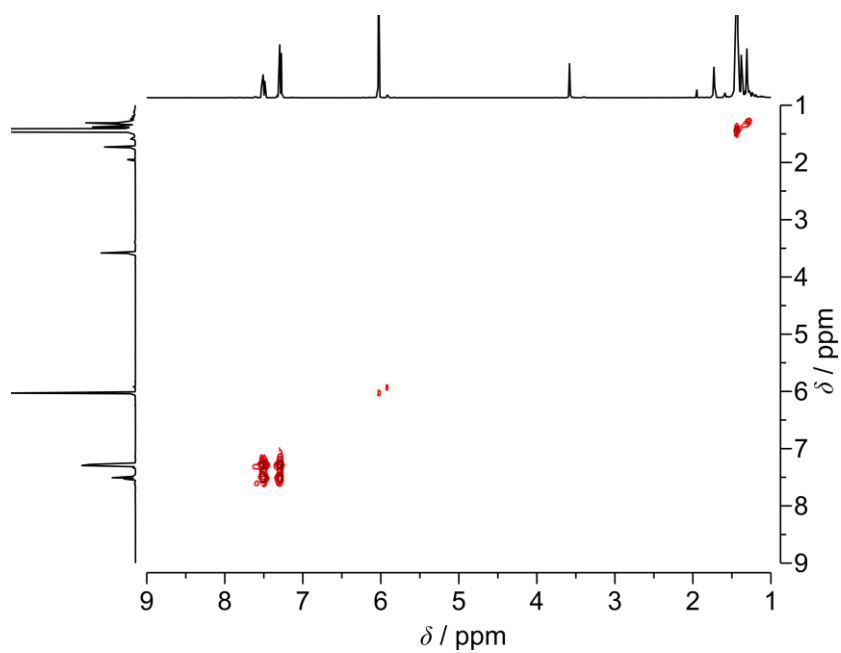


Figure S4. $^1\text{H},^1\text{H}$ COSY NMR spectrum of **1** in tetrahydrofuran- d_8 .

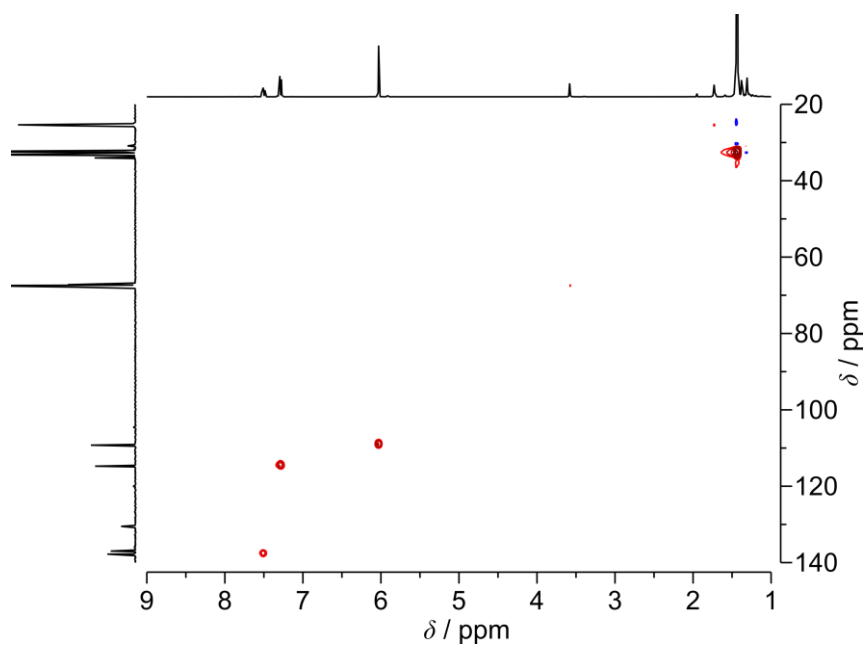


Figure S5. $^{13}\text{C},^1\text{H}$ HSQC NMR spectrum of **1** in tetrahydrofuran- d_8 .

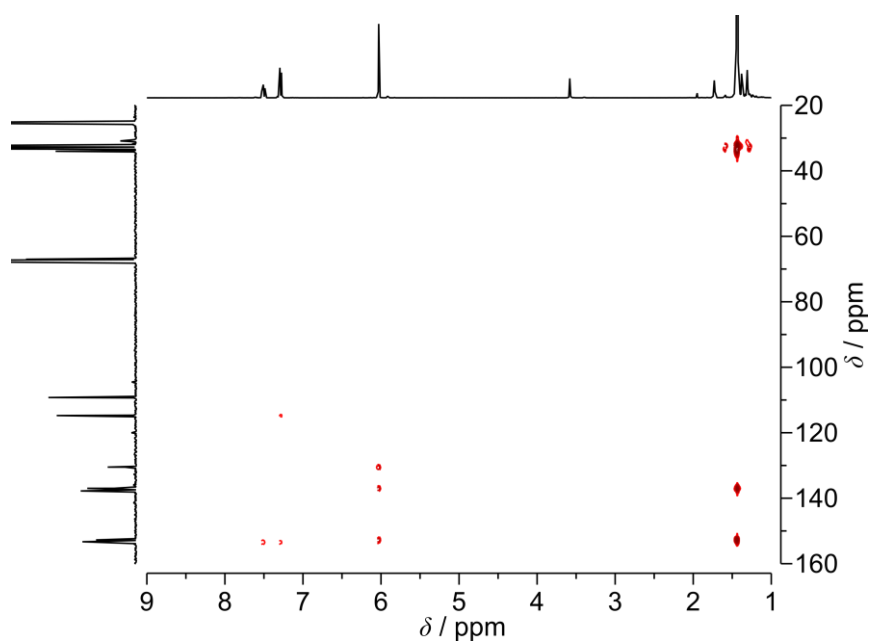


Figure S6. $^{13}\text{C}, ^1\text{H}$ HMBC NMR spectrum of **1** in tetrahydrofuran- d_8 .

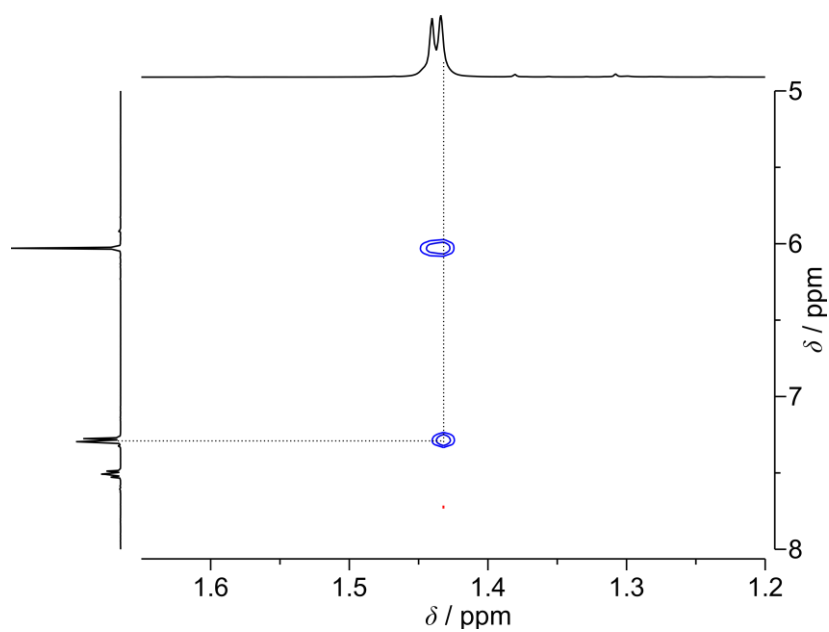


Figure S7. Part of the $^1\text{H}, ^1\text{H}$ NOESY NMR spectrum of **1** in tetrahydrofuran- d_8 for assignment of the *tert*-butyl resonances

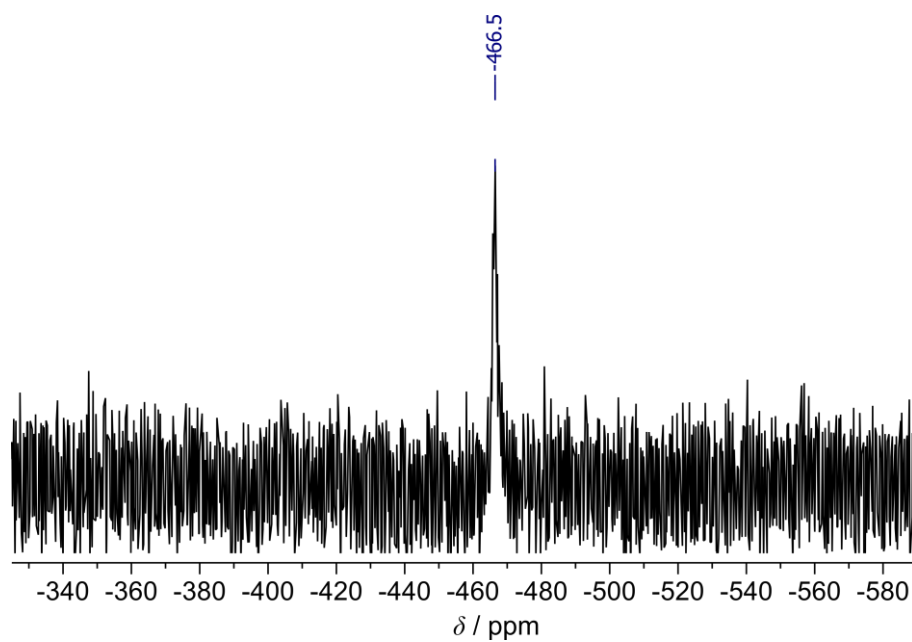


Figure S8. ^{119}Sn NMR spectrum of **1** in tetrahydrofuran- d_8 .

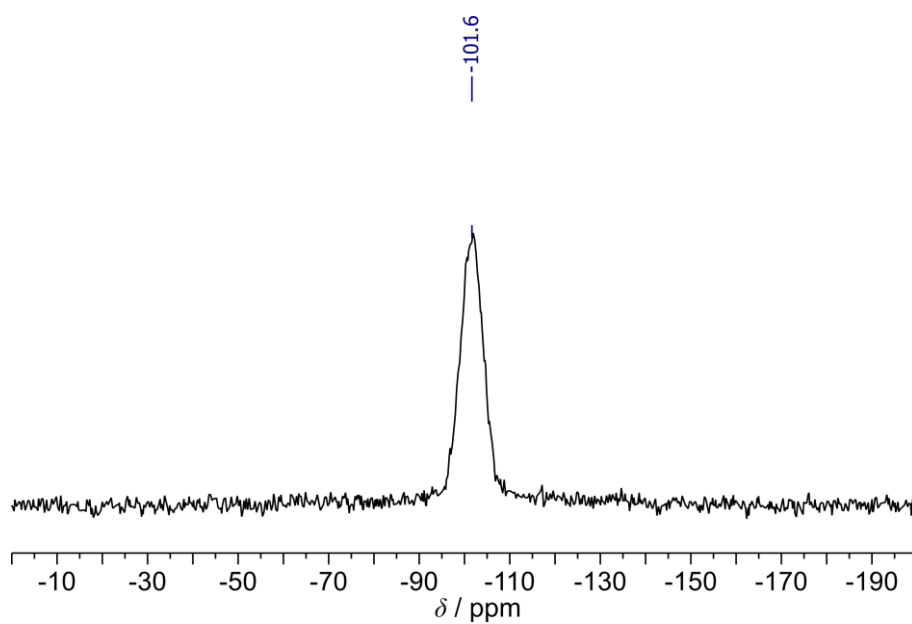


Figure S9. ^{119}Sn CP-MAS NMR spectrum of **1** in the solid state.

Table S1. Selected structural parameters of **1** in Å and degrees [°] of the molecular structure of **1** from SC-XRD of two crystals at 120 K and in the series 100–225 K and DFT calculated geometry optimized structures of **1** in the S₀, T₁ and T₂ states.

	1 (XRD 120 K)	S ₀ (DFT)	T ₁ (DFT)	T ₂ (DFT)
Sn–N ^{py}	2.1680(16)	2.197	2.247	2.266
Sn–N ^{pyr1}	2.2197(18)	2.247	2.382	2.339
Sn–N ^{pyr2}	2.1967(15)	2.238	2.381	2.334
N ^{pyr1} –Sn–N ^{pyr2}	117.07(6)	117.04	141.06	136.08
N ^{py} –Sn–N ^{pyr1}	72.73(6)	71.87	70.49	70.07
N ^{py} –Sn–N ^{pyr2}	72.36(6)	71.82	70.57	70.39

	1 (XRD 100K)	1 (XRD 150K)	1 (XRD 175K)	1 (XRD 225K)
Sn–N ^{py}	2.1697(16)	2.1679(16)	2.1676(15)	2.1679(14)
Sn–N ^{pyr1}	2.2231(15)	2.2237(15)	2.2228(14)	2.2232(13)
Sn–N ^{pyr2}	2.1922(15)	2.1935(15)	2.1920(15)	2.1972(13)
N ^{pyr1} –Sn–N ^{pyr2}	117.04(6)	117.05(6)	117.09(5)	117.06(5)
N ^{py} –Sn–N ^{pyr1}	72.71(6)	72.58(6)	72.58(5)	72.59(5)
N ^{py} –Sn–N ^{pyr2}	72.44(6)	72.51(5)	72.56(5)	72.47(5)

Table S2. Selected structural parameters in Å and degrees [°] of the molecular structure of **2** from SC-XRD at 120 K and from DFT geometry optimization.

	1 (XRD 120 K)	S ₀ (DFT)
Sn–N ^{py}	2.224(5)	2.270
Sn–N ^{pyr1}	2.200(4)	2.237
Sn–N ^{pyr2}	2.165(4)	2.223
Sn ¹ –N ^{py1}	2.228(4)	2.270
Sn ¹ –N ^{pyr11}	2.190(4)	2.237
Sn ¹ –N ^{pyr21}	2.177(4)	2.224
N ^{pyr1} –Sn–N ^{pyr2}	99.75(16)	100.16
N ^{py} –Sn–N ^{pyr1}	73.76(16)	72.20
N ^{py} –Sn–N ^{pyr2}	97.82(17)	98.04
N ^{pyr11} –Sn ¹ –N ^{pyr21}	99.18(16)	99.83
N ^{py1} –Sn ¹ –N ^{pyr11}	73.16(16)	72.20
N ^{py1} –Sn ¹ –N ^{pyr21}	98.82(16)	98.00

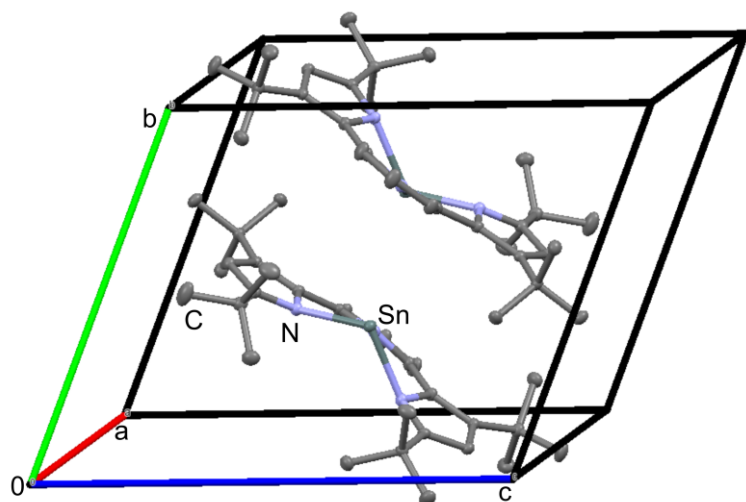


Figure S10. Unit cell of **1** in the solid state (triclinic space group $P\bar{1}$) showing the van-der-Waals pairs $[1\cdots 1]$. Hydrogen atoms omitted, thermal ellipsoids at 50% probability level.

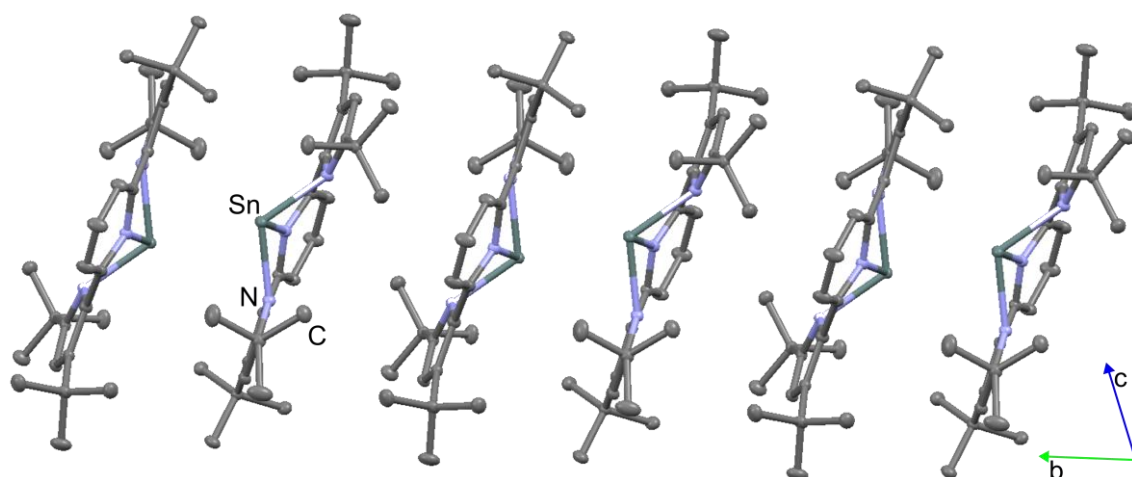


Figure S11. Selected stack of van-der-Waals pairs $[1\cdots 1]$ along the b axis in the solid state. Hydrogen atoms omitted, thermal ellipsoids at 50% probability level.

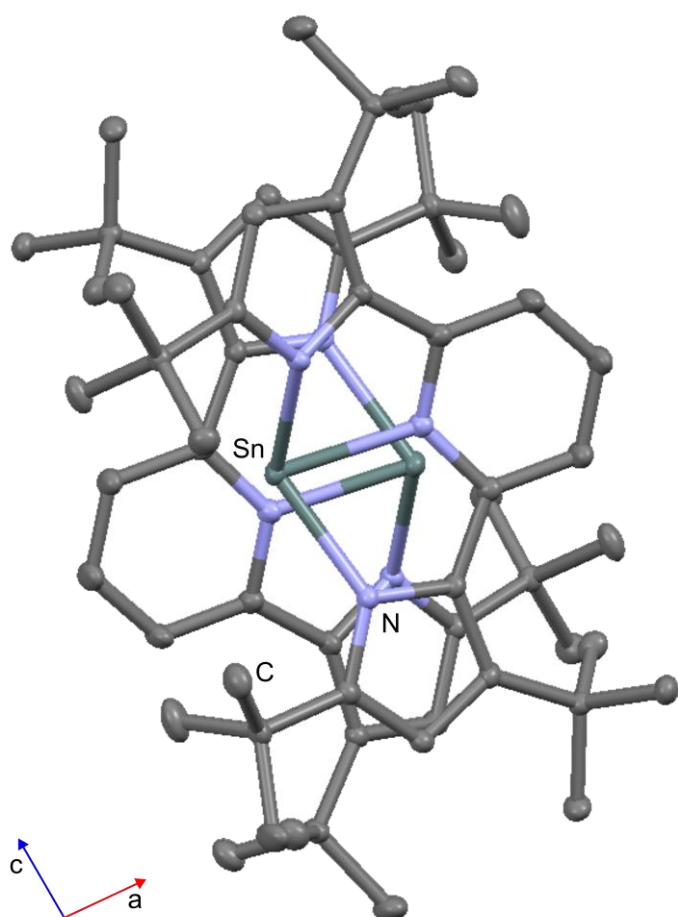


Figure S12. View of van-der-Waals pair $[1\cdots 1]$ orthogonal along the b axis. Hydrogen atoms omitted, thermal ellipsoids at 50% probability level.

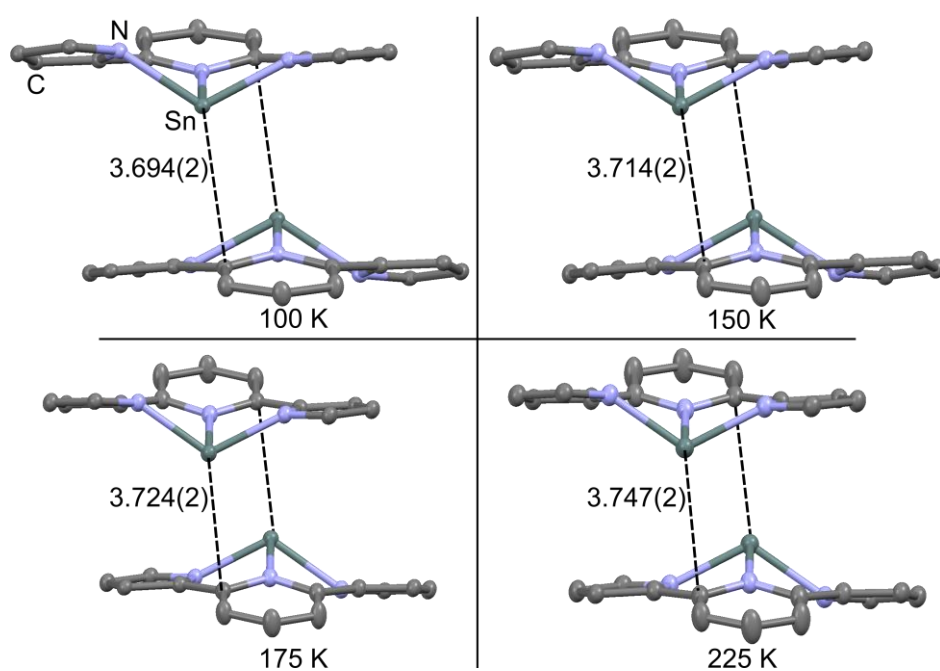


Figure S13. Van-der-Waals pairs $[1\cdots 1]$ from variable-temperature SC-XRD analyses highlighting the Sn...C17' contacts with distance given in Å. Hydrogen atoms and *tert*-butyl substituents groups omitted, thermal ellipsoids at 50% probability level.

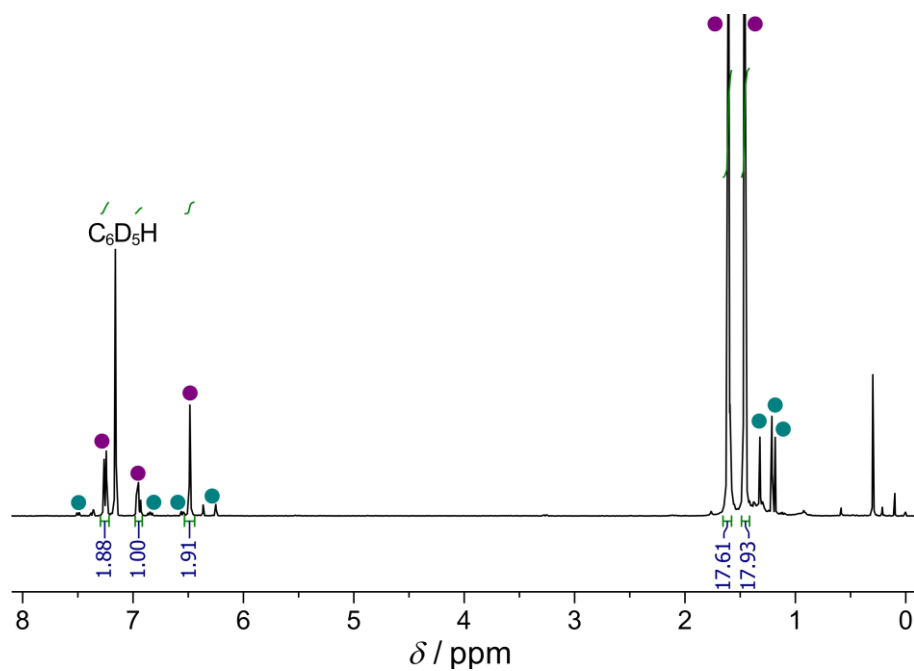


Figure S14. ^1H NMR spectrum of a mixture of **1** and **2** (1:0.08 ratio) in C_6D_6 after 20 minutes of sample preparation from solid **1** at 293 K. Resonances of **1** and **2** marked with purple and turquoise circles, respectively.

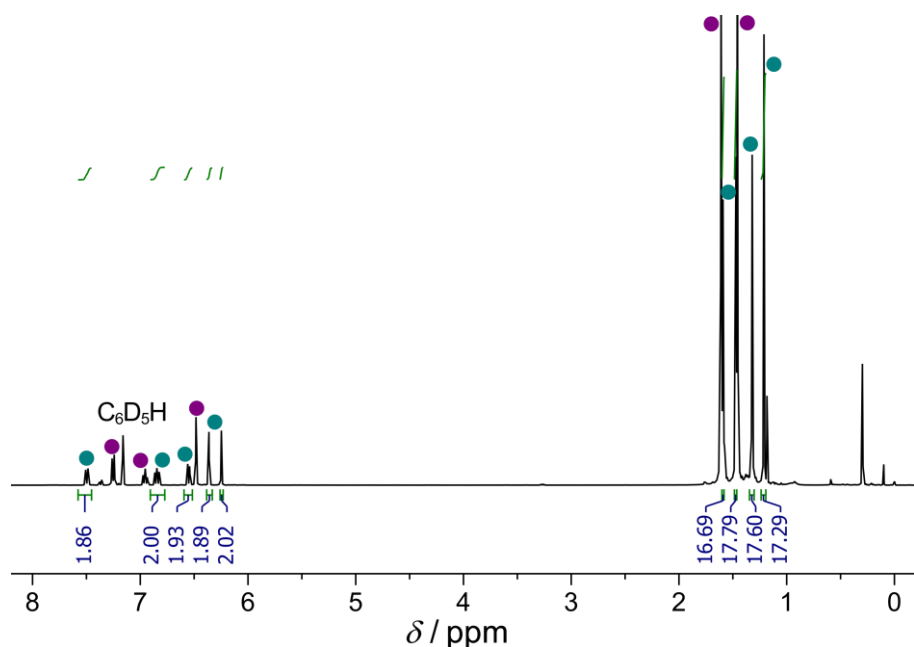


Figure S15. ^1H NMR spectrum of a mixture of **1** and **2** (1:0.59 ratio) in C_6D_6 after one day of sample preparation from solid **1** at 293 K. Resonances of **1** and **2** marked with purple and turquoise circles, respectively.

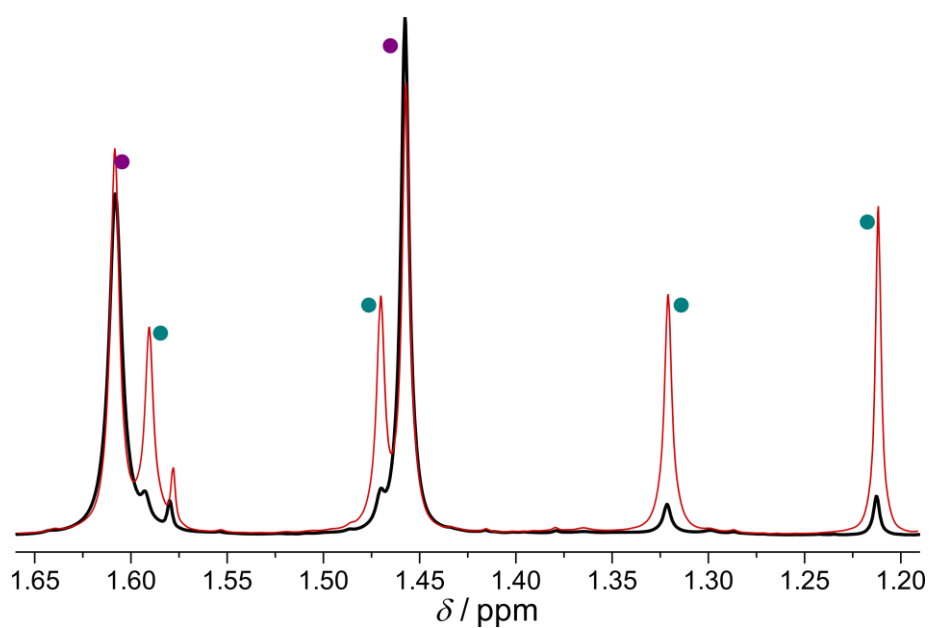


Figure S16. Comparison of the aliphatic region in the ^1H NMR spectra of a mixture of **1** and **2** in C_6D_6 after 20 minutes (black) and after one day (red) of sample preparation from solid **1** at 293 K. Resonances of **1** and **2** marked with purple and turquoise circles, respectively.

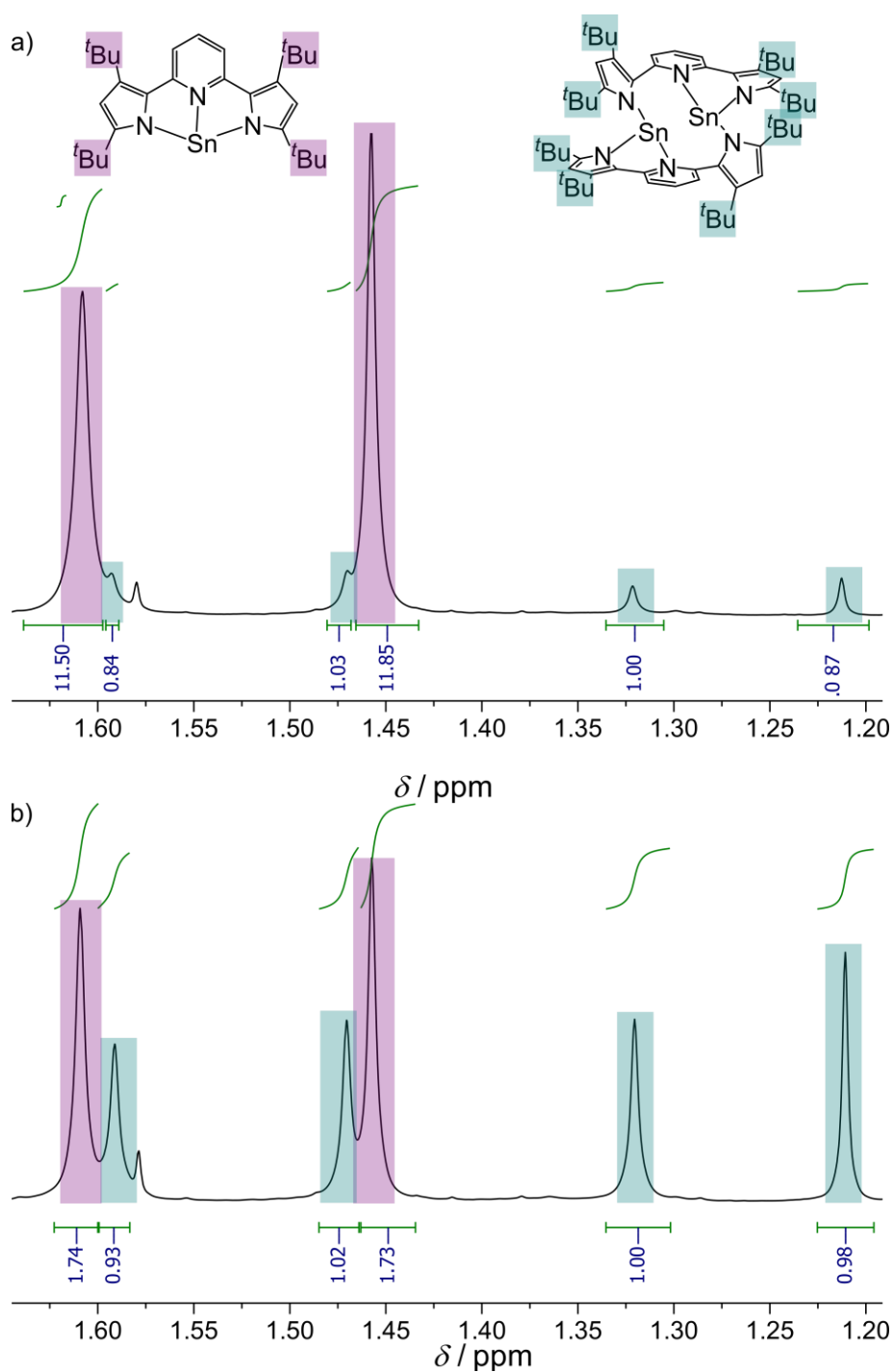


Figure S17. Integrated resonances in the aliphatic region in the ^1H NMR spectrum of a mixture of **1** and **2** after a) 20 min of sample preparation (1:0.08 ratio) and b) after one day of sample preparation (1:0.59 ratio) in C_6D_6 from solid **1** at 293K. Resonances of **1** and **2** marked with purple and turquoise bars, respectively.

