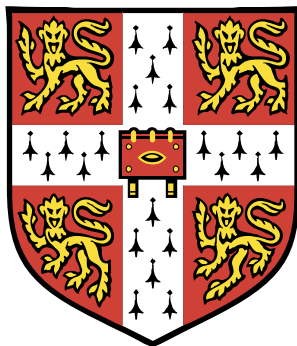


Modulated Magnetic Field Effects, Molecular Design, and Indigoids: A Mechanistic Study of Singlet Fission



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Declaration

This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the acknowledgements and specified in the text. It is not substantially the same as any work that has already been submitted before for any degree or other qualification except as declared in the preface and specified in the text. It does not exceed the prescribed word limit of 60,000 words, including appendices and footnotes. The use of the first person plural throughout is strictly a matter of style, in keeping with scientific convention.

Jessica Ruth Walton

September 2023

Abstract

Author Jessica Ruth Walton

Title Modulated Magnetic Field Effects, Molecular Design, and Indigoids:
A Mechanistic Study of Singlet Fission

Singlet fission has the potential to significantly enhance the efficiency of photovoltaic light harvesting of silicon solar cells beyond the Shockley-Queisser limit. The progress of this technology has been hindered by the limited selection of suitable molecules that can undergo singlet fission, and the methods we use to screen new materials. This thesis is constructed in two parts: the investigation of two indigoids in their candidacy for singlet fission, and the use of an alternative method, modulated magnetic field effects in photoluminescence (modMPL), as a potential screening tool for materials.

After relevant theoretical and experimental background is discussed in Chapters 2 and 3, Chapter 4 presents an alternative method for investigating singlet fission: modMPL. We employ this highly sensitive technique to examine thin films of the well-studied singlet fission system, TIPS-tetracene. This technique reveals complex lineshapes describing the spin physics in great detail. ModMPL is a rapid, low-degradation technique, that greatly enhances the screening of new potential materials. In particular, it allows comparison of sample morphologies and their impacts on singlet fission dynamics in a way that is not currently available with conventional screening techniques. A discussion of how to simulate and understand modMPL lineshapes is included in Chapter 5.

Secondly, we make use of ultrafast transient absorption spectroscopy to investigate two indigoids, a novel aza-cibalackrot (Chapter 6) and thienoisindigo (Chapter 7). Both derivatives of indigo dyes, they are highly attractive candidates for singlet fission due to their superior photostability, high extinction coefficient, and ideal predicted triplet energy. We explore these new, versatile, potential molecular families for their singlet fission capability. Furthermore, we discuss an alternative molecular design principle for creating singlet fission candidates with greater photostability, which may then be applied to other molecular families in the search for singlet fission chromophores.

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Abbreviations and Constants

Molecules

DPH	diphenyl hexatriene
INDT	indolonaphthyridine thiophene
OAC	octyl-aza-cibalackrot
OC	octyl-cibalackrot
OHAC	octyl-hexyl-aza-cibalackrot
OHC	octyl-hexyl-cibalackrot
PdTPTBP	meso-tetraphenyl-tetrabenzoporphine palladium complex
TIIG	thienoisindigo
TIIG-EH	ethyl-hexyl-thienoisindigo
TIIG-Oct	octyl-thienoisindigo
TIPS-Tc	5,12-bis((triisopropylsilyl)ethynyl)tetracene

Abbreviations

DC	drop cast
DFT	density functional theory
ESR	electron spin resonance
FRET	Förster resonant energy transfer
FWHM	full-width at half maximum
GA	genetic algorithm
GIWAXS	grazing incidence wide angle X-ray scattering
GSB	ground state bleach
HOMO	highest occupied molecular orbital
ISC	intersystem crossing
LIA	lock-in amplifier
magPL	magnetic field effect photoluminescence

MARY	magnetically altered reaction yield
MFE	magnetic field effect
modMPL	modulated magnetic field effect photoluminescence
NOPA	non-collinear optical parametric amplifier
nsTA	nanosecond transient absorption
ODE	ordinary differential equation
ODMR	optically detected magnetic resonance
PL	photoluminescence
PLQE	photoluminescence quantum efficiency
PIA	photoinduced absorption
PMPV	photon-multiplier photovoltaic
PMT	photomultiplier tube
psTA	picosecond transient absorption
PV	photovoltaic
QD	quantum dot
S	singlet
SC	spin coated
SCRP	spin-correlated radical pair
SCTEP	spin-correlated triplet exciton pair
SF	singlet fission
SE	stimulated emission
SVD	singular value decomposition
S:N	signal-to-noise ratio
T	triplet
TA	transient absorption
TT	triplet-triplet pair
TTA	triplet-triplet annihilation
TCSPC	time correlated single photon counting
TDM	transition dipole moment

XRD	X-ray diffraction
ZFS	zero-field splitting

Physical Constants

Planck's constant h	$6.626 \times 10^{-34} \text{ Js}$
Reduced Planck's constant $\hbar$	$1.055 \times 10^{-34} \text{ Js}$
Bohr magneton μ_B	$9.274 \times 10^{-24} \text{ JT}^{-1}$
Electron g -factor g_e	-2.002

Chapter 1

Background and Motivation

In 2022, a milestone for solar energy was reached. Global solar energy generation capacity hit 1 TW (terra-watt); the culmination of 70 years of deployment and development [1–3]. However, to meet the 2015 Paris agreement of less than 2 °C global heating [4], it is estimated we need to deploy 70 TW by 2050 [3, 5]. It is clear that, to reach our target, the installation of solar energy harvesting must be accelerated.

The deployment of solar energy faces many challenges, ranging from their use of silver [3, 5], or reduced device performance due to increased prevalence of dust as conditions become hotter and more arid. Some of these challenges are being tackled already, such as the implementation of machine learning techniques to monitor and predict energy generation in solar farms, and identify issues such as dust [6, 7]. Some issues are yet to be fully faced; it is estimated solar panels will have consumed more than 80% of current global silver reserves by 2050 [3]. Meanwhile, solar energy faces a fundamental barrier to its efficacy and thus its deployment: energy harvesting efficiency.

For popular silicon solar cells, the energy harvesting efficiency is intrinsically limited to 29%, known as the Shockley-Queisser Limit [8, 9]. However, even the most efficient silicon solar cells fall short of this theoretical maximum, with 27.6% as the current highest value according to NREL [10]. Increasing the energy harvesting efficiency beyond the Shockley-Queisser limit would ease the barrier to large scale deployment of solar, and accelerate the global transition to low-carbon energy sources.

A silicon solar cell can only absorb a photon of energy greater than the band-gap of 1.1 eV, and any photon absorbed with energy above the band-gap will dissipate this excess as heat, reducing efficiency through *thermal losses* (discussed further in **Section 2.6**). Photon-multiplication technology is promising approach to mediate thermal losses in silicon photovoltaics (PVs). This process down-converts one high energy photon into two photons with half-energy at high efficiency. As detailed in **Chapter 2**, this down-conversion utilises singlet fission (SF), a quantum spin phenomenon, where the overlap of an excited singlet state and a ground singlet state produces two triplet states in a spin-conserved manner. The incorporation of singlet fission technologies has the potential to greatly enhance single junction silicon solar cell efficiencies beyond the Shockley-Queisser Limit up to 35-45% [9, 11–13]. Furthermore, the addition of photon-multiplication materials to a silicon solar cell may increase the device lifetime by reducing the thermal degradation experienced [14]. Such a technology to increase device efficiency and lifetime would greatly accelerate the deployment of solar panels.

The research of singlet fission and its integration with solar cells in photon-multiplication photovoltaics (PMPVs) has been ongoing for over a decade. The idea of sensitising a PV with singlet fission was first suggested by Dexter in 1979 [15], and gained popularity in the late 2000s [13]. However, the limited availability of suitable molecules that can meet the criterion for singlet fission has hindered the progress of this technology [9]. Singlet fission is a rare property, possessed only by some organic molecules which meet strict energetic requirements. Additionally, there must also be an ideal material morphology that allows for sufficient interchromophore coupling for singlet fission to occur. Furthermore, many current singlet fission molecules are unstable, making them unsuitable to use within solar cells. The search for an *ideal* singlet fission chromophore, with correct energetics and morphology, and desirable properties such as stability and high extinction coefficient, is ongoing [16], and requires consideration of the molecular design principles we employ in our search.

The scope of this research is in two parts. Firstly, in **Chapter 4**, this research considers the way in which we can screen the materials we consider, and offers an alternative experimental technique: modulated magnetic field effects in photoluminescence (modMPL). Conventional

methods for investigating singlet fission often require the comparison of many different techniques, such as transient absorption spectroscopy and electron spin resonance. Investigations require expert knowledge, are time intensive, and cause photodegradation. Furthermore, each technique often requires different sample preparations, and are each strongly influenced by sample morphology, meaning the complementary results of the techniques may actually be disparate. The alternative technique of modMPL, reported previously for exploration of spin correlated radical pair systems [17, 18], is highly sensitive, rapid, boasts low sample degradation, and interrogates the whole sample as an ensemble. ModMPL promises to bridge the gaps between the existing techniques, as it can be used on any sample before further measurements. Furthermore, it offers a unique insight into the <100 mT regime of magnetic field effects, allowing us to probe the spin system of singlet fission materials in great detail.

We employ modMPL to investigate thin films of the archetypal singlet fission system, TIPS-tetracene. With this highly sensitive technique, we can explore differences in singlet fission dynamics due to thin film morphologies. We gather evidence relevant to the ongoing debate in the singlet fission community on the emission from a triplet-pair or excimeric state. We make use of simulations in **Chapter 5** to understand the lineshapes generated from the technique, giving direct insight into the singlet fission dynamics. ModMPL offers a solution to investigating samples where morphology presents a barrier to understanding the material, and where signals may be too small to investigate with ESR or more traditional PL methods. It presents an excellent ‘first point of call’ methodology in the investigation of thin films of singlet fission materials.

Secondly, in **Chapters 6** and **7**, we focus on collaboration with synthetic chemists to characterise new, potential singlet fission candidates, based on derivatives of the highly stable, naturally derived, indigo dye [19–22]. **Chapter 6** examines a novel aza-cibalackrot, whose parent molecule is postulated to have ideal energetics, yet does not undergo singlet fission. We propose a simple chemical alteration to change the crystal structure of cibalackrot, and investigate whether this change has successfully ‘turned on’ singlet fission. **Chapter 7** investigates a previously reported thienoisindigo ([23–25]) through the lens of singlet fission. We predict that thienoisindigo follows a similar molecular motif to other recently reported

singlet fission chromophores [19] and explore its photophysics, with examination of the impacts of side-chain engineering. This exploration of indigo derivatives aims to broaden the pool of suitable materials by considering molecular engineering strategies, and by furthering understanding how crystal structure may influence singlet fission properties.

Through finding more suitable molecular families, and introducing alternative methods for screening them more quickly, robustly, with a deeper understanding of the signals we observe, we aim to consequently accelerate the field of singlet fission research for photovoltaic application.

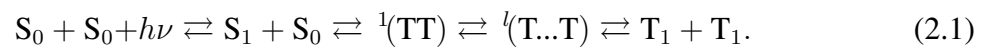
Chapter 2

Scientific Theory

2.1 Introduction

The theme of this research, as discussed in **Chapter 1**, is to investigate magnetic field effects and new potential materials for singlet fission. We aim to also gain a deeper mechanistic understanding of the photophysical processes involved. Ultimately, our findings about singlet fission materials aim to accelerate their deployment in photovoltaics, using the exciton multiplication properties of singlet fission to overcome the Shockley-Queisser limit of silicon solar cells [9].

Briefly, singlet fission is the conversion of a singlet excited state, S_1 , to two free triplet excited states, T_1 . The term ‘excited’ refers to a higher energy state, accessed through some initial absorption of a photon, $h\nu$. The terms ‘triplet’ and ‘singlet’ are referring to states of electron *spin*. The mechanism of singlet fission, to be further explained and understood throughout this chapter, is



The mechanism includes the intermediate state, the *triplet pair*, which is a four-electron state. This triplet pair state can be *strongly coupled*, ${}^1(TT)$, or *weakly coupled*, ${}^l(T...T)$. To explain this mechanism, we introduce the relevant physics in two parts: the spin physics, and the photophysics.

We begin by addressing electron spin, explaining singlet and triplet states, and understanding the four-electron triplet pair intermediate state relevant to the mechanism of singlet fission. We lay out the spin hamiltonian, and discuss the influence a magnetic field can have on singlets and triplets, relevant to **Chapters 4** and **5**. Secondly, we address the general photophysics of organic materials, including processes involved in singlet fission, such as absorption and emission, but also those that offer competing pathways to singlet fission.

After setting out the necessary spin physics and photophysics of singlet fission materials, we discuss the general molecular design principles and strict requirements governing singlet fission behaviour, relevant to **Chapters 6** and **7**. We then discuss how singlet fission can be applied to photovoltaics to circumvent the Shockley-Queisser limit on efficiency.

2.2 Electron Spin

Singlet fission is a phenomenon that utilises singlets and triplets, which are states that arise from electron *spin*: a quantum mechanical, intrinsic angular momentum with no classical analogue. Spin is characterised by two quantum numbers, s spin magnitude, and $m_s = s, s - 1, s - 2 \dots - s$, the spin projection, often represented in Dirac bra-ket notation, $|s, m_s\rangle$. The operators for total spin magnitude and z -axis projection are given by

$$\hat{\mathbf{S}}^2 |s, m_s\rangle = s(s + 1)\hbar^2 |s, m_s\rangle \quad (2.2)$$

$$\text{and } \hat{S}_z |s, m_s\rangle = m_s \hbar |s, m_s\rangle. \quad (2.3)$$

For an electron ($s = \frac{1}{2}$), two orthonormal states arise: $|\alpha\rangle = |\frac{1}{2}, +\frac{1}{2}\rangle$ and $|\beta\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle$, often referred to as ‘up’ and ‘down’ spins. In the absence of an external magnetic field, the $|\alpha\rangle$ and $|\beta\rangle$ states are degenerate.

A consequence of spin is that an electron has a magnetic moment, which can interact with external magnetic fields through the *Zeeman interaction*, the magnetic moment of nuclear spins through the *hyperfine interaction*, or with other electron spins through *dipolar* or *exchange couplings*. Each of these interactions are introduced below.

Zeeman Interaction

Electron spin gives rise to a magnetic moment,

$$\hat{\boldsymbol{\mu}} = -g_e \mu_B \hat{\mathbf{S}}, \quad (2.4)$$

where g_e is the electron g -factor, and $\mu_B = \frac{e\hbar}{2m_e}$ is the Bohr magneton, defined by electron charge, e and electron mass, m_e . The z -axis projection of the spin magnetic moment, $\hat{\mu}_z$, is given by

$$\hat{\mu}_z |s, m_s\rangle = -g_e \mu_B m_s |s, m_s\rangle. \quad (2.5)$$

The interaction of this magnetic moment with an external magnetic field, $\mathbf{B}$ is given by $-\hat{\boldsymbol{\mu}} \cdot \mathbf{B}$, and is described by the Hamiltonian

$$\hat{H}_Z = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} = g_e \mu_B \hat{\mathbf{S}} \cdot \mathbf{B}. \quad (2.6)$$

As a field is applied, the energy of the spin state is split depending on its spin projection, m_s . For a field applied in the z -direction, spin states with $m_s = 0$ are invariant under the Zeeman interaction, such that their energies remain constant with increasing magnetic field. For a sufficiently strong field in the z -direction, $\hat{\boldsymbol{\mu}}$ can be replaced with the z -component of the spin magnetic moment, $\hat{\mu}_z$, such that the energy eigenvalues are $E = g_e \mu_B m_s B_0$, where B_0 is the strength of the magnetic field along the z -axis. For an electron with $m_s = \pm \frac{1}{2}$, this gives an energy splitting of

$$\Delta E = g_e \mu_B B_0. \quad (2.7)$$

Depending on molecular geometry and spin-orbit coupling, the g -factor may be anisotropic, and so the more general form of the Zeeman interaction includes the g -tensor, $\mathbf{g}$,

$$\hat{H}_Z = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \hat{\mathbf{S}}. \quad (2.8)$$

In the presence of a field, a spin will precess around the field vector with a frequency called the Larmor frequency, ω_L , given by

$$\omega_L = \frac{g_e \mu_B}{\hbar} B_0. \quad (2.9)$$

Larmor precession plays a key role in processes such as spin mixing and relaxation. A summary of the $|\alpha\rangle$ and $|\beta\rangle$ states is shown in **Figure 2.1**. The spins are represented in the vector model in **(a)**, showing the cone of precession. The magnetic moments arising from the spins, $\boldsymbol{\mu}$, are also shown. The resulting energy level splitting from the Zeeman interaction is shown in **(b)**.

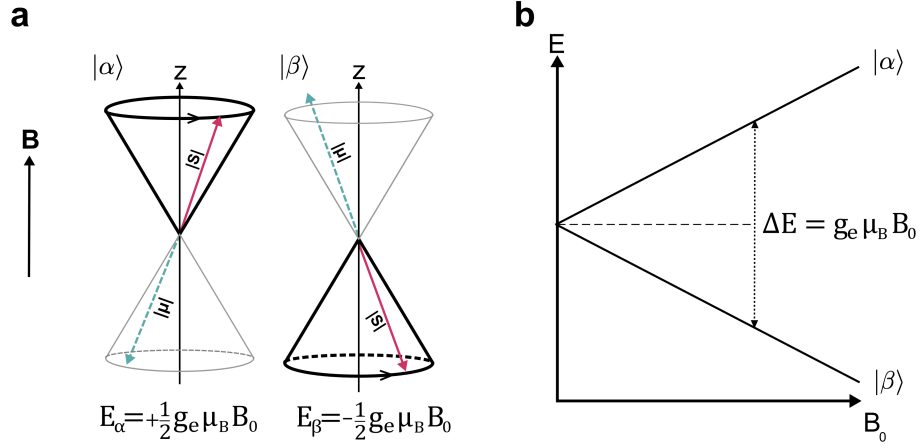


Figure 2.1: One electron spin: **(a)** the $|\alpha\rangle$ and $|\beta\rangle$ states represented by the vector model. The magnetic moment (dashed arrow) arising from the spin is also represented, and is anti-parallel to the spin vector. **(b)** The Zeeman interaction for a one electron system, resulting in the splitting of the degenerate $|\alpha\rangle$ and $|\beta\rangle$ states as an external field is applied. [26, 27]

Hyperfine Interaction

Electron spins can interact with the magnetic moments of nuclear spins, giving rise to the hyperfine interaction. The strength of this interaction is far smaller than that of the Zeeman interaction, on the μT - mT scale. The hyperfine interaction plays a large role in the field of spin-correlated radical pairs [28–31]. However, it is often neglected in the singlet fission community due to its relatively small contribution to the Hamiltonian. Nonetheless, the hyperfine interaction impacts Larmor precession, and has an influence over spin relaxation processes.