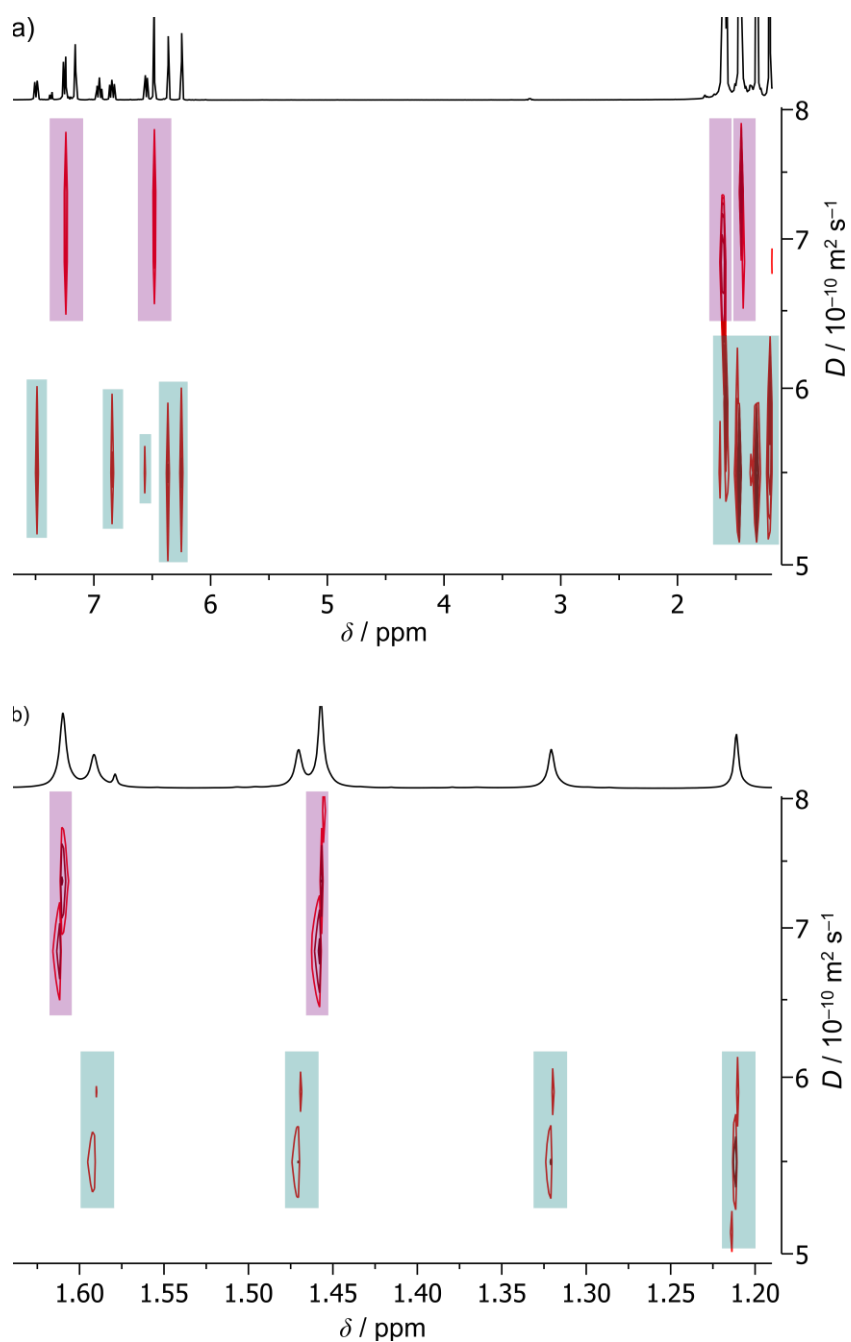


Figure S18. a) ^1H NMR DOSY of an equilibrated mixture of **1** and **2** (1:0.57 ratio) in C_6D_6 at 293 K, b) excerpt of the aliphatic region. Correlation peaks of **1** and **2** marked with purple and turquoise bars, respectively

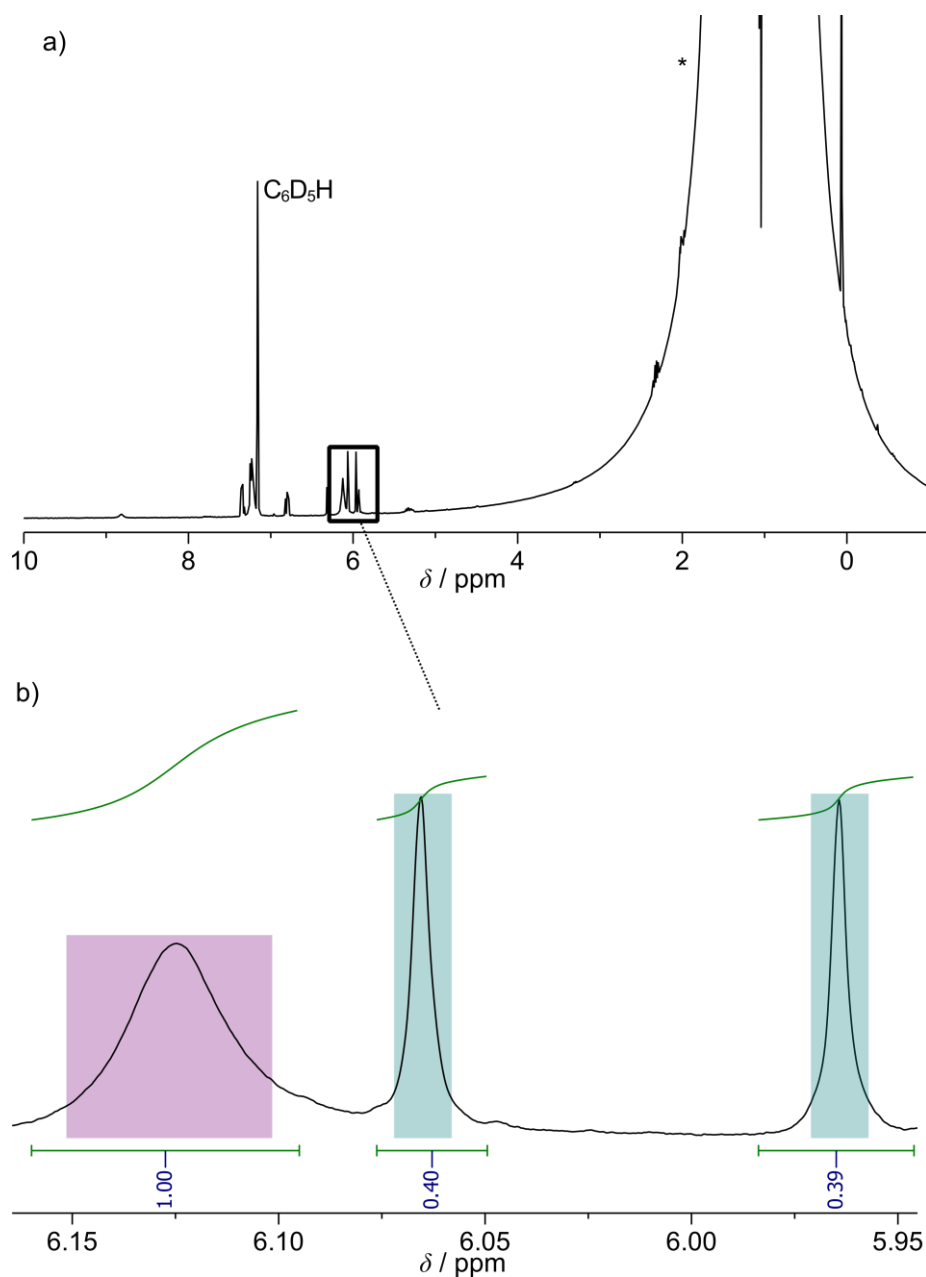


Figure S 19. a) ^1H NMR spectrum of a mixture of **1** and **2** in 3-methylpentane (asterisk) with C_6D_6 (for locking) 30 minutes after sample preparation from **1** at 293 K and b) integrated pyrrolate proton resonances of **1** and **2** marked with purple and turquoise bars, respectively.

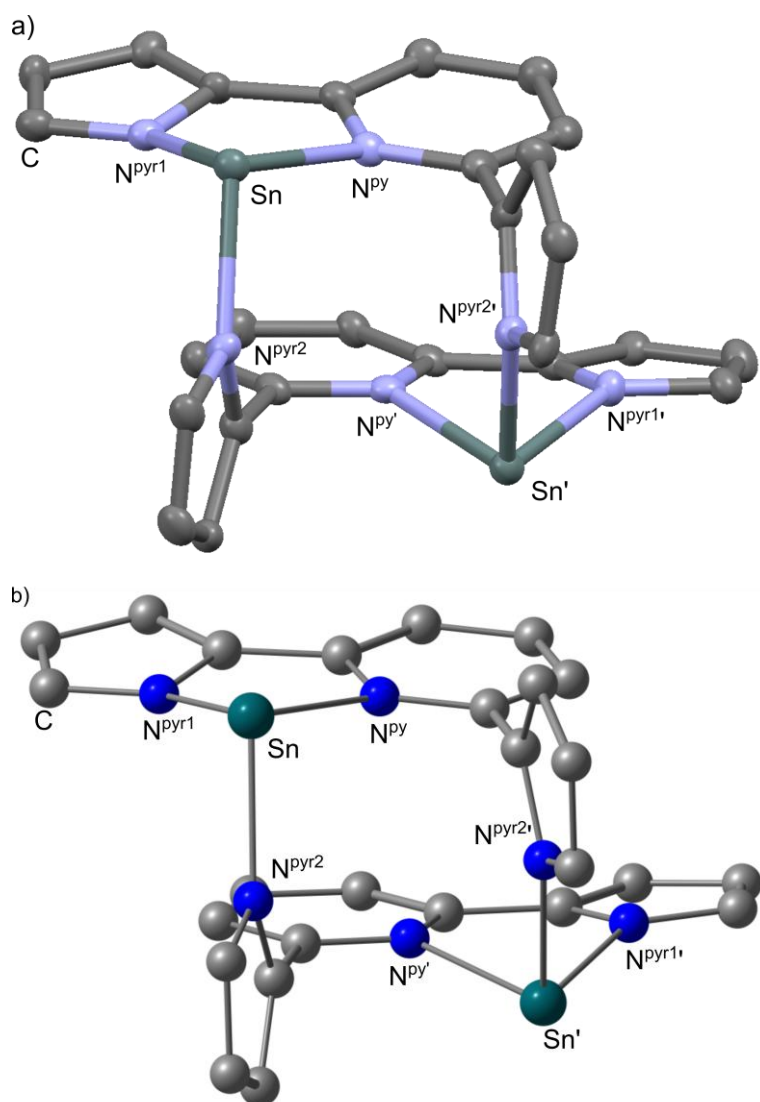


Figure S20. Molecular structure of **2** from a) SC-XRD analysis and b) from DFT calculations, hydrogen atoms and *tert*-butyl substituents omitted, thermal ellipsoids at 50% probability level. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-ZORA-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn).

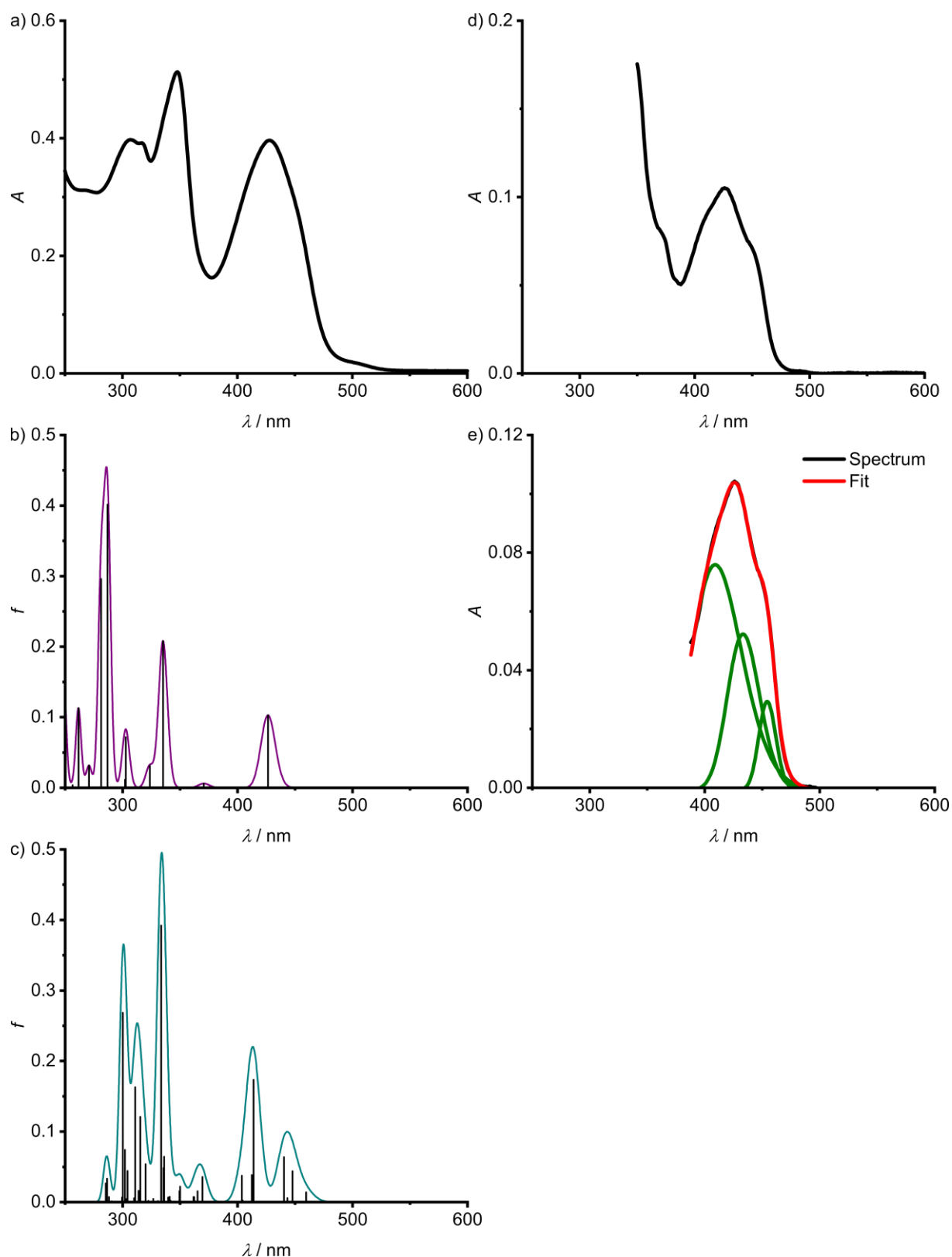


Figure S21. a) Absorption spectrum of a mixture of **1** and **2** in *n*-pentane at 293 K, 30 minutes after sample preparation from **1**, TDDFT calculated oscillator strengths b) of the monomer **1** shifted by +3500 cm⁻¹ to higher energies with Voigtian line broadening (FWHM = 800 cm⁻¹) and c) of the dimer **2** shifted by -1650 cm⁻¹ to lower energies with Voigtian line broadening (FWHM = 800 cm⁻¹), d) absorption spectrum of a mixture of **1** and **2** at 77 K, 25 minutes after sample preparation from **1** and e) sum fit (red) consisting of three Voigt functions (green) of the low-energy band of the absorption spectrum at 77 K. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-ZORA-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

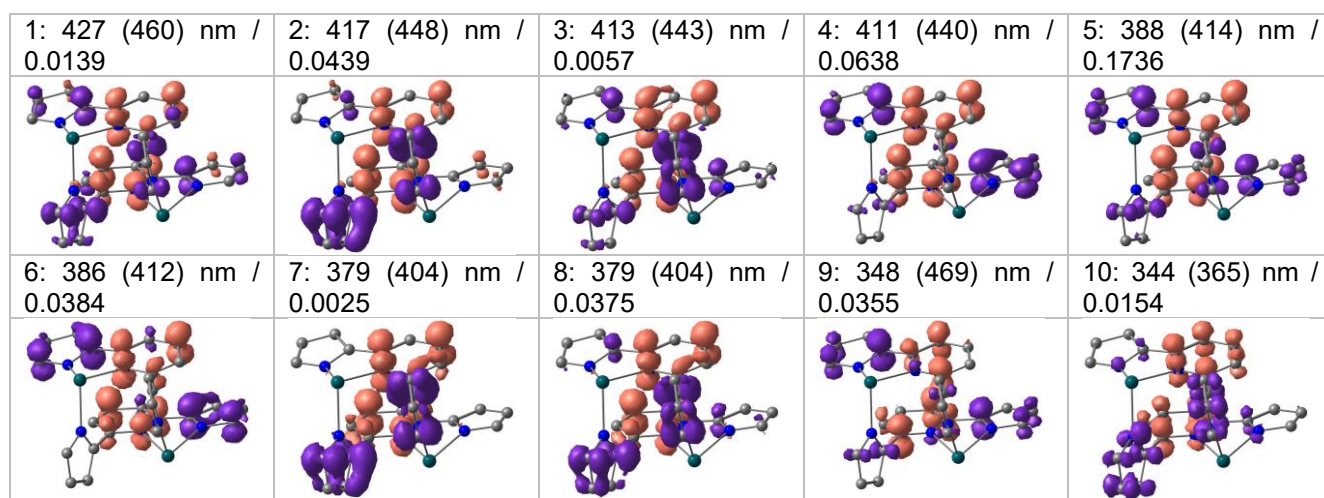


Figure S22. Difference electron densities of the 10 lowest spin-allowed transitions of **2** with the respective wavelength and oscillator strength (purple = electron loss; orange = electron gain) displayed at an isosurface value of 0.003 a.u.. The values in parentheses are shifted by -1650 cm^{-1} to lower energies to fit the absorption spectra depicted in Figure S20. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-ZORA-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn), hydrogen atoms and *tert*-butyl substituents omitted.

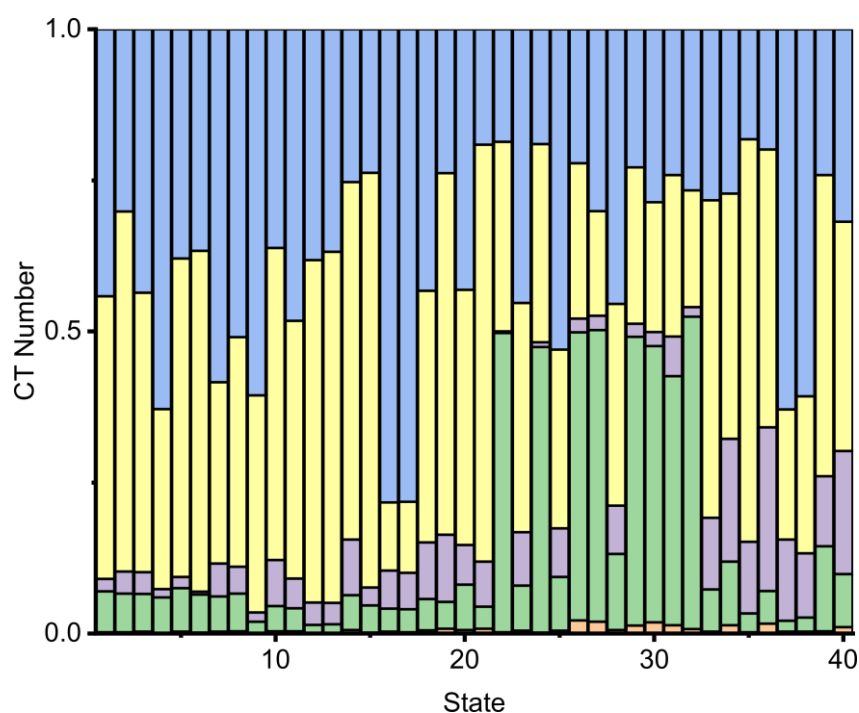


Figure S23. Charge transfer analysis of the 50 lowest spin-allowed transitions of **2** (green: LMCT, yellow: ILCT, purple: MLCT; orange: MC, blue: LL'CT).

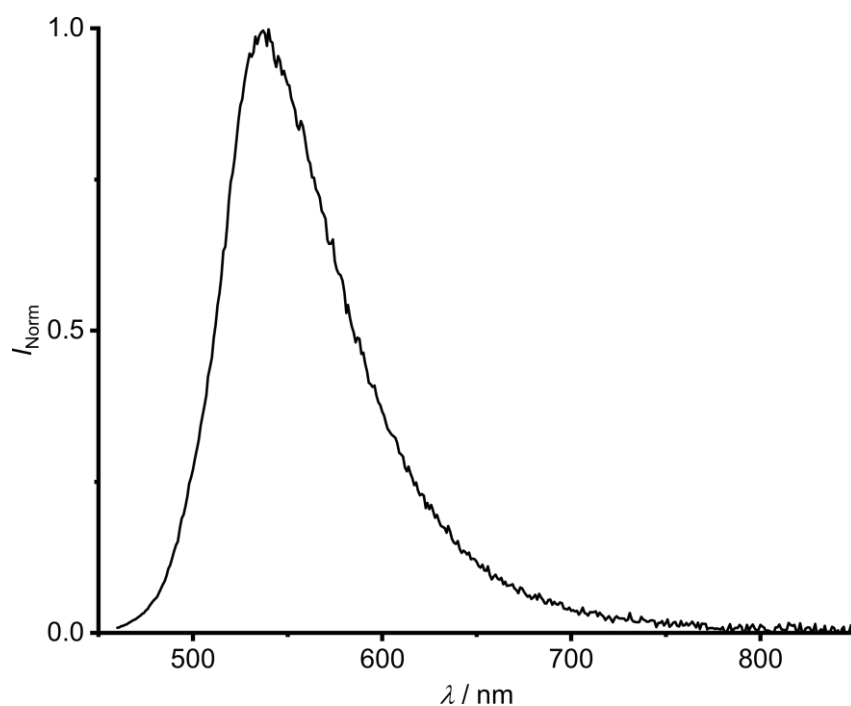


Figure S 24. Emission spectrum of **2** measured from a mixture of **1** and **2** in 3-methylpentane solution at 293 K with $\lambda_p = 540$ nm, respectively ($\lambda_{\text{exc}} = 450$ nm). Only the luminescence of **2** is observed due to the much higher quantum yield.

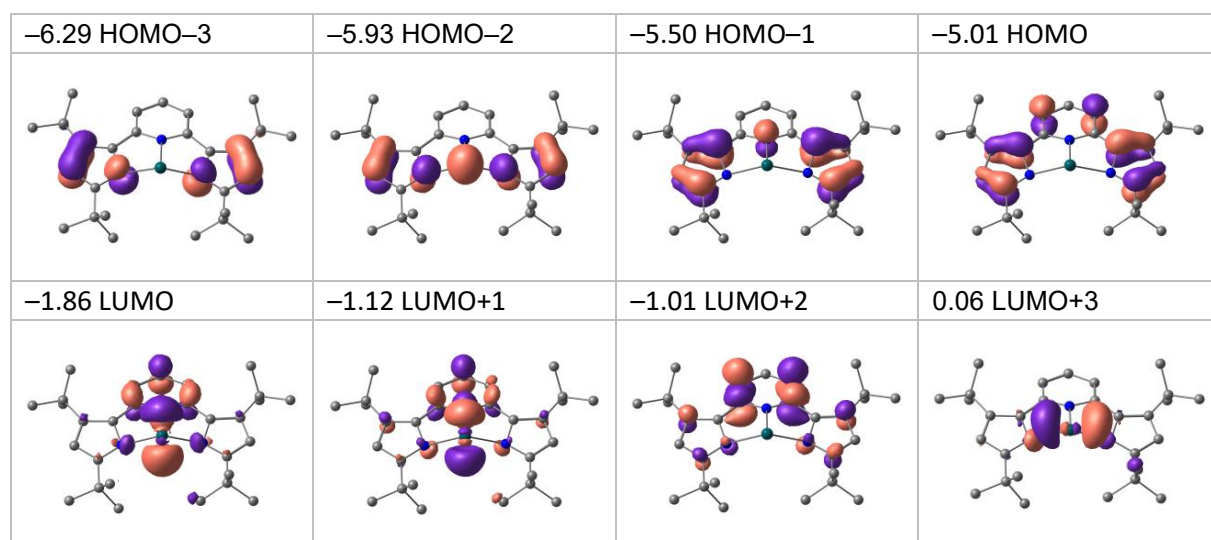


Figure S25. Selected molecular orbitals of **1** with energies given in eV, displayed at an isosurface value of 0.05 a.u.. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-ZORA-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn), hydrogen atoms omitted.

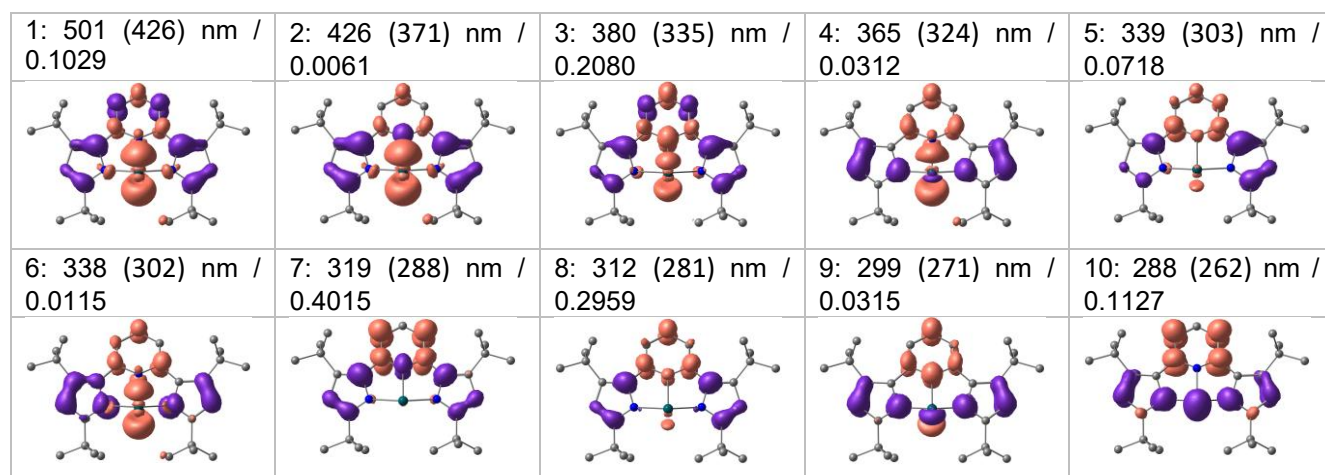


Figure S26. Difference electron densities of the 10 lowest spin-allowed transitions of **1** with the respective wavelength and oscillator strength (purple = electron loss; orange = electron gain) displayed at an isosurface value of 0.003 a.u.. The values in parentheses are shifted by +3500 cm^{-1} to higher energies to fit the absorption spectra depicted in Figure S20. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-ZORA-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn), hydrogen atoms omitted.

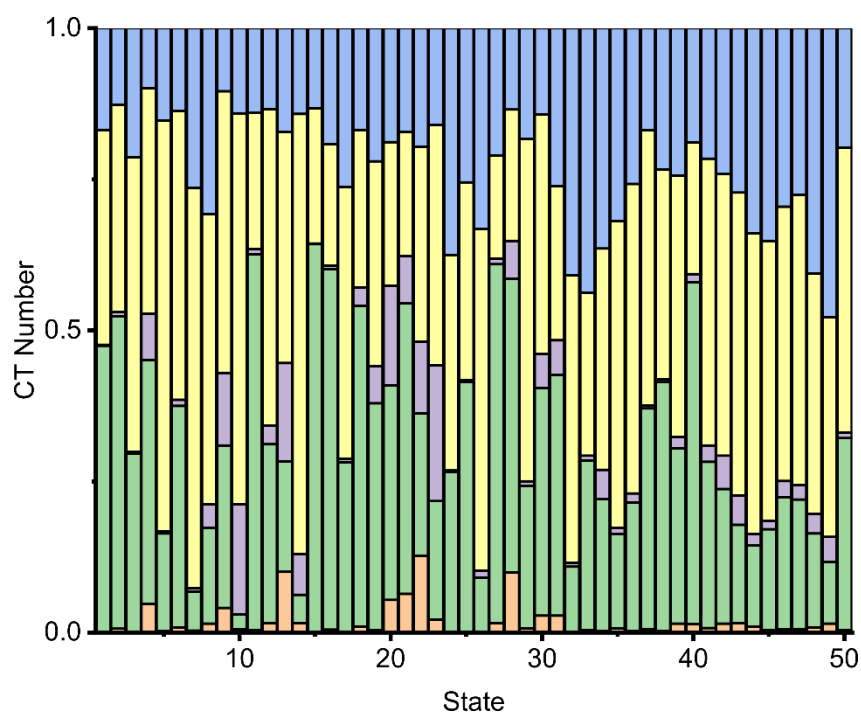


Figure S27. Charge transfer analysis of the 50 lowest spin-allowed transitions of **1** (green: LMCT, yellow: ILCT, purple: MLCT; orange: MC, blue: LC)

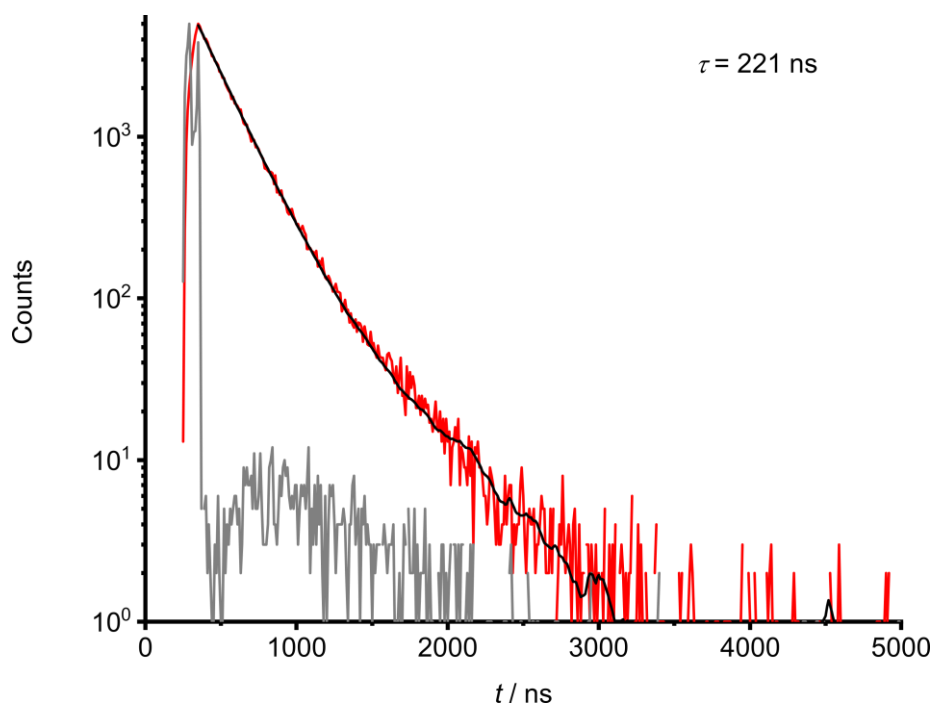


Figure S28. Emission decay curve of **1** in the solid state upon $\lambda_{\text{exc}} = 450$ nm excitation at $\lambda_{\text{em}} = 700$ nm at 293 K (red) superimposed with monoexponential reconvolution fit (black) and IRF (gray).

Table S3. Emission properties of **1** in the solid state.

	λ_p / nm	τ_p	Φ_p	k_{obs} / s^{-1}	k_r / s^{-1}	k_{nr} / s^{-1}
293 K	710	221 ns	0.0044 ^b	4.52×10^6	20000	4.5×10^6
77 K	690	128 μs (97%) 313 μs (3%) ^a	0.0116 ^b	7.81×10^3 ^c	100 ^c	7.7×10^3 ^c

^a Relative emission amplitude in parentheses. ^b Photoluminescence quantum yields include the emission band tail in NIR region. ^c Determined for the main component $\tau_{p1} = 128 \mu\text{s}$.

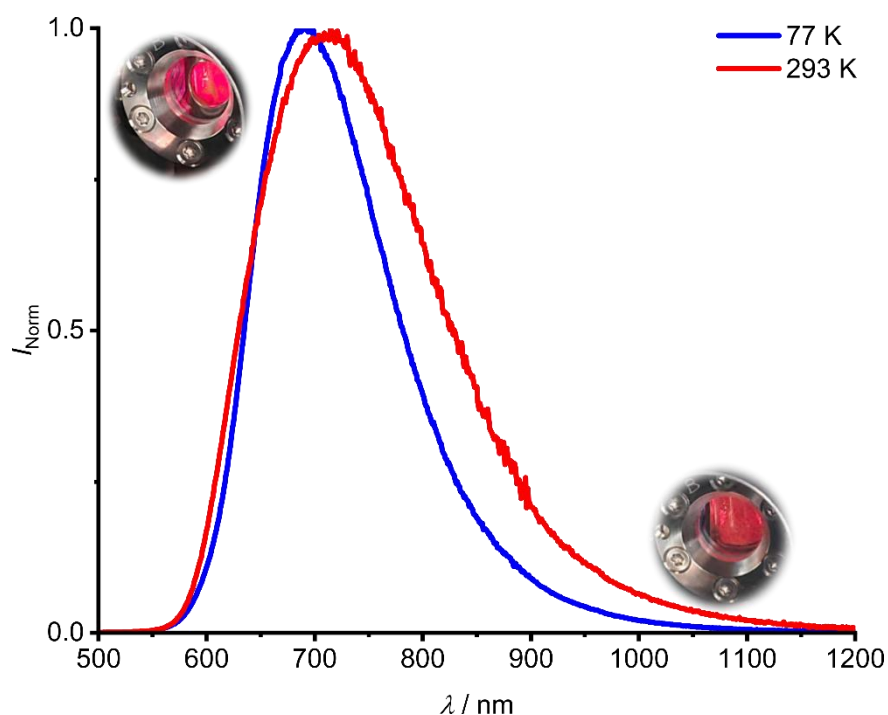


Figure S29. Normalized emission spectra of **1** in the solid state upon $\lambda_{\text{exc}} = 450$ nm excitation at 77 K (blue) and 293 K (red). Inset: Photographs of the red emission at 77 K (left) and 293 K (right).

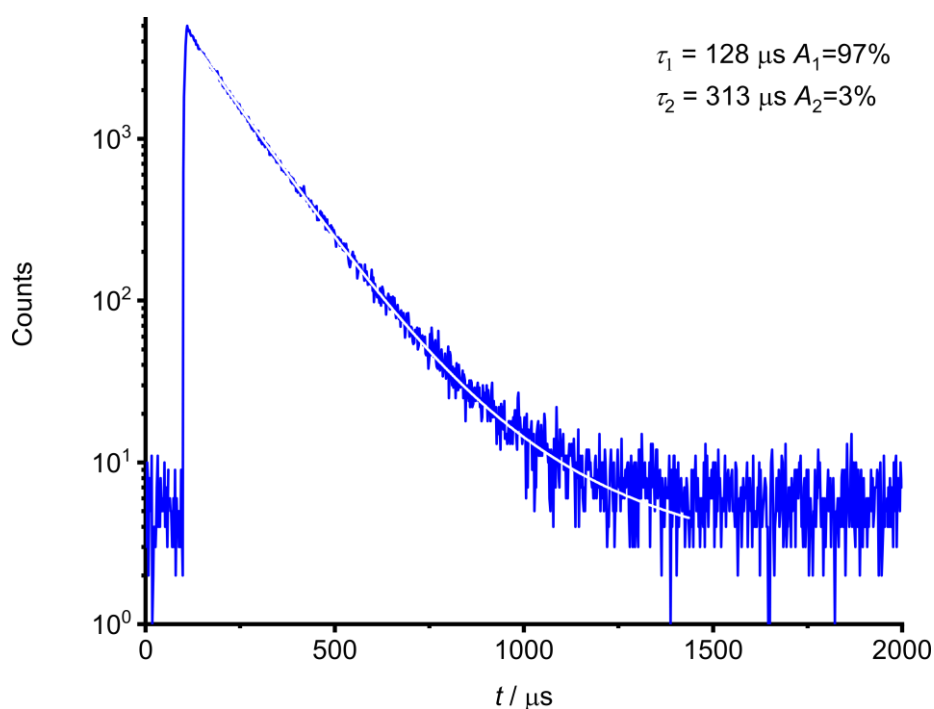


Figure S30. Emission decay curve of **1** in the solid state (blue) upon $\lambda_{\text{exc}} = 450$ nm excitation at $\lambda_{\text{em}} = 700$ nm at 77 K superimposed with biexponential fit (white).

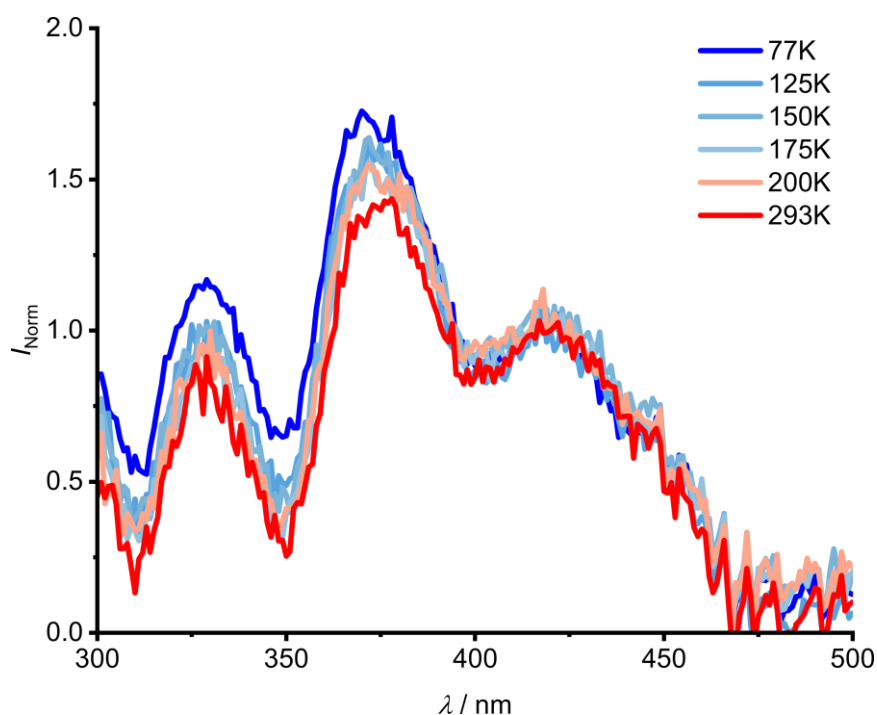


Figure S31. Excitation spectra of **1** at various temperatures in the solid state ($\lambda_{\text{obs}} = 700$ nm). The high absorbance in the solid state and filter effects lead to distorted spectra in the high energy region of the spectra.

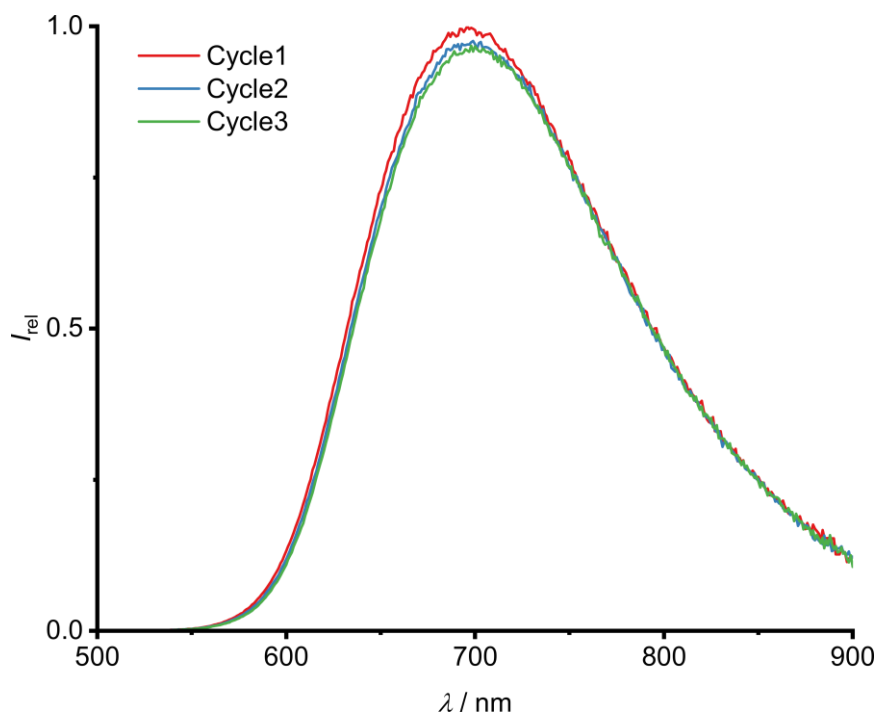


Figure S32. Emission spectra of **1** upon excitation at $\lambda_{\text{exc}} = 450$ nm in the solid state at 150 K after repeating heating and cooling cycles (77–200 K).

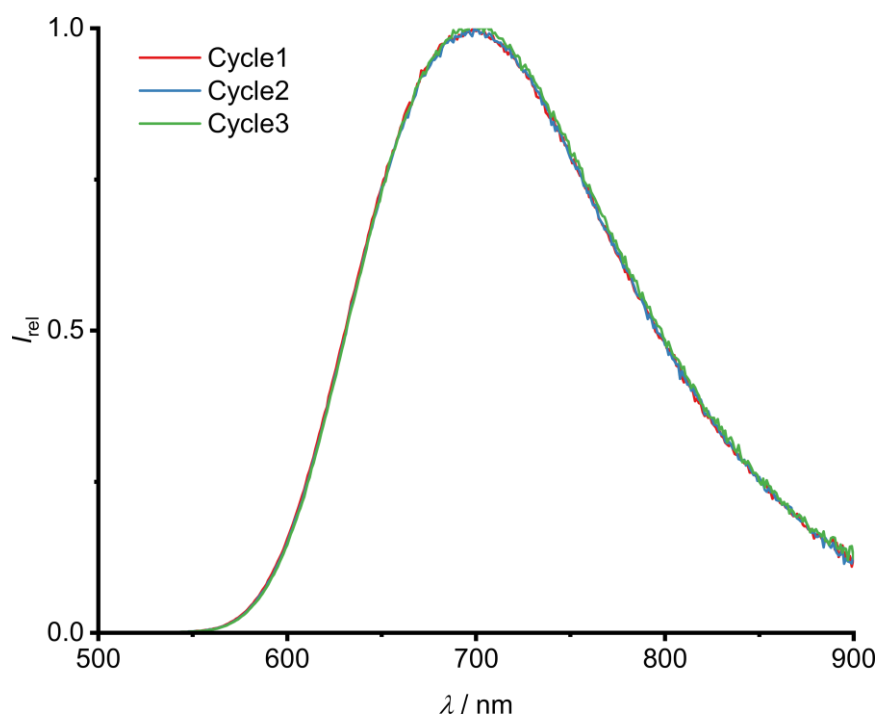


Figure S33. Emission spectra of **1** upon excitation at $\lambda_{\text{exc}} = 450$ nm in the solid state at 175 K after repeating heating and cooling cycles (77–200 K).

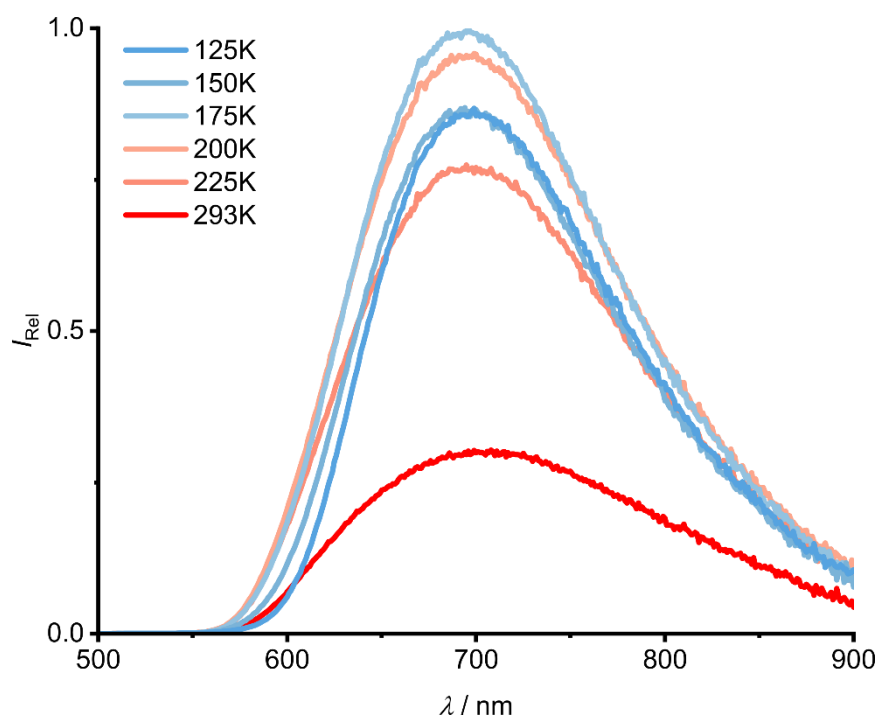


Figure S34. Temperature-dependent emission spectra of **1** upon $\lambda_{\text{exc}} = 420$ nm excitation in the solid state.

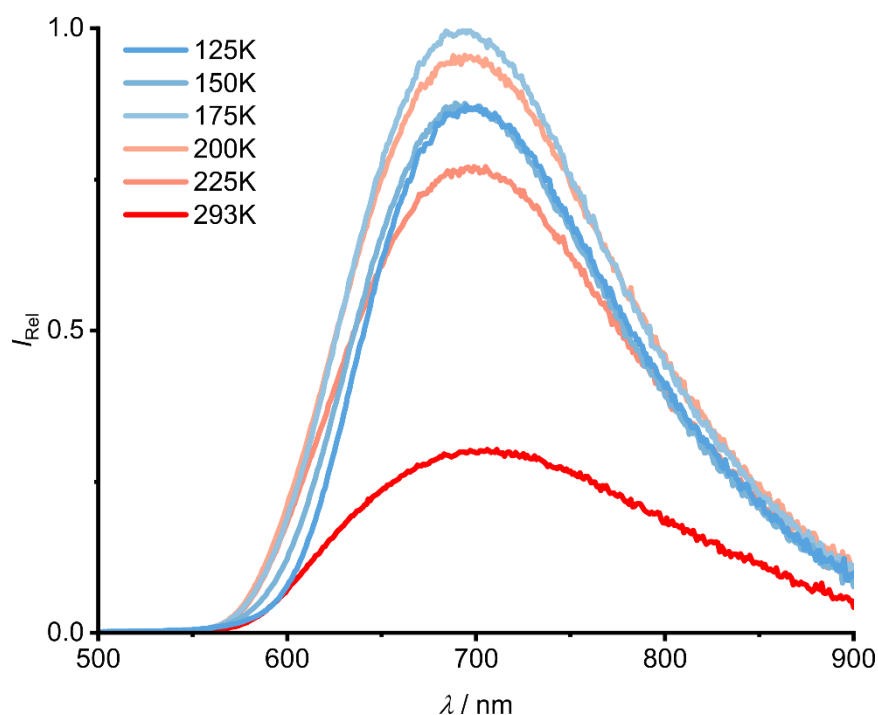


Figure S35. Temperature-dependent emission spectra of **1** upon $\lambda_{\text{exc}} = 480$ nm excitation in the solid state.

Table S4. Fit parameters for the emission decays k_{obs} , k_{nr} and k_r of solid **1** obtained from Arrhenius fits for given temperature regions.

	k_{obs}	temperature regions / K
$E_{a,1} / \text{eV (cm}^{-1}\text{)}$	0.01 (81)	77–100
A_1 / s^{-1}	4.40×10^4	
$E_{a,2} / \text{eV (cm}^{-1}\text{)}$	0.19 (1533)	225–293
A_2 / s^{-1}	7.86×10^9	
	k_{nr}	
$E_{a,1} / \text{eV (cm}^{-1}\text{)}$	0.01 (81)	77–100
A_1 / s^{-1}	4.44×10^4	
$E_{a,2} / \text{eV (cm}^{-1}\text{)}$	0.19 (1533)	225–293
A_2 / s^{-1}	7.70×10^9	
	k_r	
$E_{a,r} / \text{eV (cm}^{-1}\text{)}$	0.11 (887)	175–293
A_r / s^{-1}	1.52×10^6	

Table S5. Relative integrals of the emission bands of solid **1** at various temperatures with photoluminescence quantum yields $\Phi_{p,rel}$ determined relative to the absolute quantum yield Φ_p at 293 K given in Table S3, emission lifetimes τ_p with respective rate constants k_{obs} and radiative and nonradiative rate constants k_r and k_{nr} determined from $\Phi_{p,rel}$ and k_{obs} .

T / K	relative integral	$\Phi_{p,rel}$	$\tau_p / \mu s$	k_{obs} / s^{-1}	k_r / s^{-1}	k_{nr} / s^{-1}
293	1.00	0.0044 ^a	0.221	4.52×10^6	20000	4.5×10^6
275	1.29	0.0056	0.385	2.60×10^6	15000	2.6×10^6
250	1.79	0.0078	0.892	1.12×10^6	8700	1.1×10^6
225	2.35	0.010	2.12 ^b	4.73×10^5	4800	4.7×10^5
200	2.80	0.012	5.00 ^b	2.00×10^5	2400	2.0×10^5
175	2.84	0.012	12.0 ^b	8.33×10^4	1000	8.2×10^4
150	2.48	0.011	27.0 ^b	3.70×10^4	400	3.7×10^4
125	2.54	0.011	51.0 ^b	1.96×10^4	220	1.9×10^4
100	3.78	0.017	86.0 ^b	1.16×10^4	190	1.1×10^4
77	5.52	0.024	128 ^b	7.81×10^3	190	7.6×10^3

^a Absolute photoluminescence quantum yield Φ_p and emission lifetime τ_p see Table S3. ^b Main component (94–98%) of biexponential decay.

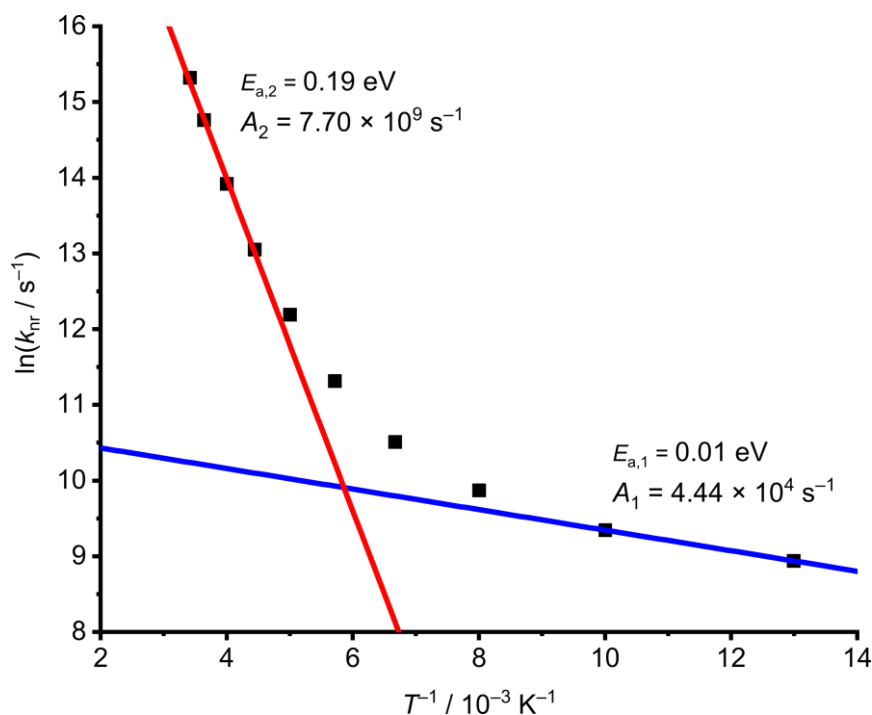
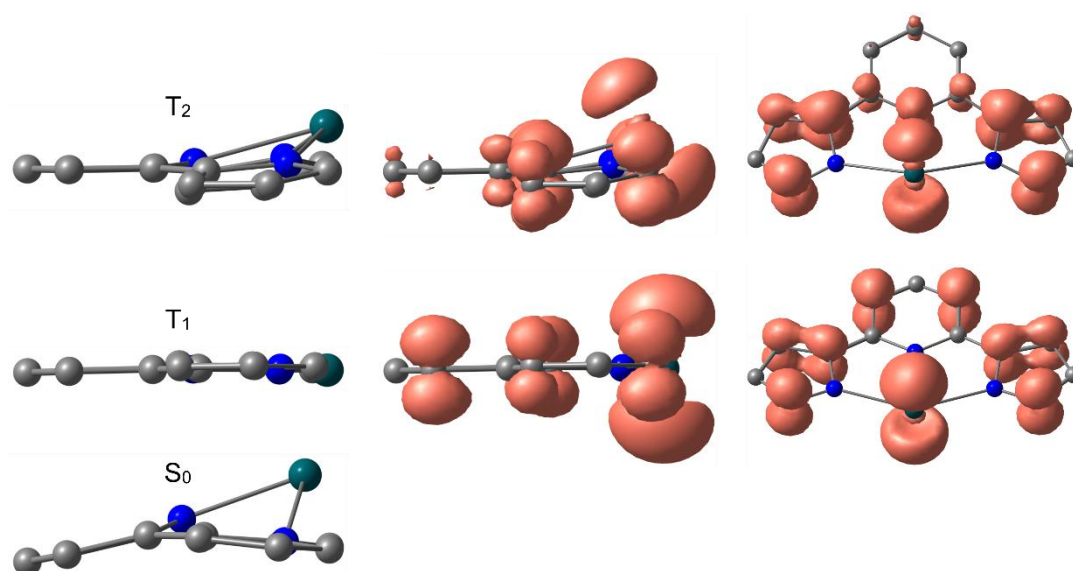
**Figure S36.** Arrhenius plot of the nonradiative rate constants ($k_{nr}(T)$, $T = 77$ – 293 K) of solid **1** with fit parameters obtained from Arrhenius fits in the temperature regions 293 – 225 and 100 – 77 K, respectively.

Table S6. SOC-TDDFT calculated SOCCs in cm^{-1} of **1** as square-root of sum of squares of the SOC matrix elements at the FC geometry.

	T₁	T₂	T₃
S₀	19	69	163
S₁	31	106	72
S₂	46	40	2
S₃	95	70	88

**Figure S37.** DFT optimized geometries of the singlet ground state S_0 and the triplet states T_1 and T_2 with respective spin density plots from the side and front view of **1**. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-ZORA-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn), hydrogen atoms and *tert*-butyl substituents omitted (isosurface value: 0.005).

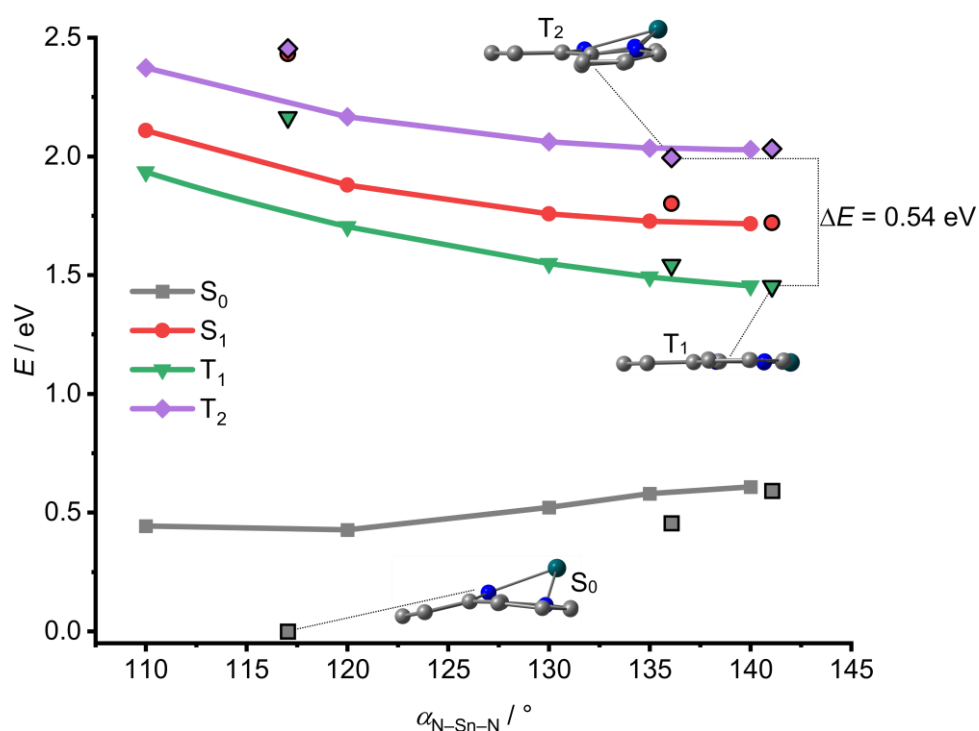


Figure S38. Relaxed potential energy surface scan of **1** as projection along the $\text{N}^{\text{Pyr1}}\text{-Sn-N}^{\text{Pyr2}}$ bending mode on the T_1 hypersurface with energies from TDDFT calculations for the respective S_0 , S_1 , T_1 and T_2 hypersurfaces. Symbols with frame indicate the TDDFT calculated energies from the geometry optimized S_0 , T_1 and T_2 states with energy difference between the relaxed T_1 and T_2 states indicated. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-ZORA-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn), hydrogen atoms and *tert*-butyl substituents omitted.

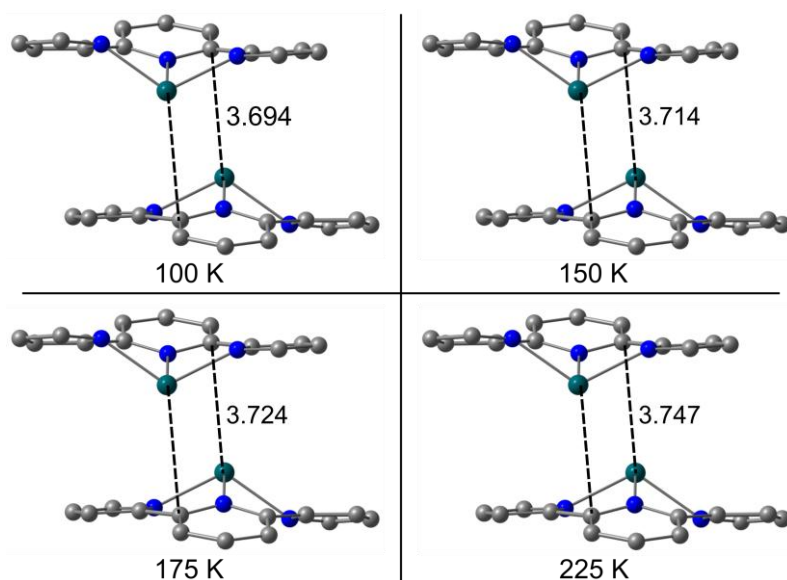


Figure S39. DFT optimized structures (only hydrogen atom positions optimized) of $[\mathbf{1} \cdots \mathbf{1}]^{\text{H}}$ based on the SC-XRD structures of **1** determined at variable temperatures. *tert*-butyl groups were replaced by hydrogens and only the hydrogen carbon bonds were optimized. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-ZORA-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn), hydrogen atoms omitted. $\text{Sn} \cdots \text{C17}'$ distances indicated.

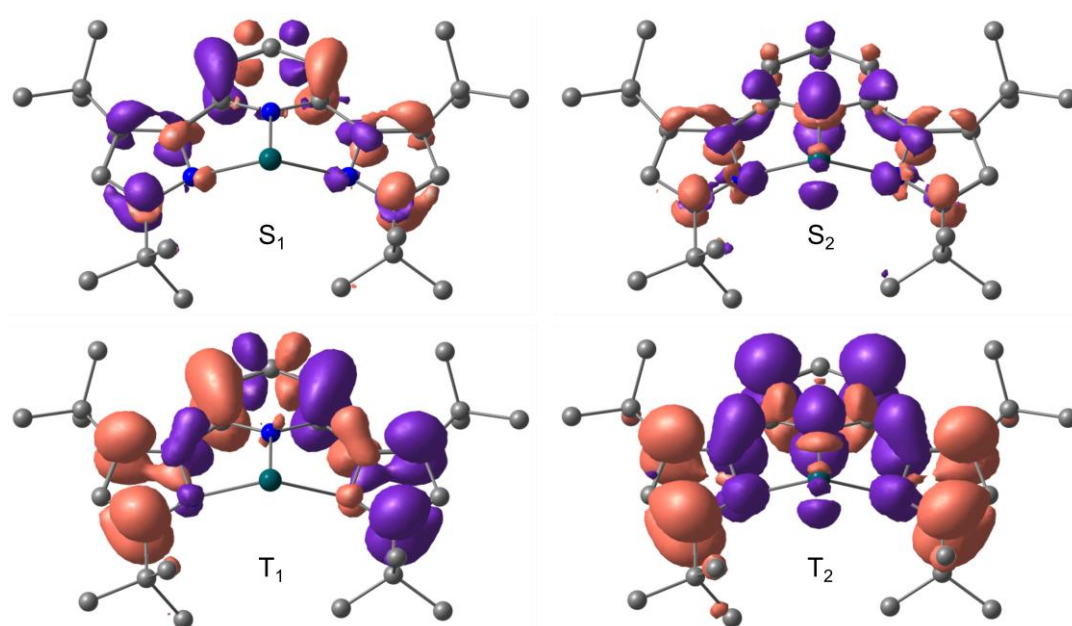


Figure S40. TDDFT calculated transition densities of $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, $S_0 \rightarrow T_1$ and $S_0 \rightarrow T_2$ transitions in **1** (isosurface value: 0.001 a.u.).

Table S7. Selected SOC corrected TDDFT data of $[1\cdots 1]^H$ based on the SC-XRD structures of **1** at variable temperatures. The electronic states of $[1\cdots 1]^H$ deriving from the same state in monomeric **1** are denoted $T_{n,+}/T_{n,-}$ and $S_{n,+}/S_{n,-}$ without distinguishing the M_S spin sublevels of the triplet states.

100 K				150 K		
states	energy / cm^{-1}	λ / nm	f	energy / cm^{-1}	λ / nm	f
$T_{1,-}$	18577	538.3	0	18584	538.1	0
$T_{1,-}$	18578	538.3	0	18585	538.1	0
$T_{1,-}$	18578	538.3	0	18585	538.1	0
$T_{1,+}$	18593	537.8	1.37×10^{-6}	18607	537.4	2.06×10^{-6}
$T_{1,+}$	18593	537.8	3.470×10^{-7}	18607	537.4	4.63×10^{-7}
$T_{1,+}$	18594	537.8	7.91×10^{-6}	18608	537.4	7.23×10^{-6}
$T_{2,+}$	20862	479.3	4.21×10^{-3}	20897	478.5	5.65×10^{-3}
$T_{2,+}$	20877	479.0	1.48×10^{-6}	20914	478.2	1.49×10^{-6}
$T_{2,+}$	20877	479.0	4.47×10^{-6}	20914	478.2	2.00×10^{-9}
$S_{1,-}$	20893	478.6	0	20914	478.2	6.40×10^{-6}
$T_{2,-}$	20943	477.5	0	20990	476.4	0
$T_{2,-}$	20943	477.5	0	20990	476.4	0
$T_{2,-}$	21074	474.5	0	21078	474.5	0
$S_{1,+}$	21363	468.1	1.51×10^{-1}	21337	468.7	1.51×10^{-1}
175 K				225 K		
states	energy / cm^{-1}	λ / nm	f	energy / cm^{-1}	λ / nm	f
$T_{1,-}$	18571	538.5	0	18525	539.8	0
$T_{1,-}$	18572	538.5	0	18526	539.8	0
$T_{1,-}$	18572	538.5	0	18526	539.8	0
$T_{1,+}$	18595	537.8	1.50×10^{-6}	18553	539	1.62×10^{-6}
$T_{1,+}$	18595	537.8	2.62×10^{-7}	18553	539	2.28×10^{-7}
$T_{1,+}$	18596	537.8	7.05×10^{-6}	18554	539	7.05×10^{-6}
$T_{2,+}$	20912	478.2	5.74×10^{-3}	20867	479.2	0
$T_{2,+}$	20923	478	1.70×10^{-8}	21005	476.1	1.60×10^{-2}
$T_{2,+}$	20929	477.8	1.68×10^{-6}	21036	475.4	2.37×10^{-6}
$S_{1,-}$	20929	477.8	3.50×10^{-6}	21036	475.4	2.75×10^{-6}
$T_{2,-}$	21002	476.1	0	21100	473.9	0
$T_{2,-}$	21002	476.1	0	21100	473.9	0
$T_{2,-}$	21085	474.3	2.00×10^{-9}	21128	473.3	0

$S_{1,+}$	21349	468.4	1.51×10^{-1}	21274	470.1	1.29×10^{-1}
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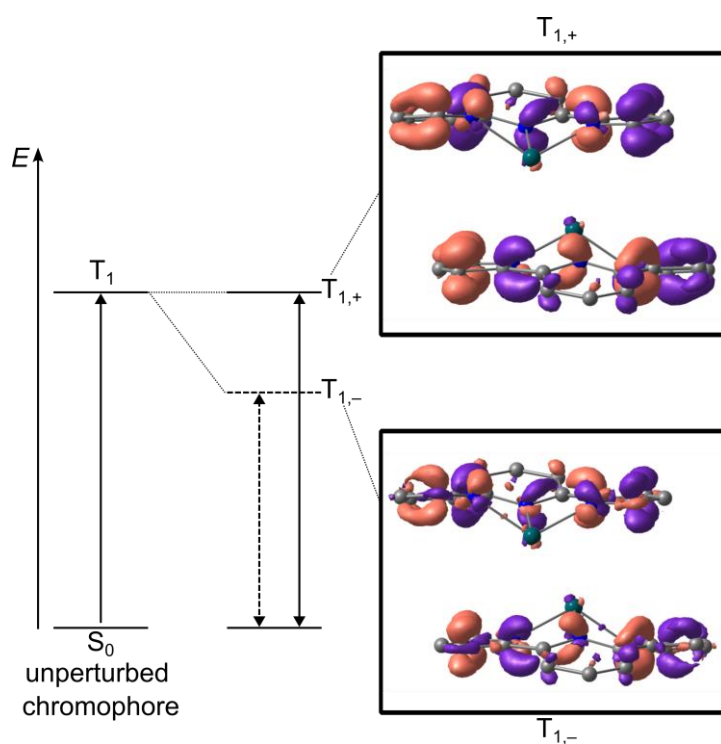


Figure S41. Qualitative energy diagram and SOC-TDDFT calculated $S_0 \rightarrow T_{1,-}/T_{1,+}$ transition densities of $[1 \cdots 1]^H$ derived from the $S_0 \rightarrow T_1$ transition of **1** (isosurface value: 0.001 a.u.).

6.3 Supporting Information: The Overlooked Dual Phosphorescence in *Lappert's* Diamino Stannylene

Supplementary Information

General

All reactions and measurements were performed under argon atmosphere unless otherwise noted. Gloveboxes (UniLab/MBraun – Ar 4.8, O₂ < 1 ppm, H₂O < 0.1 ppm) were used to store and weigh sensitive compounds for synthesis as well as to prepare samples that require absence of oxygen and water. The reagents were purchased from commercial suppliers (ABCR, Acros Organics, Alfa Aesar, Fischer Scientific and Sigma Aldrich). *n*-pentane and 3-methylpentane were dried and distilled from sodium. C₆D₆ was purchased from euriso-top and Deutero GmbH and was dried and distilled from potassium and stored over molecular sieve (3 Å).

NMR spectra were recorded on a *Bruker Avance NEO* or a *Bruker Avance DRX 400* spectrometer at 400.42 MHz (¹H) and 149.23 MHz (¹¹⁹Sn). All data were evaluated with the software *MestReNova 12.0.4-22023*. All resonances are reported in ppm versus the solvent signal as internal standard ¹H NMR: C₆D₆: δ = 7.16 ppm^[1] or versus an external standard for ¹¹⁹Sn NMR (SnMe₄, δ = 0 ppm). (s) = singlet.

UV/Vis absorption spectra were recorded on a V-770 from JASCO or a Cary-5000 spectrometer from Agilent using *d* = 1.00 cm quartz cuvettes with a Schott valve. Measurements at low temperatures were carried out using a liquid nitrogen cooled cryostat *Optistat DN* from Oxford Instruments equipped with 1 cm quartz tubes. Concentration dependent measurements at low temperatures and room temperature were conducted with a special self-made quartz cell (*d* = 0.2 cm) surrounded with a PEEK frame.

Steady-state emission spectra and photoluminescent decay curves (solution and solid-state samples) were measured with a *FLS1000* spectrometer from Edinburgh Instruments equipped with a cooled photomultiplier PMT-980 and a high-speed photomultiplier HSPMT-920 (< 300 ps resolution). A xenon arc lamp Xe2 (450 W) was used for excitation in steady-state measurements. Time-resolved luminescence experiments were conducted using the μ s-xenon-flashlamp μ F2 (pulse width ca. 2 μ s) or a picosecond pulsed diode laser EPL-375 as excitation source. For time resolved emission spectra, a pulsed diode laser VPL-450 was used as excitation source. Measurements at low temperature were carried out using a liquid nitrogen cooled cryostat *Optistat DN* from Oxford Instruments. Single lifetime decays were evaluated with the software *Fluoracle* provided by Edinburgh Instruments. The data of the time-resolved emission spectra were analysed globally with the open-source Python based data analysis tool *KiMoPack 7.4.9*.^[2] Absolute luminescence quantum yields Φ were determined using a *MicrostatN* from Oxford Instruments combined with a Cryosphere from Edinburgh Instruments. Relative uncertainty of Φ is estimated to be $\pm 10\%$.