The hyperfine interaction can be separated into two parts, the isotropic Fermi contact interaction, and the anisotropic dipole-dipole interaction. The Fermi contact interaction is dependent on the s -character of the electronic wavefunction, or how much electron density penetrates the nucleus. The total hyperfine Hamiltonian, defined by hyperfine interaction tensor $\mathbf{A}$, between an electron spin $\hat{\mathbf{S}}$ and nuclear spin $\hat{\mathbf{I}}$, is given by

$$\hat{H}_{hf} = \hat{\mathbf{S}} \cdot \mathbf{A} \cdot \hat{\mathbf{I}}, \quad (2.10)$$

which can be separated into the isotropic contact interaction,

$$\hat{H}_{hf}^{contact} = a_0 \hat{\mathbf{S}} \cdot \hat{\mathbf{I}} \quad (2.11)$$

and the anisotropic dipolar interaction,

$$\hat{H}_{hf}^{dipolar} = a \left(\frac{\hat{\mathbf{S}} \cdot \hat{\mathbf{I}}}{r^3} - 3 \frac{(\hat{\mathbf{S}} \cdot \mathbf{r})(\hat{\mathbf{I}} \cdot \mathbf{r})}{r^5} \right), \quad (2.12)$$

where a_0 is the strength of the contact coupling, and $a = -\frac{\mu_0}{4\pi} g_e g_N \mu_B \mu_N$. μ_B and μ_N are the Bohr and nuclear magneton, g_e and g_N the electronic and nuclear g -factors, and $\mathbf{r}$ is the nuclear-electron spin separation [32, 33].

2.2.1 Interactions of Two Electron Spins

The spin angular momenta of multiple electrons in a system can be considered together, giving rise to new states beyond $|\alpha\rangle$ and $|\beta\rangle$.

There are two ways to describe the spin system for two electrons: the coupled and uncoupled representations. The uncoupled representation describes the two spins with separate vectors, such that the system is described as $|s_1, m_{s1}; s_2, m_{s2}\rangle$, giving rise to the eigenkets $|\alpha\alpha\rangle$, $|\alpha\beta\rangle$, $|\beta\alpha\rangle$ and $|\beta\beta\rangle$. The coupled representation specifies the system as $|s_1, s_2; S, M_S\rangle$, where S is the total angular momentum for the two electrons s_1 and s_2 , and is defined by the Clebsch-Gordan series $S = s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2|$. The total spin projection, M_S , is defined as $M_S = S, S - 1, \dots, -S$. One result of these representations is that $\hat{s}_{1z}$ and $\hat{S}^2$ do not commute, meaning the projection of one of the spins and the total spin angular momentum cannot both be specified simultaneously and precisely. This highlights the key difference between the uncoupled and coupled representations: the uncoupled precisely defines the individual magnitudes and projections of the spins, but cannot describe the total spin angular momentum; the coupled representation defines the total spin angular momentum and its projection, but cannot precisely define the individual spin components. However, the coupled representation can be written as a linear combination of the uncoupled states, as shown in **Table 2.1** [26, 34].

For a two-electron system, the interaction of spins gives rise to four possible states: three triplet states ($S = 1$), symmetric with respect to permutation, and an antisymmetric singlet state ($S = 0$). As a consequence of the Pauli principle, this implies that the singlet state must have a symmetric spatial wavefunction, and the triplets must have an antisymmetric spatial

$ S, M_S\rangle$	$ \Psi\rangle$		
$ 1, +1\rangle$	$ \alpha\alpha\rangle$	$ T_+\rangle$	} triplet
$ 1, 0\rangle$	$\frac{1}{\sqrt{2}}(\alpha\beta\rangle + \beta\alpha\rangle)$	$ T_0\rangle$	
$ 1, -1\rangle$	$ \beta\beta\rangle$	$ T_-\rangle$	
$ 0, 0\rangle$	$\frac{1}{\sqrt{2}}(\alpha\beta\rangle - \beta\alpha\rangle)$	$ S\rangle$	singlet

Table 2.1: Spin states for a two electron system, showing the coupled representation $|S, M_S\rangle$, where S and M_S are total spin magnitude and projection respectively, expressed as a linear combination of uncoupled states $|s_1, m_{s1}; s_2, m_{s2}\rangle$, where s_i is the spin quantum number of the individual electrons of the system. Shown are three triplet states ($S = 1$) and one singlet state ($S = 0$).

wavefunction, such that the total electron wavefunction

$$\Psi_{el} = \phi_{spatial}\psi_{spin} \quad (2.13)$$

is overall anti-symmetric under permutation. Similarly, the symmetric triplet states must have an antisymmetric spatial wavefunction. This is important to the *exchange interaction*, introduced shortly.

It is also worthwhile to mention that there are many possible eigenbases available to describe a multielectron system. The basis taken above, which gives rise to the triplet states $|T_+\rangle$, $|T_0\rangle$, and $|T_-\rangle$, is often referred to as the *high-field basis*. Another relevant basis set to consider is from the molecular coordinate system, x, y, z . This basis gives rise to the triplet states

$$\begin{aligned} |T_x\rangle &= \sqrt{\frac{1}{2}}(|T_-\rangle - |T_+\rangle) = \sqrt{\frac{1}{2}}(|\beta\beta\rangle - |\alpha\alpha\rangle) \\ |T_y\rangle &= i\sqrt{\frac{1}{2}}(|T_-\rangle + |T_+\rangle) = i\sqrt{\frac{1}{2}}(|\beta\beta\rangle + |\alpha\alpha\rangle) \\ |T_z\rangle &= |T_0\rangle = \sqrt{\frac{1}{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle), \end{aligned} \quad (2.14)$$

which we often refer to as the *zero-field basis* [35].

The spin states can be represented in the vector model, as shown in **Figure 2.2**. Under an external field, the spin states with non-zero spin projection, namely $|T_+\rangle$ and $|T_-\rangle$, will separate in energy with increasing field according to the Zeeman interaction, as shown in **(b)**. Each spin state will also have hyperfine structure due to the interaction of the electron spins with the

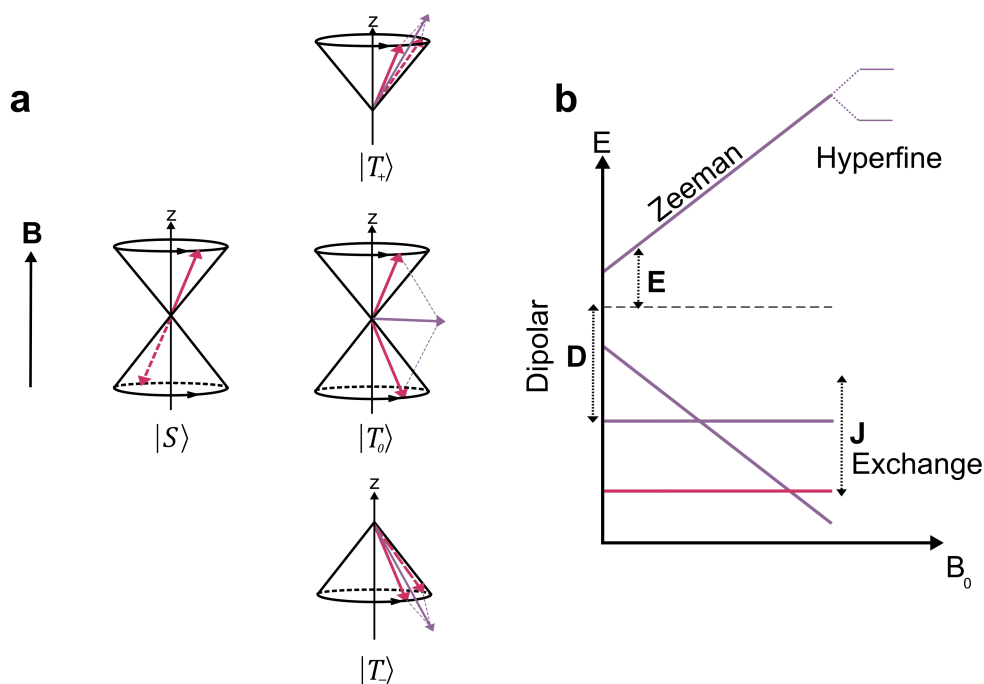


Figure 2.2: Two electron spins: (a) The singlet state and three triplet states, as described in **Table 2.1**, visualised with the vector model. (b) The energy levels of singlet and triplets under an applied magnetic field, showing the impacts of the dipolar interaction at zero field, the exchange interaction, the Zeeman interaction, and an example of the hyperfine interaction.

nuclear environment. Furthermore, electron spin will also interact with other electron spins, through electron-electron interactions. Similarly to the hyperfine interaction, the electron-electron interactions can be separated into isotropic and anisotropic parts: the isotropic *exchange* interaction, and anisotropic *dipolar* interaction, or *zero-field splitting*.

Exchange Interaction

The exchange interaction takes a similar mathematical form to the hyperfine contact interaction, but arises from a different physical basis. The exchange interaction results in spin states of different multiplicities having different energies. This is a result of symmetry in the wavefunction. As mentioned, the singlet has an antisymmetric spin wavefunction and a symmetric spatial wavefunction. The lowest energy symmetric spatial wavefunction has no nodes, while the lowest anti-symmetric spatial wavefunction has one node. The presence of a node in the antisymmetric spatial wavefunction allows for overall greater spatial separation of the electrons, resulting in reduced Coulombic or electrostatic repulsion of the two negatively charged

particles. The indirect result of the symmetry of the triplet spin wavefunction, therefore, is that the total wavefunction has been lowered in energy compared to the singlet state.

Mathematically, we describe the exchange interaction as

$$\hat{H}_{ex} = -J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = -J\left(\frac{1}{2}S_{tot}(S_{tot} + 1) - \frac{3}{4}\right) \quad (2.15)$$

where $J = 2K$, where K is the exchange integral from the Coulombic treatment of electronic wavefunctions in the literature [26, 36]. For $S_1 = S_2 = \frac{1}{2}$, then $E_{ex} = \frac{3}{4}J$ for $S = 0$ and $-\frac{1}{4}J$ for $S = 1$, giving an energy difference of J between the singlet and triplet states. J can be positive or negative, which determines whether the singlet is higher or lower than the triplet state in energy.

Zero-Field Splitting

In the absence of a magnetic field, the energy levels of the three triplet states are separated according to the zero-field splitting (ZFS), or dipolar interaction¹. The general form of the ZFS arising from the electron magnetic moments, $\boldsymbol{\mu}$, is

$$\hat{H}_{zfs} = \frac{\mu_0}{4\pi} \left(\frac{\hat{\boldsymbol{\mu}}_1 \cdot \hat{\boldsymbol{\mu}}_2}{r^3} - 3 \frac{(\hat{\boldsymbol{\mu}}_1 \cdot \mathbf{r})(\hat{\boldsymbol{\mu}}_2 \cdot \mathbf{r})}{r^5} \right), \quad (2.16)$$

similarly to the anisotropic hyperfine interaction. From the definition of the electron magnetic moment, we find

$$\hat{H}_{zfs} = g_1 g_2 \mu_B^2 \frac{\mu_0}{4\pi} \left(\frac{\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2}{r^3} - 3 \frac{(\hat{\mathbf{S}}_1 \cdot \mathbf{r})(\hat{\mathbf{S}}_2 \cdot \mathbf{r})}{r^5} \right). \quad (2.17)$$

We define a $\mathbf{D}$ tensor in the x, y, z molecular basis

$$\mathbf{D} = \frac{\mu_0 g_1 g_2 \mu_B^2}{8\pi} \begin{bmatrix} \langle \frac{r^2 - 3x^2}{r^5} \rangle & \langle \frac{-3xy}{r^5} \rangle & \langle \frac{-3xz}{r^5} \rangle \\ & \langle \frac{r^2 - 3y^2}{r^5} \rangle & \langle \frac{-3yz}{r^5} \rangle \\ & & \langle \frac{r^2 - 3z^2}{r^5} \rangle \end{bmatrix} \quad (2.18)$$

¹as we study organic molecules in this thesis, we consider only the dipolar interaction of ZFS, and neglect any contribution from spin-orbit coupling.

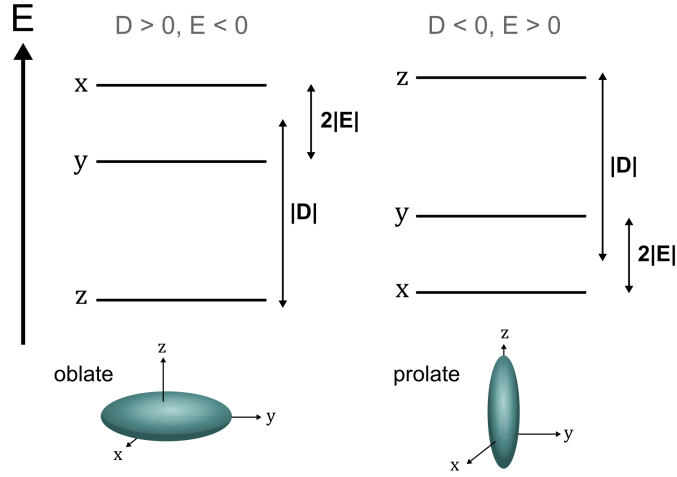


Figure 2.3: Zero-field splitting parameters, D and E , for an oblate (disc-like) and prolate (rod-like) spin density distributions for a field parallel to z . Reproduced from [37].

where angular brackets denote expectation values, and r is the distance between the two spins.

With the $\mathbf{D}$ tensor, we can write the ZFS Hamiltonian as

$$\hat{H}_{zfs} = \hat{\mathbf{S}} \cdot \mathbf{D} \cdot \hat{\mathbf{S}}. \quad (2.19)$$

Taking the eigenvalues of $\mathbf{D}$, $D_{x,y,z}$, we rewrite this as

$$\hat{H}_{zfs} = D_x \hat{S}_x^2 + D_y \hat{S}_y^2 + D_z \hat{S}_z^2. \quad (2.20)$$

As we can select $\mathbf{D}$ to be traceless, meaning $D_x + D_y + D_z = 0$, we can write $\hat{H}_{zfs}$ as

$$\hat{H}_{zfs} = D \left(\hat{S}_z^2 - \frac{1}{3} S(S+1) \right) + E \left(\hat{S}_x^2 - \hat{S}_y^2 \right) \quad (2.21)$$

where $D = \frac{3}{2} D_z$, $E = \frac{1}{2} (D_x - D_y)$. By convention, $|D| \geq 3|E|$, and $|D_z| \geq |D_x| \geq |D_y|$ [33, 35, 37]. The key result of the ZFS interaction is that $T_{x,y,z}$ are not degenerate at zero-field, as seen in **Figure 2.2 (b)**. The sign of the D parameter is related to the electron spin density distribution. E is a measure of the rhombicity of the $\mathbf{D}$ tensor. The resulting splitting of triplet sub-levels for an oblate and prolate spin density distribution with respect to a field applied along z can be seen in **Figure 2.3** [37].

2.2.2 The Triplet Pair

Within singlet fission, there is an intermediate state made up of 4 electrons. From the one electron basis, we can find 16 possible states for the 4-electron system: $|\alpha\alpha\alpha\alpha\rangle, |\alpha\alpha\alpha\beta\rangle, \dots, |\beta\beta\beta\beta\rangle$ [35]. By taking linear combinations of these states, we arrive at 16 pure spin states: two singlets ($S=0$), 9 triplets ($S=1$), and 5 quintets ($S=2$). Much theoretical consideration of the 4-electron state has been performed by Kollmar [38] and Scholes [39], as reviewed by Musser and Clark [35]. To simplify the spin physics, we take a more simple basis, and consider the system as two pairs of electrons, or two $S=1$ triplets, interacting. In this basis, we tend to only consider the 9 lowest lying states, as prescribed by Merrifield [40], giving one singlet state, three triplet states, and five quintet states. The singlet state is written as

$$|S\rangle = \sqrt{\frac{1}{3}}(|+-\rangle + |-+\rangle - |00\rangle) \quad (2.22)$$

in the high-field basis, or

$$|S\rangle = \sqrt{\frac{1}{3}}(|xx\rangle + |yy\rangle + |zz\rangle) \quad (2.23)$$

in the low-field basis, where $|++\rangle$ denotes $|T_+, T_+\rangle$ and $|xx\rangle$ denotes $|T_x, T_x\rangle$ for each of the constituent triplets within the pair. This singlet $S=0$ state is considered to be the correlated triplet pair state, denoted as $^1(TT)$. In the low-field basis, we write the triplet and quintet states as

$$\begin{aligned} |T_x\rangle &= \sqrt{\frac{1}{2}}(|yz\rangle - |zy\rangle) \\ |Q_a\rangle &= \sqrt{\frac{1}{2}}(|xx\rangle - |yy\rangle) \\ |Q_b\rangle &= \sqrt{\frac{1}{6}}(|xx\rangle + |yy\rangle - 2|zz\rangle) \\ |Q_x\rangle &= \sqrt{\frac{1}{2}}(|yz\rangle + |zy\rangle) \end{aligned} \quad (2.24)$$

with $|T_y\rangle, |T_z\rangle, |Q_y\rangle, |Q_z\rangle$ obtained through cyclic permutation. In the high-field basis, the triplet and quintet states are written as

$$\begin{aligned}
|T_{\pm}\rangle &= \sqrt{\frac{1}{2}}(|\pm 0\rangle - |0\pm\rangle) \\
|T_0\rangle &= \sqrt{\frac{1}{2}}(|+-\rangle - |-+\rangle) \\
|Q_{\pm 2}\rangle &= |\pm\pm\rangle \\
|Q_{\pm 1}\rangle &= \sqrt{\frac{1}{2}}(|\pm 0\rangle + |0\pm\rangle) \\
|Q_0\rangle &= \sqrt{\frac{1}{6}}(|+-\rangle + |-+\rangle + 2|00\rangle)
\end{aligned} \tag{2.25}$$

The role of this so called triplet pair, with its 9 spin sublevels, is to act as an intermediate state to the mechanism. The existence of the triplet-pair state has been observed through numerous experiments, such as transient absorption spectroscopy [35, 41–45], vibrational spectroscopy [46, 47], optically detected magnetic resonance, and electron spin resonance [48–50]. There are reports the triplet pair can be emissive, again evidencing the existence of this state [41, 42, 45, 51].