Stern-Volmer quenching experiments were carried out in long-neck inert gas quartz cuvettes (*d* = 1.0 cm) with a Schott valve. Emission lifetimes and emission spectra were recorded at various concentrations of Sn in pentane. The emission lifetimes were measured with a picosecond pulsed diode laser EPL-375 as excitation source. The corresponding emission spectra were recorded upon excitation λ_{exc} = 490 nm (S₀ $\rightarrow$ T₁) to guarantee a homogenous excitation in the sample within the concentration range. UV/Vis absorption spectra were measured for each concentration to correct the emission intensities by the respective absorbance.

fs-Transient absorption experiments were conducted using a *Helios* pump-probe setup from Ultrafast Systems paired with a regeneratively amplified 1030 nm laser (*Pharos, Light Conversion*, 1030 nm, < 175 fs, 2 mJ). The effective laser repetition rate of 2 kHz was set via an internal pulse picker. A small portion of the 1030 nm fundamental was directed to the optical delay line and was subsequently used to generate broadband probe light by focusing the beam onto a sapphire for measurements in the Vis/NIR range (450 nm – 900 nm). In the UV/Vis spectral range (330 nm – 500 nm), the second harmonic was focused onto a second sapphire. The pump pulse was generated with an optical parametric amplifier (*Apollo Y, Ultrafast Systems*) and the beam diameter at the sample was adjusted to 100 μ m – 150 μ m at the sample to assure homogeneous excitation of the observation volume, which is defined by the probe diameter (ca. 20 μ m). At room temperature, the samples were measured under argon atmosphere in a quartz cuvette (*d* = 1 mm). To correct artefacts due to emission and scattering, a second chopper was installed along the probe beam. Measurements at low temperature were carried out using a liquid nitrogen cooled cryostat *Optistat DN* from Oxford Instruments. For measurements at

low temperatures, samples were prepared in an air and moisture tight special quartz cell ($d = 0.2$ cm) surrounded with a PEEK frame (time resolution of ≤ 200 fs for all experiments). Preprocessing of the data, including chirp and baseline correction, has been performed using the *Surface Xplorer 4.3.0* software from *Ultrafast Systems*. The open-source *Python* based data analysis tool *KiMoPack 7.4.9*^[2] was employed for global analysis of the TA data.

ns-Transient absorption experiments were carried out using a modified version of the described fs-transient absorption spectroscopy setup. For this purpose, the *EOS* add-on has been employed, which uses a photonic crystal fiber-based supercontinuum laser as probe light source. In contrast to the fs measurements, the pump-probe time delay is controlled electronically with a time resolution of < 1 ns. The sample preparation and data analysis were carried out as described for the fs-transient absorption experiments.

Photolysis experiments were conducted by irradiating deaerated solutions of **Sn** in inert gas cuvettes ($d = 1$ cm). An Ultra-High Power collimated LED from *Prizmatix* (UHP-T-405-DI) with an emission maximum at 412 nm was used for irradiation. The output power (determined with a high-sensitive thermal power head S425C from *Thorlabs*) was adjusted to $P = 0.55$ W with an UHPTLCC-02-USB controller for all experiments. The beam was focused onto the cuvette with a plano convex lens. At the cuvette, the beam diameter amounts to 0.5 cm. The temperature of the irradiated solution was kept at 20 °C with a Peltier module.

Irradiation (total irradiation time 15 min) of **Sn** at $\lambda_{exc} = 412$ nm in *n*-pentane leads to tin(III) radical formation, which was followed by UV/Vis absorption spectroscopy and confirmed by EPR spectroscopy. The absorption (A_{350nm} , initial two minutes) versus time plots were fitted linearly for all concentrations (see Figure S43.). Using Lambert-Beer's law, the degradation rates $\dot{N}_{deg}$ were obtained from the slopes $\dot{A}_{350nm}$ of the fits (eq. 1)

$$\frac{dA_{350nm}}{dt} = \dot{A}_{350nm} = \Delta\epsilon_{350nm}d\dot{c} = \frac{\Delta\epsilon_{350nm}d}{VN_A}\dot{N}_{deg} \Leftrightarrow \dot{N}_{deg} = \frac{\dot{A}_{350nm}VN_A}{\Delta\epsilon_{350nm}d} \quad (1)$$

$\Delta\epsilon_{350nm}$ is the difference between the molar absorption coefficients of the photolysis product and **Sn** at 350 nm, d is the optical path length (1 cm), V is the volume of the sample (3 mL) and N_A is the Avogadro constant.

For a non-monochromatic light source, the rate of photon absorption $\dot{N}_{abs}(\lambda)$ is given by eq. 2.

$$\dot{N}_{abs}(\lambda) = \dot{N}_{LED}(\lambda) (1 - 10^{-A(\lambda)}) \quad (2)$$

$\dot{N}_{LED}(\lambda)$ is the rate of photons emitted at the corresponding wavelength and is obtained from the emission spectrum of the UHP-LED, which is multiplied with the photon energy $\frac{hc}{\lambda}$ at the respective wavelength. The spectral area is approximated as sum of intensities in 0.5 nm steps and normalised to the output power of $P = 0.55$ W. The number of emitted photons is obtained from division by $\frac{hc}{\lambda}$. $A(\lambda)$ is the initial absorbance of the sample and is assumed to be constant for the first two minutes. The total rate of photon absorption $\dot{N}_{abs}$ is given by the sum of all $\dot{N}_{abs}(\lambda)$ in the wavelength range 370 – 480 nm (eq. 3).

$$\dot{N}_{abs} = \sum_{\lambda} \dot{N}_{abs}(\lambda) \quad (3)$$

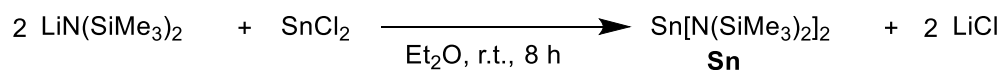
The photodegradation quantum yield Φ_{deg} is defined as the ratio between the number of degraded molecules N_{deg} and the total number of absorbed photons N_{abs} , which equals with the ratio between the degradation rate $\dot{N}_{deg}$ of the chromophore and the total rate of photon absorption $\dot{N}_{abs}$ (eq. 4).

$$\Phi_{deg} = \frac{N_{deg}}{N_{abs}} = \frac{\dot{N}_{deg}}{\dot{N}_{abs}} \quad (4)$$

X-band cw-electron paramagnetic resonance measurements were carried out using a *Magnettech Miniscope MS 300* in 3-methylpentane at 293 K. *g* values are referenced to external Mn^{2+} in ZnS ($g = 2.118(1), 2.066(1), 2.027(2), 1.986(2), 1.946(1), 1.906(1)$). Microwave frequency: 9.427917 GHz, center field: 338 mT, sweep: 20 mT, modulation amplitude 0.2 mT, receiver gain = 10, microwave attenuation 10 dB, sweep time: 90 s. Simulations of the experimental spectra were performed with *garlic* (isotropic, fast-motional cw-EPR spectra) of *EasySpin* (5.2.35) for *Matlab R2020a*.^[3]

Density functional theory calculations were performed with *Orca 5.0.4*.^[4,5] Geometry optimisation was performed using (un-)restricted Kohn-Sham orbitals DFT (UKS/RKS) and the B3LYP functional^[6–8] in combination with Ahlrich's split valance triple-zeta basis set def2-TZVPP^[9] and SARC-ZORA-TZVPP^[10] (Sn) with the auxiliary basis SARC/J^[11–14]. Tight convergence criteria were chosen for DFT calculations (keywords TIGHTSCF and TIGHTOPT). All DFT calculations make use of the resolution of identity (Split-RI-J) approach for the Coulomb term in combination with the chain-of-spheres approximation for the exchange term (keyword RIJCOSX^[15,16]). The zeroth order regular approximation was used to describe relativistic effects in all calculations (keyword ZORA).^[11–14,17,18] To account for solvent effects, a conductor-like screening model (keyword CPCM(hexane)) modelling hexane was used in all calculations.^[19,20] Atom-pairwise dispersion correction was performed with the Becke-Johnson damping scheme (keyword D3BJ^[21,22]). A numerical frequency calculation confirmed that the optimised geometry corresponds to a minimum structure or a transition state structure, respectively. The 2D relaxed potential energy surface scans with 72 points were performed on the CPCM(hexane)-RIJCOSX-(U)B3LYP-D3BJ-def2/J-def2-SVP level with subsequent single-point calculations at higher level (CPCM(hexane)-RIJCOSX-(U)B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)). Transition states were localised, using the OPTTS keyword and assigned with a subsequent calculation of the internal reaction coordinate (keyword IRC). Fifty spin-allowed transitions were calculated by TDDFT. Spin Orbit Coupling (SOC) TDDFT calculations were performed using the additional keyword RI-SOMF(1X).^[23] Twenty vertical spin-forbidden transitions were localised with TRIPLETS TRUE as keyword. The charge transfer number analyses of the TDDFT calculated transitions were done using *TheoDORE 2.4*.^[24] All calculations were computed on the supercomputer Elwetritsch and advisory services offered by the RPTU Kaiserslautern-Landau (<https://hpc.rz.rptu.de>); which is a member of the AHRP. All coordinates are provided in an additional xyz file.

I Synthesis



Sn[N(SiMe₃)₂]₂ (Sn): Sn was prepared according to modified literature procedures.^[25–27] In a Schlenk tube, lithium bis(trimethylsilyl)amide (21.20 g, 127 mmol, 2 eq) was combined with tin dichloride (12.00 g, 63 mmol, 1 eq). Diethylether (300 mL) was added slowly under strong stirring and cooling (ice-water bath). Immediately, the cloudy colourless mixture turned orange and the reaction was stirred for 8 h at room temperature. The resulting LiCl was removed from the solution by filtration and the solvent was removed under reduced pressure resulting an orange oil. The crude product was distilled under reduced pressure leading the desired product as a red-orange oil, which solidified with liquid nitrogen cooling to a yellow-orange solid. (20.22 g, 46 mmol, 73%), ¹H NMR (400 MHz, C₆D₆): δ = 0.29 (s, CH₃) ppm. ¹¹⁹Sn NMR (149 MHz, C₆D₆): 766.6 ppm. UV/Vis (*n*-pentane): λ (ε) = 490 (31), 389 (1830), 287 nm (3080 M⁻¹ cm⁻¹). The data match literature values.^[27–29]

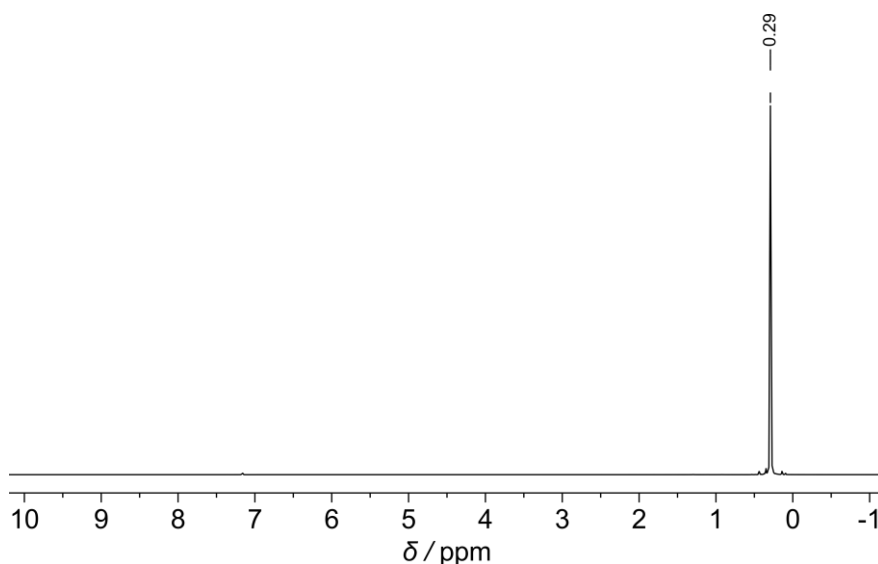


Figure S1. ¹H NMR spectrum of **Sn** in C₆D₆.

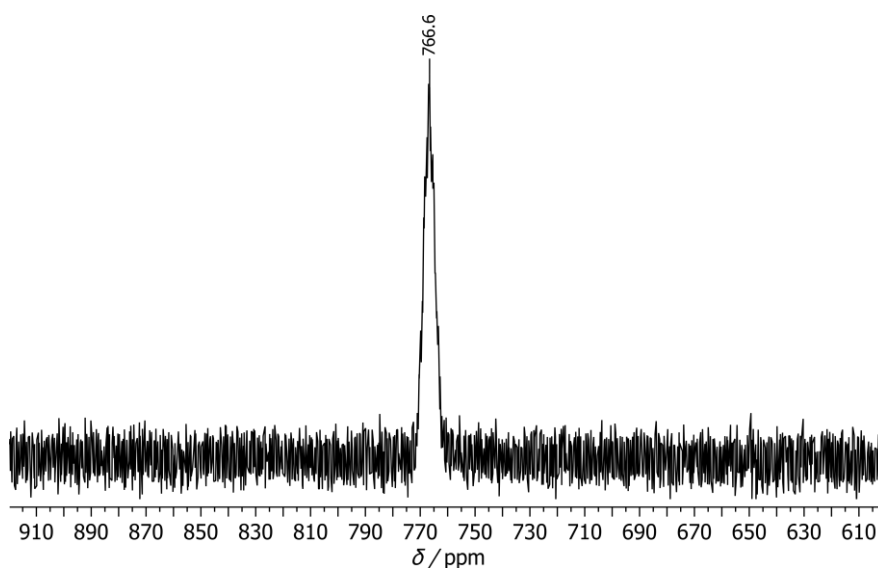


Figure S2. ¹¹⁹Sn NMR spectrum of **Sn** in C₆D₆.

II Photophysical Properties

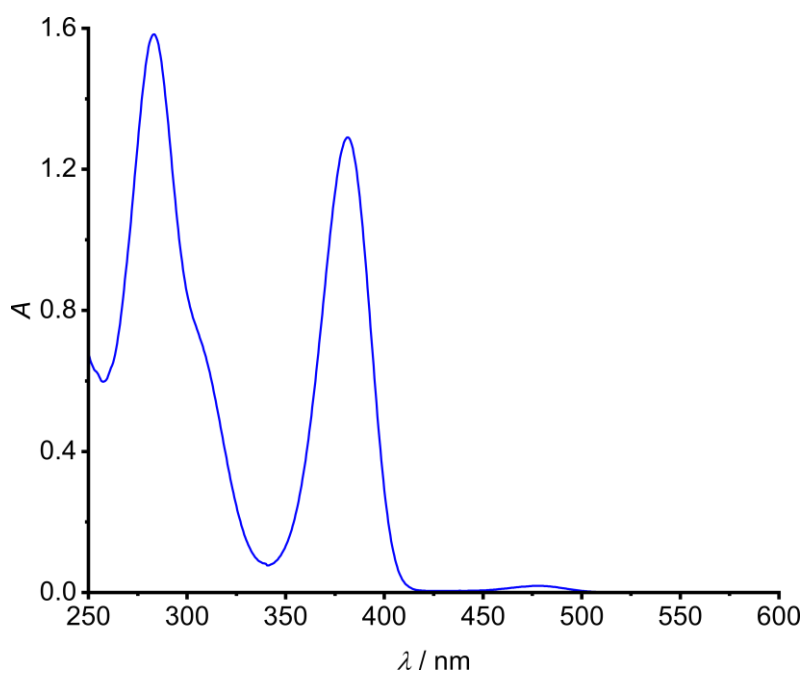


Fig. S3. UV/Vis absorption spectrum of **Sn** ($c = 0.36$ mM) in 3-methylpentane at 77 K.

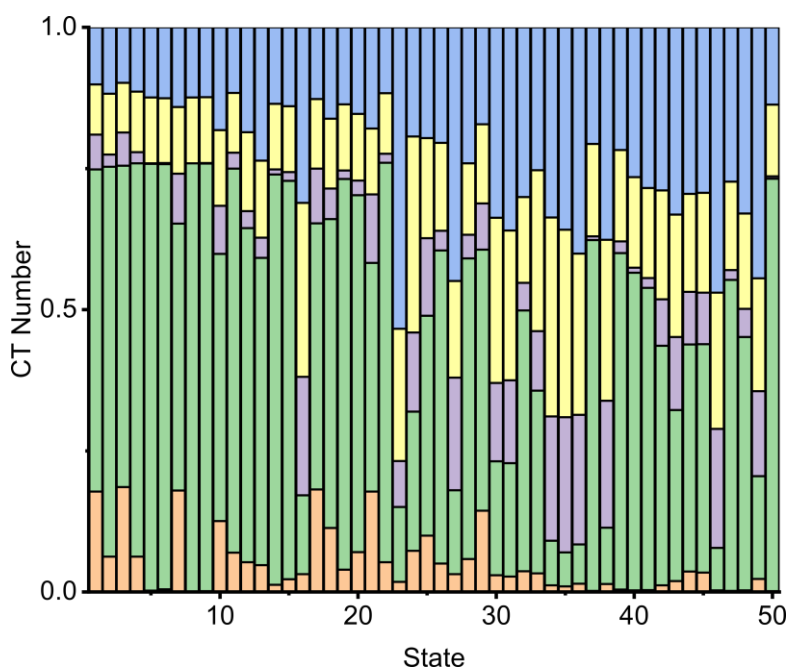


Figure S4. Charge transfer number analysis of the 50 lowest spin-allowed transitions of **Sn** (orange: MC, green: LMCT, purple: MLCT; yellow: LLCT, blue: LC). CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn).

Table S1. Selected molecular orbitals of **Sn** with energies given in eV, displayed at an isosurface value 0.06 a.u.. Mulliken symbol of the orbital character given in idealised C_{2v} point group of the N-Sn-N unit. Hydrogen atoms omitted. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

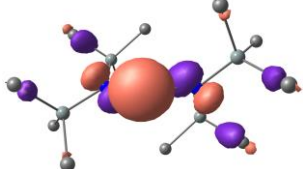
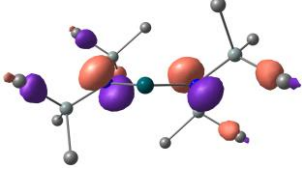
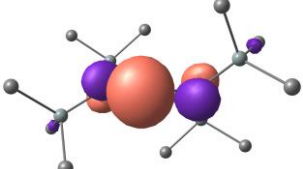
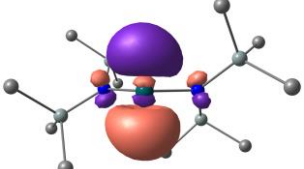
HOMO-2(a ₂) / -6.8171	HOMO-1(b ₂) / -6.4389	HOMO(a ₁) / -5.9203	LUMO(b ₂) / -1.9977
			

Table S2. SOC constants as square root of the sum of the squares of SOC matrix elements in cm^{-1} between the lowest singlet and triplet states derived from SOC-TDDFT calculations on the geometry optimised GS structure of **Sn**. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

triplet states	singlet states			
	S ₀	S ₁	S ₂	S ₃
T ₁	945	94	282	120
T ₂	63	194	48	112
T ₃	654	15	224	8

Table S3. SOC corrected TDDFT transitions of **Sn** with energies E in cm^{-1} and wavelengths λ in nm and oscillator strengths f . CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

State	Energy / cm^{-1}	λ / nm	f
S ₁	24927	401.2	0.033964539
S ₂	29745	336.2	0.013170607
S ₃	32309	309.5	0.059986636
T ₁	19510	512.6	0.000000300
	19534	511.9	0.000273717
	19569	511.0	0.002700203
T ₂	26223	381.3	0.000000473
	26228	381.3	0.000005283
	26259	380.8	0.001629286
T ₃	28386	352.3	0.003692885
	28402	352.1	0.000013474
	28412	352.0	0.000021312

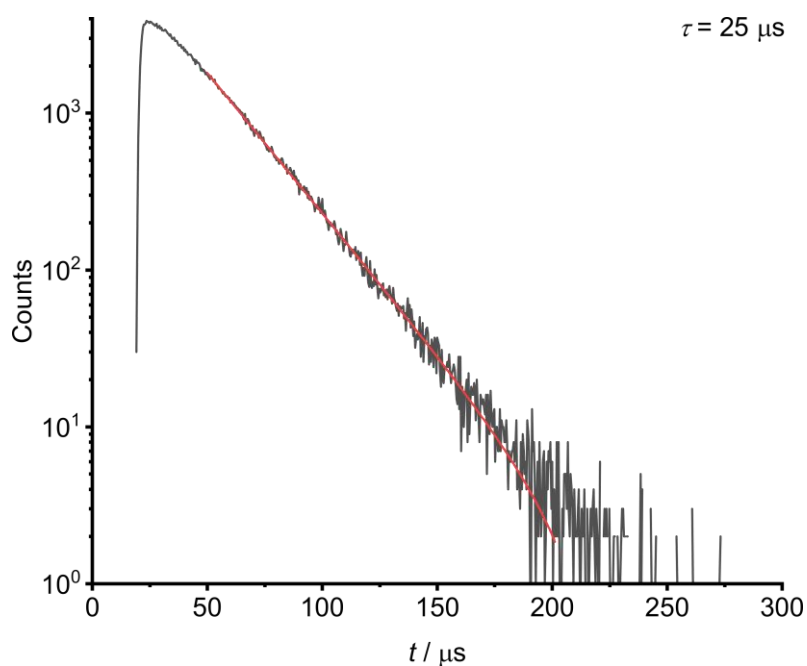


Figure S5. Emission decay curve of **Sn** in 3-methylpentane at $\lambda_{\text{em}} = 560$ nm upon $\lambda_{\text{exc}} = 390$ nm excitation (pulse width = 2 μs) at 77 K superimposed with monoexponential fit (red curve).

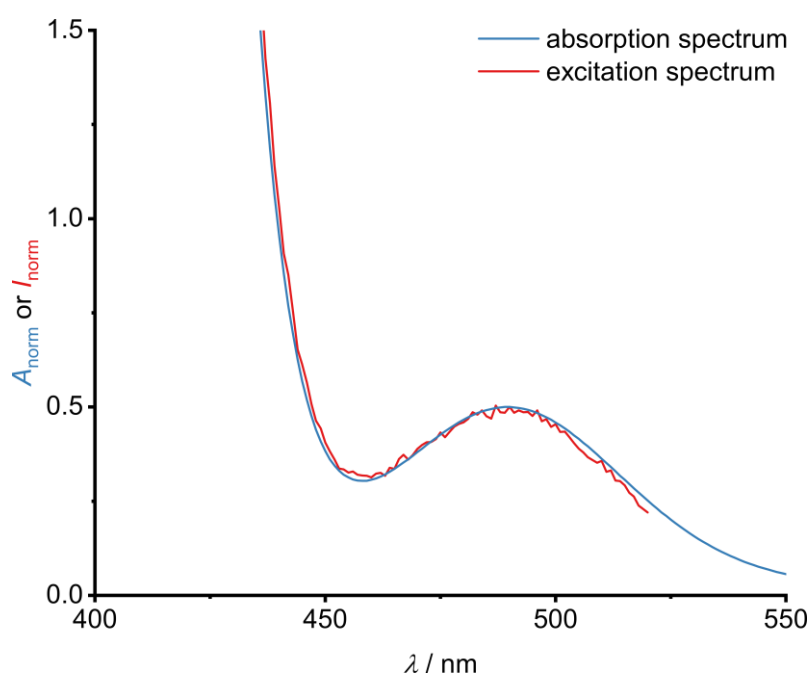


Figure S6. Excitation spectrum of **Sn** in 3-methylpentane at 293 K ($\lambda_{\text{em}} = 640$ nm $c = 2.5$ mM, red) and UV/Vis absorption spectrum of **Sn** in 3-methylpentane at 293 K ($c = 1.7$ mM, blue).

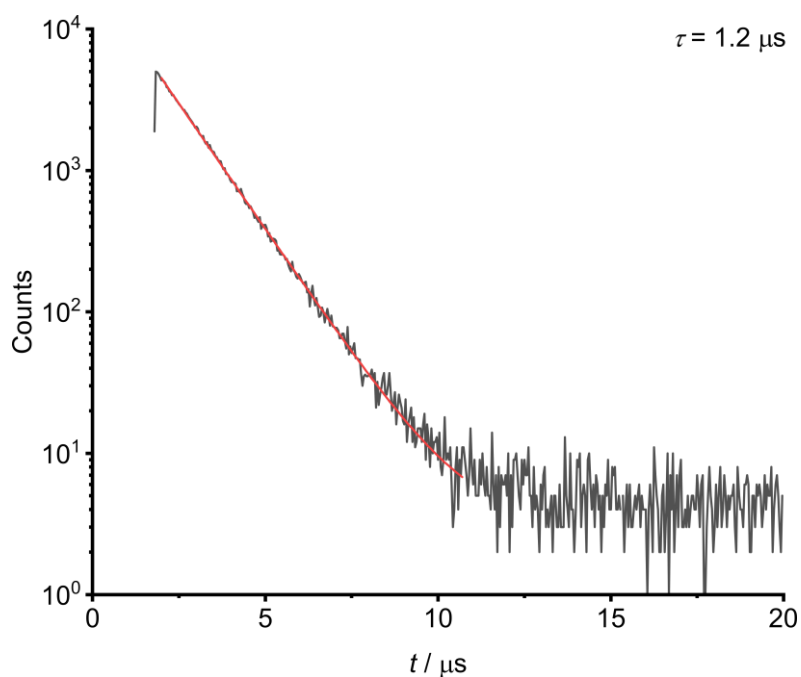


Figure S7. Emission decay curve of **Sn** in *n*-pentane upon $\lambda_{\text{exc}} = 375$ nm excitation at $\lambda_{\text{em}} = 640$ nm at 293 K superimposed with monoexponential fit (red curve) ($c = 0.32$ mM).

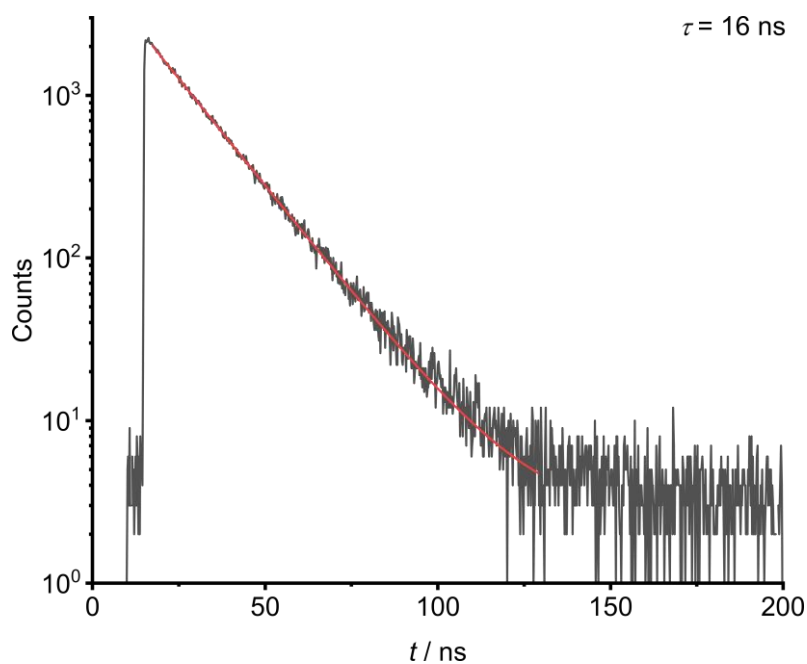
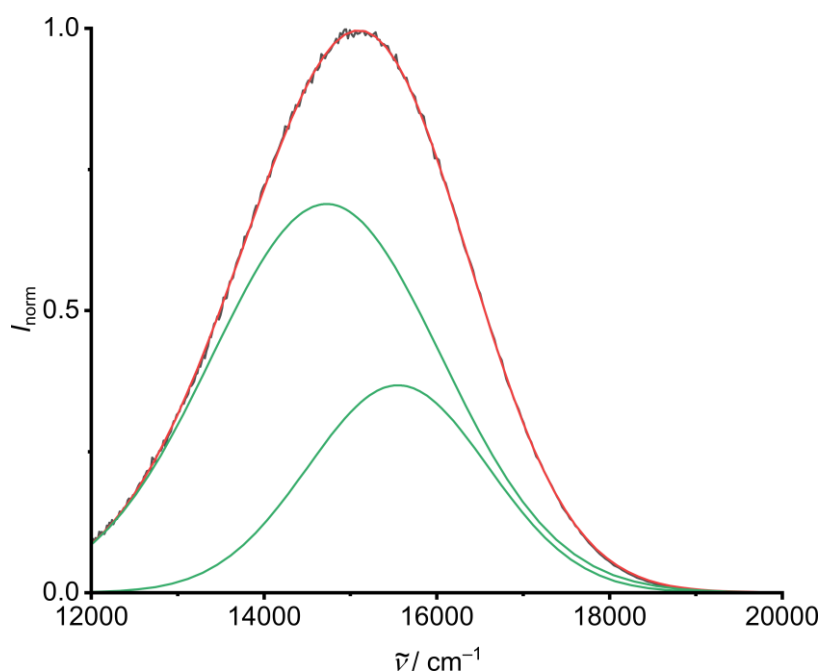


Figure S8. Emission decay curve of **Sn** in *n*-pentane upon $\lambda_{\text{exc}} = 375$ nm excitation at $\lambda_{\text{em}} = 640$ nm at 293 K superimposed with monoexponential fit (red curve) ($c = 25$ mM).



Type	Area	FWHM / cm ⁻¹	Max Height	Centre / cm ⁻¹	Area ratio / %
Voigt	2268	3134	0.69	14725	70
Voigt	961	2459	0.37	15552	30

Figure S9. Emission spectrum of **Sn** in 3-methylpentane at 293 K in black overlayed with two Voigt functions. Fit components shown in green and the cumulative fit in red with fit parameters.

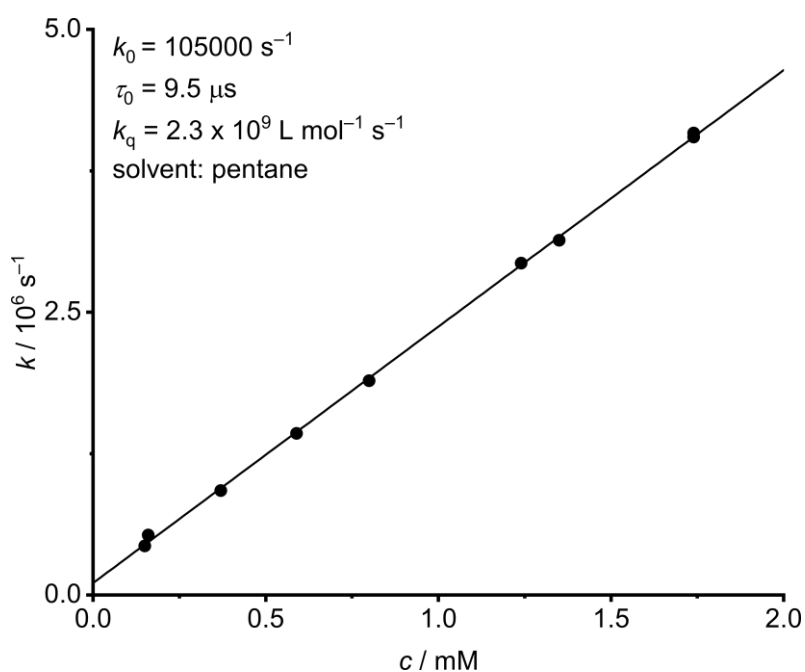


Figure S10. Modified Stern-Volmer plot of quenching rate constants of **Sn** in *n*-pentane upon $\lambda_{\text{exc}} = 375$ nm excitation ($S_0 \rightarrow S_1$) with $\lambda_{\text{em}} = 640$ nm at 293 K at various concentrations with linear fit.

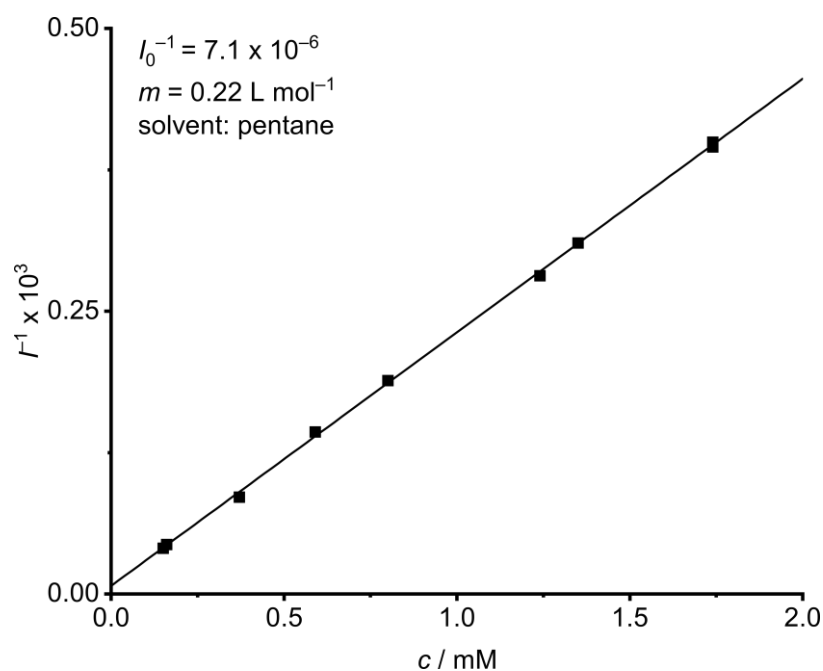


Figure S11. Modified Stern-Volmer plot of the reciprocal emission intensity from absorption corrected integration of **Sn** in *n*-pentane, emission upon $\lambda_{\text{exc}} = 490 \text{ nm}$ excitation ($S_0 \rightarrow T_1$, to omit self-absorption) at 293 K at various concentrations with linear fit.

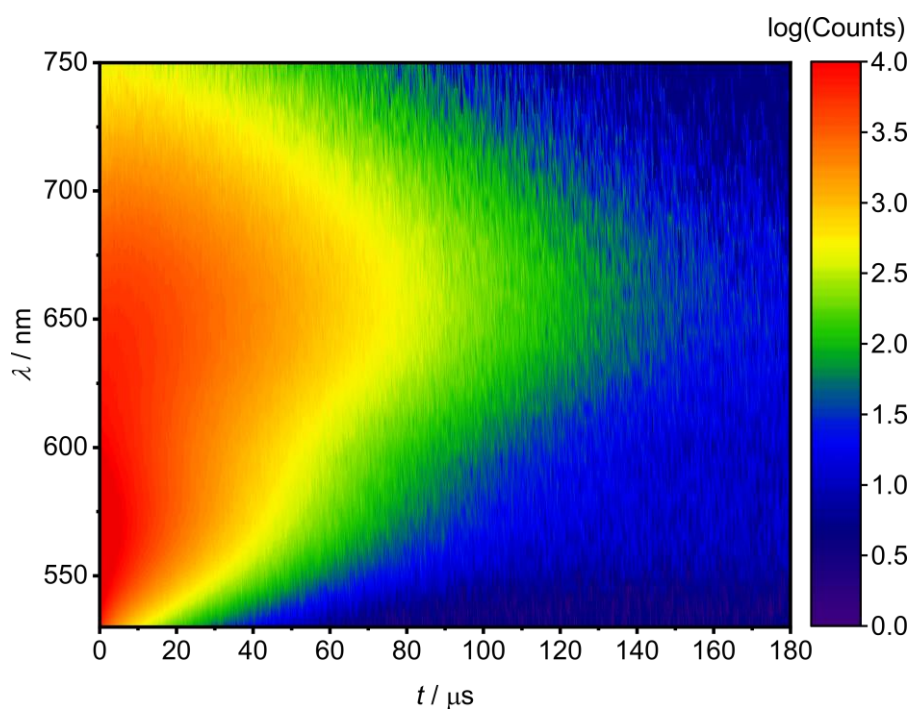


Fig. S12. Colour map of the time-resolved emission spectra of **Sn** in 3-methylpentane obtained upon $\lambda_{\text{exc}} = 450 \text{ nm}$ laser excitation at 95 K.