A summary of the 9 considered sublevels of the triplet pair state are shown in **Figure 2.4**, with a representation of an $M_S = 2$ quintet state in the vector model, and a summary of the energy level splittings in an applied magnetic field. The states with $M_S = 0$ remain unchanged with applied field. The zero-field splitting is a feature of both the triplet and the quintet sublevels, which have distinct ZFS parameters, D_T and E_T for the triplet states and D_Q and E_Q for the quintet states [50].

2.2.3 The Spin Hamiltonian

Piecing together all the relevant information from the previous sections, we can now assemble the spin Hamiltonian for the triplet pair state. Only one interaction remains undiscussed: the intertriplet dipolar coupling. In the framework we have considered, the triplet pair state is formed of two interacting triplets. Each triplet will have an intratriplet dipolar coupling, or zero-field splitting. The two triplets will also have a dipolar coupling, which depends on the distance r between the two triplets. Whilst this takes a similar form to the ZFS previously discussed, the tensor defining this interaction will be labelled as $\mathbf{X}$ for clarification. Typically,

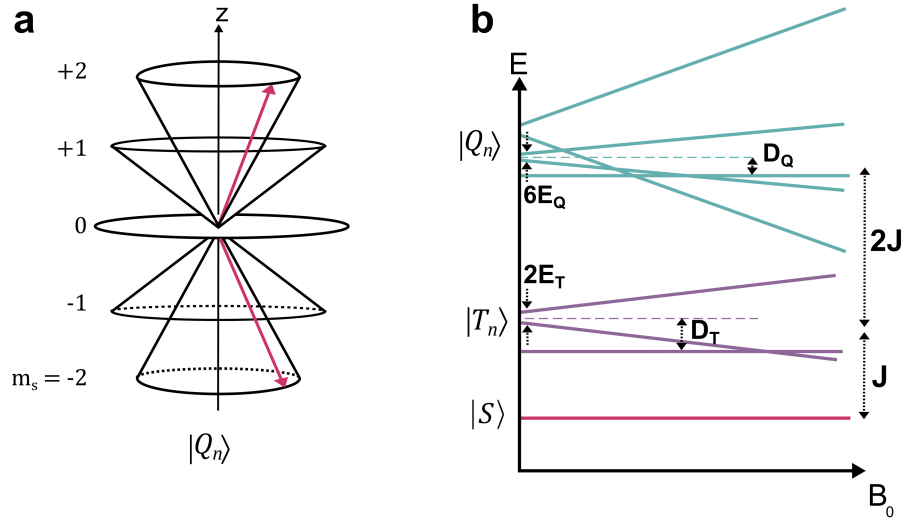


Figure 2.4: The triplet pair with 9-sublevels: one singlet, three triplets, and five quintets. The quintet is represented in the vector model in (a). The energy level splittings under an external magnetic field are shown in (b).

$X \approx D/100$. This then gives us the Hamiltonian

$$\begin{aligned}
 \hat{H} = & \underbrace{J\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B}_{\text{Exchange}} + \underbrace{X[3(\hat{\mathbf{S}}_A \cdot \hat{\mathbf{r}})(\hat{\mathbf{S}}_B \cdot \hat{\mathbf{r}}) - \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B]}_{\text{Intertriplet dipolar}} \\
 & + \sum_{i=A,B} \underbrace{[g\mu_B \mathbf{B} \cdot \hat{\mathbf{S}}_i]}_{\text{Zeeman}} + \underbrace{D(\hat{S}_{i,z}^2 - \hat{S}_i^2/3) + E(\hat{S}_{i,x}^2 - \hat{S}_{i,y}^2)}_{\text{ZFS}}
 \end{aligned} \tag{2.26}$$

[52, 53]. The nine spin states in the zero-field basis are eigenstates of this Hamiltonian. However, as noted by Tapping and Huang [54], caution must be taken when considering the two molecular bases x, y, z for the ZFS of the individual triplets. One way to appropriately treat this is to calculate the ZFS for one of the triplets, A , then apply an Euler rotation operation to find the ZFS of the second triplet, B . We detail this in **Section 5.2**.

As alluded to earlier, there are two regimes of the triplet pair: the *strongly coupled* and *weakly coupled*. In the strongly coupled pair, the interactions between the two triplets, namely the exchange interaction, is strong ($J \gg D$). In this case, the spin states are well defined, and often denoted as $^1(\text{TT})$, $^3(\text{TT})$, and $^5(\text{TT})$. However, as the spins evolve in time, with processes described shortly, the interactions between the two triplets can be reduced in magnitude, such that $J \ll D$. This is the weakly coupled triplet pair, often denoted as $^l(\text{T}...\text{T})$. The states

of the weakly coupled pair are no longer eigenstates, and spin is no longer a ‘good’ quantum number. The states are often of mixed spin character. We will later ascribe importance to the degree of singlet state character in these states. The mixed nature of the spin states results in quantum beating [35, 55], an example of spin evolution.

2.2.4 Spin Evolution

Spins can evolve through a number of mechanisms or dynamic processes, particularly within an *ensemble* of spins. Spins can be quenched through chemical reactions, such as a triplet spin state reacting with molecular oxygen [56], or transferring triplet energy to other molecules such as in sensitisation experiments. Moreover, the spins themselves evolve over time, undergoing processes such as relaxation and spin mixing.

Relaxation

Spin relaxation is the phenomenon by which the thermal equilibrium of the spin projection onto an external field is reached. Spin relaxation is well observed in resonance techniques, such as electron spin resonance or nuclear magnetic resonance, where polarisations of the spin projections are achieved. Relaxation is typically classed as two separate processes: spin-lattice relaxation, and spin-spin relaxation.

Spin-lattice relaxation, thought of as the loss of spin polarisation in the z -direction, is caused by fluctuating local fields. Fluctuating local fields can be caused by processes such as molecular tumbling, and are the result of changes in the local dipolar or hyperfine couplings. If the oscillations of the local fields are resonant with the Larmor frequency, transitions between spin states can occur, ultimately destroying any z -direction polarisation of spins. The spin-lattice relaxation is characterised by time constant T_1 .

Spin-spin relaxation, or *dephasing*, is the loss of spin coherence in the xy plane. Spin coherence is the ‘bunching up’ of spins, allowing them to precess together in time [57]. However, if the spins precess with different frequencies, then phase coherence is lost through destructive interference. The spin-spin relaxation is characterised by time constant T_2 . Both T_1 and T_2 intimately depend on the rotation correlation time, τ_c , the time taken for the root-mean-square

deflection of molecules to be 1 radian. As such, spin relaxation processes in solution can be slowed through decreasing temperature or increasing viscosity.

Spin Mixing

As described, transitions between spin states, or coherences, can occur. A good visual example can be demonstrated with the vector-model representation of singlet and triplet states, shown previously in **Figure 2.2**. In the presence of a field, if the two spins have different Larmor precession frequencies (due to changes in hyperfine environment, for example), then the $|S\rangle$ and $|T_0\rangle$ states can readily interconvert, as the system exists as a linear combination of the two states during the transition. One such way to describe these non-stationary states is as the superposition of several eigenfunctions that are subject to time evolution.

Spin mixing is involved within the weakly coupled $^l(\text{T...T})$ pair, where J is small, such as mixing between $^1(\text{T...T})$ and $^5(\text{T...T})$. As such, we consider the weakly coupled pair to comprise triplets, $|T\rangle$, quintets, $|Q\rangle$, and singlet-quintet mixtures $|SQ\rangle$. For some processes, such as reverse singlet fission from the TT state to S_1 , the amount of singlet-state character will impact the rate at which the process will occur. The efficiency of spin mixing will depend on the Zeeman interaction: if the spin states are energetically separated, spin mixing is inefficient. This phenomenon leads to the observation of magnetic field effects, as discussed in **Section 2.4.1**.

Quantum Beating

In the case of weak exchange coupling, $|S\rangle$ is not in fact an eigenstate of the Hamiltonian, and must be expressed as the superposition of the eigenstates $|xx\rangle$, $|yy\rangle$, and $|zz\rangle$. Each of these eigenstates evolve in time with a phase proportional to the eigenvalue. The singlet state, therefore, will evolve in time:

$$|S(t)\rangle = \frac{1}{\sqrt{3}}(e^{-iE_{xx}t/\hbar}|xx\rangle + e^{-iE_{yy}t/\hbar}|yy\rangle + e^{-iE_{zz}t/\hbar}|zz\rangle) \quad (2.27)$$

The coupling between the singlet weakly coupled triplet pair, $^1(T...T)$, with the singlet state S_1 will therefore change in time, resulting in oscillating S_1 state fluorescence intensity. The frequency of the oscillation, called quantum beating, is determined by the ZFS parameters. It has been observed on the nanosecond timescale in tetracene crystals [55, 58], and is considered as strong evidence for the existence of the weakly coupled triplet pair state.

Now we have addressed some of the fundamental spin physics required for investigating singlet fission, we now explore some principles of photophysical processes.

2.3 Photophysical Processes

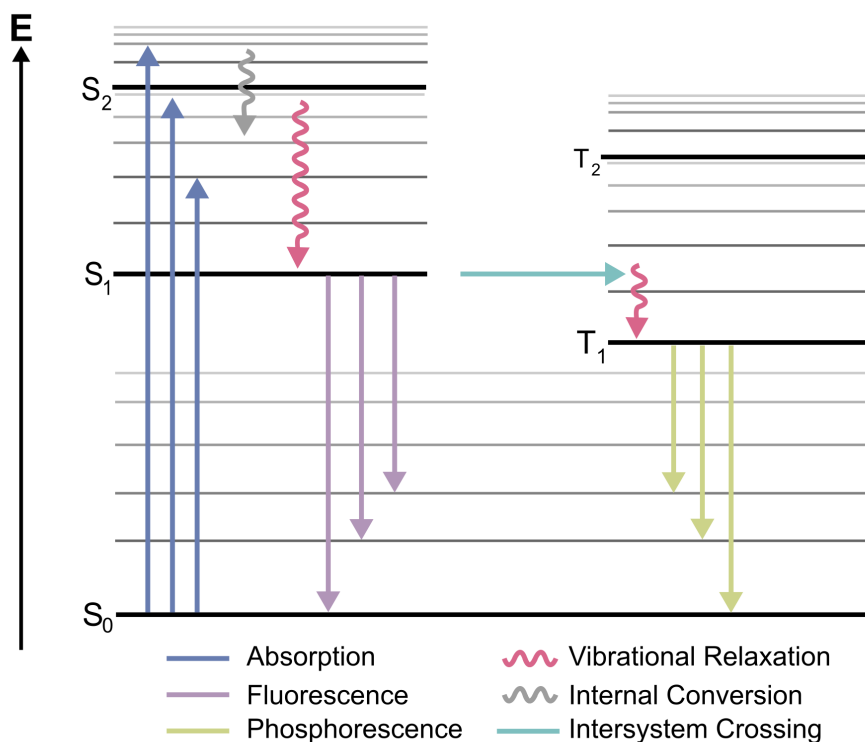


Figure 2.5: A partial Jablonski diagram, summarising key photophysical processes. The key processes shown that compete with singlet fission pathways are fluorescence, *reversible* intersystem crossing (ISC), and non-radiative processes (wavy lines) such as internal conversion.

A summary of the most common photophysical processes is summarised in a Jablonski diagram in **Figure 2.5**. A ground state (closed shell) S_0 state can absorb a photon, resulting in transitions to higher energy states. High energy excited electronic states, such as S_2 and S_1 , can undergo *non-radiative transitions* such as vibrational relaxation between vibrationally excited levels, and internal conversion. As according to Kasha's law, the lowest energy excited state can then emit a photon to spontaneously return to the ground state. This *photoluminescence*, or *fluorescence* if from a singlet excited state, is very rapid. Excited states can also undergo formally *spin-forbidden* transitions such as *intersystem crossing* to the triplet excited states, T_1 . These triplet excited state can also emit a photon, known as *phosphorescence*. Each of these processes are explored in further detail, as follows.

2.3.1 Absorption and Emission

Absorption and emission of photons causes transitions between electronic states of a molecule, with fine-structure arising from the various vibrational levels of each electronic state. As mentioned, an organic molecule can absorb a photon to promote an electron from the ground state (highest occupied molecular orbital, HOMO) to an excited state. This is a *radiative transition*. When considering radiative transitions, the rate of the transition, k_{if} , between initial and final states (described by wavefunctions Ψ_i and Ψ_f), is dictated by Fermi's Golden Rule:

$$k_{if} = \frac{2\pi}{\hbar} \left| \langle \Psi_f | \hat{H}' | \Psi_i \rangle \right|^2 \rho(E_f), \quad (2.28)$$

where $\hat{H}'$ is the Hamiltonian describing the perturbation of the transition, and $\rho(E_f)$ is the density of the final states. From the Born-Oppenheimer approximation, the wavefunctions can be separated as products of their electronic, vibrational and spin counterparts, where only the transitions arising from the electronic part is dependent on electron position, r . Consequently, the rate of transition can be written as

$$k_{if} = \frac{2\pi}{\hbar} \underbrace{|\langle \Psi_{el,f} | \hat{\mu}(r) | \Psi_{el,i} \rangle|^2}_{\text{TDM}} \underbrace{|\langle \Psi_{spin,f} | \Psi_{spin,i} \rangle|^2}_{\text{SSR}} \underbrace{|\langle \Psi_{vib,f} | \Psi_{vib,i} \rangle|^2}_{\text{FCO}} \rho(E_f). \quad (2.29)$$

Here, the rate of transition is separated into three terms: the transition dipole moment (TDM), or orbital selection rule, the spin selection rule (SSR), and the Franck Condon Overlap (FCO). Each term has important consequences on radiative transitions. The rate of the transition also depends on the density of states for the final state.

Transition Dipole Moment

The TDM creates strict symmetry requirements for transitions to be allowed between orbitals: a radiative transition must occur with a change in dipole. This is due to the odd parity of the transition dipole operator, $\hat{\mu}(r)$, which transforms as x, y, z . For a transition from state $\Psi_{el,i}$ to $\Psi_{el,f}$ to have significant intensity, there must be a change in the parity, or symmetry, of the electronic orbital wavefunction. This can be understood through group theory analysis of molecular symmetries [59]. For example, if we take the initial state of a centrosymmetric

molecule to have *gerade*, *g*, symmetry (symmetric under inversion), then the final state must have *ungerade*, *u*, symmetry. This is due to the fact a photon has *u*-symmetry. The TDM also increases in strength with overlap and orbital extent of the initial and final electronic wavefunctions.

The symmetry restrictions from the TDM can be relaxed through processes such as Herzberg-Teller intensity borrowing [45, 60]. A ‘dark’ state, forbidden from absorbing or emitting through the dipole symmetry, can couple to a symmetry breaking vibrational mode, and ‘borrows’ intensity from a bright state that is close in energy. This intensity borrowing is the proposed mechanism allowing emission from the $^1(\text{TT})$ state in singlet fission.

Spin-Selection Rule

The SSR term is the overlap integral of the spin states, such that overlap between orthogonal spin states will give a transition probability close to zero. A radiative transition cannot result in a change of spin state. This implies that the $S=1$ triplet state cannot be directly accessed by absorbing or emitting a photon. This is due to a photon not possessing spin angular momentum; absorption of a photon can not cause a change in the total spin angular momentum of the system. However, this can be relaxed by spin-orbit coupling mechanisms, such as those caused by the presence of heavy atoms.² Emission from a triplet state is spin-forbidden, but can occur; this is phosphorescence. Phosphorescence, the emission from a triplet state, is an example of violation of the SSR, but is quite common. In the absence of heavy atoms, phosphorescence is often slow, and in low yield.

Frank-Condon Overlap

The FCO captures the vibrational contribution to radiative transitions, and is the origin of most spectroscopic line-shapes in organic molecules. Each electronic level has vibrational sublevels. Different vibrational sublevels can be accessed when a photon is absorbed or emitted. A radiative transition is considered ‘vertical’ on the nuclear coordinate system. This is visualised in **Figure 2.6**, which shows the electronic energy potentials for two states along an

²The spin-orbit coupling Hamiltonian $\hat{H}_{SOC}$ transforms as R_x, R_y, R_z , and scales with atomic number Z^4 .

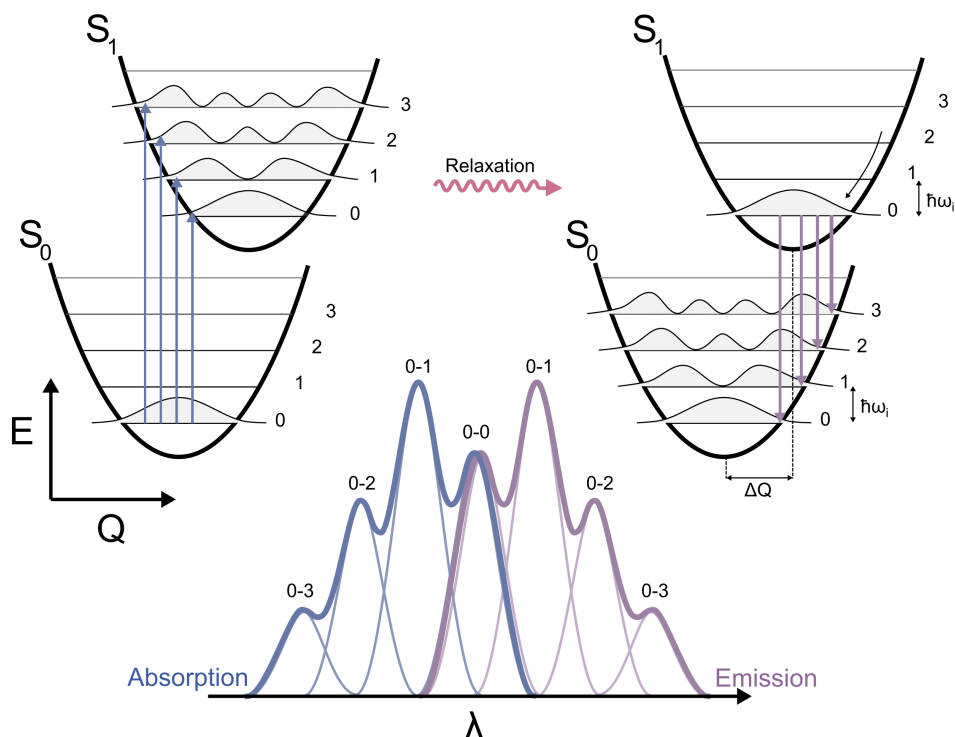


Figure 2.6: Absorption, emission, and vibronic progressions: absorption of a photon populates many of the vibrational levels of the electronic excited state. Rapid vibrational relaxation occurs to the lower vibrational level. Emission of a photon from the excited state then populates many vibrational levels of the ground electronic state. This vibrational fine structure to the absorption and emission spectra is termed the Frank-Condon progression, or vibrational progression. Figure adapted from Allardice [61].

axis of nuclear coordinate, Q . As electronic transitions occur far faster than nuclear movement, the absorption of a photon does not coincide with simultaneous nuclear motion; the transition is vertical with respect to nuclear coordinate. The strongest intensity for such a vertical transition will occur where there is greatest overlap between vibrational states of the initial and final states.

As seen in **Figure 2.6**, a small shift in nuclear coordinate between the initial and excited state means the 0-0 transition (lowest vibrational state in both the initial and final states) is less intense than the 0-1 transition. The transitions for the radiative emission from the excited state, fluorescence from a singlet state, follows a similar shape, or *vibronic progression*, as the absorption.

As according to Kasha's law, emission occurs from the lowest lying excited state. Rapid vibrational relaxation between the vibrational levels of the excited state means emission comes from the lowest vibrational level. This vibrational relaxation of the excited state results in a

smaller energy for photons emitted compared to those absorbed; the emission is red-shifted compared to the absorption wavelengths. The shift in the peak wavelength, λ_{max} , of the absorption and emission spectra is the Stokes shift [62]. The Stokes shift can be increased through processes such as bathochromic shift, where solvent reorganisation further stabilises the excited state, causing a further red-shift of the emission wavelengths.

If the vibrational level separations are similar in both the excited and singlet state, as in **Figure 2.6**, the emission spectrum will be an almost mirror image of the absorption spectrum, red-shifted on account for smaller energy-gaps. The shape of the spectra is termed the vibrational (or vibronic) progression, as the shape arises from the vibrational transitions. This ‘mirror-image’ of the vibrational progressions is most common with rigid molecules. Exceptions to the mirror-image rule occur when there are changes in excited state molecular geometry, photoinduced redox reactions, excited state dissociation, or more commonly, excitation to a low lying higher excited state, such as S_2 , with rapid internal conversion to and emission from S_1 . The vibrational progression is also impacted by phenomena such as molecular aggregation.

The Effects of Molecular Aggregation

When small molecules aggregate, they form preferential close packing structures through interactions such as Van der Waals, or π - π interactions. We consider two types of packing: cofacial, known as H-aggregation, and slipped-stack (edge-on, or head-to-tail) packing, known as J-aggregation. The impact of such aggregation on absorption and emission has been widely studied [63, 64].

For the H-aggregation, the lowest lying excited state is where the dipole moments of the monomers are antiparallel. However, the net dipole moment of this state is zero, meaning radiative transitions to and from this state are forbidden; it is a dark state. The higher lying excited state, with dipoles parallel, is radiative. This impacts the absorption and emission spectra such that the 0-0 transition is lowered in intensity, and higher level transitions are relatively increased in transition intensity. Overall, H-aggregation results in an apparent blue-shifted absorption spectrum in comparison to the monomer. Furthermore, the emission from

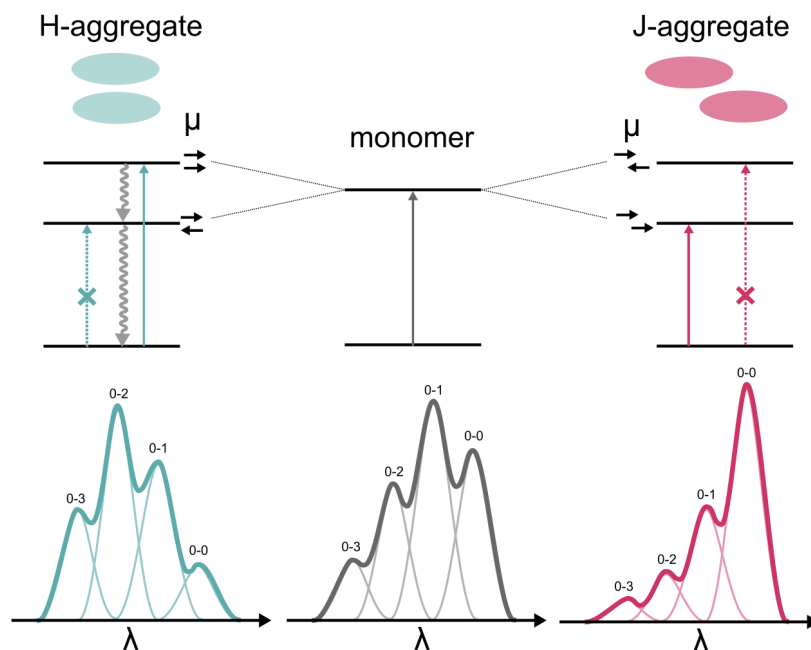


Figure 2.7: Effects of molecular aggregation: alignment of dipole moments in aggregates impact the TDM. Cofacial aggregation (H-aggregation) is characterised by a blue-shifted spectrum and weak emission. Slip-stack or edge-on aggregation is characterised by a red-shifted spectrum and strong emission.

an H-aggregate is red-shifted and sub-radiant, due to rapid non-radiative decay (internal conversion) through the dark state.

The opposite case is true for J-aggregates. The lower lying state, with dipole moments parallel in the head-to-tail packing, is now radiative, whereas the higher lying state, with no net dipole moment, is now dark. This leads to increased transition intensity for the lowest lying transitions, and reduced intensity of the higher lying peaks. The absorption spectrum appears red-shifted for J-aggregates compared to the monomer.

2.3.2 Non-Radiative Transitions

As previously discussed in the Jablonskii diagram in **Figure 2.5**, there are transitions between states that are not mediated by a photon; these are non-radiative transitions. They include processes such as vibrational relaxation, internal conversion, and intersystem crossing.

Vibrational relaxation is the transition to lower energy vibrational states; the energy difference can be dissipated to the surrounding environment as heat. The vibrational levels are populated as a Maxwell-Boltzmann distribution for a large sample of molecules.

Transitions between vibrational levels of different electronic states can also occur. If the spin state of the two levels is the same, then this is *internal conversion*. If the spin state changes, this is *intersystem crossing*. The rate of a non-radiative transition takes the form

$$k_{if} \propto \exp\left(-\gamma \frac{\Delta E}{\hbar \omega_M}\right), \quad (2.30)$$

where γ is a constant which depends on the structure of the molecule, ω_M is the angular frequency of the highest energy vibration of the final electronic state, and ΔE is the energy gap between the electronic states [65].

Non-radiative transitions are commonly thought as being mediated by phonons (quasi-particles of vibrational energy). As previously mentioned, spin orbit coupling (the relativistic interaction between the electron's spin and its orbital motion around the nucleus [66]) can increase the rate and yield of intersystem crossing by relaxation of spin selection rules. Non-radiative transitions can also be facilitated by conical intersections: the intersection of two electronic potential energy surfaces [67, 68]. As the two energy surfaces intersect, no nuclear motion or vibration is required to change the electronic state at the point of the conical intersection. The transition through a conical intersection is therefore highly rapid, and extremely efficient.

2.3.3 Exciton Transfer

Once excited states are generated, in the solid state they are able to migrate. In the solid state, we refer to an excited state as an *exciton*. An exciton is a Coulombically bound electron-hole pair formed from processes such as the promotion of an electron from the HOMO or valence band to the LUMO or conduction band. The term exciton is more general to organic and inorganic solids, whereas an excited state is more well-defined for isolated organic molecules. Here, we strictly refer to Frenkel (localised) excitons, and use the terms exciton and excited state quasi-synonymously.

Excitons transport through the transfer of energy from one molecule to a nearest neighbour. There are two mechanisms of interest for exciton transfer: Förster resonant energy transfer,

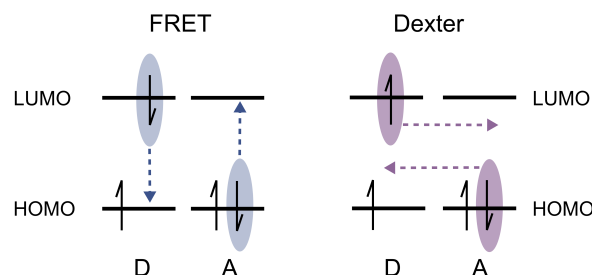


Figure 2.8: Förster resonance (FRET) and Dexter energy transfers: energy is donated from an excited molecule to neighbouring acceptor molecule. FRET is mediated by a ‘virtual’ photon, while Dexter is mediated by the correlated transfer of two electrons [61].

FRET, or Dexter energy transfer, both shown in **Figure 2.8**. The energy transfer process is mediated by the Coulomb and exchange mechanisms respectively [65, 69, 70].

FRET is mediated by the coupling of electric dipoles between neighbouring molecules. FRET is described as mediated by a ‘virtual’ photon, where the emission of a photon from a donor molecule leads to subsequent absorption by the acceptor. The rate of FRET therefore depends on the oscillator strengths of the donor and acceptor emission and absorption, the overlap of the emission and absorption spectra, and also is related to their separation by $\propto 1/r^6$.

Dexter transfer, on the other hand, is mediated by the correlated transfer of two electrons. As Dexter is not mediated by a virtual photon, there is no dependence on the oscillator strengths of the donor or acceptor. This allows states with poor oscillator strength, such as triplets, to transfer. Dexter is a shorter range transfer interaction, dependent on separation by $\propto \exp(-2\beta r)$, and is only appreciable between molecules with less than a few nanometres separation [71].

Singlet states usually transfer *via* FRET, whereas triplets tend to transfer through Dexter mechanisms. While FRET is a longer range interaction, the diffusion lengths of triplet excitons tend to be longer than that of singlets due to the former having a longer lifetime.

2.3.4 Exciton-Exciton Annihilation

As asserted, excitons can transfer energy to nearest neighbours, and so can diffuse or ‘hop’ through a solid-state material. This exciton hopping plays an important role in the separation of the triplet pair, and is morphology dependent [72].

Excitons that diffuse through the material can encounter other excitons and interact, transferring energy between them, such that one exciton is de-excited and the other assumes a higher energy state. This is termed exciton-exciton annihilation. Both singlets and triplets can annihilate, through singlet-singlet annihilation (SSA) or triplet-triplet annihilation (TTA). For some materials, TTA will result in the formation of one higher energy excited singlet spin state. This is the opposite process to singlet fission, and will be discussed in **Section 2.4**. Both SSA and TTA are dependent on the excitation density, or the effective concentration of the excitons, as they are bimolecular processes.

There are two further processes for diffusing excitons to undergo that are worthwhile noting: triplet sensitisation, and excimer formation. These processes can occur in both the solid state and the solution state.

Triplet Sensitisation

Triplet sensitisation is the process through which a triplet exciton donates its energy to a neighbouring molecule of a *different* identity. This allows for the generation of triplet excited states of a material without direct photoexcitation of that material. This experiment is particularly useful to ascertain the triplet absorbance spectrum, as we discuss in **Section 3.6.5**. For this process to be efficient and in high yield, the triplet ‘donor’ must generate triplet excitons rapidly, through processes such as intersystem crossing. Materials such as Palladium II complexes work well, as they have large spin-orbit coupling interactions and so fast, efficient intersystem crossing. Furthermore, the triplet energy of the donor must be close to or greater than the triplet energy of the acceptor molecule.

Excimer Formation

An excited state can form a loosely coupled ‘dimer’ with another molecule (M^*-M), referred to as an ‘excited dimer’ or excimer. An excimer state is coupled through either a Van der Waals interaction, or a Coulombic interaction, but are not formally chemically bonded [65]. Excimers of a singlet state can emit, giving a broad, featureless emission spectrum, and subsequently dissociate; the ‘ground state’ of an excimer is unbound. The formation of excimers

is seen as a competing process to singlet fission, reducing device performance [65, 73]. However, their role in singlet fission mechanisms is uncertain. Broad, red emissions in singlet fission systems are often attributed to either excimer states, or the TT pair state emission, with assignment of either state debated within the community [41, 73–76].

2.4 Singlet Fission: The Mechanism

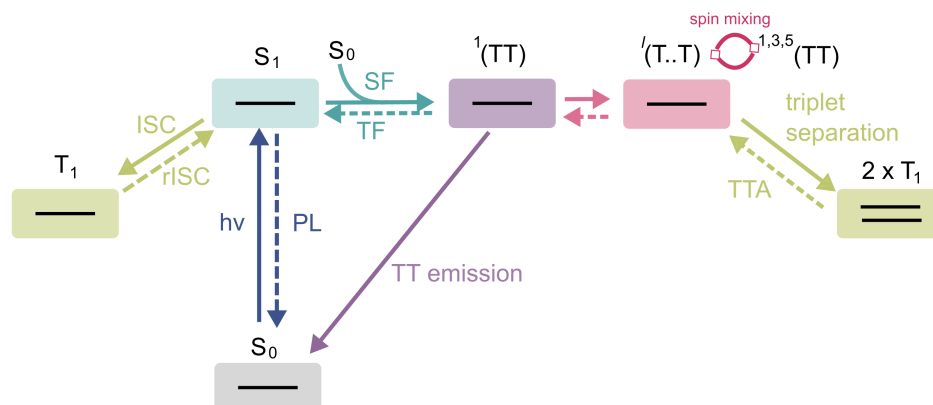


Figure 2.9: A proposed photocycle for singlet fission. The energy of the T_1 must be approximately half the energy of the S_1 state. Pathways competing with singlet fission include fluorescence and intersystem crossing (shown in **Figure 2.5**). Spin mixing of the spin-correlated triplet-triplet pair can result in an observable magnetic field effect, discussed in Chapter 4.

From the previous descriptions of spin chemistry and photophysics, we can now address the mechanism of singlet fission, as shown in **Figure 2.9**.

A ground singlet state, S_0 absorbs a photon, giving the singlet excited state S_1 . Overlap with (or collision with, in concentrated solution) a neighbouring ground state molecule yields a strongly-coupled triplet pair state in an initial singlet spin state, $^1(TT)$. Both the S_1 and $^1(TT)$ can undergo emission³.

The triplet pair evolves, forming the weakly coupled triplet pair, $^l(T...T)$, comprising the superposition of spin states. Spin mixing occurs within this state, which can be modulated by a magnetic field. The triplet pair can separate to form two free triplets, T_1 , which possess half the energy of the S_1 state. This separation has two aspects: a physical separation of the excitons, through diffusion or hopping, and the accompanying spin decoherence of the two triplets.

Each step in the photocycle in **Figure 2.9** is considered to have a reverse process. The triplet pair can reform the singlet state, and the weakly coupled $^l(T...T)$ state can reform the strongly coupled $^1(TT)$ (or $^3(TT)$ and $^5(TT)$). The free triplet excitons can ultimately recombine through annihilation to reform the triplet pair. As a result, we can observe a ‘prompt’

³Emission from $^1(TT)$ occurs through Herzberg Teller intensity borrowing from the S_1 state [45]

fluorescence from the S_1 state, but also a delayed fluorescence due to a late time repopulation of the singlet state. This property of delayed fluorescence led to the discovery and research of singlet fission in the 1960s [77–80]. The yield of prompt and delayed fluorescence can be modified with the application of an external field, as discussed in **Section 2.4.1** [40, 78, 80, 81].

Singlet fission is referred to as an exciton multiplication process, as one singlet exciton is rapidly and efficiently converted to two triplet excitons. Triplet-triplet annihilation (TTA) is the reverse process; two triplet excitons combine to form one singlet exciton with a higher energy. TTA can be used as an upconversion process, as the resulting state is higher in energy than the two initial states. Singlet fission, therefore, can be used as a downconversion process.

An alternative pathway to form free triplets is through intersystem crossing directly from the S_1 state. ISC is much slower than singlet fission in the absence of heavy atoms. Confirmation of the origin of triplet states can be achieved through electron spin resonance.

Charge Transfer States

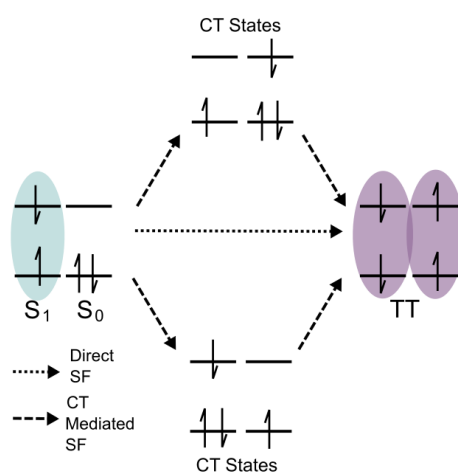


Figure 2.10: The direct and indirect (charge transfer mediated) mechanisms of singlet fission. Reproduced from Rao and Friend [9].

The mechanism for forming the triplet pair state from the S_1 state is widely hypothesised to be mediated through charge transfer states, as shown in **Figure 2.10** [9, 13, 82]. The charge transfer states may be real or virtual, and some states may possess partial charge-transfer character. A charge-transfer state intermediate to singlet fission has been reported [83], although uncommon.

Triplet Pair Emission

Direct emission from the strongly coupled $^1(TT)$ has been reported [41, 45, 84]. While the assignment of the emission has been widely debated to belong to an excimer [76], evidence that the TT state does in fact emit is still growing [85]. Interestingly, the emission from $^1(TT)$ is symmetry forbidden [86], and occurs through Herzberg Teller intensity borrowing [45]. The TT pair emission and its tentative assignment within archetypal singlet fission molecule TIPS-tetracene is featured in **Chapters 4 and 5**.