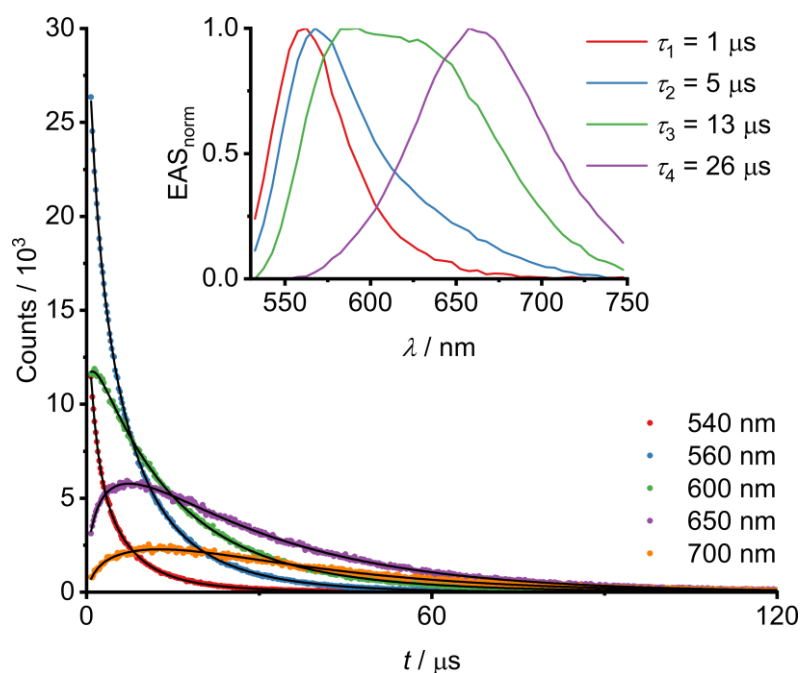


Figure S13. Emission decay curves of **Sn** in 3-methylpentane upon $\lambda_{exc} = 450$ nm laser excitation at 95 K at selected wavelengths with multiexponential fits obtained by global analysis (black curve, $\tau_1 = 1 \mu$ s, $\tau_2 = 5 \mu$ s, $\tau_3 = 13 \mu$ s, $\tau_4 = 26 \mu$ s, sequential model). Inset: Evolution associated spectra acquired from global analysis.

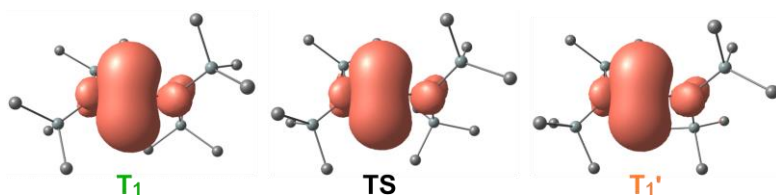


Figure S14. DFT calculated optimised geometries of the triplet states T_1 and T_1' and the $T_1 \leftrightarrow T_1'$ transition state of **Sn** with spin densities (isosurface value 0.005 a.u.). Hydrogen atoms omitted. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

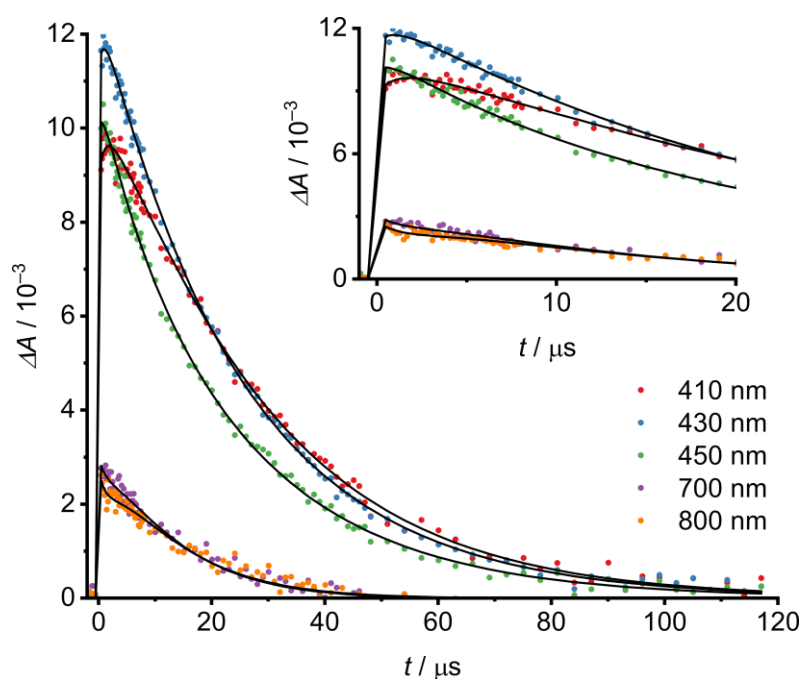


Figure S15. TA decay curves of **Sn** in 3-methylpentane upon $\lambda_{\text{pump}} = 390$ nm excitation at 95 K at selected wavelengths with multiexponential fits obtained from global analysis ($\tau_1 = 1$ μs , $\tau_2 = 5$ μs , $\tau_3 = 13$ μs , $\tau_4 = 26$ μs , sequential model). The inset shows a zoom in the 0–20 μs range.

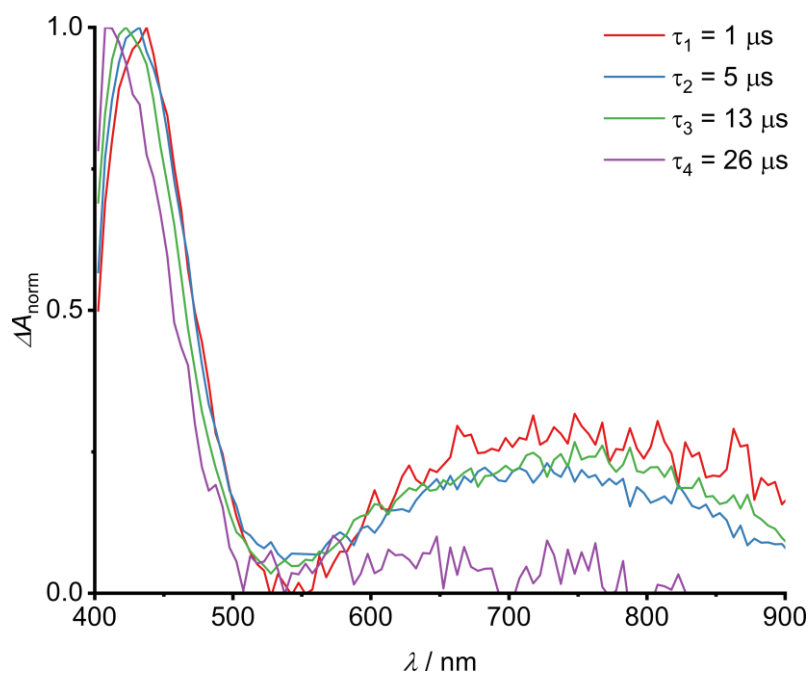


Figure S16. Evolution associated difference absorption spectra of **Sn** in 3-methylpentane upon $\lambda_{\text{pump}} = 390$ nm excitation at 95 K obtained from global analysis with corresponding lifetimes of the respective components.

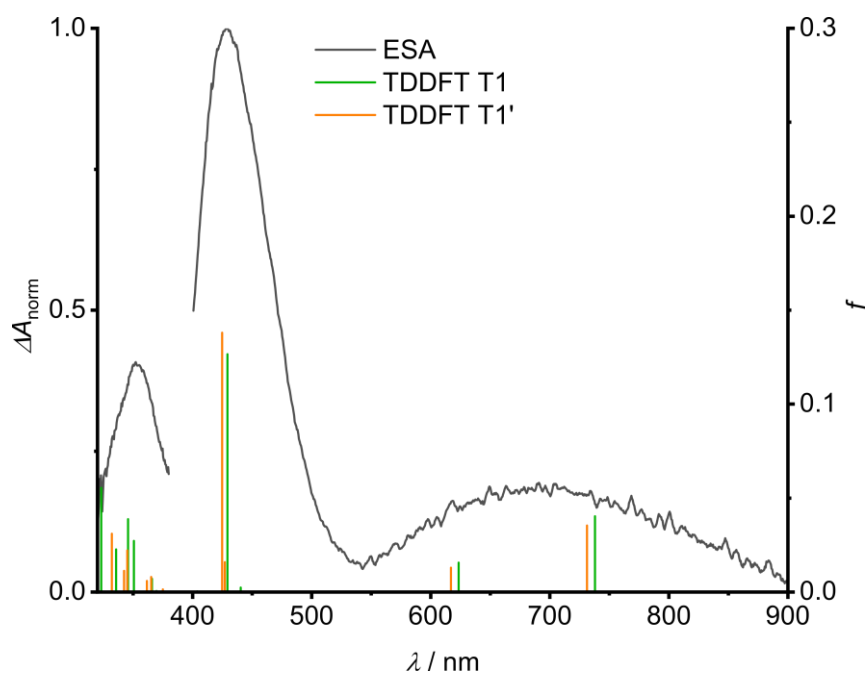
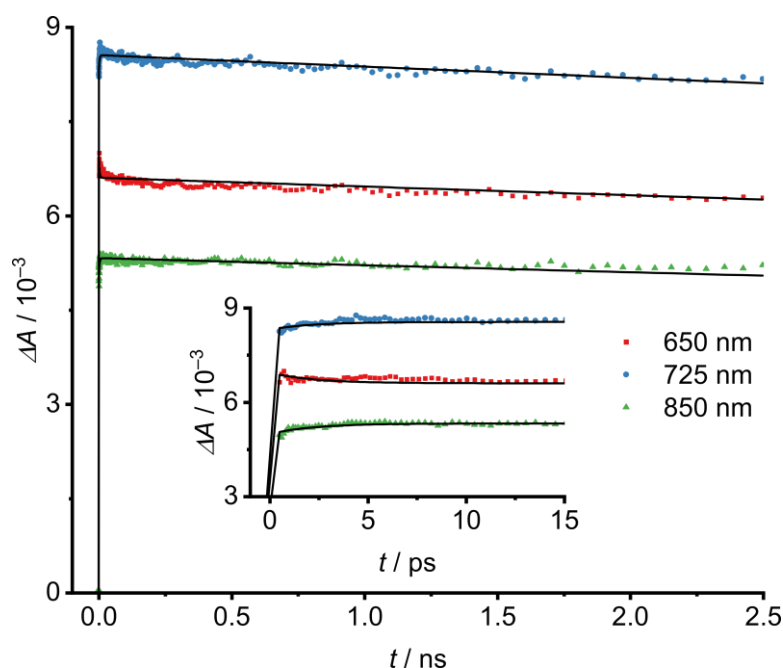


Figure S17. Normalised, time-averaged (5–40 ns) excited state absorption (ESA) spectrum of **Sn** in 3-methylpentane ($c = 4.8$ mM) at 293 K after $S_0 \rightarrow S_1$ excitation at $\lambda_{\text{pump}} = 390$ nm with TDDFT calculated oscillator strengths of T_1 and T_1' , shifted by 0.5 eV to higher energies, at the relaxed triplet geometries in green and orange, respectively. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).



FigureS18. TA decay curves of **Sn** in 3-methylpentane at 77 K upon $S_0 \rightarrow T_1$ $\lambda_{\text{pump}} = 480$ nm excitation at selected wavelengths with biexponential fits obtained from global analysis (black curves $\tau_1 = 2.2$ ps, $\tau_2 =$ non decaying, sequential model). The inset shows a zoom in the 0–15 ps range.

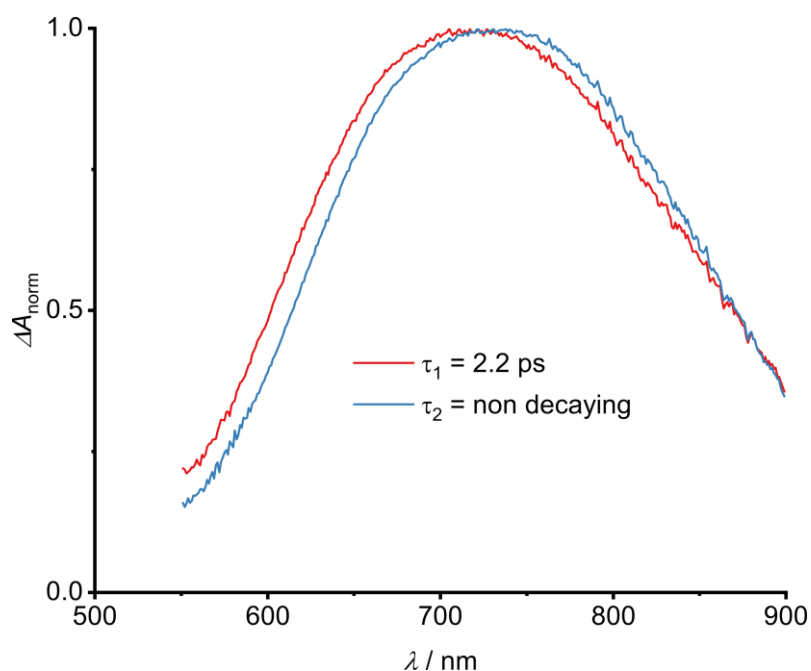


Figure S19. Evolution associated difference absorption spectra of **Sn** in 3-methylpentane at 77 K after $S_0 \rightarrow T_1$ excitation at $\lambda_{\text{pump}} = 480$ nm obtained from global analysis with corresponding lifetimes of the respective components.

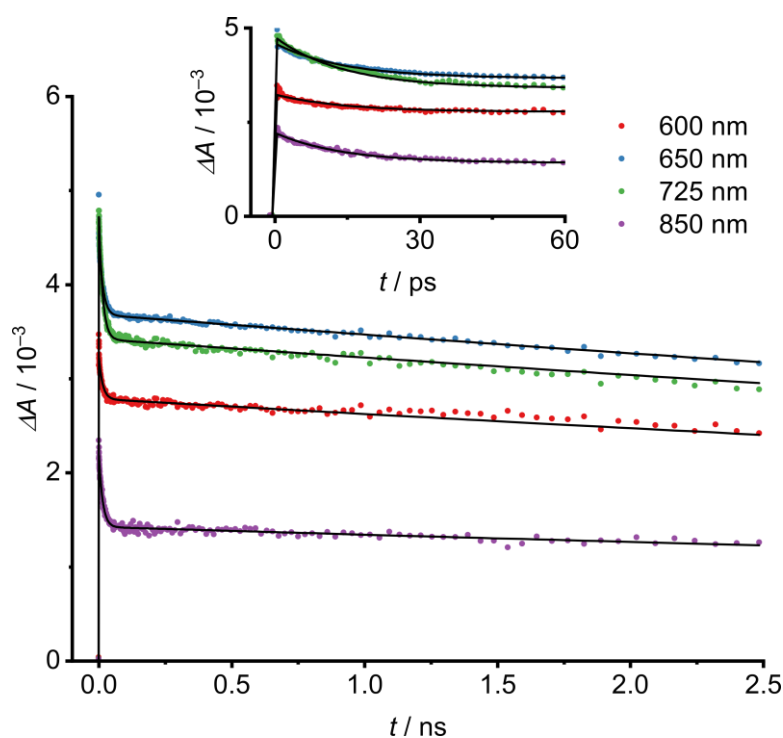


Figure S20. TA decay curves of **Sn** in 3-methylpentane at 293 K upon $S_0 \rightarrow T_1$ $\lambda_{\text{pump}} = 490$ nm excitation at selected wavelengths with biexponential fits obtained from global analysis (black curves, $\tau_1 = 14$ ps, $\tau_2 = \text{non decaying}$ (17 ns), sequential model). The inset shows a zoom in the 0–60 ps range.

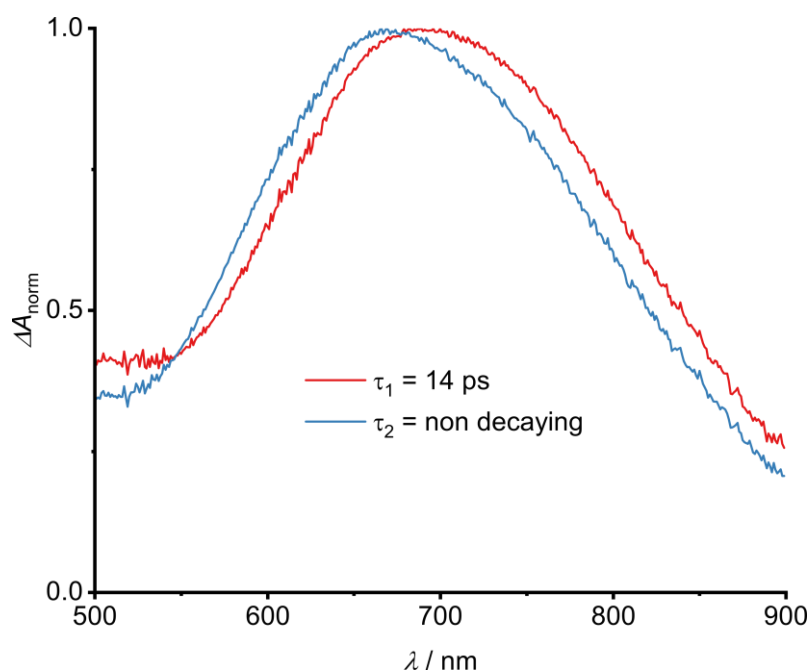


Figure S21. Evolution associated difference absorption spectra of **Sn** in 3-methylpentane at 293 K after $S_0 \rightarrow T_1$ excitation at $\lambda_{\text{pump}} = 490$ nm obtained from global analysis with corresponding lifetimes of the respective components.

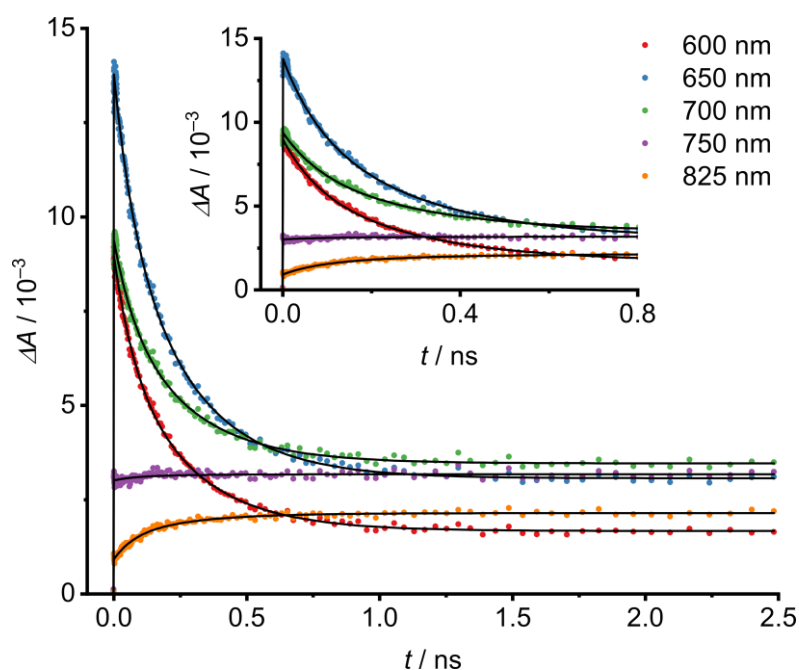


Figure S22. TA decay curves of **Sn** in 3-methylpentane at 77 K upon $S_0 \rightarrow S_1$ $\lambda_{\text{pump}} = 390$ nm excitation at selected wavelengths with triexponential fits obtained from global analysis (black curves, $\tau_1 = 76$ ps, $\tau_2 = 262$ ps, $\tau_3 = \text{non decaying}$, sequential model). The inset shows a zoom in the 0–0.8 ns range.

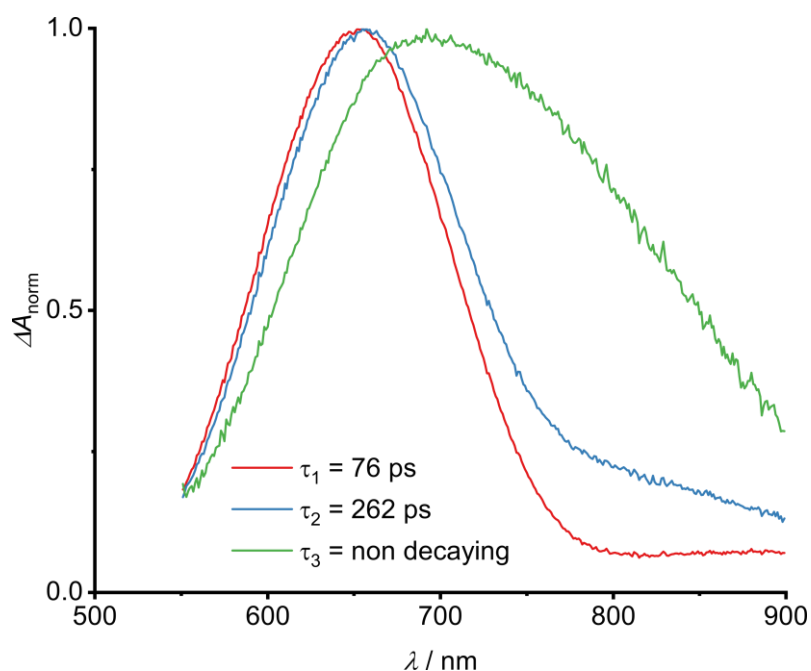


Figure S23. Evolution associated difference absorption spectra of **Sn** in 3-methylpentane at 77 K after $S_0 \rightarrow S_1$ excitation at $\lambda_{\text{pump}} = 390 \text{ nm}$ obtained from global analysis with corresponding lifetimes of the respective components.

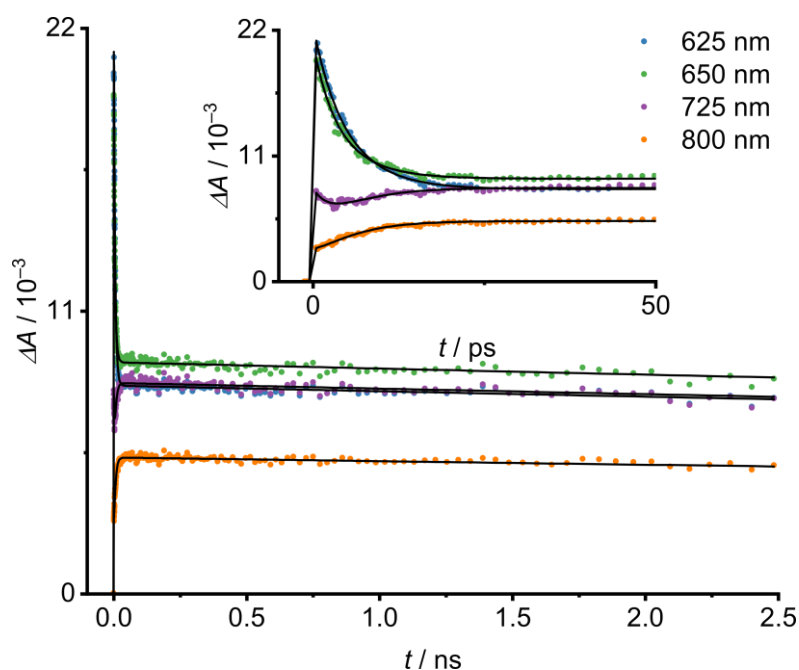


Figure S24. TA decay curves of **Sn** in 3-methylpentane at 293 K upon $S_0 \rightarrow S_1$ $\lambda_{\text{pump}} = 390 \text{ nm}$ excitation at selected wavelengths with triexponential fits obtained from global analysis (black curves, $\tau_1 = 2.6 \text{ ps}$, $\tau_2 = 5.4 \text{ ps}$, $\tau_3 = \text{non decaying}$, sequential model). The inset shows a zoom in the 0–50 ps range.

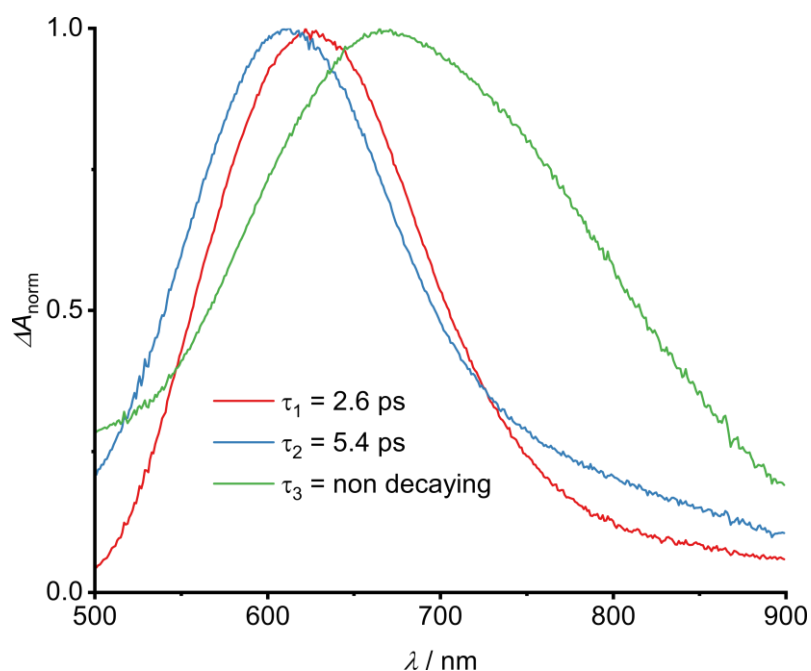


Figure S25. Evolution associated difference absorption spectra of **Sn** in 3-methylpentane at 293 K after $S_0 \rightarrow S_1$ excitation at $\lambda_{\text{pump}} = 390$ nm obtained from global analysis with corresponding lifetimes of the respective components.

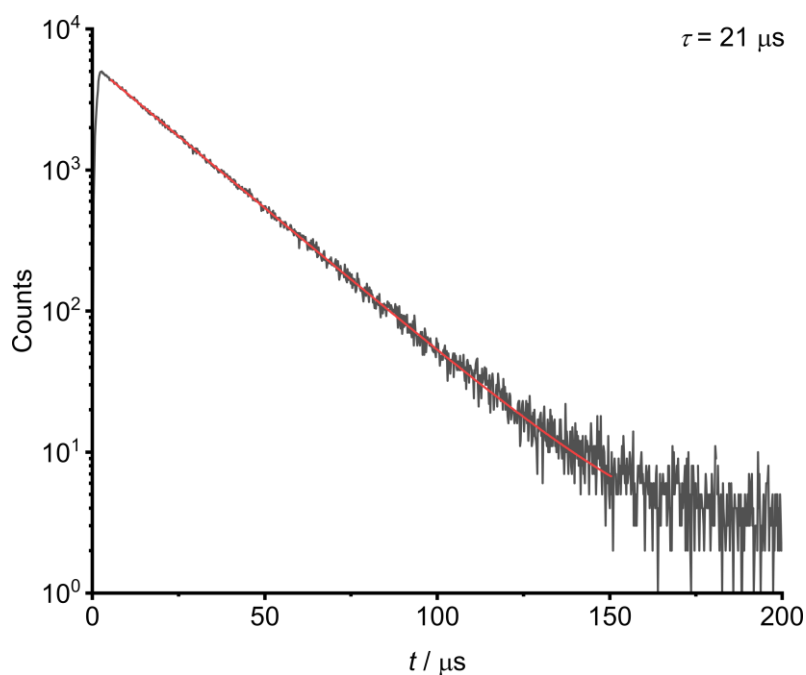


Figure S26. Emission decay curve of **Sn** (solid) at 77 K at $\lambda_{\text{em}} = 550$ nm upon $S_0 \rightarrow T_1$ $\lambda_{\text{exc}} = 450$ nm excitation superimposed with monoexponential fit (red curve).

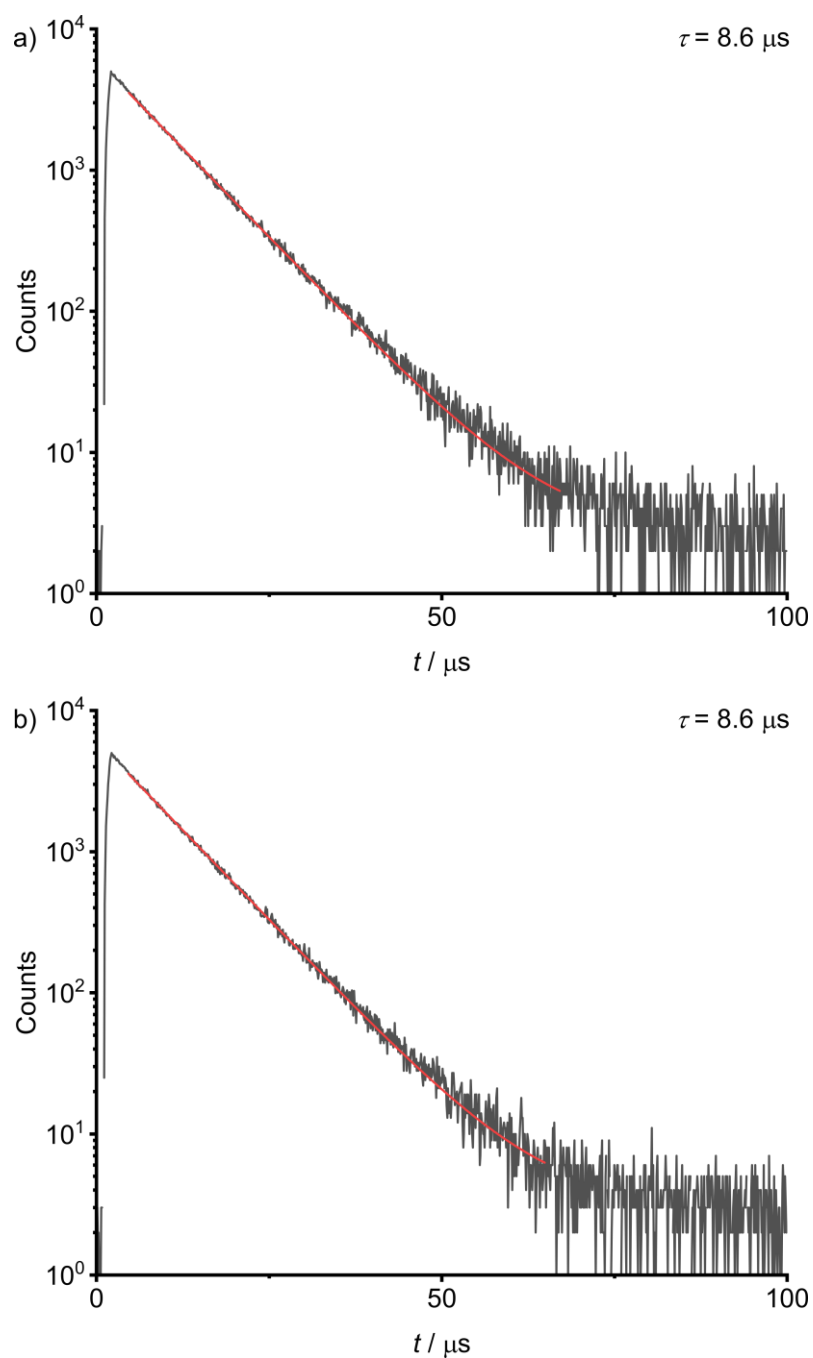
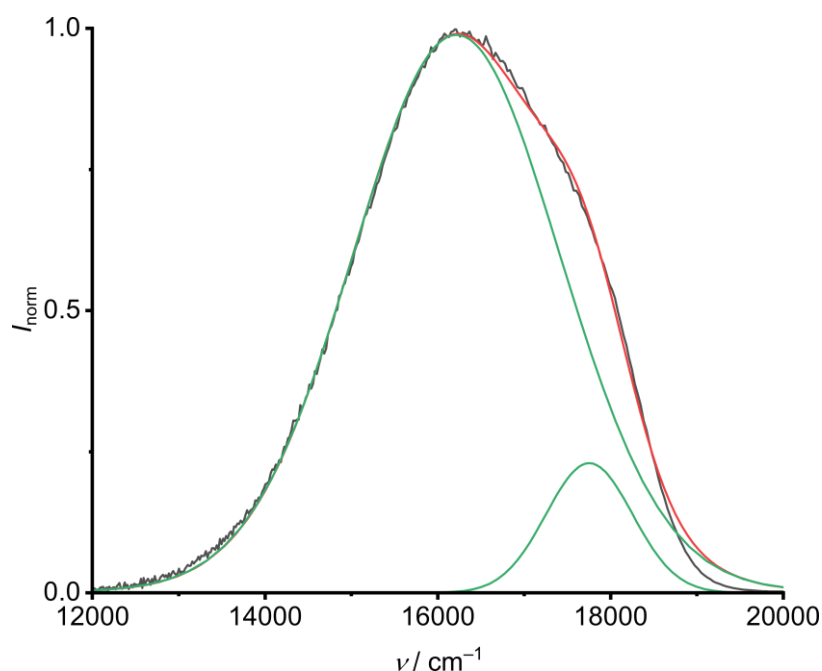


Figure S27. Emission decay curves of **Sn** (solid) at 293 K at a) $\lambda_{\text{em}} = 550 \text{ nm}$ upon $S_0 \rightarrow T_1$ $\lambda_{\text{exc}} = 450 \text{ nm}$ excitation and b) $\lambda_{\text{em}} = 650 \text{ nm}$ upon $S_0 \rightarrow T_1$ $\lambda_{\text{exc}} = 450 \text{ nm}$ excitation superimposed with monoexponential fits (red curves).



Type	Area	FWHM / cm ⁻¹	Max Height	Centre / cm ⁻¹	Area ratio / %
Voigt	2982	2820	0.99	16216	91
Voigt	288	1179	0.23	17754	9

Figure S28. Emission spectrum of **Sn** (solid) upon $S_0 \rightarrow T_1$ $\lambda_{\text{exc}} = 450$ nm excitation at 293 K in black overlaid with two Voigt functions. Fit components shown in green and the cumulative fit in red with fit parameters.