2.4.1 Magnetic Field Effects in Singlet Fission

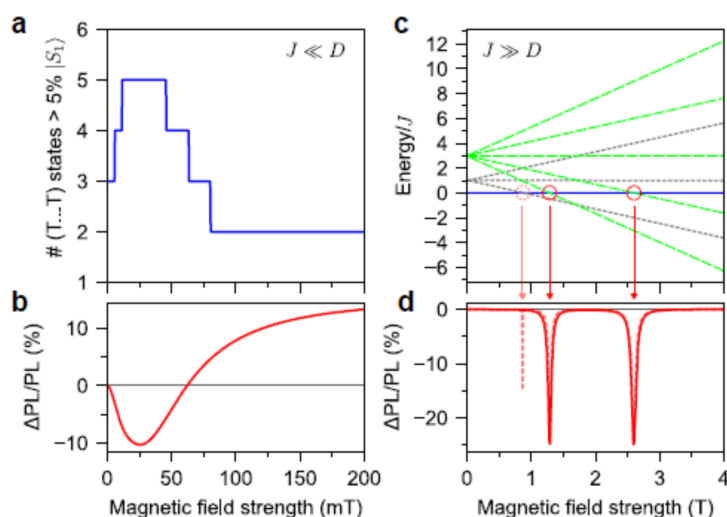


Figure 2.11: Magnetic field effects in singlet fission: at low fields, spin mixing in the weakly coupled T...T pair causes a change in the fluorescence intensity from the S_1 state. Initially, more states with significant singlet character are accessible, shown in (a), which causes a decrease in fluorescence, shown in (b). As the field strength increases, the spin levels become energetically separated, and spin mixing reduces in efficiency, causing an increase in fluorescence. At very high fields, level crossings in the energies of the strongly coupled TT pair, shown in (c), causes dips in fluorescence, shown in (d). In this thesis, we consider only MFEs in the weakly coupled pair at relatively low fields. Reproduced from Bossanyi *et al.* [52, 53].

At this point, we have discussed how magnetic fields impact the spin Hamiltonian that described the triplet pair states. Within the TT pair, different spin sublevels become energetically separated with increasing field strength due to the Zeeman interaction. The energetic separation of states will impact the efficiency of spin mixing between them. For the singlet fission mechanism, we are most concerned with the amount of singlet character each of the

mixed-spin states exhibits. This amount of singlet state character will impact the rate, k_{TF} , of transition from the TT pair back to the S_1 state. Formation of the TT pair initially populates the singlet $^1(TT)$. As we apply small field values, the number of states with significant singlet-character increases, and so spin mixing *away* from the $^1(TT)$ state is facilitated. The return to the S_1 state reduces in rate, and fluorescence intensity decreases. Conversely, at sufficiently high fields, the energetic separation of spin states reduces spin mixing efficiency away from the $^1(TT)$ state. Thus, return to the S_1 state is favoured and fluorescence intensity increases. This modulation of the fluorescence intensity with applied field is an example of a *magnetic field effect* (MFE). An example of an MFE lineshape is shown in **Figure 2.11 (b)**, with the number of states within the $^l(T...T)$ manifold with significant singlet character shown in **(a)**, reproduced from Bossanyi *et al.* [52, 53].

Spin mixing can be caused through a number of mechanisms, but ultimately depends on the comprising spins of the triplet pair experiencing fluctuating local fields. A similar spin mixing and resulting MFE is observed in the spin-correlated radical pair mechanism (SCRPM), where the spin mixing is mediated through changes in the hyperfine environment at low fields, and changes in the electron g tensor at high fields (called the Δg mechanism) [28, 34, 87]. In singlet fission, the spin mixing is driven by changes in the ZFS couplings. As such, the magnetic field effects in singlet fission systems are highly dependent on the molecular axis orientation.

Since first reports in the late 1960s, magnetic field effects of singlet fission systems have been widely observed at both low field (<1 T) and high field ranges (>1 T) [40, 45, 48, 52, 54, 78–81, 88–91]. A common framework employed to understand the kinetics of MFEs is that of Merrifield, which we discuss in **Chapter 5** [78]. The low-field MFEs are attributed to the impact of spin mixing within the weakly coupled pair, as described. At high-fields (> 1 T), we see dips in the fluorescence intensity, which are attributed to level-crossings within the TT manifold with the $^1(TT)$ state. High-field MFEs have been reported for TIPS-Tc and DPH [48, 90]. An example of a high-field MFE, due to level-crossings in the strongly coupled TT pair, is shown in **Figure 2.11 (c) and (d)** [52, 53].

MFEs are not unique to singlet fission. As mentioned, the SCRP mechanism also gives rise to an appreciable MFE, for example. However, the shape and scale of the low-field MFE lineshape are indicators of singlet fission. Simulation of the MFE lineshape with either spin density matrix formulation or kinetic modelling can further confirm the singlet fission origin of an MFE lineshape. MFEs will be explored in greater detail in **Chapters 4** and **5**.

2.5 Singlet Fission Chromophores

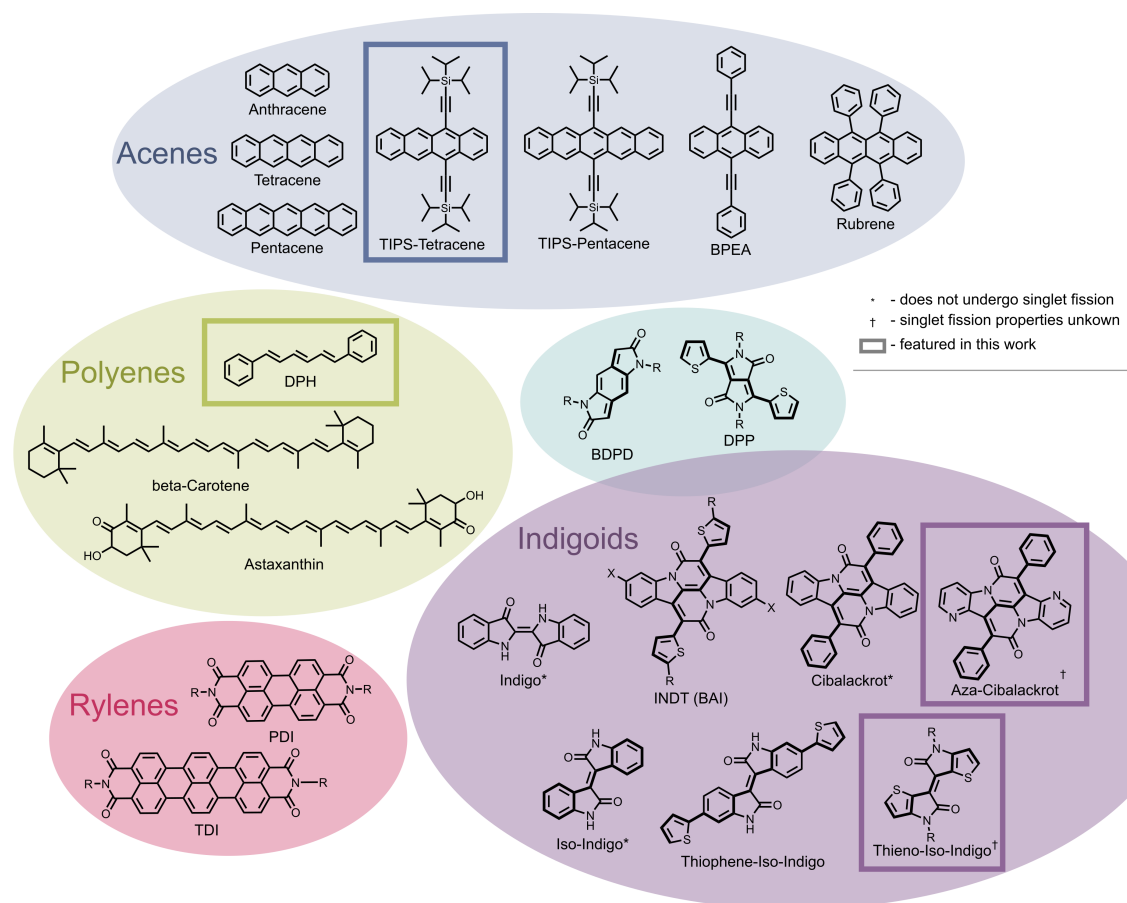


Figure 2.12: Families of singlet fission molecules: acenes, polyenes, rylenes, and indigoids. Each molecule is discussed in the main text. Molecules surrounded with a border feature in the investigations in this thesis. Figure adapted from Budden and Bossanyi [53, 92].

For a molecule to undergo singlet fission, there are many requirements in place. The energy of the singlet excited state must be approximately twice the energy of the triplet state, $E(S_1) \approx 2E(T_1)$ [11, 13]. While singlet fission can be exothermic or endothermic [42], this energy requirement serves as a good rule of thumb when considering the energetic landscape of a material. For singlet fission to occur efficiently, there must be sufficient intermolecular coupling for the triplet pair to form, but not such strong coupling that the triplet pair cannot separate efficiently [13]. For singlet fission to outcompete other processes, such as non-radiative decay and photoluminescence, it must be fast; on the picosecond timescale or faster [13, 93].

Beyond these requirements for singlet fission to occur, we must also consider the material requirements for use within optoelectronic devices such as solar cells:

1. The triplet yield must be high ($\sim 200\%$); something that has been previously reported for some systems [94, 95].
2. The molecule must exhibit high ambient and photo- stability.
3. The absorption coefficient must be high, so that only a thin layer of material is used to minimise triplet diffusion losses [93].
4. Ideally, the molecule would be solution processable, for roll-to-roll processing [20] and incorporation with triplet harvesters [96].
5. For use with conventional silicon solar cells, the energy of the triplet state must be greater than the band-gap of silicon, $E(T_1) > 1.1$ eV.

The main obstacle for successful deployment of singlet fission materials for solar cells is the lack of molecules that exhibit both high singlet fission yield (with a triplet energy above 1.1 eV) *and* molecular stability. As such, a vast survey of material families have been conducted over the past decade, both computationally and experimentally, to search for the ‘holy grail’ singlet fission material that boasts high yield and stability [11, 13, 19, 93, 97].

A short summary of singlet fission compounds is shown in **Figure 2.12**. The molecules are grouped by ‘family’: acenes, rylenes, polyenes, and indigoids.

Acenes

The acenes (anthracene, tetracene, pentacene, and their derivatives) have been widely studied for their singlet fission properties for decades. Singlet fission was first reported in anthracene crystals in 1965 [77], with singlet fission in tetracene crystals reported shortly after [78, 79]. The acenes present a series of molecules with decreasing triplet energy as molecular length increases, from 1.83 eV for anthracene, 1.25 eV for tetracene, and 0.81 eV for pentacene [11, 98]. While anthracene typically has low triplet yield from singlet fission ($\sim 6\%$ [11]), tetracene and pentacene have been reported to have high yields of close to 200% [99–102]. However, a large drawback of the suitability of acenes for device applications is their poor stability. Tetracene and pentacene readily photooxidise in the presence of oxygen, and can

also photodimerize [103, 104]. Furthermore, tetracene and pentacene are very weakly soluble. Functionalisation with groups such as bis(triisopropylsilylethynyl), TIPS, allows the acenes to be more soluble and minimise photodimerisation [93]. TIPS-tetracene and TIPS-pentacene are shown in **Figure 2.12**. However, the triplet energy of TIPS-tetracene is reduced from 1.25 eV to 1.06 eV [105], reducing its feasibility for use with silicon solar cells. Nonetheless, we use TIPS-tetracene in **Chapter 4**, as it is one of the most studied singlet fission materials [41, 42, 96, 106].

Other materials in the acene family are 9,10-bis(phenylethynyl)anthracene (BPEA) and rubrene, which have been reported to undergo singlet fission [107, 108]. Rubrene is also commonly used for triplet-triplet annihilation up-conversion [52].

Rylenes

The search for singlet fission chromophores outside of acenes has yielded other molecular families, such as rylenes, amongst others. Rylenes have far greater photostability than acenes and have large absorption coefficients [109], and are used as industrial pigments [110] (suggesting synthesis is well characterised in high yield, and the pigment is intense and stable). Perylene diimide (PDI) and terrylene diimide (TDI), shown in **Figure 2.12**, have both been reported to undergo singlet fission with >100% triplet yield [109, 111–113].

Polyenes

Singlet fission has been investigated in polyenes, with particular attention on diphenyl-hexatriene (DPH), and naturally occurring carotenoids, β -carotene and astaxanthin. Polyenes are identified as promising singlet fission candidate [11, 46]. Polyenes possess a characteristic low-lying dark Ag state, which from a theoretical basis is similar to the weakly coupled triplet pair and may facilitate intramolecular fission [114, 115]. While this occurs in some polymers, for some polyenes singlet fission does not invoke the Ag state, but instead two triplets are formed directly from the bright 1Bu state [46, 116]. This is in stark contrast to the mechanisms reported for acenes.

DPH has been investigated, with many possible functionalisations and dimerisations, and is shown to have very high yields of triplets ($\sim 200\%$) [73, 89, 90, 95, 117]. Carotenoid aggregates have shown very rapid singlet fission [46, 118, 119], with asaxanthin aggregates reported as having a time constant of <70 fs [46, 93]. Polyenes are a highly interesting family of high yield, rapid singlet fission materials. However, while highly air stable, DPH in particular suffers from poor photostability [120].

Indigoids: Our Molecules of Interest

Indigo is one of the oldest known dyes, dating to over 6000 years old [121–123]. Indigo is inexpensive, highly stable, and used globally. Indigo was historically derived from natural products, but is now created through a one-pot synthesis on a multitonne scale [20]. Indigo itself undergoes rapid relaxation after photoexcitation, through excited state intramolecular proton transfer and rotation around its central bond [20, 124, 125]. This property means excellent photostability, allowing indigo to exist for centuries. This deactivation pathway, however, means indigo is not suitable for optoelectronic device applications. However, its isomer, isoindigo, has wide applications in optoelectronics [126]. Similarly, annulation of indigo yields new molecular families with interesting photophysical processes.

Annulation of indigo opens a long, uninterrupted conjugation pathway through the molecule, as highlighted with boldened bonds in **Figure 2.12** [127]. This conjugation pathway moiety is also present in other amide-based monomers, such as diketopyrrolopyrrole (DPP) and benzodipyrrolidone (BDPD). DPP and BDPD have also been shown to undergo singlet fission [128–131].

Annulated derivatives of indigo, such as cibalackrot and indolonaphthyridine thiophene (INDT, or bay-annulated indigo, BAI [127]) have been investigated for singlet fission potential [19, 21, 132]. INDT was found to be a highly stable, versatile monomer, with much availability for substitutions or manipulation of the core structure [19, 133]. INDT with suitable substitutions of the core yielded efficient singlet fission. However, the triplet energies of the INDT variants are below the desired 1.1 eV. Cibalackrot, on the other hand, while being isolated as having perfect energetic alignment for singlet fission [13], with triplet energy above 1.1 eV,

does not undergo singlet fission [132]. Altering the molecular structure of cibalackrot, giving aza-cibalackrot, in the aim of facilitating singlet fission, is the focus of **Chapter 6**.

A thiophene derivative of isoindigo, thienoisindigo, follows similar molecular design principles as the INDs, and has favourable energetics according to theoretical calculations [19]. Thienoisindigo (TIIG) has previously been reported for application in organic field effect transistors, OFETs, [23–25], but not yet considered as a potential singlet fission chromophore. This is the focus of **Chapter 7**.

Our interest in the indigoids for singlet fission is motivated by their well known stability and wide availability, compounded by their hypothesised ideal energetics. Moreover, the monomers have a lot of potential for further modification, whether through adding solubilising alkyl chains, adding electron withdrawing or donating groups to further tweak the energetic landscape of the molecule, or even dimerisation or polymerisation. If singlet fission could be successfully identified in molecules such as aza-cibalackrot or thienoisindigo, many new potential modifications would be of interest to explore.

Molecular Design Approaches

In the search for stable, efficient singlet fission materials, many molecular design approaches have been taken. With the energetic guidelines prescribed by Smith and Michl, computational investigations of molecular structures with density functional theory have been carried out [19, 97, 134–140]. From a molecular perspective, approaches include either making a singlet fission material more stable [120, 141], or make a stable material undergo singlet fission [19, 22]. As organic molecules are highly tunable, adding or changing electron withdrawing or donating groups can adjust the triplet energy levels to reach the desirable 1.1 eV [19]. Adding side-chains to alter the molecular packing properties can also impact the singlet fission properties of a material to make them more efficient [95, 130, 142, 143]. We further discuss these molecular design approaches in **Chapter 6**, where we suggest a new crystal engineering strategy to employ in the search for singlet fission materials.

2.6 Singlet Fission For Photovoltaics

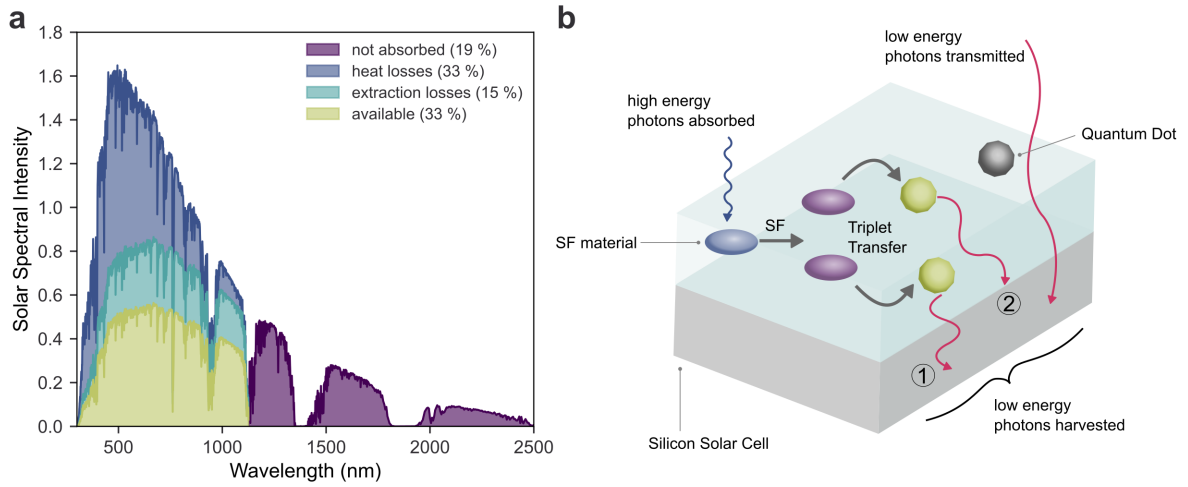


Figure 2.13: (a) Solar radiance and the Shockley-Queisser limit, showing that only 33% of solar radiation is available for harvesting by silicon solar cells. Singlet fission technology aims to harvest some of the 33% of energy lost to thermalization. (b) Schematic of a photon-multiplier photovoltaic (PMPV), showing the triplet transfer from the SF sensitizer material to quantum dots, where lower energy photons are emitted and subsequently absorbed by the silicon PV. Reproduced from Rao and Friend [9].