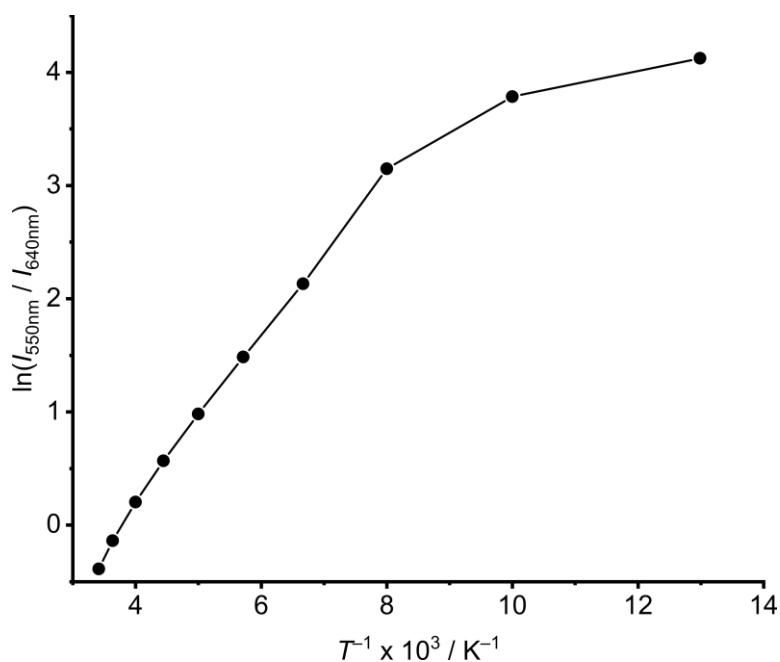


Figure S29. Logarithmic luminescence intensity ratio between the intensities at $\lambda = 550$ nm and $\lambda = 640$ nm plotted against the reciprocal temperature in the solid state.

III Photochemical Properties

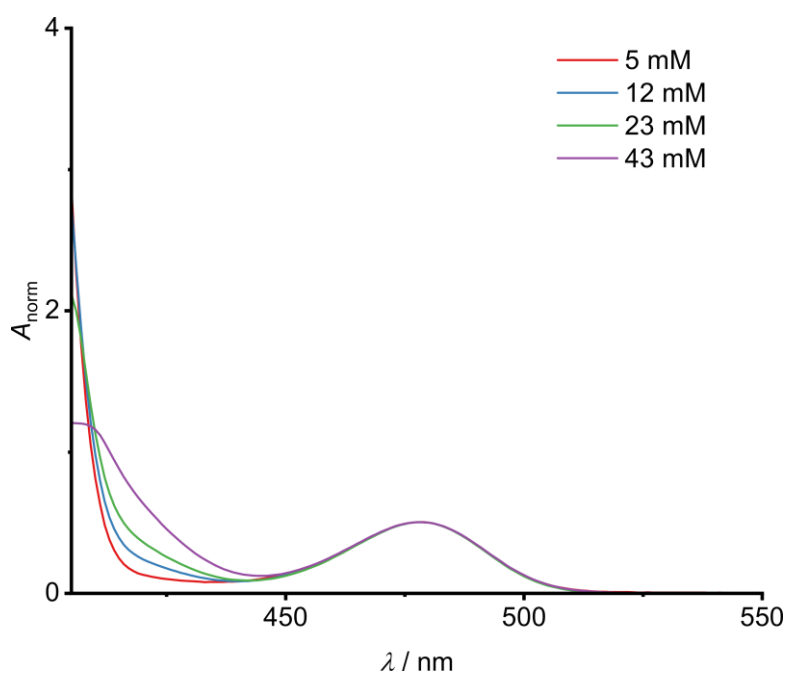


Figure S30. UV/Vis absorption spectra of **Sn** in 3-methylpentane at 77 K, normalised to the $S_0 \rightarrow T_1$ absorption band at various concentrations.

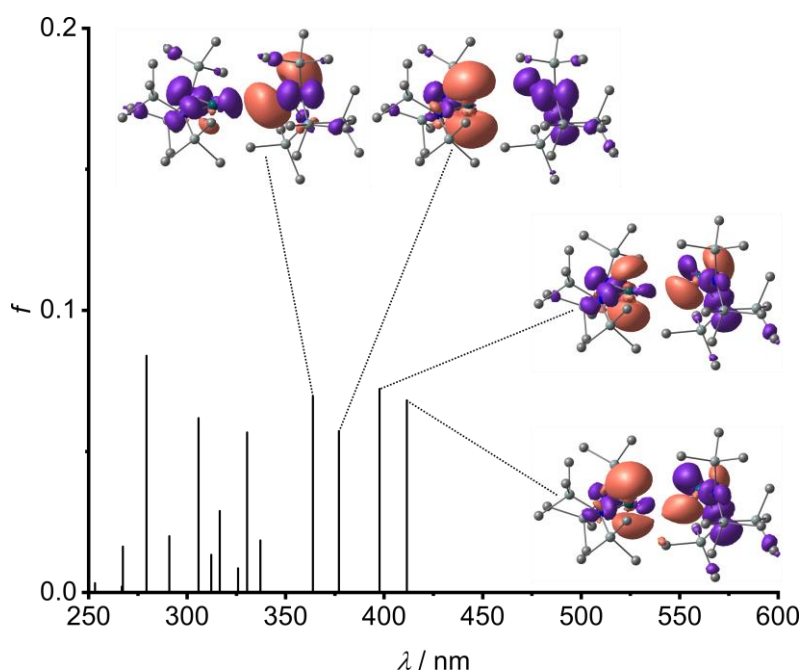


Figure S31. TDDFT calculated spectrum of the geometry optimised dimer ***cis*-1[Sn...Sn]** with difference electron densities of selected transitions (isosurface value 0.002 a.u., purple = electron loss, orange = electron gain). Hydrogen atoms omitted. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

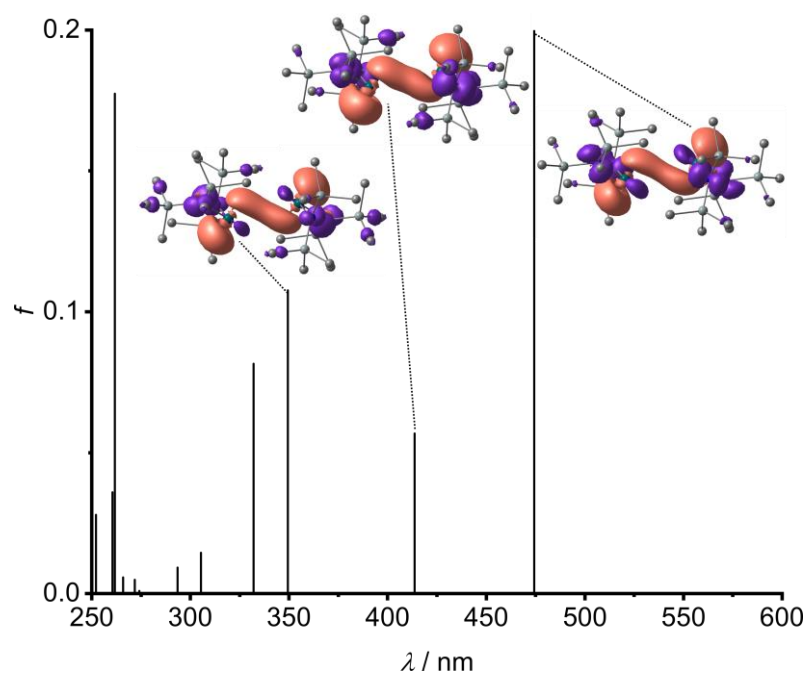


Figure S32. TDDFT calculated spectrum of the geometry optimised dimer *trans*-1[Sn...Sn] with difference electron densities of selected transitions (isosurface value 0.002 a.u., purple = electron loss, orange = electron gain. Hydrogen atoms omitted. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

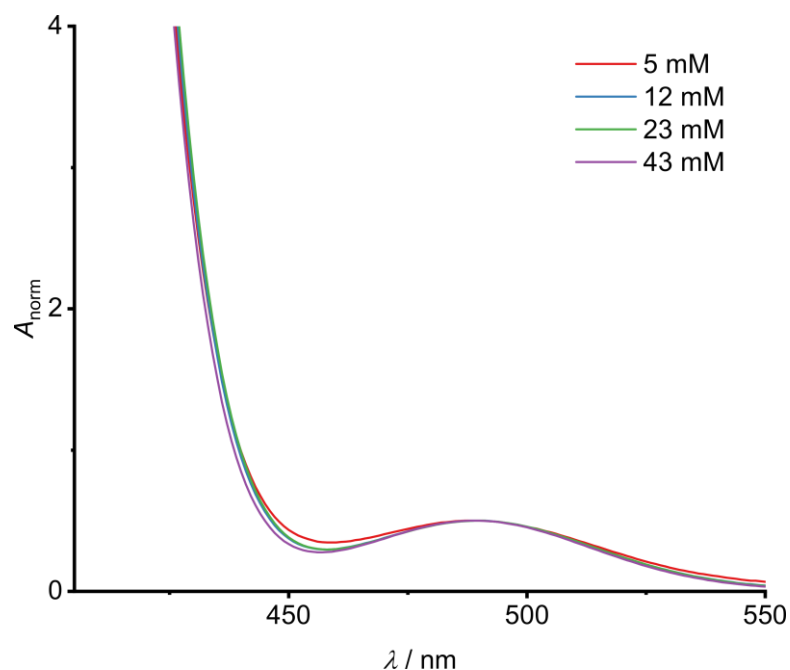


Figure S33. UV/Vis absorption spectra of **Sn** in 3-methylpentane at 293 K, normalised to the $S_0 \rightarrow T_1$ absorption band at various concentrations.

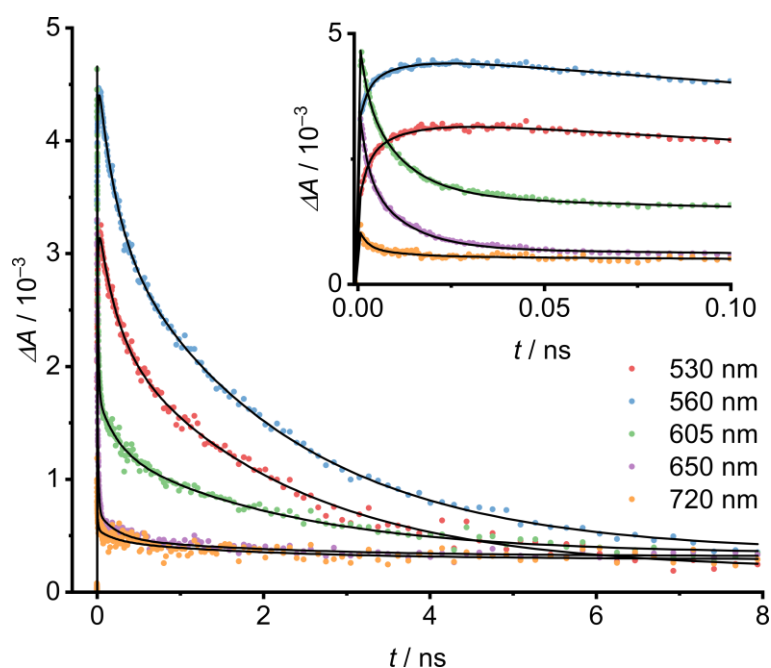


Figure S34. TA decay curves of a sample of **Sn** in 3-methylpentane ($c = 22$ mM) at 77 K upon $\lambda_{\text{pump}} = 430$ nm excitation at selected wavelengths with multiexponential fits obtained from global analysis (black curves, $\tau_1 = 2.2$ ps, $\tau_2 = 11$ ps, $\tau_3 = 222$ ps, $\tau_4 = 2.2$ ns, $\tau_5 =$ non decaying, sequential model). The inset shows a zoom in the 0–0.1 ns range.

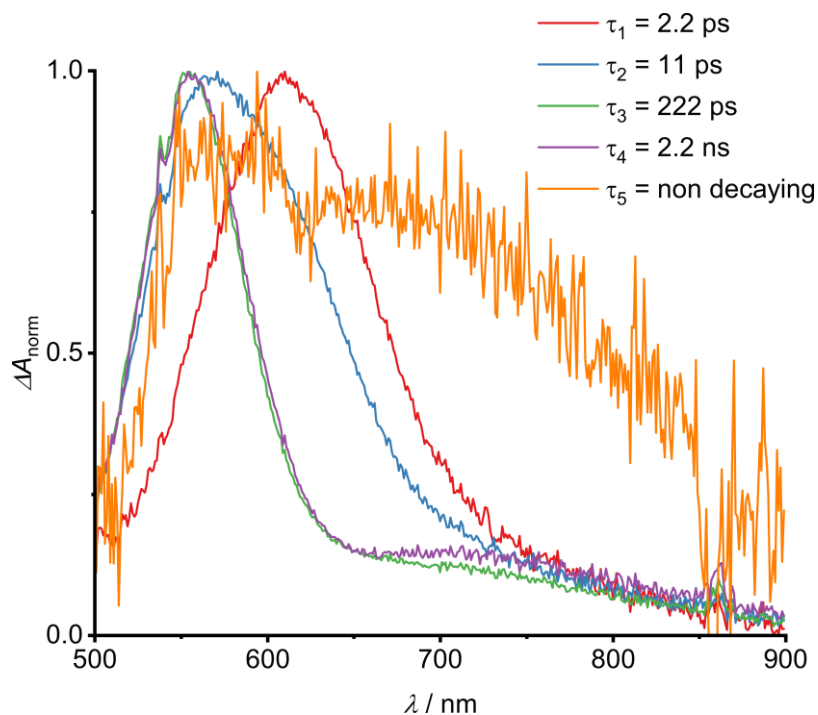


Figure S35. Evolution associated difference absorption spectra of **Sn** ($c = 22$ mM) in 3-methylpentane at 77 K after $\lambda_{\text{pump}} = 430$ nm excitation obtained from global analysis with corresponding lifetimes of the components of a sample.

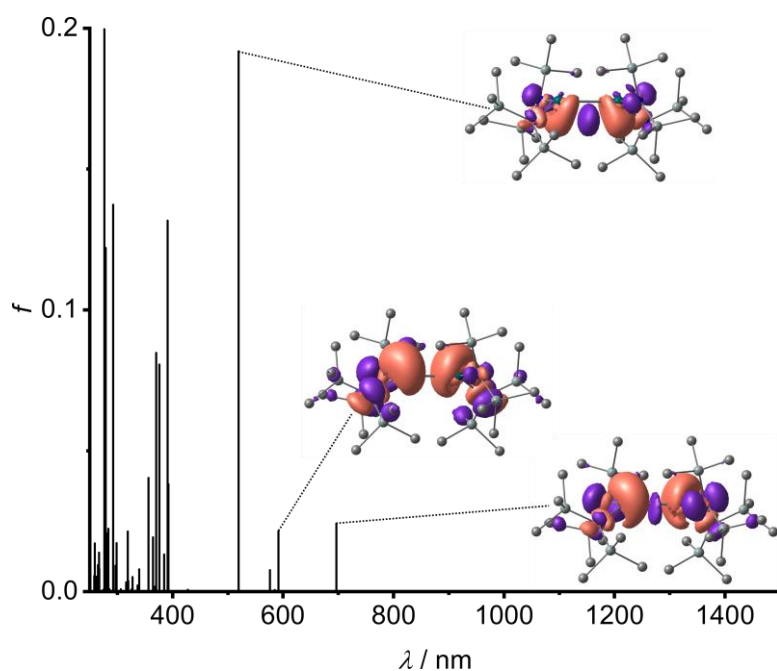


Figure S36. TDDFT calculated spectrum of the geometry optimised triplet excimer *cis*- $^3[\text{Sn}_2]$ (isosurface value 0.002 a.u., purple = electron loss, orange = electron gain. Hydrogen atoms omitted. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

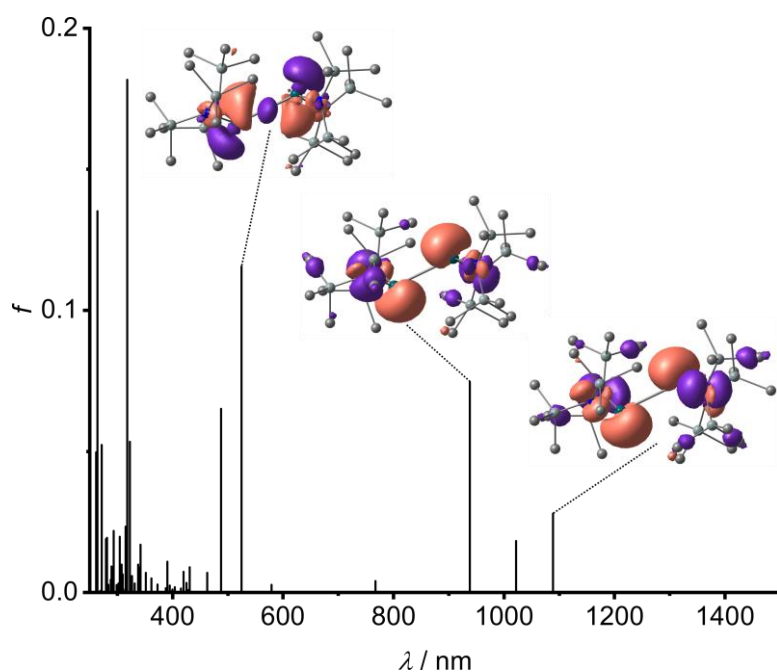


Figure S37. TDDFT calculated spectrum of the geometry optimised triplet excimer *trans*- $^3[\text{Sn}_2]$ (isosurface value 0.002 a.u., purple = electron loss, orange = electron gain. Hydrogen atoms omitted. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

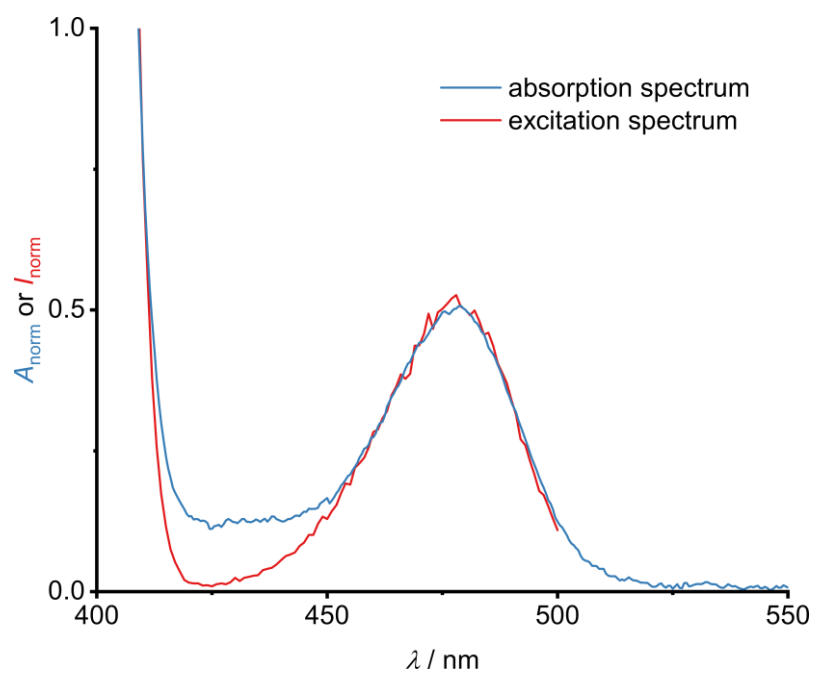


Figure S38. Excitation spectrum of **Sn** in 3-methylpentane at 77 K ($\lambda_{\text{em}} = 560$ nm, $c = 0.42$ mM, red) and UV/Vis absorption spectrum of **Sn** in 3-methylpentane at 77 K ($c = 0.36$ mM, blue).

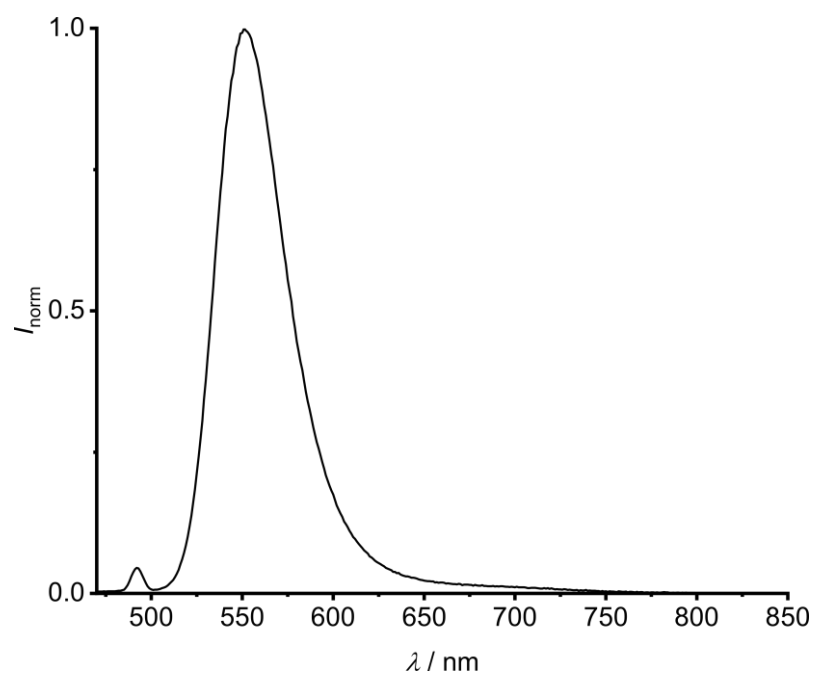


Figure S39. Emission spectrum of **Sn** in 3-methylpentane at 77 K upon $\lambda_{\text{exc}} = 430$ nm excitation.

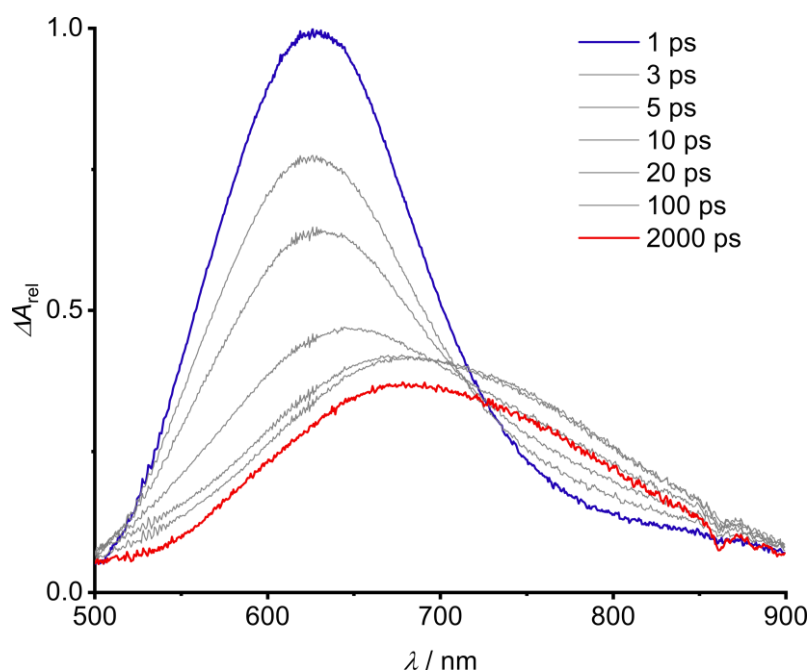


Figure S40. fs-Transient absorption spectra of **Sn** in 3-methylpentane at 293 K upon $\lambda_{\text{pump}} = 430$ nm excitation at $c = 22$ mM.

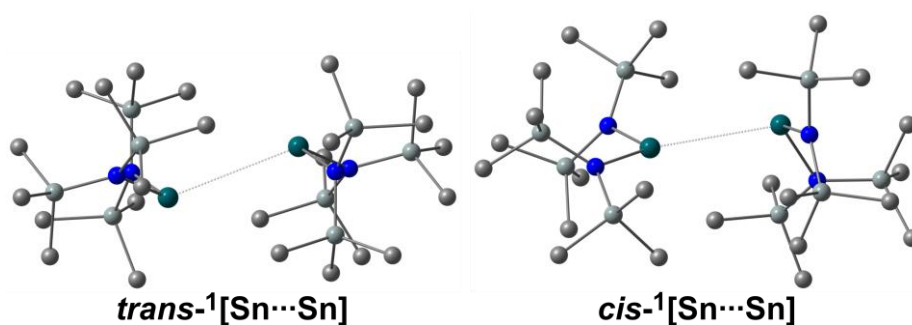


Figure S41. DFT calculated dimers of two **Sn** molecules in the trans-bent ***trans*-1[Sn...Sn]** and cis-bent ***cis*-1[Sn...Sn]** orientation. Hydrogen atoms omitted. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

Table S4. Selected molecular orbitals of the model $[\text{SnH}_2]_2$ in the triplet state at C_{2v} and C_{2h} symmetry and in the GS at D_{2h} symmetry, displayed at an isosurface value of 0.06 a.u.. Mulliken symbol of the orbital character given in the respective point group. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

C_{2v}	D_{2h}	C_{2h}
b_1	$\sigma^*(b_{3u})$	b_u
b_1	$\pi^*(b_{1g})$	a_g
a_1	$\pi(b_{2u})$	b_u

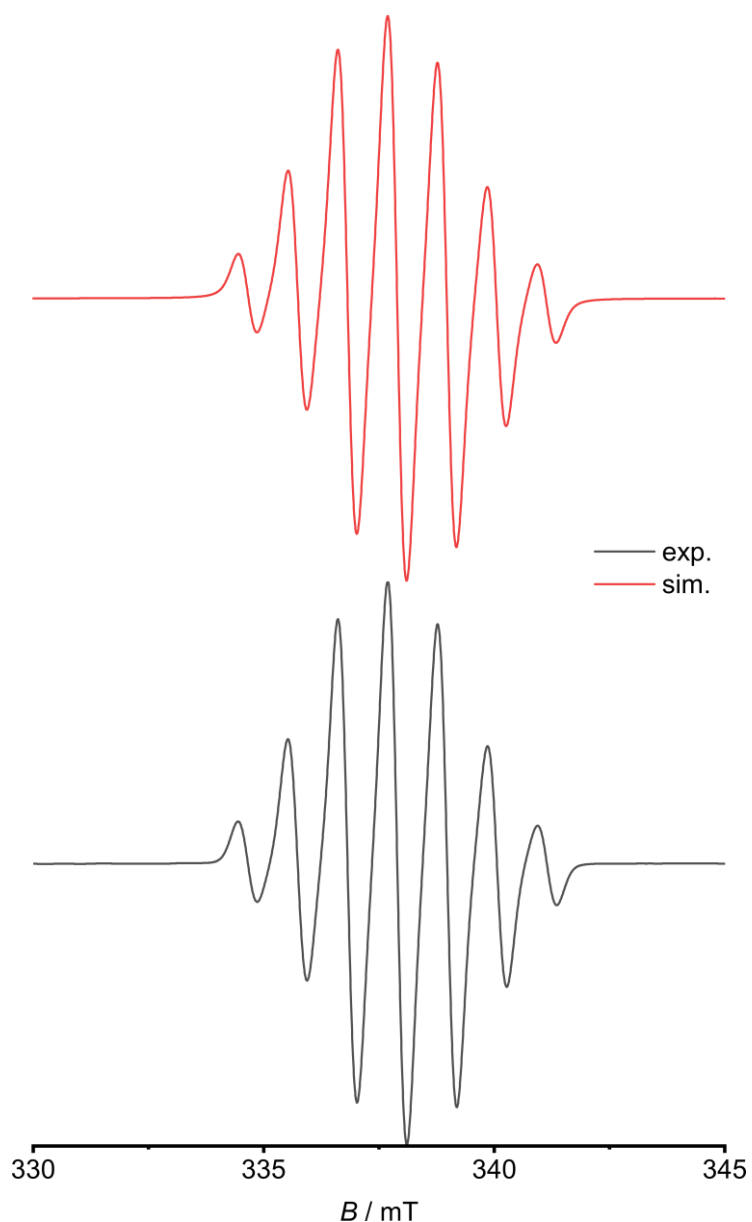
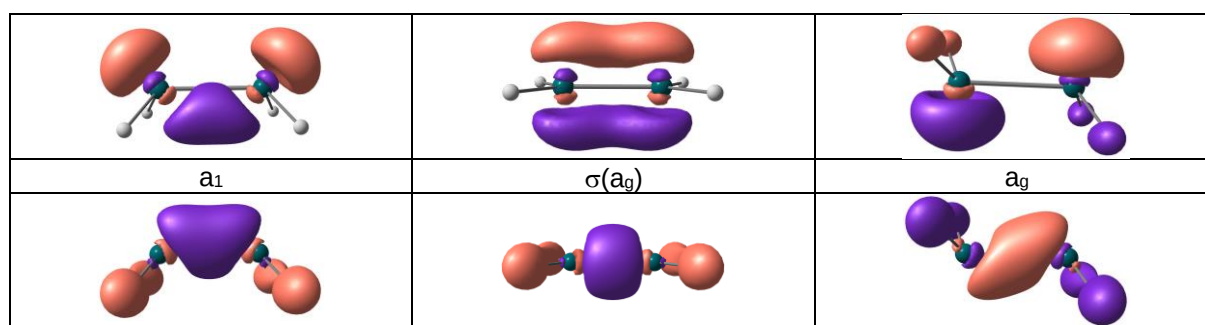


Figure S42. X-band cw-EPR spectrum of $\bullet\text{Sn}[\text{N}(\text{SiMe}_3)_2]_3$ in *n*-pentane at 293 K (black) and simulated spectrum (red) in the isotropic, fast motional regime with $g = 1.996$, $A(^{14}\text{N}) = 30.21$ MHz with peak-to-peak Gaussian/Lorentzian line widths 0.38/0.06 mT. The $^{117/119}\text{Sn}$ satellites could not be detected, being outside the instrument's spectral window.

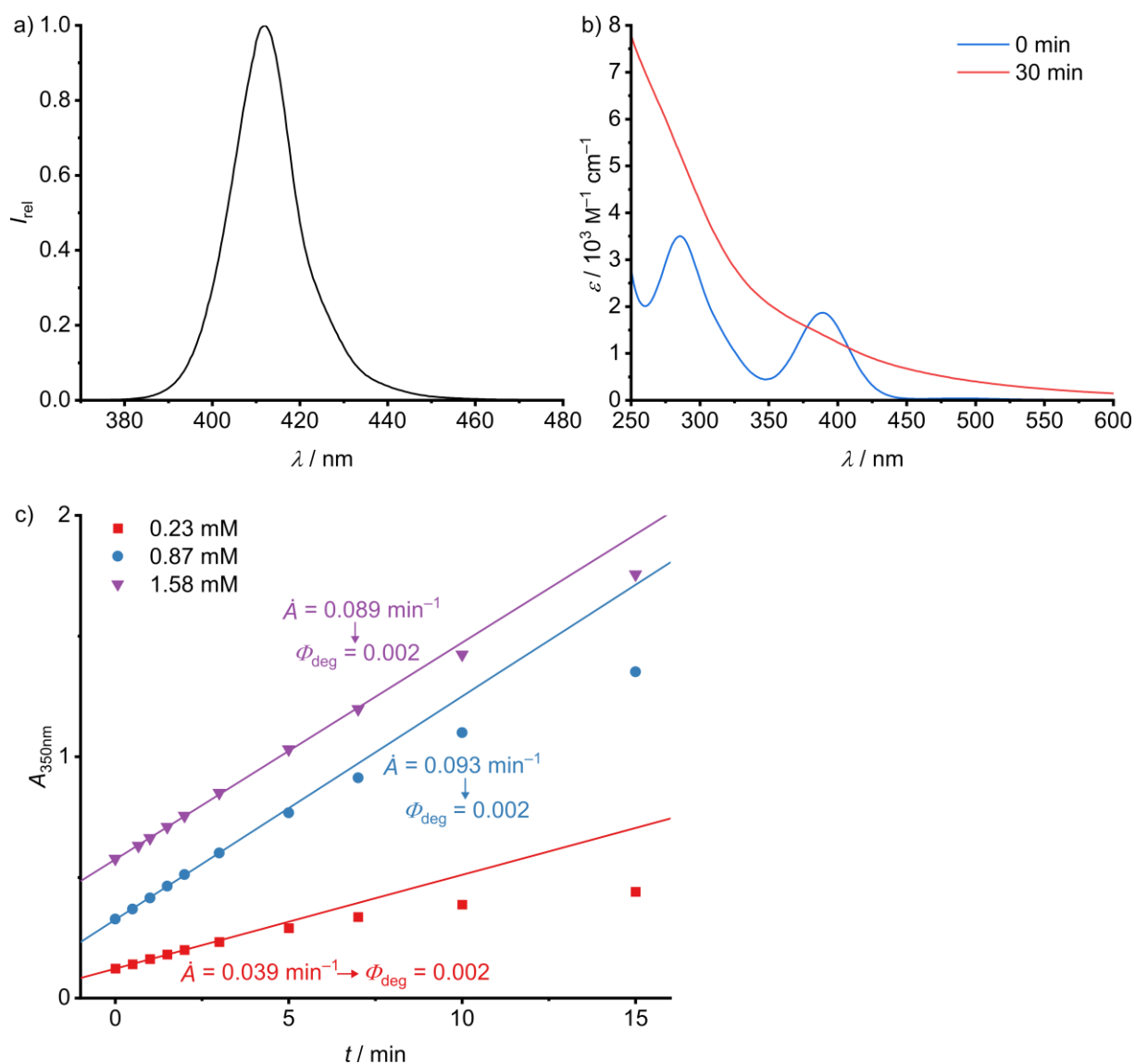


Figure S43. a) Emission spectrum of the used UHP-LED, b) UV/Vis absorption spectrum of **Sn** at $t = 0$ min in blue and the UV/Vis absorption spectrum of the photolysis product in *n*-pentane after complete conversion $t = 30$ min in red. c) UV/Vis absorption versus time plots of **Sn** in *n*-pentane at $\lambda = 350$ nm of photolysis measurements at $c = 0.23, 0.87$ and 1.58 mM with linear fits of the data points within the 0–2 min time interval (5 data points).