The photovoltaic market is dominated by single-junction silicon solar cells [144, 145]. However, as mentioned, a silicon solar cell has a fundamental maximum harvesting efficiency of 29-33.7%, known as the Shockley-Queisser limit [9, 12, 144]. Current solar cell technology has increased device performance from 24% to 26.7% over the past two decades [12]. Progress toward increasing device efficiency is slow and limited as we approach the Shockley-Queisser limit.

This limit on harvesting efficiency arises from only being able to efficiently absorb energy at a narrow window of energies close to the band gap in silicon. Any photons below the band gap cannot be absorbed. Higher energy (blue) photons are inefficiently converted, as high energy excitations thermalise to the band-gap before extraction [146]. These thermalization losses account for 33-39% power loss [9, 145]. This is shown in **Figure 2.13 (a)**, where the solar spectrum is divided into the component ‘loss’ contributions [9, 147]. The thermalisation is the dominant loss mechanism for a silicon solar cell.

Many strategies have been proposed over the past decade as to how to reduce thermalisation losses. Research includes finding alternative solar cell materials to silicon [148, 149] where

the Shockley-Queisser limit for that material is at a higher efficiency [150]; tandem solar cells [145]; multi-junction cells [151]; up and down conversion solar cells [9], to name but a few. While devices such as multi-junction cells could offer maximum harvesting efficiencies of above 40%, additional complexity to fabrication processes increase device costs beyond feasible global deployment [145].

Singlet fission has the potential to increase the maximum harvesting efficiency to 35-45% [9, 11, 12]. The idea of sensitising a solar cell with singlet fission was proposed in 1979 by Dexter [15]. However, harvesting the triplet excitons from singlet fission is a difficult feat to achieve. Several architectures have been suggested, making use of charge transfer, Dexter transfer, FRET transfer, and photon multiplication [9, 12, 152]. All require very small singlet fission layers, <1 nm, to minimise losses from triplet diffusion [12]; this again highlights the importance of a highly absorptive material.

A promising design in this field is that of the photon-multiplier photovoltaic (PMPV): a device that integrates a singlet fission (SF) material with a triplet-emitter, such as quantum dots, that re-emit lower energy photons directly into a silicon solar cell [9]. An illustration of PMPVs is shown in **Figure 2.13 (b)**. This optical integration of singlet fission with silicon PVs could be employed with solar cells already in the domestic market. For a silicon cell with efficiency of 26.7%, incorporation of singlet fission material in the PMPV architecture is suggested to increase the harvesting efficiency to 29-32.5 % [12, 145]. Much research has been undertaken in developing efficient systems for transferring triplet excitons to QDs to achieve photon multiplication [96, 144, 153, 154].

Not only does singlet fission offer opportunity to improve the efficiency limit for silicon, its has the ancillary benefit of reducing the thermal load of the silicon PV. By filtering out higher energy photons, less thermalisation occurs, and the silicon cell operating temperature is reduced. This increases the lifespan of the solar cell, again reducing the cost of solar energy deployment [14].

While the deployment of singlet fission for photovoltaics may be some years away, singlet fission promises to offer a low-cost improvement to silicon solar cell efficiency.

Chapter 3

Experimental Methods

The techniques used to explore singlet fission properties in molecules are described in this chapter. We outline the techniques used for sample preparations, and the broad range of spectroscopic methods used in this study. We also include description of the numerical methods used.

3.1 Materials

5,12-Bis((triisopropylsilyl)ethynyl)tetracene (TIPS-Tc) in **Chapter 4** was obtained from Ark Pharm. Cibalackrot materials in **Chapter 6** were synthesised by Michael Purdy [21, 155]. Materials in **Chapter 7** were synthesised by Anastasia Klimash and Anastasia Leventis. The cibalackrots and thienoisindigos were supplied in <10 mg quantities. Materials for triplet sensitisation were purchased from Frontier Scientific, Inochem. All other chemicals were purchased from Sigma-Aldrich/Merck and used as delivered.

3.2 Sample Preparation

All samples were prepared in a glovebox under nitrogen environment. Solutions were prepared in quartz cuvettes with a 1 mm path length, sealed with a PTFE stopper cap, PTFE tape and parafilm, or in a microcuvette (rectangle borosilicate tubing, CM Scientific) with 200 μm path length sealed with a UV-cure epoxy resin. Solutions in micro-cuvettes were prepared by Dr Jurjen Winkel and Dr Simon Dowland.

Thin films were prepared through a number of methods, and encapsulated. All substrates were washed with acetone and iso-propyl-alcohol, and then cleaned with an ozone plasma. Samples were encapsulated with an 18x18mm coverslip and a choice of resin. Two part Araldite rapid cure epoxy, or with polyisobutylene (PIB). A UV-cure epoxy, Blufixx, was used as this offered far easier and cleaner encapsulation. However, most small organics used in this thesis were highly soluble in the Blufixx epoxy, meaning that the resin was unable to fully cure and would destroy the sample through dissolution within a few days. Therefore, the encapsulant of choice throughout this thesis was the Araldite two-part rapid cure.

3.2.1 Preparation of Thin Films

Thin films were prepared through spin coating, drop casting, blade coating, or thermal evaporation at $2 \text{ \AA s}^{-1}$. Blade coating was performed by Dr Simon Dowland, and thermal evaporation was performed by Nipun Sawhney, Aswathy Girja, and Rituparno Chowdhury. Substrates for spin coating, drop casting and evaporating were circular ITO Silica. Blade coating and some drop casting done on Menzel gläser 24×24mm borosilicate glass cover slips.

Each sample preparation methods comes with advantages and disadvantages. Thermal evaporation deposition can coat many films simultaneously, with highly consistent results. However, it requires a lot of material, is highly wasteful, and takes time and expertise to find the correct evaporation settings for a new material. Furthermore, some small organics may decompose. For TIPS-Tc in **Chapter 4**, as a readily available and well characterised material, thermal evaporation was implemented. However, for **Chapters 6 and 7**, where material was uncharacterised and limited in quantity, thermal evaporation was not appropriate.

Solution processing methods are highly desirable, as they are rapid, cheap, and ultimately a desirable method for implementation of SF materials in PMPVs [96]. Blade coating is excellent for making multiple identical samples simultaneously. Solution is spread evenly over a substrate by a fast moving ‘blade’, similar to screen printing. It is less wasteful than methods such as spin coating. However, as the blade requires cleaning when changing solutions, it is not ideal for when only making a few samples, and can be prone to contamination.

Drop casting is by far the simplest method for thin film preparation. However, there is very limited control over the crystallite formation within the thin film, and so films are highly varied and difficult to reproduce. Furthermore, drop cast films are typically very thick and absorbing, making them suboptimal for absorbance measurements. However, this is something that may be preferred for fluorescence measurements.

Spin coating was selected as the most desirable and suitable method for thin film preparation within this study. Spin coating forms films (nm - μm thickness) by depositing solution onto a rotating substrate. A comprehensive guide to spin coating has been written by Ossila [156]. In this work, small organics were spin coated from solvents such as toluene, chloroform or chlorobenzene. Stock solutions were typically made to be 5-20 mg ml^{-1} . Films were cast at spin speeds of 1000-2000 rpm.

Spin coating is a cheap, quick way to create solution processed samples with superior uniformity when compared to other methods such as drop casting. However, it is wasteful, using only around 10% of the sample, with the rest being wasted in the spinning-off. However, overall, only a small volume of stock solution is required per sample (10-50 μl). Furthermore, with each sample being made sequentially, fine tuning settings such as spin speed and solvent choice can be done very quickly, with identical methods being applied to different materials within the same preparation slot.

One caveat of spin coating is that the method may not drive off all the solvent in the sample. Further steps such as heating or putting the film under vacuum can help with this. One interesting result of residual solvent is that the film morphology can evolve over time. The growth of spherulites after spin coating is well observed, particularly within TIPS-Tc thin films [106, 157]. This can lead to very exciting photophysics, as illustrated in **Chapter 4**. Moreover, even changing the solvent choice for preparing thin films from can cause dramatic changes in morphology such that the singlet fission dynamics are impacted [158].

3.3 Morphology Characterisation

Materials have a hierarchy of order. The arrangement of atoms within a molecule is the molecular structure. Changes in molecular structure, such as substituting atoms or making alkyl chains longer or shorter, have impacts on the electronic wavefunction of the molecule. Changes in the wavefunction can impact things such as energies of excited states.

Changes to molecular structure can also impact the crystal structure, which is the nanoscale arrangement of molecules within the crystal unit cell. The crystal structure can be examined with X-ray diffraction of single crystals. Changes to the crystal structure can impact intermolecular interactions, such as $\pi - \pi$ stacking and wavefunction overlaps. In **Chapter 6**, we make use of an atomic substitution in the molecular structure to induce effects in the crystal structure, and thus the intermolecular interactions. In **Chapter 7**, we change the solubilising chains (alkyl chains which help make the small molecules soluble in organic solvents) to also impact the crystal structure.

There may be more than one crystal structure for a certain material, known as polymorphism [159]. This is a characteristic of materials such as pentacene [160]. If a material is truly amorphous, this means every molecule in a material is randomly oriented, and regular formations of crystal packing is not present. A material being amorphous is an example of morphology, the microstructure of a material. The morphology describes whether the material forms regions of crystal packing, referred to as a crystal grain. The size of the grains, and the orientation of the crystal grains with respect to each other, is the morphology.

3.3.1 GIWAXS

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) was performed and analysed by Dr Daniel Toolan and Dr Rachel Kilbride at the University of Sheffield, Department of Chemistry, as previously reported [21]. GIWAXS provides insight into the microstructure of thin films. This includes the degree of crystallinity, the crystal grain size and preferential orientation, and interlayer spacings. GIWAXS requires the samples to be prepared on silicon substrates, which were treated in the same procedure as the ITO substrates for optical studies

to reproduce the substrate surface conditions. A review on interpretation of GIWAXS patterns has been reported by Mahmood and Wang [161].

Debye-Scherrer rings indicate large, randomly orientated crystal grains. Arcs indicate some preferential stacking of crystal grains with respect to the substrate. A large peak at low Q may indicate the lamellae packing distance. Comparisons between the radially integrated data can be made to the single crystal X-ray diffraction data to confirm similarities or differences between the thin film environment and the single crystal.

Examples of different GIWAXS patterns for thin films of TIPS-tetracene prepared through different preparation methods are shown in **Figure 3.1**. Spin coating and evaporation are shown to give a highly amorphous morphology, with very broad and diffuse Debye-Scherrer rings. Spin coating from chloroform appears to give a thicker sample than from toluene, likely due to chloroform being more volatile and evaporating faster during the spinning-off than toluene. The drop cast samples show highly crystalline films. The toluene drop cast film shows clear arcs, rather than rings, suggesting preferential packing of the molecule with respect to the substrate. This is more prominent for the toluene film than the chloroform film, as the less volatile solvent toluene allows for longer crystallisation time and more organisation of the molecules. When drop cast from 100 °C solution in toluene, these arcs are replaced with rings, suggesting the crystallites are now more randomly oriented.

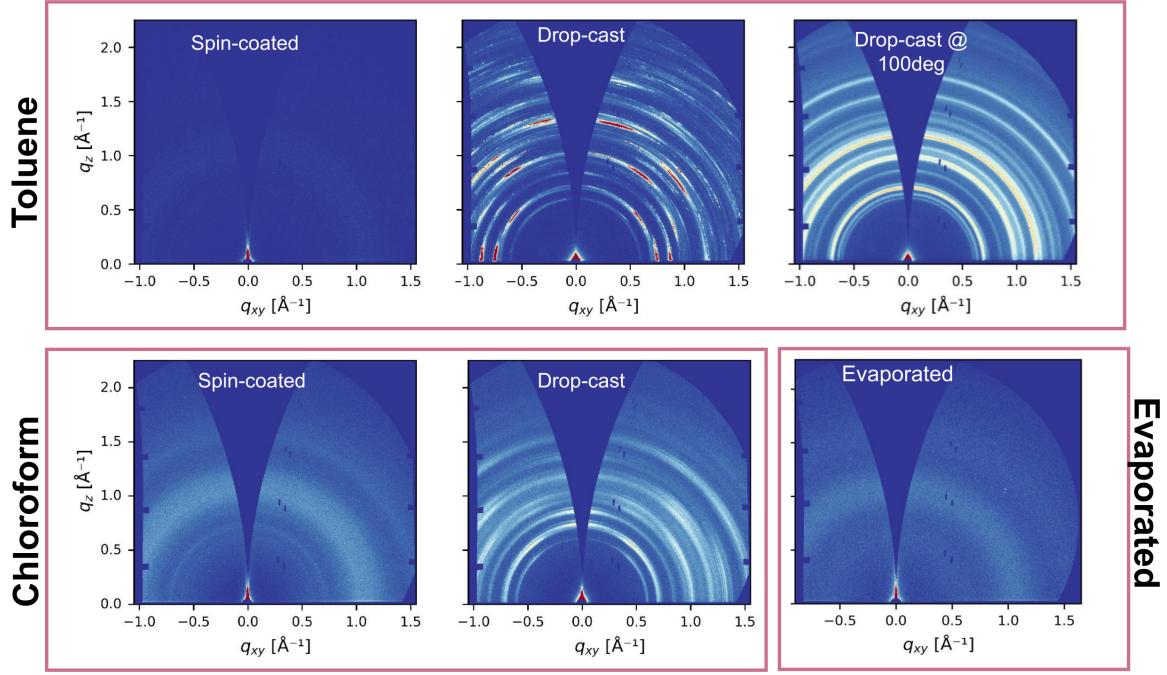


Figure 3.1: Examples of GIWAXS patterns for different thin film morphologies. Films of TIPS-Tc were prepared through different methods: spin coating (1500 rpm, 30 mg ml⁻¹), drop casting (30 mg ml⁻¹), from toluene and chloroform, and thermal evaporation (2 Ås⁻¹).

3.4 Absorbance and Photoluminescence Methods

3.4.1 Absorbance and Emission Spectra

The measurement of absorbance and emission spectra are similar in principle. The sample is irradiated with a continuous-wave (cw) excitation source. For absorbance measurements, the beam is transmitted through the sample, and its spectra recorded by a detector. Comparison to a reference beam allows for the change in transmission with and without the sample to be recorded. The sample absorbance, A , can then be related to its concentration, c , by the Beer-Lambert law:

$$A = -\log_{10} \left(\frac{I}{I_0} \right) = \epsilon cl, \quad (3.1)$$

where I and I_0 are output and reference output light intensities respectively, ϵ is the decadic molar extinction coefficient and l is path length through the sample.

In this thesis, UV-Vis spectra were measured using a Shimadzu UV3600 Plus UV-Visible spectrometer with reference beam. Black card or electrical tape was used to mask the sample

where appropriate.

Photoluminescence (PL) spectra are recorded similarly. An excitation beam is directed to the sample, which then emits. The resultant emission is then directed to a detector and spectrally resolved. In this thesis, PL spectra were either recorded with a cw-laser, a free-optics set up, and an Andor iDus 420 Si-CCD detector, or with a commercially available fluorometer, Edinburgh Instruments FLS1000-DD-stm Steady State, Fluorescence Lifetime and Phosphorescence Lifetime Spectrometer.

The fluorometer can also record excitation spectra, where the intensity of an emission wavelength is monitored for different excitation wavelengths (giving a result similar to the UV-Vis spectrum). Excitation spectra are useful for highly scattering or thick samples used for fluorescence measurements. Time resolved PL at certain emission wavelengths were also measured with the fluorometer. Time resolved PL was measured with time correlated single photon counting (TCSPC) with a maximum time resolution of 300 ps. TCSPC detects single photons and measures their arrival times with respect to a reference signal. It uses a high repetition light source to accumulate photons to gain a statistical data set which can be interpreted for the PL decay, from which lifetimes of states can be determined. The resolution is often limited by the instrument response time, which can be measured by using a non-fluorescent scattering material. Measurements on the fluorometer were performed by Lars Van Turnhout.

3.4.2 Photoluminescence Quantum Efficiency

Photoluminescence quantum yield (PLQE) was measured using adapted methods as previously reported [162, 163]. PLQE is the percentage of photons emitted per photons absorbed by a sample. Three measurements are required within an integrating sphere: a. the measurement of the cw-excitation source irradiating a blank sample, giving the intensity of the laser beam and accounting for any scattering; b. the measurement of the sample inside the integrating sphere *without* direct excitation, which takes into account the absorption of the photons scattered within the integration sphere due to the presence of the sample; and c. the measurement of sample being directly irradiated, and its subsequent emission spectrum, and attenuation of the laser peak due to absorbance. From these three measurements, we can

compare the area under the laser peak, L_n , to the area under the PL spectrum, P_n , such that the PLQE can be defined as:

$$\text{PLQE} = 100\% \frac{P_c - \frac{L_c}{L_b} P_b}{L_a(1 - \frac{L_c}{L_b})}. \quad (3.2)$$

The samples were excited with 520 nm laser (Coherent, ~ 1 mW) inside an integrating sphere, and emission was detected with an Andor iDus 420 Si-CCD detector. PL spectra obtained from within the integrating sphere may be attenuated at the 0-0 peak due to self-reabsorption.

3.4.3 Magnetic Field Effect Photoluminescence (magPL)

Magnetic field effects in photoluminescence, referred to as MagPL or MPL, were measured at the University of Cambridge. With the same lasers and camera as described for the PLQE measurements, the sample was irradiated and PL collected with an optical fibre. The sample was placed in the centre of an electromagnet, driven by a current amplifier and a Keithley 2400 variable voltage source to achieve different field strengths (-600 - 600 mT). The magnetic field value was calibrated with a Gauss-meter (GM08, RS components). As the full PL spectrum was recorded with the silicon camera, the wavelength dependence of the magnetic field effect could be observed. Each field value was randomly selected, and measured with a corresponding $B = 0$ measurement before or after. Inspection of the PL spectrum with respect to the zero field measurements aimed to minimise the effect of laser or sample fluctuations throughout the measurement.