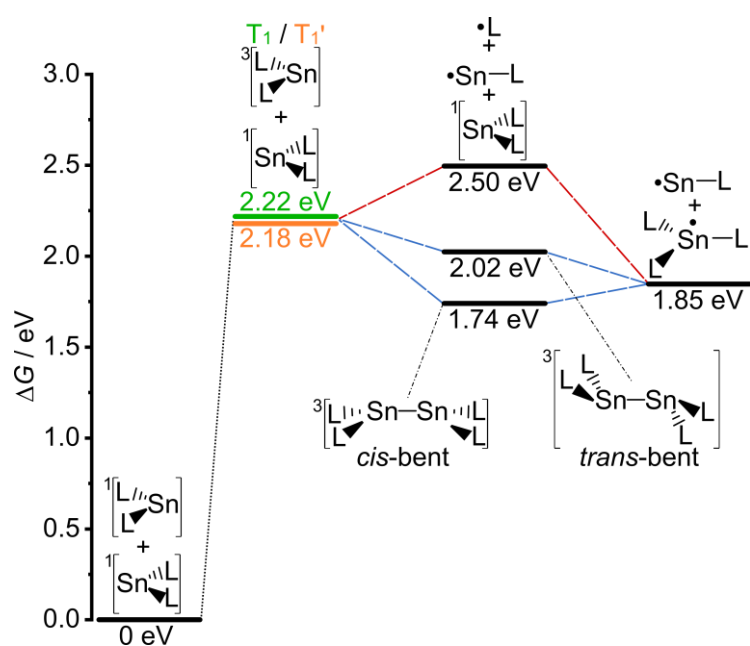


Figure S44. Energy profile diagram with Gibbs free energies in eV for the $\bullet\text{Sn}[\text{N}(\text{SiMe}_3)_2]_3$ radical formation, starting from two molecules of **Sn** in the GS via the T_1/T_1' states after single molecule excitation with Sn–L bond homolysis and $\bullet\text{L}$ radical to **Sn** addition (mechanism A, red path) or via excimer formation with ligand migration and dissociation (mechanism B, blue paths). CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

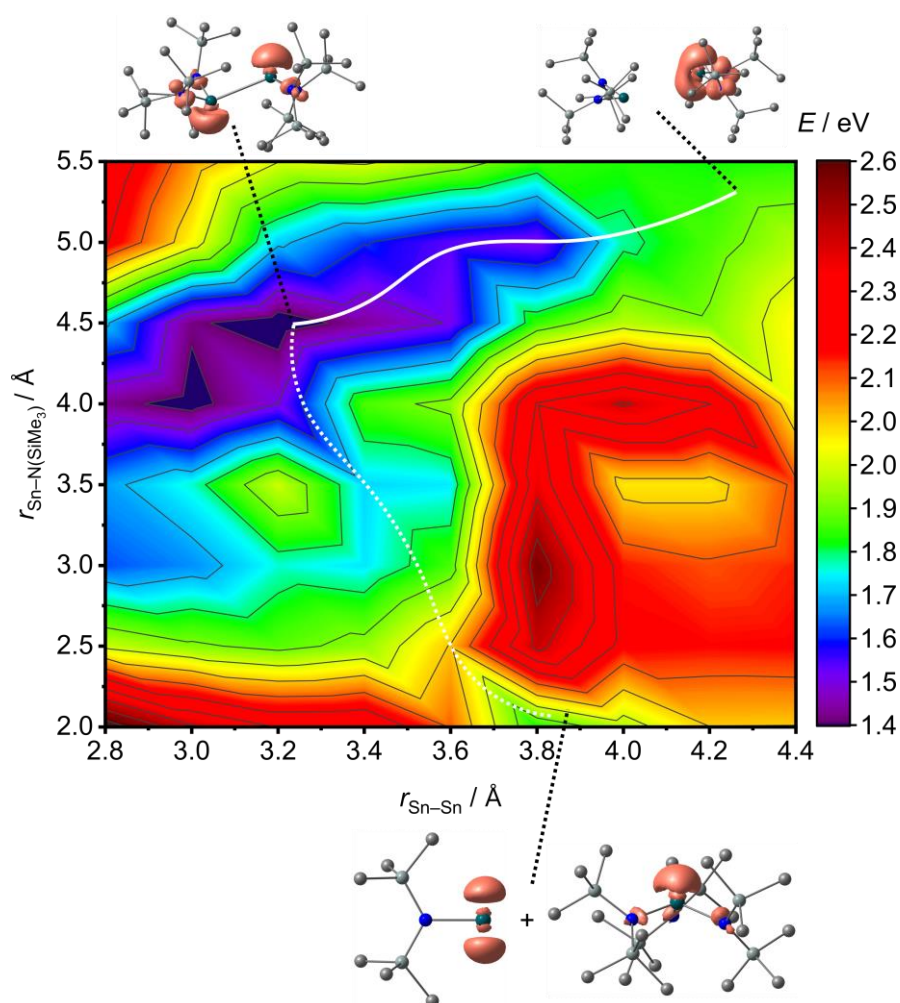


Figure S45. Contour plot of 2D relaxed potential energy surface scans as projection along the Sn-Sn distance and the Sn-N^{HMDs} transfer on the triplet hypersurface of **Sn** with selected geometry optimised molecular structures with spin densities (isosurface value 0.01 a.u.). Energies are given vs. the respective singlet ground state energy (Figure S46). Hydrogen atoms omitted. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

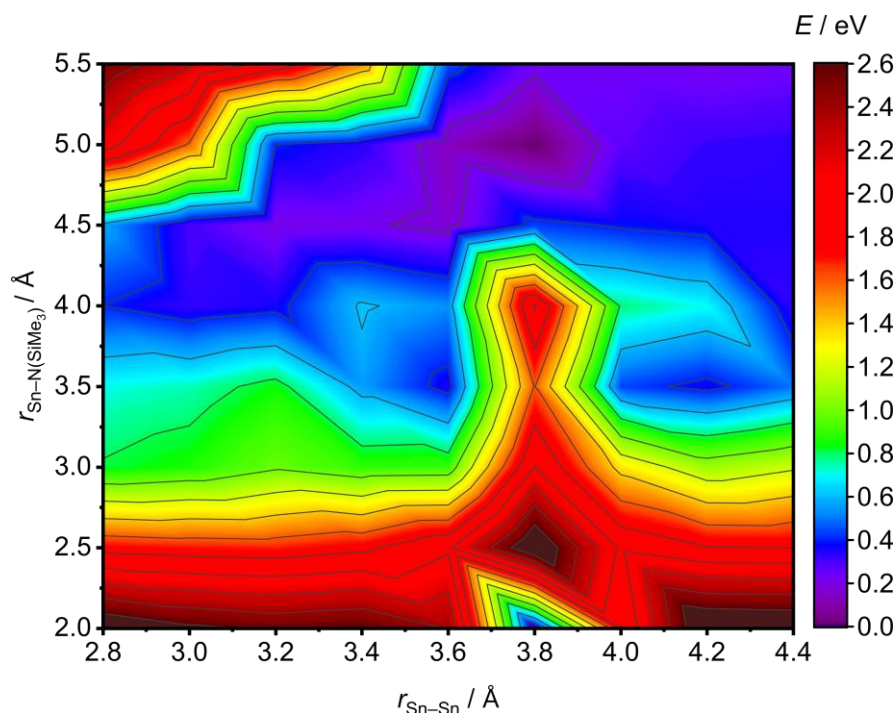


Figure S46. Contour plot of 2D relaxed potential energy surface scans as projection along the Sn-Sn distance and the Sn-N^{HMDS} transfer on the singlet hypersurface of **Sn**. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

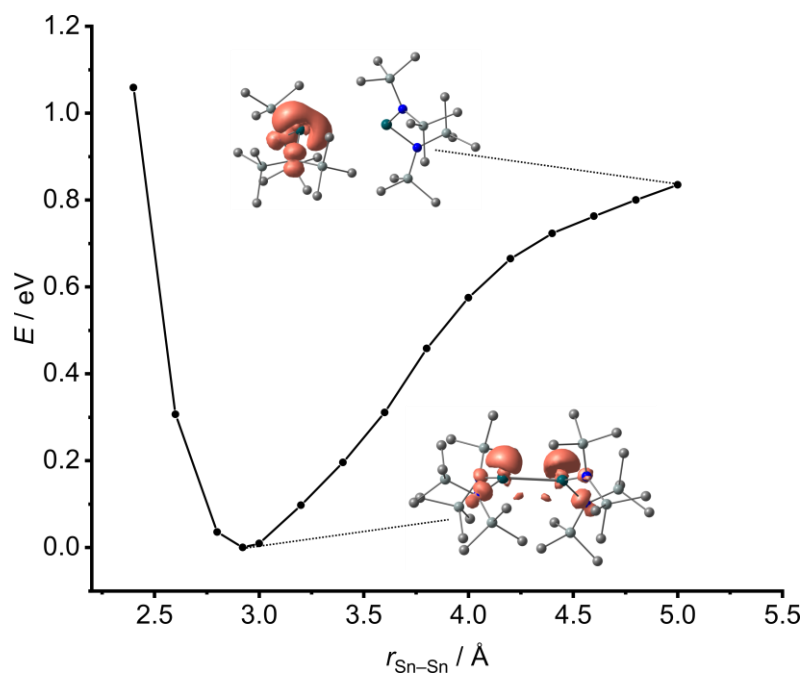


Figure S47. Relaxed potential energy surface scan as projection along the Sn-Sn distance of the *cis*-³[Sn] excimer. Hydrogen atoms omitted. Spin densities of selected geometries with isosurface value of 0.01 a.u.. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

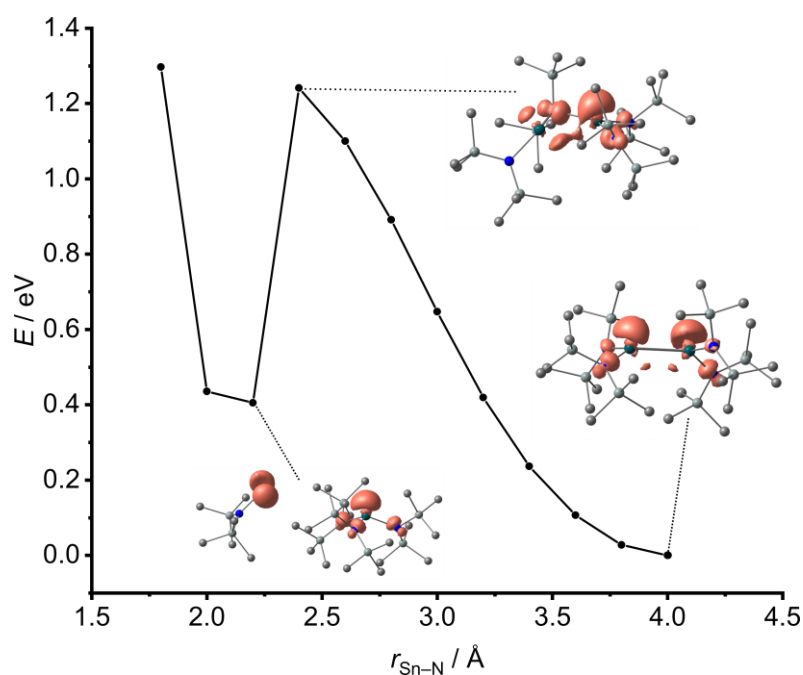


Figure S48. Relaxed potential energy surface scan as projection along the Sn-N^{HMDs} transfer of the *cis*-³[Sn] excimer. Hydrogen atoms omitted. Spin densities of selected geometries with isosurface value of 0.01 a.u.. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn))

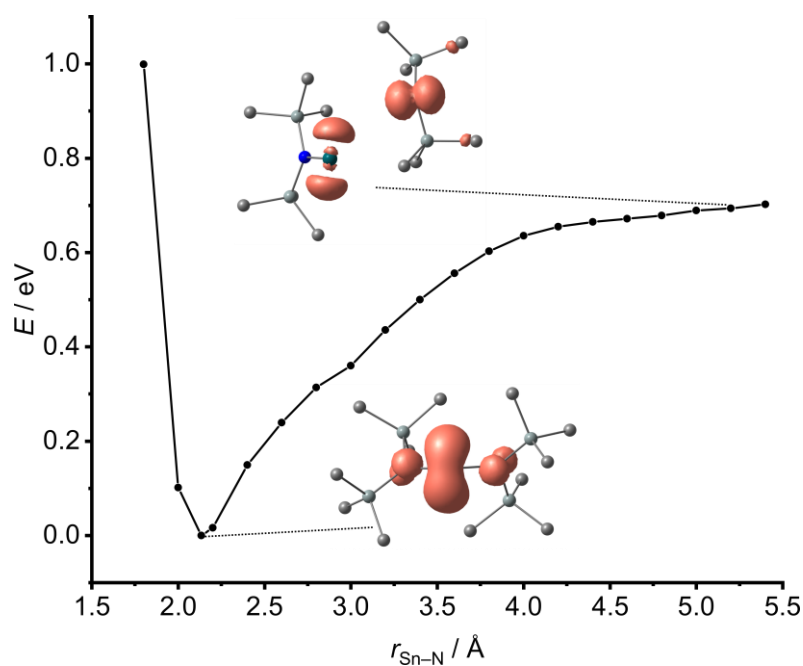


Figure S49. Relaxed potential energy surface scan as projection along the Sn-N^{HMDs} distance of ³Sn. Hydrogen atoms omitted. Spin densities of selected geometries with isosurface value of 0.01 a.u.. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

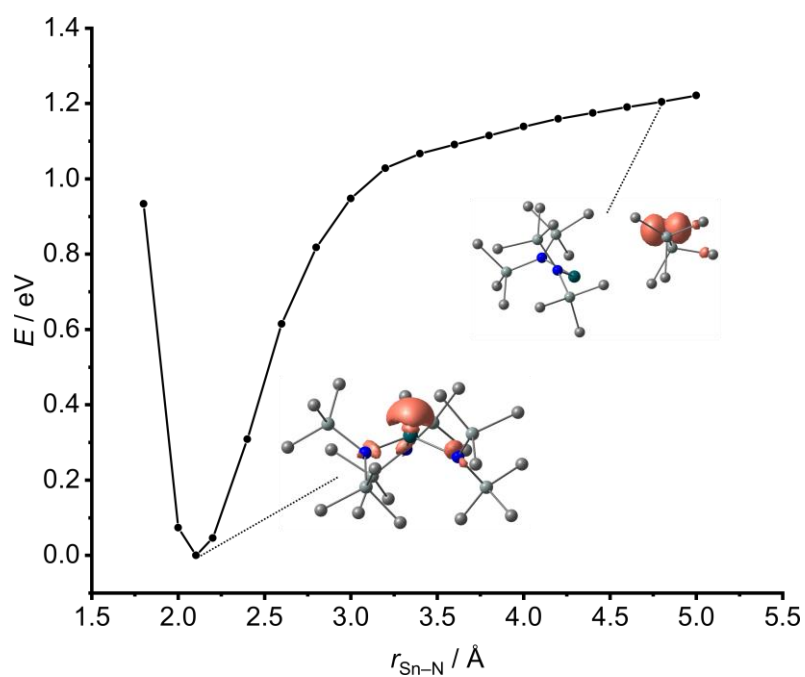


Figure S50. Relaxed potential energy surface scan as projection along the Sn–N^{HMDs} distance of the •Sn[N(SiMe₃)₂]₃ radical. Hydrogen atoms omitted. Spin densities of selected geometries with isosurface value of 0.01 a.u.. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Sn)).

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6.4 Supporting Information: The Photophysics of Lappert's Diamino Plumbylene

All reactions and measurements were performed under argon atmosphere unless otherwise noted. Gloveboxes (UniLab/MBraun – Ar 4.8, O₂ < 1 ppm, H₂O < 0.1 ppm) were used to store and weigh sensitive compounds for synthesis as well as to prepare samples that require the absence of oxygen and water. The reagents were purchased from commercial suppliers (ABCR, Acros Organics, Alfa Aesar, Fischer Scientific and Sigma Aldrich). *n*-pentane and 3-methylpentane were dried and distilled from sodium. C₆D₆ was purchased from euriso-top and Deutero GmbH and was dried and distilled from potassium and stored over molecular sieve (3 Å).

NMR spectra were recorded on a *Bruker Avance NEO* or a *Bruker Avance DRX 400* spectrometer at 400.42 MHz (¹H) and 83.79 MHz (²⁰⁷Pb). All data were evaluated with the software *MestReNova 12.0.4-22023*. All resonances are reported in ppm versus the solvent signal as internal standard ¹H NMR: C₆D₆: δ = 7.16 ppm^[1] or versus an external standard for ²⁰⁷Pb NMR (PbMe₄, δ = 0 ppm). (s) = singlet.

UV/Vis absorption spectra were recorded on a *V-770* from *JASCO* or a *Cary-5000* spectrometer from *Agilent* using *d* = 1.00 cm quartz cuvettes with a *Schott* valve. Measurements at low temperatures were carried out using a liquid nitrogen cooled cryostat *Optistat DN* from *Oxford Instruments* equipped with 1 cm quartz tubes. Concentration dependent measurements at low temperatures and room temperature were conducted with a special self-made quartz cell (*d* = 0.2 cm) surrounded with a PEEK frame.

Steady-state emission spectra and photoluminescent decay curves (solution and solid-state samples) were measured with a *FLS1000* spectrometer from *Edinburgh Instruments* equipped with a cooled photomultiplier PMT-980 and a cooled NIR-sensitive photomultiplier detector N-G09 PMT-1700. A xenon arc lamp Xe2 (450 W) was used for excitation in steady-state measurements. Time-resolved luminescence experiments were measured in the multi-channel scaling mode employing a pulsed diode laser VPL-450 (λ_{exc} = 451.3 nm) as excitation source. Measurements at low temperature were carried out using a liquid nitrogen cooled cryostat *Optistat DN* from *Oxford Instruments*. Single lifetime decays were evaluated with the software *Fluoracle* provided by *Edinburgh Instruments*. For these measurements, **PbH** was freshly distilled no more than one day beforehand.

Photolysis experiments were conducted by irradiating deaerated solutions of Pb(HMDS)₂ **PbH** in inert gas cuvettes (*d* = 1 cm). An Ultra-High Power collimated LED from *Prizmatix* (UHP-T-460-DI) with an emission maximum at 455 nm was used for irradiation. The output power (determined with a high-sensitive thermal power head S425C from *Thorlabs*) was adjusted to *P* = 0.03 W with an UHPTLCC-02-USB controller for all experiments. The beam was focused on the cuvette with a plano convex lens. At the cuvette, the beam diameter amounts to 0.5 cm. The temperature of the irradiated solution was kept at 20 °C with a Peltier module.

Irradiation (total irradiation time 480 s) of **PbH** at $\lambda_{\text{exc}} = 455 \text{ nm}$ in *n*-pentane forms directly lead particles and a lead mirror after longer irradiation (Figure S 18). This was followed by UV/Vis absorption spectroscopy. The scattering in the UV/Vis absorption spectra, caused by the lead particles, were corrected with a fit function based on Mie light scattering, with the slope m , off-set value b and the wavelength λ [Eq (1)].^[2]

$$m \cdot \lambda^3 + b \quad (1)$$

The absorption ($A_{410\text{nm}}$) versus time plots were fitted linearly for all concentrations. The spectra below an offset of 0.1 were considered for each measurement (initial 120 s - 8 data points for $c = 0.27 \text{ mM}$, initial 60 s - 6 data points for $c = 0.64 \text{ mM}$, initial 40 s - 5 data points for $c = 1.2 \text{ mM}$, Figure S 21). Using Lambert-Beer's law, the degradation rates $\dot{N}_{\text{deg}}$ were obtained from the slopes $\dot{A}_{410\text{nm}}$ of the fits [Eq (2)].

$$\frac{dA_{410\text{nm}}}{dt} = \dot{A}_{410\text{nm}} = \Delta\varepsilon_{410\text{nm}} d \dot{c} = \frac{\Delta\varepsilon_{410\text{nm}} d}{V N_A} \dot{N}_{\text{deg}} \Leftrightarrow \dot{N}_{\text{deg}} = \frac{\dot{A}_{410\text{nm}} V N_A}{\Delta\varepsilon_{410\text{nm}} d} \quad (2)$$

$\Delta\varepsilon_{410\text{nm}}$ is the difference between the molar absorption coefficients of the photolysis product and **PbH** at 410 nm (the molar absorption coefficients for the lead particles is approximately assumed as 0), d is the optical path length (1 cm), V is the volume of the sample (3 mL) and N_A is the Avogadro constant.

For a non-monochromatic light source, the rate of photon absorption $\dot{N}_{\text{abs}}(\lambda)$ is given by Eq (3).

$$\dot{N}_{\text{abs}}(\lambda) = \dot{N}_{\text{LED}}(\lambda) (1 - 10^{-A(\lambda)}) \quad (3)$$

$\dot{N}_{\text{LED}}(\lambda)$ is the rate of photons emitted at the corresponding wavelength and is obtained from the emission spectrum of the UHP-LED, which is multiplied with the photon energy $\frac{h c}{\lambda}$ at the respective wavelength. The spectral area is approximated as sum of intensities in 1 nm steps and normalized to the output power of $P = 0.03 \text{ W}$. The number of emitted photons is obtained from division by $\frac{h c}{\lambda}$. $A(\lambda)$ is the initial absorbance of the sample and is assumed to be constant for the respective time intervals of each concentration. The total rate of photon absorption $\dot{N}_{\text{abs}}$ is given by the sum of all $\dot{N}_{\text{abs}}(\lambda)$ in the wavelength range 390 – 530 nm [Eq (4)].

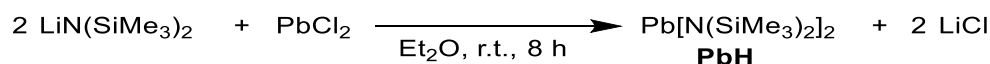
$$\dot{N}_{\text{abs}} = \sum_{\lambda} \dot{N}_{\text{abs}}(\lambda) \quad (4)$$

The photodegradation quantum yield Φ_{deg} is defined as the ratio between the number of decomposed molecules N_{deg} and the total number of absorbed photons N_{abs} , which equals the ratio between the degradation rate $\dot{N}_{\text{deg}}$ of the chromophore and the total rate of photon absorption $\dot{N}_{\text{abs}}$ [Eq (5)].

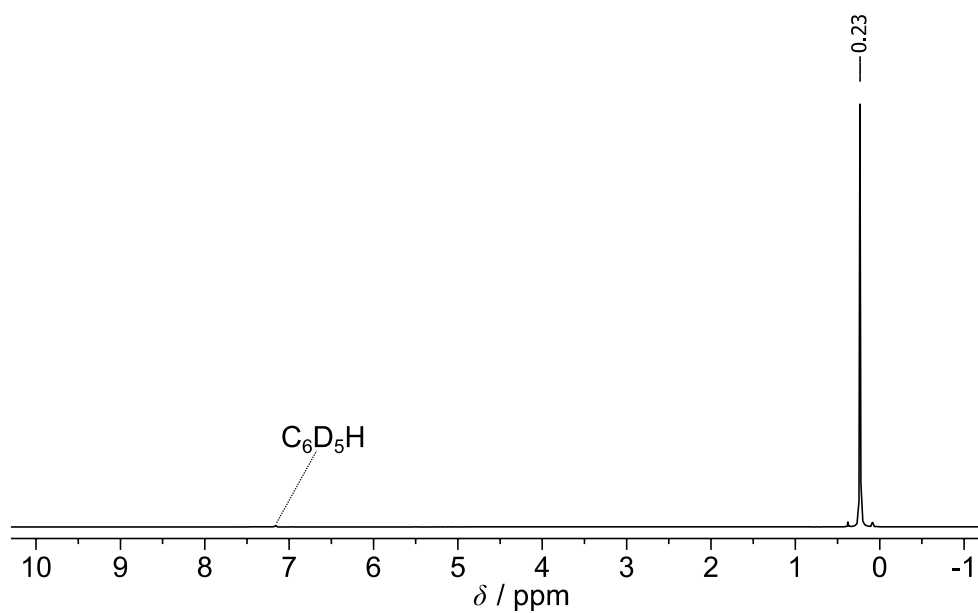
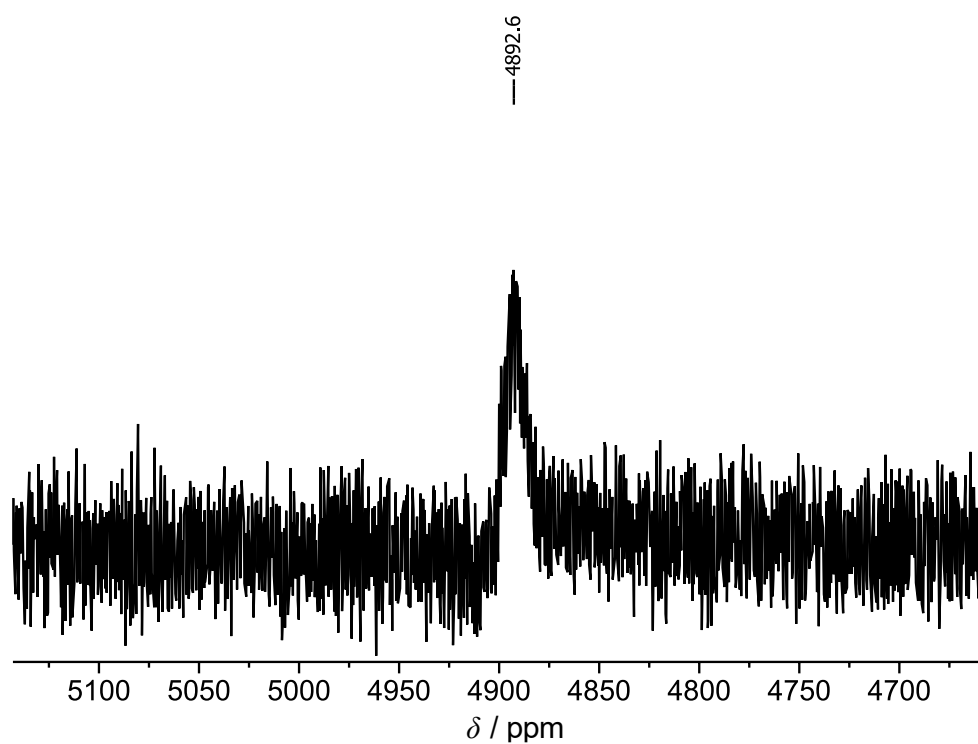
$$\Phi_{\text{deg}} = \frac{N_{\text{deg}}}{N_{\text{abs}}} = \frac{\dot{N}_{\text{deg}}}{\dot{N}_{\text{abs}}} \quad (5)$$

Density functional theory calculations were performed with *Orca 6.1.0*.^[3,4] Geometry optimizations were performed using (un)restricted Kohn-Sham orbitals DFT (RKS or UKS) and the B3LYP functional^[5–7] in combination with the ZORA-def2-TZVPP basis as recontracted *Ahlrich's* basis set def2-TZVPP^[8] or the SARC-ZORA-TZVPP basis^[9–13] with the auxiliary basis SARC/J^[9–12] as decontracted def2/J^[14] basis up to Kr to use the zeroth order regular approximation to describe relativistic effects in all calculations (keyword *ZORA*).^[15,16] Tight convergence criteria were chosen for (TD)DFT calculations (keywords *tightscf* and *tightopt*). All DFT calculations make use of the resolution of identity (Split-RI-J) approach for the Coulomb term in combination with the chain-of-spheres approximation for the exchange term (keyword *RIJCOSX*).^[17–20] To account for solvent effects, a conductor-like screening model (keyword *CPCM(hexane)*) modelling hexane was used in all calculations.^[21,22] Atom-pairwise dispersion correction was performed with the *Becke-Johnson* damping scheme (keyword *D3BJ*).^[23,24] A numerical frequency calculation confirmed that the optimized geometry corresponds to a minimum structure. Explicit solvent molecules were not considered. The 2D relaxed potential energy surface scans with 130 points were performed on the CPCM(hexane)-RIJCOSX-(U)B3LYP-D3BJ-def2/J-def2-SVP level with subsequent single-point calculations at higher level (CPCM(hexane)-RIJCOSX-(U)B3LYP-D3BJ-SARC/J-ZORA/def2-TZVPP/SARC-ZORA-TZVPP(Pb)). Transition states were localized, using the OPTTS keyword and assigned with a subsequent calculation of the internal reaction coordinate (keyword IRC). The charge transfer number analyses of the TDDFT calculated transitions were done using *TheoDORE*.^[25,26] Fifty spin-allowed and spin-forbidden transitions were calculated by TDDFT with and without the keyword *triplets true*. SOC-TDDFT calculations were performed using the additional keywords *DoSOC true*, *TDA false* and *RI-SOMF(1X)*.^[27] All calculations were computed on the supercomputer Elwetritsch with advisory services offered by the RPTU Kaiserslautern-Landau (<https://hpc.rz.rptu.de>), which is a member of the AHRP. All coordinates are provided in an additional xyz file.

Synthesis



Pb[N(SiMe₃)₂]₂ (PbH): PbH was prepared according to modified literature procedures.^[24–26] In a Schlenk tube, lithium bis(trimethylsilyl)amide (18.00 g, 108 mmol, 1.86 eq) was combined with dry lead dichloride (16.00 g, 58 mmol, 1.00 eq). Diethylether (100 mL) was added slowly under strong stirring and cooling (ice-water bath). Immediately, the cloudy colorless mixture turned yellow, and the reaction was stirred for 12 h at room temperature. The resulting LiCl was removed from the solution by filtration, and the solvent was removed under reduced pressure resulting in a red oil. The crude product was distilled under reduced pressure yielding the desired product as a red oil, which solidified with liquid nitrogen cooling to a yellow solid. (19.00 g, 36 mmol, 62%), ¹H NMR (400 MHz, C₆D₆): δ = 0.23 (s, CH₃) ppm. ²⁰⁷Pb NMR (149 MHz, C₆D₆): 4892.6 ppm. UV/Vis (*n*-pentane): λ (ε) = 410 (1500), 350 (sh, 1400), 315 (2000 M^{−1} cm^{−1}).

Figure S 1: ^1H NMR spectrum of **PbH** in C_6D_6 .Figure S 2: ^{207}Pb NMR spectrum of **PbH** in C_6D_6 .

Photophysical Properties

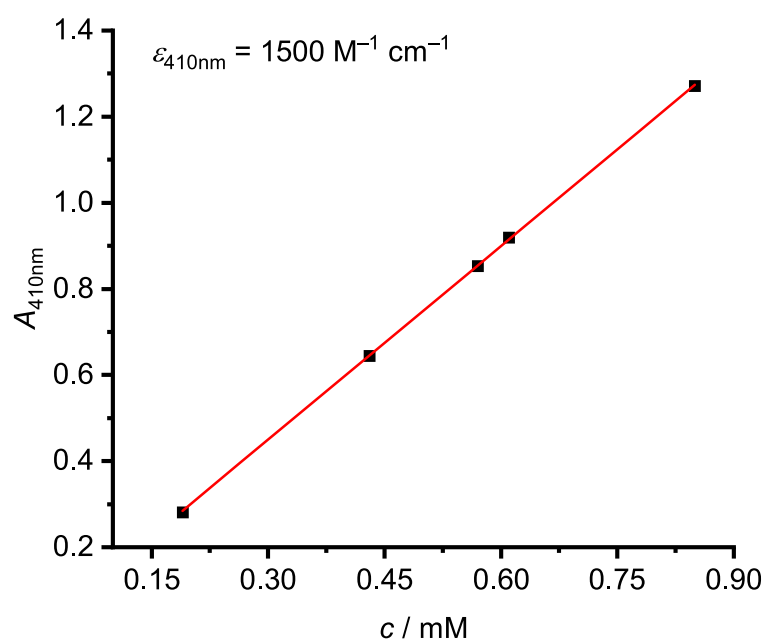


Figure S 3: UV/Vis absorption versus concentration plot of **PbH** in *n*-pentane at $\lambda = 410$ nm with linear fit in red. The intercept of the fit is set to 0 mM.

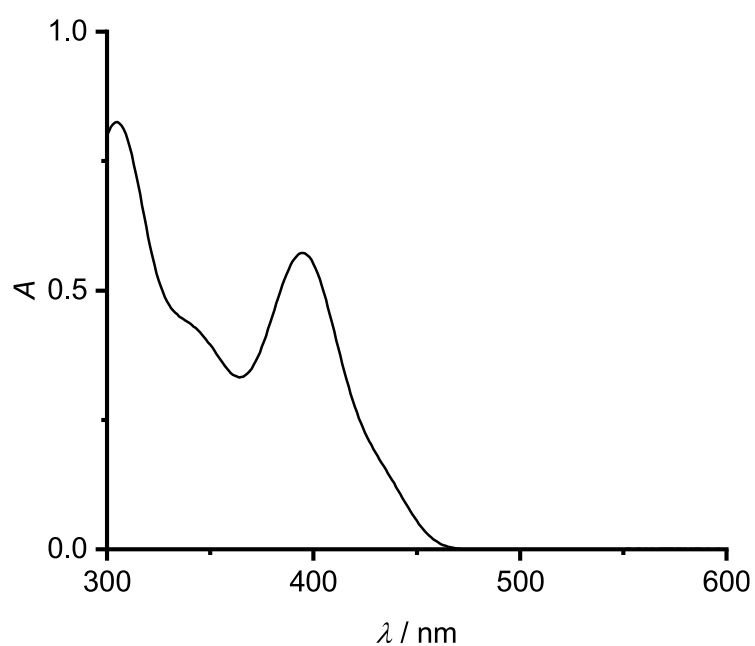


Figure S 4: UV/Vis absorption spectrum of **PbH** ($c = 2.1$ mM) in 3-methylpentane at 77 K

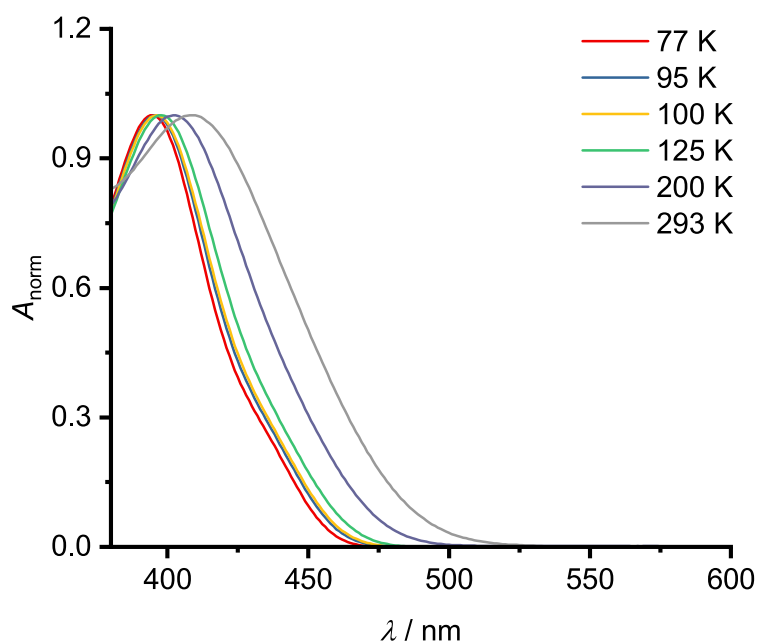


Figure S 5: Normalized UV/Vis absorption spectra of **PbH** in 3-methylpentane between 77 K (red) and 293 K (grey).