The magnetic field effect is calculated as

$$\% \text{MFE} = 100\% \frac{I(B, \lambda) - I(B = 0, \lambda)}{I(B = 0, \lambda)}. \quad (3.3)$$

MagPL is relatively slow to perform a ‘sweep’ of all the desired field values due to the field voltage ramping time, taking at least 20 minutes per sweep for a relatively fast exposure time for the PL spectrum. If the sample is weakly emissive, long exposure time or a greater number of accumulations can be made, or greater laser power used. However, this has limited

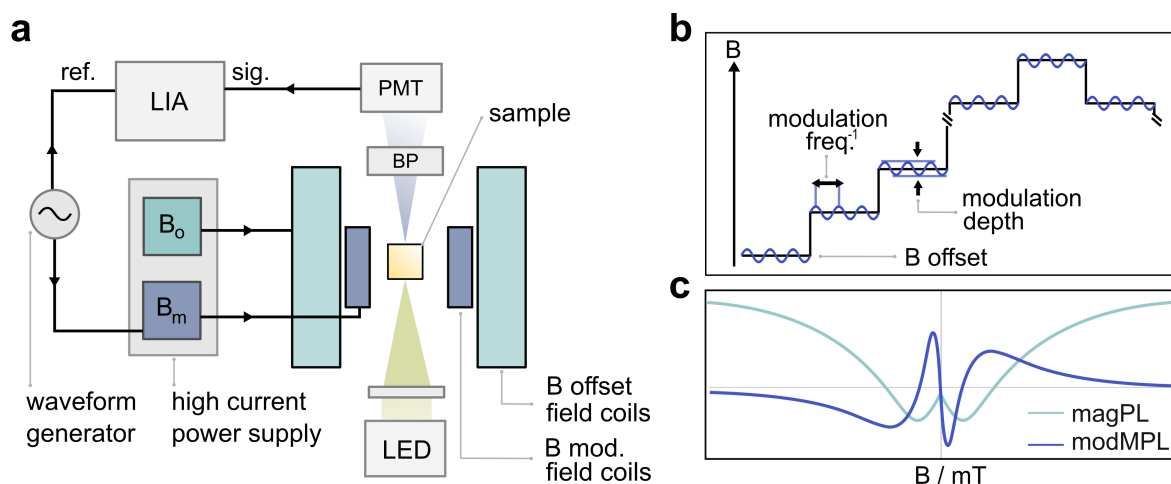


Figure 3.2: (a) ModMPL apparatus, showing the collinear offset and modulation field coils. (b) A example of how the offset field is swept forth-and-back across field values over time, with a constant amplitude and frequency modulation field applied at each offset field value. (c) Illustrative magPL and modMPL curves, showing how the modMPL signal is proportional to the derivative of the magPL signal.

success in producing a better signal-to-noise ratio (S:N) due to fluctuations in the laser, sample degradation, and field fluctuations.

3.4.4 Modulated Magnetic Field Effect Measurements (modMPL)

Modulated magnetic field effects in photoluminescence, referred to as modMPL or mod-MARY (modulated magnetically altered reaction yield) within the literature, was performed by the author using apparatus at the University of Oxford, as a collaboration with the Timmel Group. The apparatus has been previously reported for application with spin correlated radical pairs in solution [17, 18]. Similarly to the magPL measurements in Cambridge, the sample is irradiated, and an ‘offset’ magnetic field applied (-40 - 40 mT), with corresponding PL collected. For modMPL, a secondary, oscillating ‘modulation’ field is applied (67 Hz, 1 mT amplitude). This oscillating field causes the MFE in the PL to also oscillate at the applied frequency. This oscillating signal now allows for detection with a lock-in amplifier (LIA, Stanford Research Systems SR865A), proffering extremely high S:N.

The sample was excited by a 505/365 nm LED (Thorlabs M505L2) which was powered with an LED driver. The LED output was collimated and focused to a wide spot (approx. 10 mm). The power was measured with a Thorlabs power meter with a power head detector of 9.3 mm

diameter. The beam was assumed as top-hat, and fluence was calculated with a commercial energy density calculator [164].

The PL was collected with a light guide, 90° to the direction of irradiation. The thin films were oriented approximately 45° to incident light, and the detected PL through the back face of the sample. The light guide directed the PL to a shielded photomultiplier tube (PMT, Hamamatsu) through a bandpass filter (Thorlabs FKBV40, 40 nm FWHM bandpass filter set of ten).

The field was applied by two pairs of Helmholtz coils with magnetic field axis co-parallel. Each pair of coils had an independent power supply (University of Oxford Physical and Theoretical Chemistry Laboratory workshops). A sample holder (3D printed plastic block with hole for sample) was wedged between the magnets. A hall probe Gauss-meter was affixed in the sample holder to measure the applied field throughout the measurement. The magnetic field was adjusted with a Ziegler-Nicols proportional integral derivative (PID) controller [165] (LabView) to minimise the effects of magnet hysteresis. Due to this fine control of the field value, the magnetic field was swept back-and-forth through the $\pm$ maximum field values rather than being randomly sampled, which was much faster to perform a full ‘sweep’ than that used in Cambridge. The reference for the oscillating field and the LIA was generated by a Rigol DG1022 waveform generator.

A summary of the apparatus is shown in **Figure 3.2 (a)**, with an illustration of the direct and oscillating fields shown in panel **(b)**. Due to the modulated nature of the experiment, the signal observed is proportional to the derivative of the conventional magPL signal, as illustrated in **(c)**.

Lock-in detection is a widely used method, from applications in electron spin resonance (ESR) [32] through to complex methods such as two-dimensional ultrafast spectroscopy with photocurrent detection [47]. The principles of lock-in detection are summarised well by Zurich Instruments [166]. While lock-in amplifiers are expensive, a low cost, digital lock-in amplifier has been recently reported, which may be of interest for future modMPL instrumentation [167].

modMPL Data Analysis

The PMT trace over time can be plotted, and measurements where the PMT voltage saturated (> 13 mV) could be discarded. The LIA output (mV) was given in two channels, x and y , which are phase separated. x represents the real signal, and y the imaginary part. To rephase the signal, we define the total signal as

$$S = x + iy \quad (3.4)$$

and the rotated signal, S_r , as

$$S_r = S \cdot e^{i\theta}. \quad (3.5)$$

We then solved for θ_{min} such that the sum of squared $im(S_r)$ is minimised. The rephased LIA signal, R is then taken as

$$R = re(S_r(\theta_{min})) \quad (3.6)$$

ModMPL gives a signal that is proportional to the derivative of the change in PL intensity $\frac{dI(B,\lambda)}{dB}$, as seen in **Figure 3.2 (c)**. To relate this to the derivative of the magnetic field effect, $\frac{dM}{dB}$, we take the derivative of **Equation 3.3**,

$$\frac{dM}{dB} = \frac{1}{I(B=0, \lambda)} \frac{dI(B, \lambda)}{dB}. \quad (3.7)$$

We therefore find it appropriate to normalise the modMPL signal to the value of the PL intensity at $B = 0$, which we obtain from the PMT voltage. Each field-sweep, or average, can then either be displayed together as a time evolution, or averaged together. The standard deviation across the averages can then be displayed.

3.5 Transient Electron Spin Resonance

Transient Electron Spin Resonance measurements (trESR) were made on numerous occasions at the Centre of Advanced Electron Spin Resonance, Oxford, by Aswathy Girja, Dr Jeannine

Grüne, and Dr William Myers. While all measurements related to this thesis were unsuccessful, it is still worthwhile addressing how trESR is used within the singlet fission community.

TrESR employs the Zeeman interaction, sweeping magnetic fields whilst applying a continuous microwave field to observe transitions between the spin sublevels when the Zeeman splitting is resonant with the microwave frequency. TrESR is able to probe long living ($>1 \mu\text{s}$) spin states with non-zero spin. Therefore, trESR is a useful tool for diagnosing the formation of triplets from singlet fission rather than intersystem crossing, and even the presence of quintet ($m_s = 2$) states in the TT manifold. This direct observation of $^5(\text{TT})$ states with trESR was a large breakthrough in proving the existence of TT intermediates to singlet fission [168]. The most likely reason that the ESR studies in this thesis were unsuccessful is short triplet lifetimes.

A diagram of the expected trESR signatures from intersystem crossing and singlet fission generated triplets is shown in **Figure 3.3**. For intersystem crossing born triplets, population of the T_x and T_y is observed, giving a characteristic absorption (A) and emission (E) pattern such as EEE AAA. For singlet fission born triplets, the T_0 state is populated, giving rise to ESR patterns such as AEE AAE. These characteristic patterns are hallmarks of the origin of the triplets formed. Further to distinguishing the origins of triplets, ESR is also used to find the ZFS parameters, D and E , which is achieved through fitting of ESR lineshapes with EasySpin.

Sample Preparation for trESR

TrESR samples have an unusual requirement to be less than 2 mm wide. Often, thin film samples are prepared by drop casting directly into an ESR tube. However, this does not allow fine control of morphology. To allow morphological control, thin films can be prepared upon 2 mm wide strips of glass cover slip, cut with a diamond scribe, through methods such as blade coating or evaporation. These strips of sample can then be layered within an ESR tube to achieve the desired sample thickness for a successful measurement.

A similar approach was conducted to achieve similar samples through spin coating, for more direct comparison to the spin coated films used within TA measurements. To achieve this, a

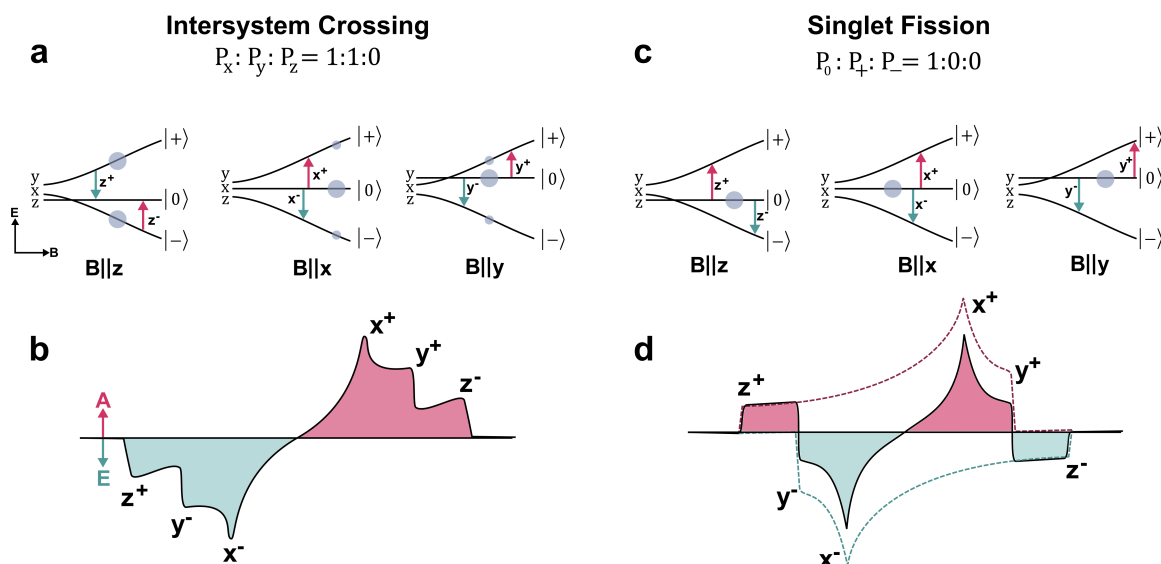


Figure 3.3: An illustrative transient electron spin resonance spectrum of triplets formed by intersystem crossing and singlet fission. The pattern given by SF, AEEAAE, is very different from that given by intersystem crossing, AAAEEE, originating from changes of initial populations of the triplet sublevels. Reproduced from [33].

cover slip was partially scored into 2 mm sections, such that the coverslip (18×18 mm) was still intact. With double-sided tape, the scored face was attached to a second, pristine coverslip (marked with indelible pen), such that the substrate was more rigid, and the unscored ‘back-face’ of the substrate was available for sample deposition. These substrates were then used for spin coating inside a glovebox, such that the two coverslips could be separated after coating, and the scored strips separated whilst under inert atmosphere. This successfully achieved thin (<2 mm), uniformly spin coated samples suitable for trESR measurements.

3.6 Transient Absorption Spectroscopy

3.6.1 Introduction to Transient Absorption Spectroscopy

A simple schematic for transient absorption (TA) spectroscopy is shown in **Figure 3.4**. The basic principle of an absorption technique is to observe how the intensity of a probe beam is modulated by the presence of a sample. For time-resolved transient absorption spectroscopy, the probe beam is pulsed, and a second pump pulse is added, which intersects the probe beam at the sample. The pump pulse induces a change in population of states of the sample, from which new transitions can be observed with the probe pulse. A change in delay between pump

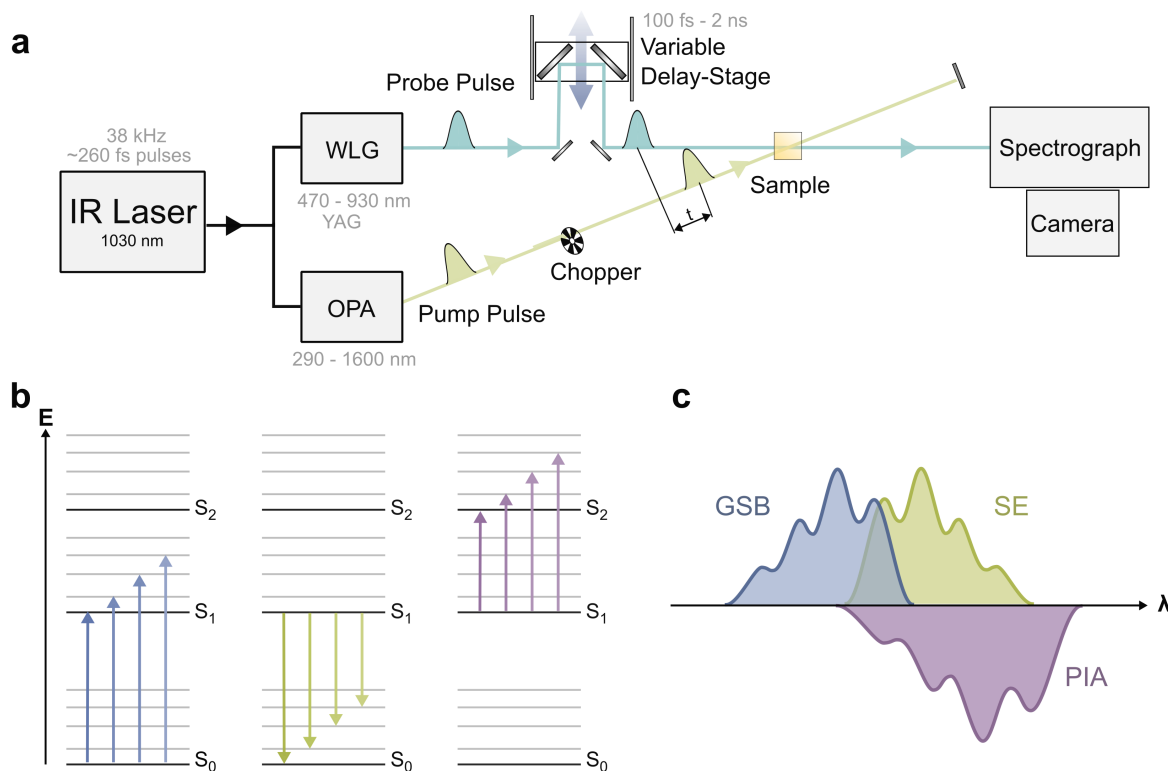


Figure 3.4: (a) picosecond transient absorption spectroscopy apparatus schematics, (b) possible transitions that can occur after photo excitation with pump pulse, giving rise to (c) signals common to TA Spectroscopy. A ground state system is photoexcited by the pump pulse, wherein subsequent absorption of the probe pulse can result in three possible signals: ground state bleach, GSB; stimulated emission, SE; and photoinduced absorption, PIA. GSB results in increased transmission in the ground state region due to depletion of population, resulting in a positive feature in the $\Delta T/T$. SE results in apparent increased transmission in a region redder than the ground state, giving a positive $\Delta T/T$ signal. PIA results in reduced probe transmission due to new possible transitions, giving a negative $\Delta T/T$ signal, often redder than the GSB. Adapted from Baikie *et al.* [169].

and probe pulse arriving at the sample creates a time resolution. This delay can be created with a mechanical delay stage for short timescales (fs-ps), or by electronic delay generation for longer timescales (ns- μ s). Changing the delay between the pulses allows observation of changes in the population of states before the pump pulse, and at desired time intervals after the pump pulse, providing key insight into the photophysics of the system.

The pump pulse is blocked at every other measurement, often mechanically by a chopper, such that the modulation of sample absorbance by the pump beam can be observed. The observable quantity of TA spectroscopy is often chosen to be $\Delta T/T$. As $\frac{I}{I_0} = T$, then

$$\frac{\Delta T}{T} = \frac{\frac{I_{\text{on}}}{I_0} - \frac{I_{\text{off}}}{I_0}}{\frac{I_{\text{off}}}{I_0}} = \frac{I_{\text{on}} - I_{\text{off}}}{I_{\text{off}}}. \quad (3.8)$$

To achieve ultrafast (faster than nanosecond) resolution of TA spectroscopy, very temporally short pulses are required for both the pump and probe. This is achieved through the use of pulsed lasers, with the wavelengths of the pulses modified through the use of nonlinear optics; second harmonic generation, third harmonic generation, white light generation, and noncollinear optical parametric amplification (NOPA) are commonplace throughout our apparatus.

TA yields a 2D $\Delta T/T$ intensity data map as a function of wavelength and time. Slices at different wavelength points can be taken to show intensity with time in that region, highlighting kinetics, or slices at different time points can be made to show how whole spectra change in time. Whilst the former can give more quantitative insight of time constants, the latter can show key signal shapes that are indicative of certain photophysical processes.