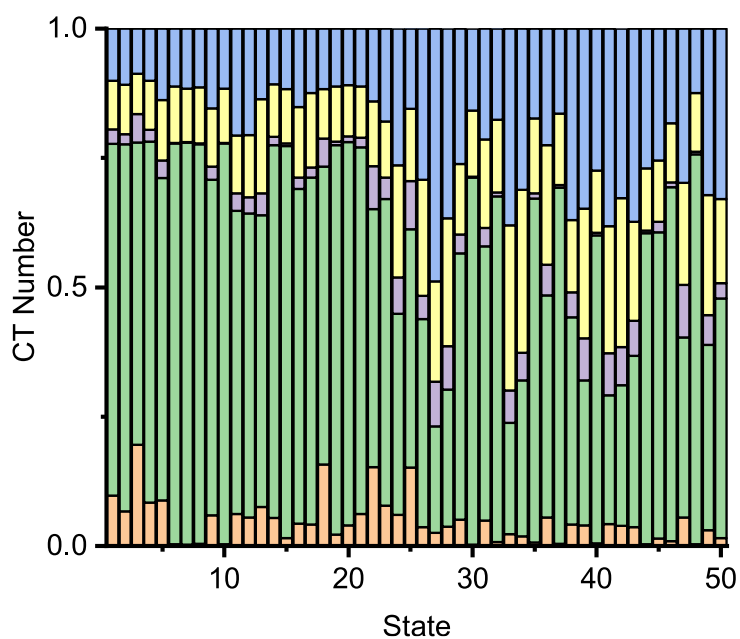


Figure S 6: Charge transfer number analysis of the 50 lowest spin-allowed transitions of **PbH** (orange: MC, green: LMCT, purple: MLCT; yellow: LLCT, blue: LC). CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Pb).

Table S 1: Selected molecular orbitals of **PbH** with energies given in eV, displayed at an isosurface value of 0.06 a.u.. Mulliken symbol of the orbital character given in idealized C_{2v} point group of the N–Pb–N unit. Hydrogen atoms are omitted. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Pb).

HOMO–2(a_1) / –6.829	HOMO–1(b_1) / –6.126	HOMO(a_1) / –5.936	LUMO(b_2) / –2.215

Table S 2: SOC constants as square root of the sum of the squares of SOC matrix elements in cm^{-1} between the lowest singlet and triplet states derived from SOC TD-DFT calculations on the geometry optimized GS structure of **PbH**. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA-def2-TZVPP/ RI-SOMF(1X)/SARC-ZORA-TZVPP(Pb).

	S_0	S_1	S_2	S_3
T_1	1528	233	416	198
T_2	125	265	179	182
T_3	2154	152	674	73

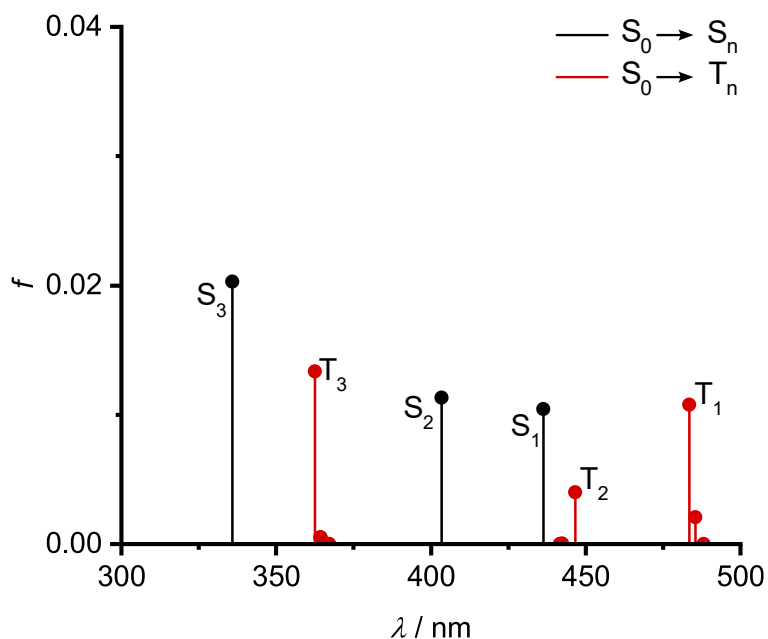


Figure S 7: Selected SOC corrected oscillator strength f from TD-DFT calculations of **PbH**. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Pb). Note the splitting of the T levels into $M_s = 0, \pm 1$ sublevels by SOC.

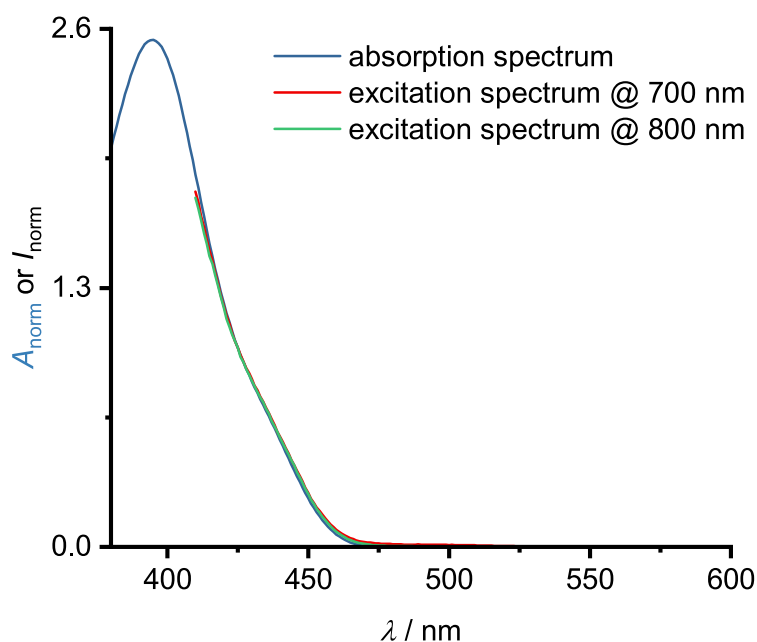


Figure S 8: Excitation spectra of **PbH** in 3-methylpentane at 77 K at $\lambda_{\text{em}} = 700$ nm in red and $\lambda_{\text{em}} = 800$ nm in green ($c = 0.08$ mM) as well as the UV/Vis absorption spectrum of **PbH** in 3-methylpentane at 77 K in blue ($c = 2.1$ mM).

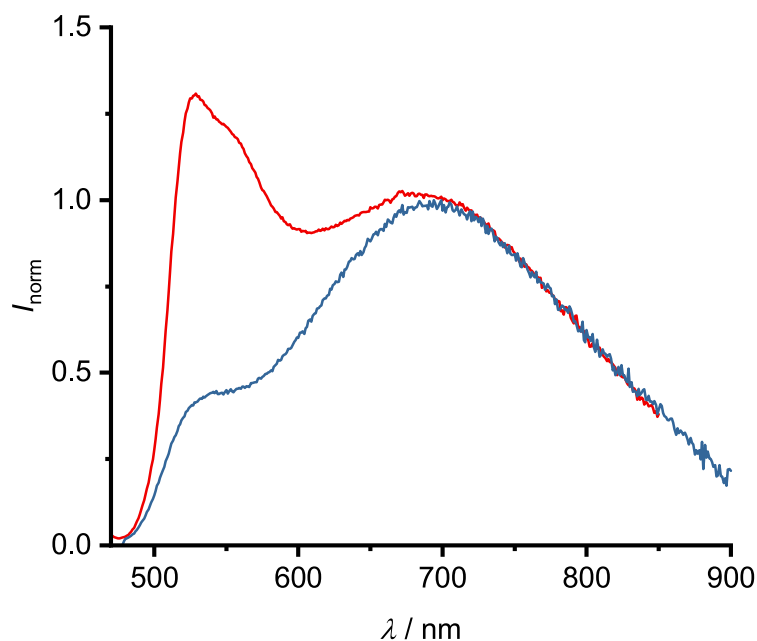


Figure S 9: Emission spectra of two different **PbH** samples in 3-methylpentane at 77 K upon $\lambda_{\text{exc}} = 410$ nm excitation. The spectrum of the freshly distilled batch is marked in blue, the spectrum of the older batch is marked in red.

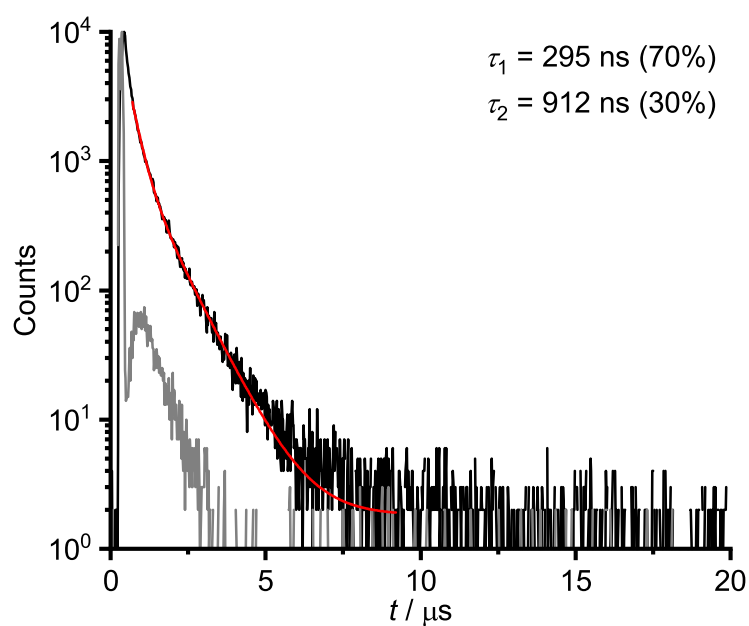


Figure S 10: Emission decay curve of **PbH** at $\lambda_{\text{em}} = 850$ nm in 3-methylpentane at 77 K upon $\lambda_{\text{exc}} = 450$ nm excitation superimposed with a biexponential fit (red) and IRF (gray).

Table S 3: Selected structural parameters in Å and deg.[°] of solid state structure of **PbH** from XRD^[27] analyses and of DFT calculated geometry optimized structures of **PbH** in the ¹GS, T₁, T₂ and transition state (TS).

	PbH (XRD) ^[27]	¹ GS (DFT)	T ₁ (DFT)	T ₂ (DFT)	TS (DFT)
Pb–N ¹	2.260	2.245	2.650	2.270	2.341
Pb–N ²	2.222	2.230	2.277	2.690	2.346
N ² –Pb–N ¹	103.56	100.54	94.93	93.38	98.90

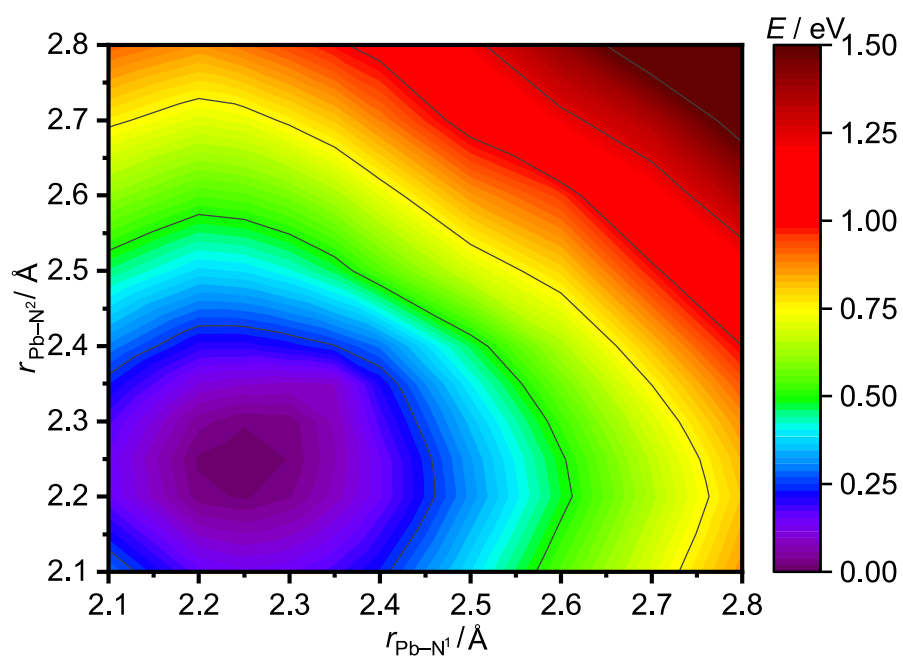


Figure S 11: Contour plot of 2D relaxed potential energy surface scan as projection along the Pb–N¹ and Pb–N² stretching mode on the singlet hypersurface of **PbH**. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Pb).

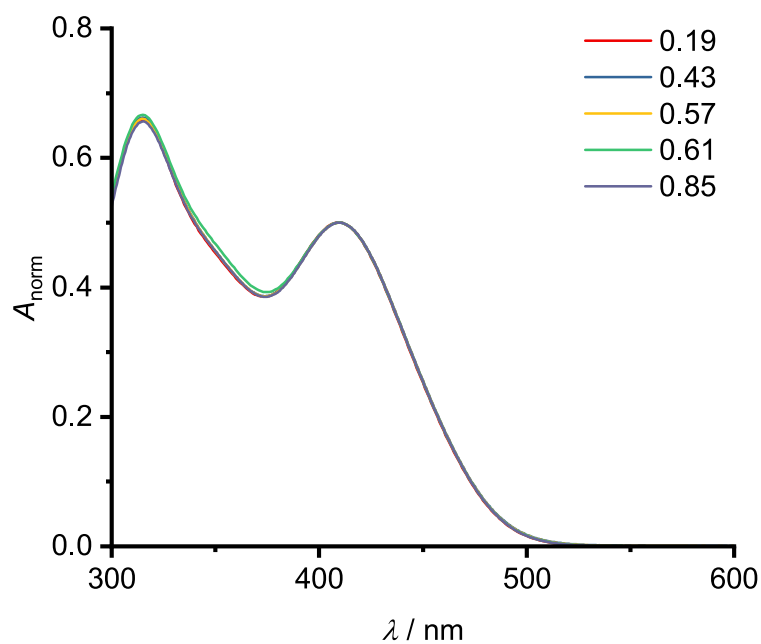


Figure S 12: Normalized UV/Vis absorption spectra of **PbH** at various concentrations in *n*-pentane at room temperature.

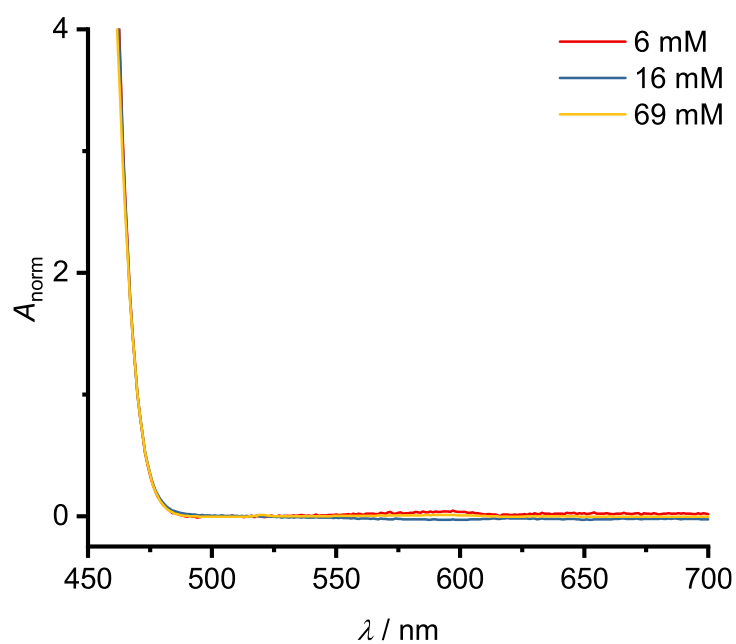


Figure S 13: Normalized UV/Vis absorption spectra of **PbH** at various concentrations in 3-methylpentane at 77 K.

Irradiation

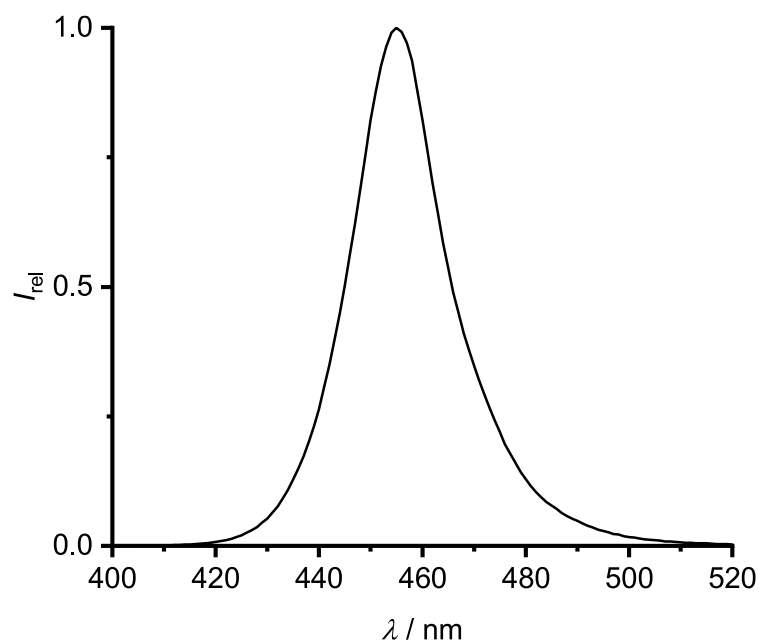


Figure S 14: Emission spectrum of the Ultra-High Power collimated LED from UHP-T-460-DI.

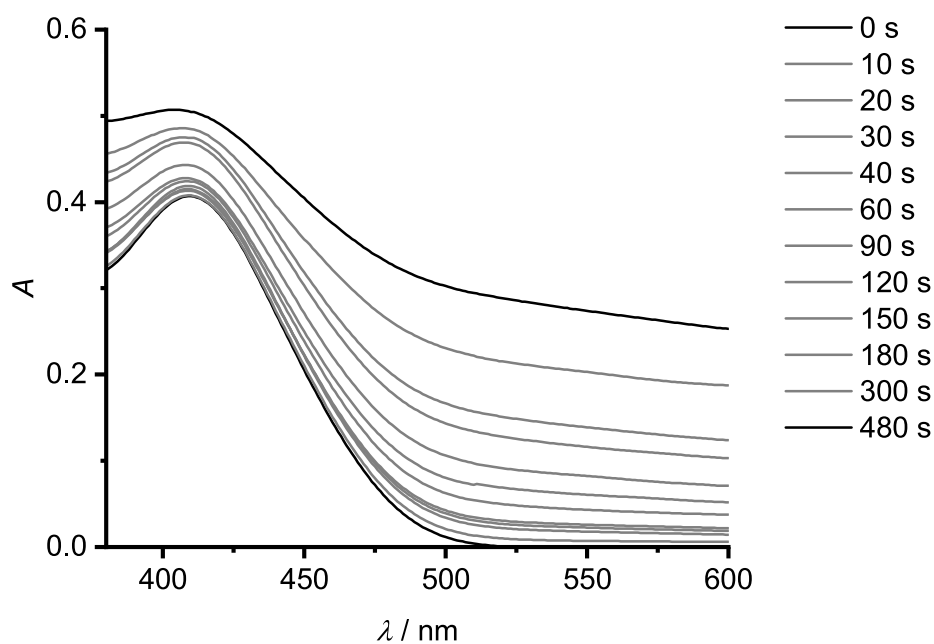


Figure S 15: Uncorrected UV/Vis absorption spectra (0 – 480 s) during the photolysis of **PbH** for $c = 0.27$ mM in *n*-pentane irradiated at $\lambda_{\text{exc}} = 455$ nm ($P = 0.03$ W).

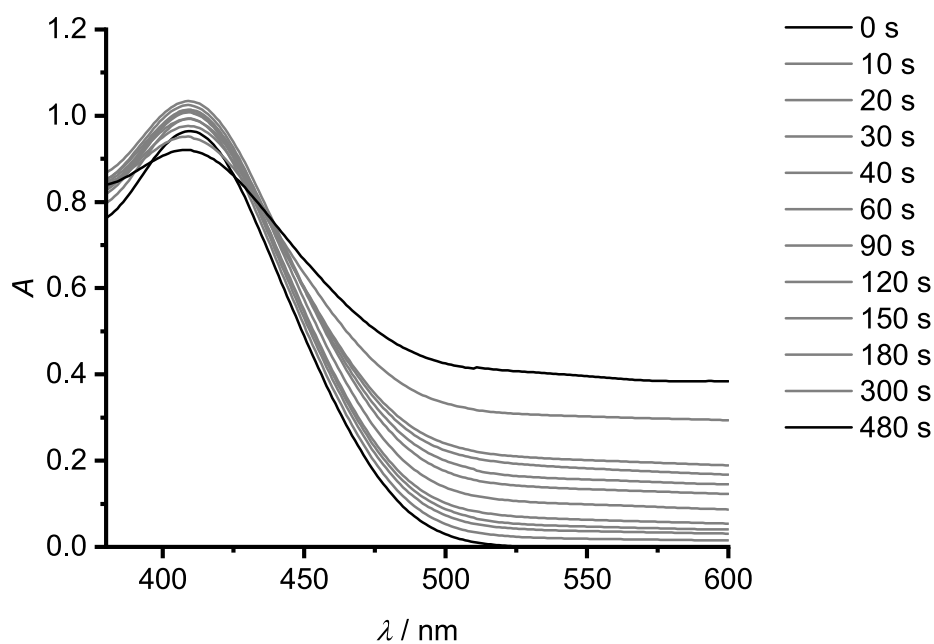


Figure S 16: Uncorrected UV/Vis absorption spectra (0 – 480 s) during the photolysis of **PbH** for $c = 0.64$ mM in *n*-pentane irradiated at $\lambda_{\text{exc}} = 455$ nm ($P = 0.03$ W).

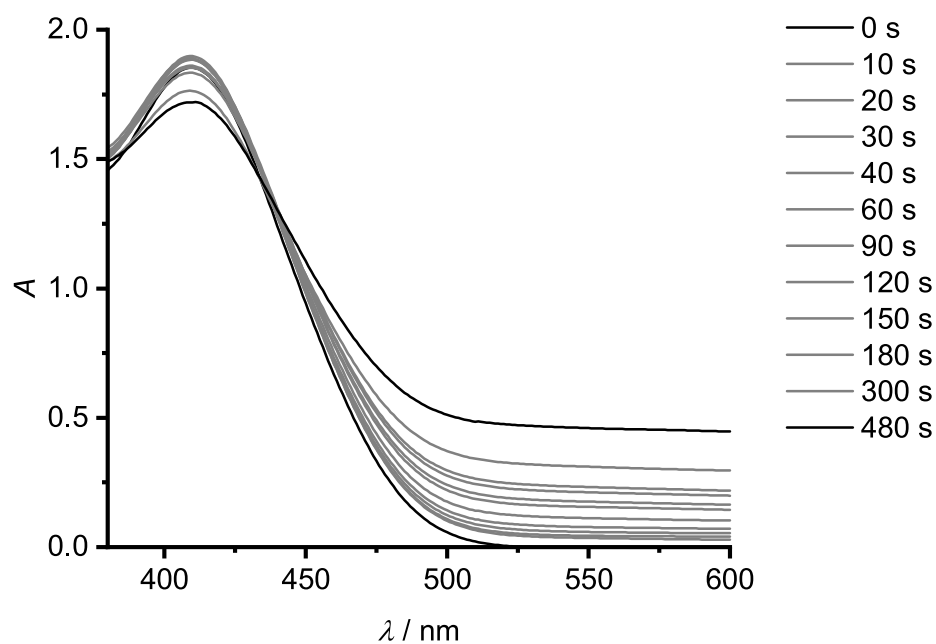


Figure S 17: Uncorrected UV/Vis absorption spectra (0 – 480 s) during the photolysis of **PbH** for $c = 1.2 \text{ mM}$ in n -pentane irradiated at $\lambda_{\text{exc}} = 455 \text{ nm}$ ($P = 0.03 \text{ W}$).

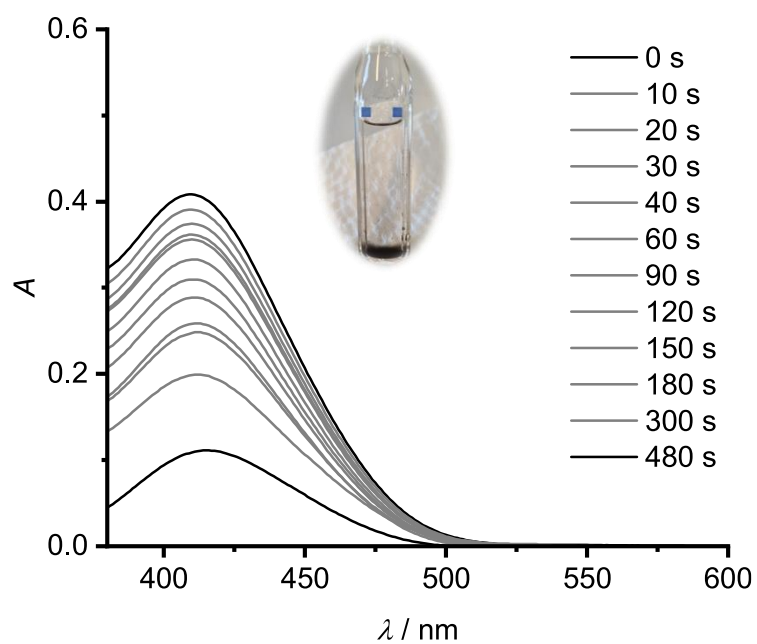


Figure S 18: Corrected UV/Vis absorption spectra (0 – 480 s) during the photolysis of **PbH** for $c = 0.27 \text{ mM}$ in n -pentane irradiated at $\lambda_{\text{exc}} = 455 \text{ nm}$ ($P = 0.03 \text{ W}$). The photograph shows the solution after irradiation.

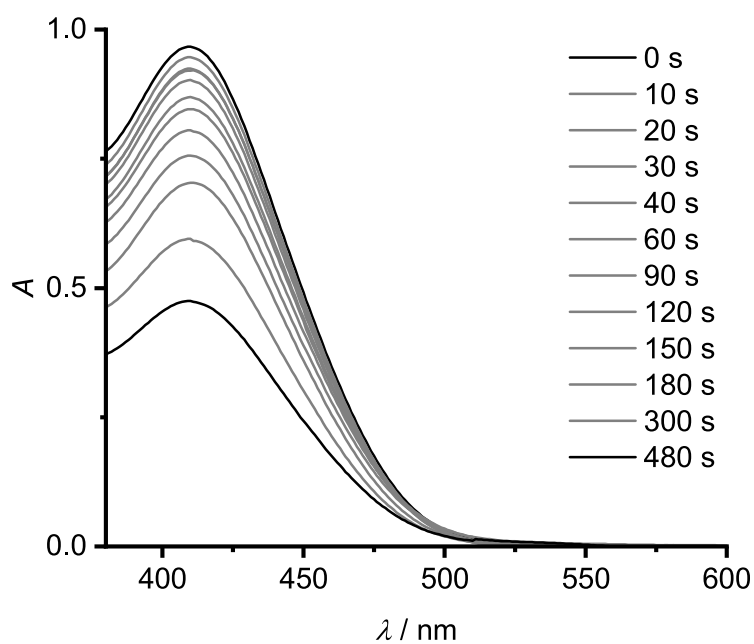


Figure S 19: Corrected UV/Vis absorption spectra (0 – 480 s) during the photolysis of **PbH** for $c = 0.64$ mM in *n*-pentane irradiated at $\lambda_{\text{exc}} = 455$ nm ($P = 0.03$ W).

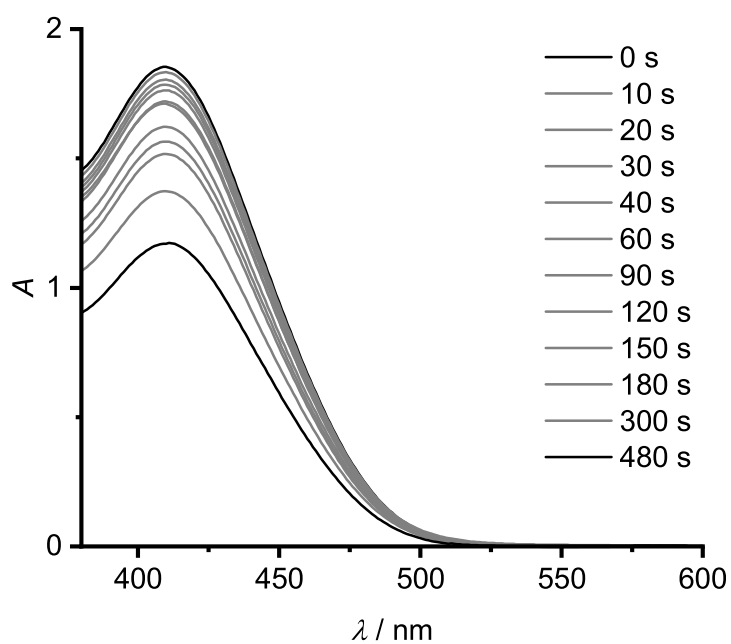


Figure S 20: Corrected UV/Vis absorption spectra (0 – 480 s) during the photolysis of **PbH** for $c = 1.2$ mM in *n*-pentane irradiated at $\lambda_{\text{exc}} = 455$ nm ($P = 0.03$ W).

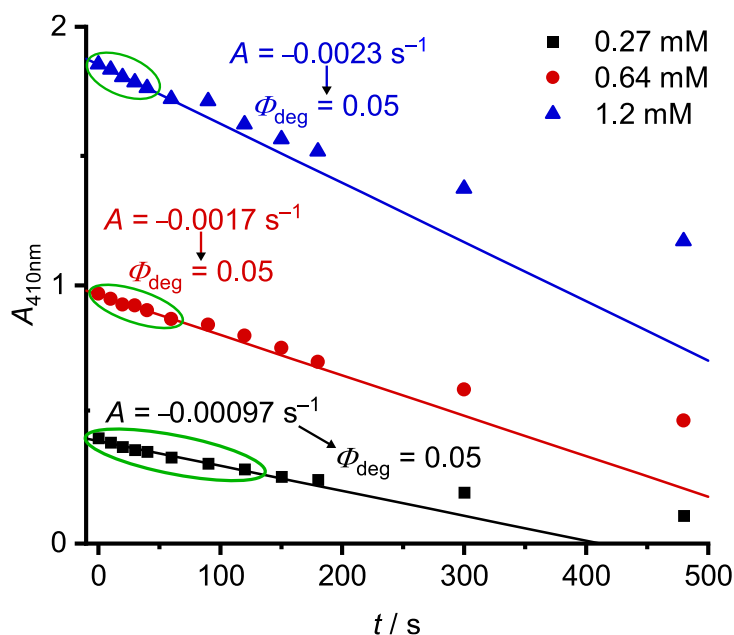


Figure S 21: UV/Vis absorption versus time plots of **PbH** in *n*-pentane at $\lambda = 410$ nm of photolysis measurements at $c = 0.27$, 0.64 and 1.2 mM with linear fits of the data points within the time interval $0 - 120$ s - 8 data points for $c = 0.27$ mM, $0 - 60$ s - 6 data points for $c = 0.64$ mM, $0 - 40$ s - 5 data points for $c = 1.2$ mM marked in green.

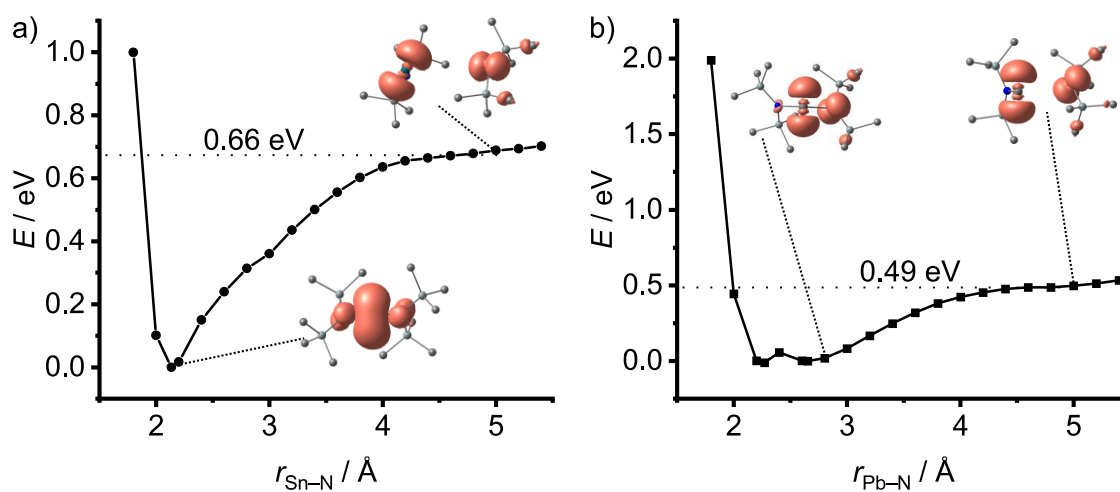


Figure S 22: Relaxed potential energy surface scans as projection along the E-N¹ distance of the respective T₁ state with estimated bond dissociation energy for a) Sn[N(SiMe₃)₂]₂ and b) **PbH**. Hydrogen atoms are omitted. Spin densities of selected geometries (isosurface value: 0.005 a.u.). CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn/Pb).

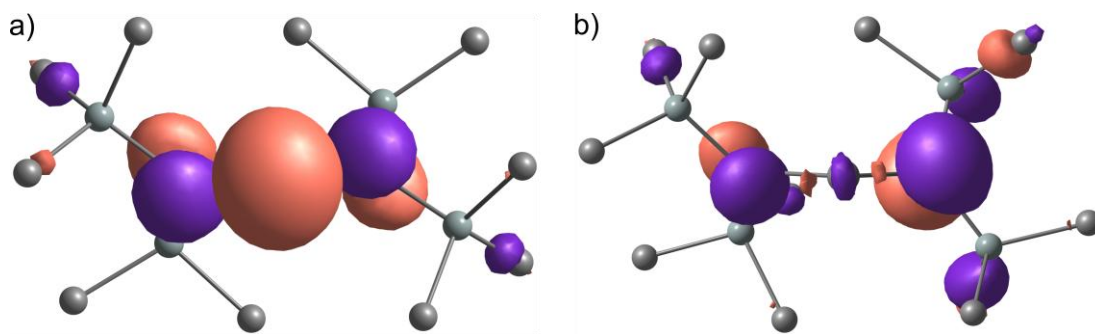


Figure S 23: Calculated HOMOs of a) $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ and b) **PbH**, displayed at an isosurface value of 0.05, Hydrogen atoms are omitted. CPCM(hexane)-RIJCOSX-B3LYP-D3BJ-SARC/J-ZORA-def2-TZVPP/SARC-ZORA-TZVPP(Sn/Pb).

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6.5 Use of AI Tools

AI tool	Used for	Why	When
ChatGPT	- Grammar checking - Dictionary and vocabulary reference - Wording and phrasing	Better readability	Throughout the entire work

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