Some signals that occur in TA spectra are shown in **Figure 3.4 (b)**. Photoexcitation with the pump pulse induces a change in population that can then be probed. As seen in the figure, there are three main processes that can occur upon absorption of the subsequent probe pulse: ground state bleach (GSB), stimulated emission (SE), and photoinduced absorption (PIA). GSB and SE both give rise to positive $\Delta T/T$ signals, whereas PIA yields a negative $\Delta T/T$. SE will often occur at slightly longer wavelengths than the GSB due to rapid vibrational relaxation to the lowest vibrational level of the excited state, as discussed in **Section 2.3**. From the correspondence principle, as states increase in energy, the energy gaps between consecutive levels typically decreases. This means that PIAs are often at longer wavelengths than both GSB and SE.

3.6.2 Non-Linear Optics for TA

Various non-linear optical processes are employed within transient absorption spectroscopy. Non-linear optics refers to the fact that the response of a material scales non-linearly with the applied optical field [170]. Second-harmonic generation, one of the first demonstrations of non-linear optics in 1961 [171], scales quadratically with the strength of the optical field. Second-harmonic generation (SHG), also called frequency doubling, is a process in which

photons interact with a non-linear material and are effectively ‘combined’ to form new photons at twice the frequency [172]. We often employ materials such as β -barium borate (BBO) crystals to achieve SHG from laser light 800 nm to an output of 400 nm. We also make use of processes such as white light generation (WLG), where a short intense pulse undergoes spectral broadening [170]. We often employ sapphire crystals to generate a visible broadband pulse from an 800 nm pulse.

The output of these two processes can be combined in a non-collinear optical parametric amplifier (NOPA). A NOPA is used to amplify broadband or narrow ultrafast pulses. A NOPA mixes two pulses in a non-linear crystal, such as BBO, resulting in an amplified pulse. This amplification requires temporal overlap and spatial overlap of the two pulses, as well as a specific angle between the two incident beams, and phase-matching with the crystal. We often overlap a white light pulse with a 400 nm pulse [173]. If the white light pulse is temporally shorter than the 400 nm pulse, the whole white light spectrum (of wavelengths up to 400 nm) is amplified in intensity. This amplified white light pulse can then be used as a probe pulse. If the white light pulse is temporally large, the 400 nm pulse can selectively amplify parts of the white light pulse. This allows for highly tunable wavelengths for a pump pulse to be chosen. A summary of the typical NOPAs used in this project can be found elsewhere [92].

3.6.3 picosecond TA

For measurements <1 ns reported in **Chapters 6** and **7**, a psTA apparatus was used, as reported [19]. The system uses a 38 kHz 1030 nm Pharos amplifier (Light Conversion) for the probe, which is used to generate white light with a yttrium aluminium garnet (YAG) crystal. The pump is generated with an ORPHEUS LYRA optical paramagnetic amplifier with tunable wavelength between 400-1300 nm. Time delay was achieved with a Newport delay stage, and on-off pulses generated by a mechanical chopper (Thorlabs). The pump and probe beams were focussed to sizes of approximately 200 μm and 80 μm diameter respectively. Probe intensity after the sample was detected with a spectrograph (Semrock 163, Oxford Instruments) and a silicon camera (AViiVA). The same light sources were used for the fsTA (< 2 ps) used in **Chapter 7**, with a smaller delay stage.

3.6.4 nanosecond TA

This apparatus was reported by Rao *et al.* [19, 174]. The nsTA system has three possible configurations for long-time measurements, making use of four possible light sources. Possible probe sources were a probe NOPA seeded by a 1 kHz 800 nm Solstice Ace Ti:Sapphire amplifier with 90 fs pulses, or a LEUKOS Disco supercontinuum laser (STM-1-UV). The NOPA offered better S:N, but a smaller probe region; the DISCO allows examination of a large window of wavelengths, but with worse S:N. Possible pump sources were a pump NOPA, again making use of the Solstice, or a INNOLAS piccolo. The piccolo allowed for greater pump powers, but only allowed pumping at 355 nm or 532 nm. The pump NOPA was weaker in intensity, but was highly tunable in wavelength. As the delay was generated electronically (Stanford Research Systems delay generator), the possible configurations were

1. DISCO probe, piccolo pump; ideal for solution state spectroscopy due to broad probe range and high pump fluence.
2. DISCO probe, NOPA pump; ideal for solution state triplet sensitisation due to broad probe range and tuneable pump wavelength.
3. NOPA probe, piccolo pump; ideal for thin films due to better S:N probe.

The nsTA made use of a second probe reference beam to give better S:N, but is problematic for inhomogeneous samples such as drop cast films. The transmitted probe was spectrally separated with a spectrograph and detected with a silicon detector (Hamamatsu G11608). Overall, due to better laser stability in the psTA apparatus, the nsTA suffered from worse S:N than the psTA data.

3.6.5 Triplet Sensitization Measurements

Triplet sensitization measurements use a molecule that forms long-lived triplet states with high yield as a sensitizer to induce triplet transfer to the chromophore of interest. Monitoring the TA of these samples in the solution state at longer timescales (ns) should show a GSB for the chromophore, and the PIA of its triplet excited states. This is best achieved if the

sensitizer absorbs in a region where the chromophore does not. For the cibalackrot systems in **Chapter 6**, triplet sensitization was measured in solutions of chlorobenzene with anthracene as sensitizer. Solutions were prepared such that anthracene in the solution had an absorbance of 0.2 OD at the excitation wavelength (355 nm), while the Cibalackrots had an absorbance of 0.5 OD at the λ_{max} . Signals were measured with the ns-TA system described above.

3.7 Numerical Methods

Throughout this thesis, we were presented with data that could be represented as a function of two dimensions, such as $\Delta T/T(\lambda, t)$, in the case of TA data ¹. Often, we wanted to reduce the data set to its component species, each with their own signature (spectrum or lineshape) that had different contributions to the total signal over time. In this thesis, we refer to this as spectral decomposition. To achieve this, we used two approaches: singular value decomposition (SVD), and a genetic algorithm (GA).

3.7.1 Singular Value Decomposition (SVD)

A good review of the principles of SVD are written by Schlens [175]. Briefly, SVD is a matrix factorisation technique that can be employed for dimensionality reduction. For an $n \times m$ matrix of data $\mathbf{X}$, SVD decomposes it to $\mathbf{X} = \mathbf{U}\mathbf{\Sigma}\mathbf{V}^T$, where $\mathbf{U}$ ($n \times n$) and $\mathbf{V}$ ($m \times m$) are unitary matrices. $\mathbf{U}$ is a matrix of *left singular vectors*, and $\mathbf{V}$ is a matrix of *right singular vectors*, while $\mathbf{\Sigma}$ is a diagonal matrix of *singular values*. From the matrix of singular values, we can find the N statistically most significant ‘species’ in the data. To best explain the subsequent analysis, we provide an example data set in **Figure 3.5**.

A ‘toy’ data set of TA data is shown in **Figure 3.5 (a)**. Three peaks at different wavelengths evolve in time. By performing SVD, we can then create a log-log plot of the singular values of $\mathbf{\Sigma}$, as shown in **(b)**. This is called a scree plot. The points represent how relatively significant each component of the data is. The first three points show some significance, whereas the points for $N > 4$ show little change. This suggests the data can be well explained or reproduced with only three components; addition of further components gives diminishing returns

¹or % MFE(B, λ), as in the case of magPL data.

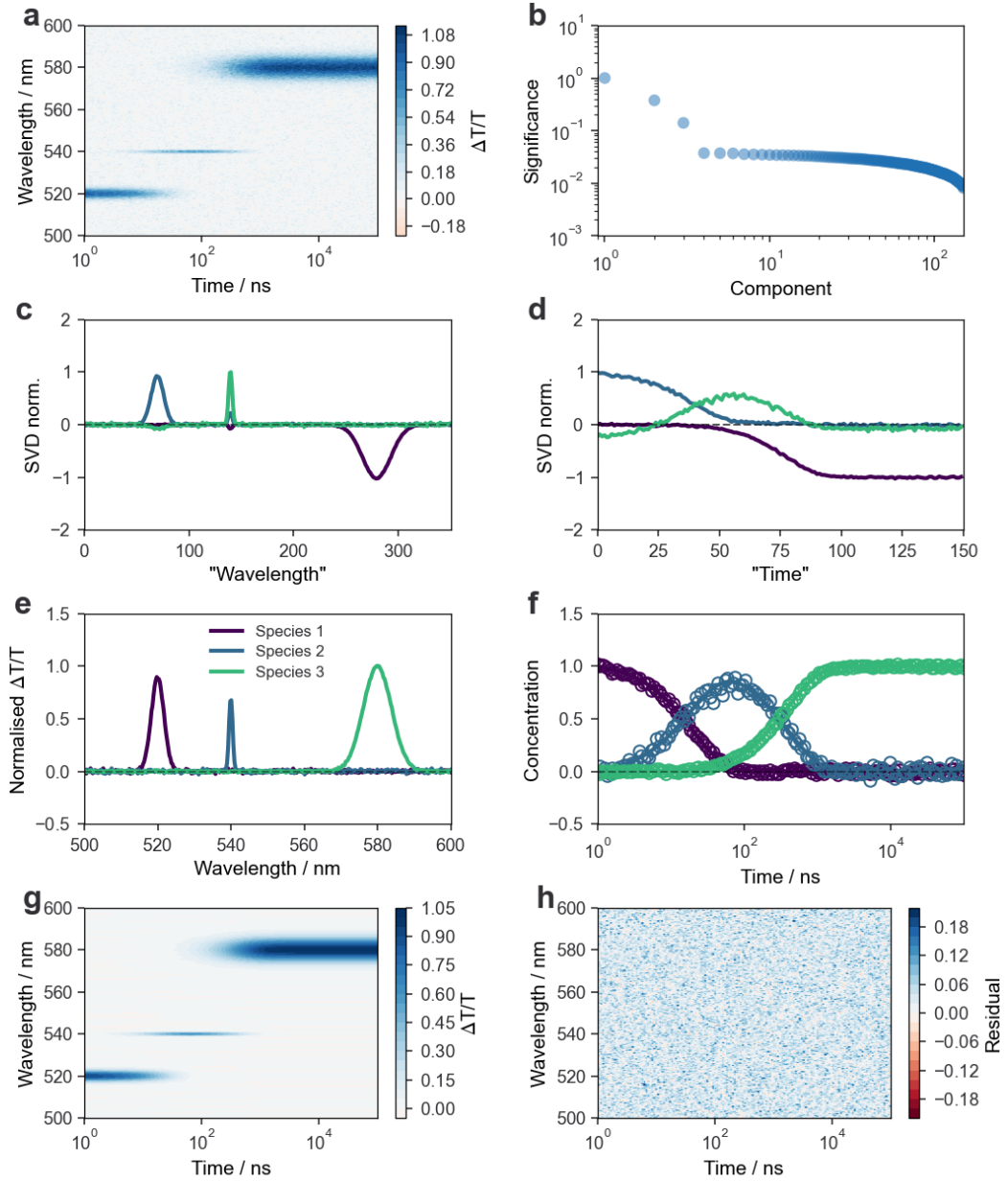


Figure 3.5: Singular value decomposition (SVD) analysis of ‘toy’ example data. (a) shows the full TA map ($\mathbf{X}$), indicating the evolution of three species with peaks at distinct wavelengths. (b) shows the scree plot obtained from Σ , confirming three species contribute to the data statistically. (c) shows the ‘spectra’ obtained from SVD ($\mathbf{P}$), with (d) showing the ‘kinetics’ ($\mathbf{T}$), of the 3 most significant components of the data. The basis of $\mathbf{P}$ and $\mathbf{T}$ is rotated such that the components are orthonormal. Through the use of an ODE model to rotate the eigenbasis, the resulting spectra and kinetics are shown in (e) and (f). The modelled data is shown in (g), and residuals of (a) and (g) shown in (h).

for the amount of information captured. We can now consider the first three components of $\mathbf{U}$ and $\mathbf{V}$. For N components, we define ‘spectra’ and ‘kinetics’ matrices in Python as

$$\mathbf{P} = \mathbf{U} @ \mathbf{S}^{**0.5}, \mathbf{P} = \mathbf{P}[:, 0:N]$$

and

$$\mathbf{T} = \mathbf{S}^{**0.5} @ \mathbf{V}, \mathbf{T} = \mathbf{T}[0:N, :]$$

(where $\mathbf{S}$ is Σ).

In the context of TA data, where we have intensity as a function of wavelength $\times$ time, $\mathbf{P}$ is a matrix of ‘wavelength’ vectors, each giving spectra of statistically unique species, while $\mathbf{T}$ shows how these spectra must evolve in ‘time’ to reproduce the data in $\mathbf{X}$. However, there is a caveat that the eigenbasis of the matrices $\mathbf{P}$ and $\mathbf{T}$ is no longer necessarily the basis of wavelength and time, but instead a rotated eigenbasis such that the singular vectors are orthonormal. The 3 components of $\mathbf{P}$ and $\mathbf{T}$ can be seen in (c) and (d). The ‘spectra’ in (c) are a linear combination of the peaks we expect to reproduce. The ‘kinetics’ in (d) are clearly physically uninterpretable, with the kinetic traces often negative. This highlights the lack of physical relevance to the output of SVD, despite the correct isolation of only 3 significant species in the data. However, because we can approximate the kinetics of the TA data with an ordinary-differential equations (ODE) model, we can rotate the data to a more suitable eigenbasis.

We set up a series of ODEs, such as

$$\begin{aligned}\frac{d[A]}{dt} &= -k_1[A] \\ \frac{d[B]}{dt} &= k_1[A] - k_2[B] \\ \frac{d[C]}{dt} &= k_2[B].\end{aligned}$$

By setting the initial concentrations, in this case $[1, 0, 0]$, we can find the three vectors of

concentrations in time with `scipy.integrate.odeint`. We now have a matrix of modelled kinetics, C_{solv} , which we can define by a vector of rate constants, $k = [k_1, k_2]$. With these modelled kinetics, we can find the rotation operation matrix of the SVD through

$$R = T @ \text{numpy.linalg.pinv}(C_{solv}).$$

The spectra can then be rotated through $P @ R$, and the data of $\mathbf{X}$ reconstructed from the rotated spectra and C_{solv} . The residuals between the input data $\mathbf{X}$ and the modelled data can be defined as a function of the rate constants, k . We then use `scipy.optimize.minimize` to perform an optimisation of the data reconstruction for the parameters of the ODE model. This approach is very similar to compartment analysis, where data is divided by the solution of an ODE model to observe the spectra generated [169]. However, this method only uses the most significant N species in the data, minimising the influence of noise. The rotated spectra are shown in **(e)**, and the kinetics from C_{solv} shown in **(f)**. The reconstructed data is shown in **(g)**, and residuals of the input data and modelled data shown in **(h)**.

This approach to model data was found to be highly successful throughout this thesis. The code for this analysis was written by the author, based on previous codes by Dr Victor Gray, and discussion with Dr Tomi Baikie. This methodology has advantages and disadvantages. The method relies only on simple linear algebra, with each step transparent to the user. The approach also allowed for the relation to physical processes very easily, with experimentation of different ODE models easy to implement. The disadvantage of this methodology is that it was highly model dependent, and required critical thinking of the user to deduce if the spectra and kinetics outputted were feasible with respect to the data. Often, a more complicated kinetic model can ‘fit’ the data better, such as $\frac{d[A]}{dt} = -k_1[A][A]$ appearing to approximate the data better than $\frac{d[A]}{dt} = -k_1[A]$. Furthermore, this methodology is somewhat prone to finding linear combinations of the species.

A way to mitigate any user bias from the kinetic modelling with this approach is to directly compare the results of the SVD to a model free approach, such as a genetic algorithm.

3.7.2 Genetic Algorithm

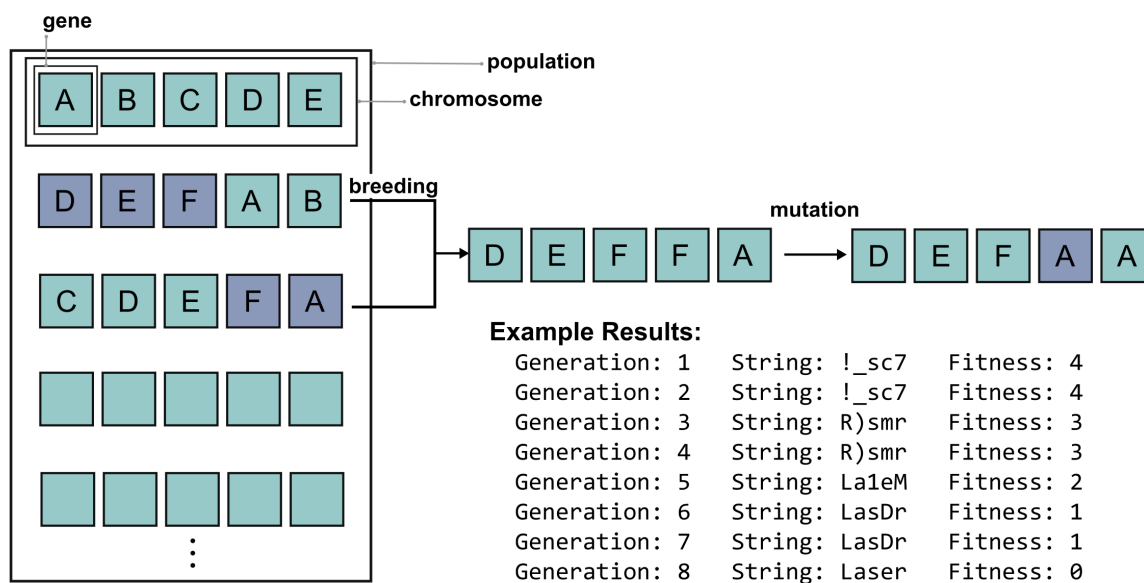


Figure 3.6: An example of genetic algorithm: random guesses of a target are generated, creating an initial random population. To liken to biology, each ‘guess’ is similar to a chromosome, made up of ‘genes’ (characters, integers, floats). Each guess is ranked according to a fitness score. Parents are selected to ‘breed’ in the attempt to create a new ‘guess’ with a better fitness score. Mutations are added to add randomness, but also to aid low scoring guesses in the next round or generation. This new population is ranked, and breeding and mutations repeats again. The highest ranking pair from each generation is passed through to the next generation without breeding or mutation. An example of the highest ranking string from 8 generations of GA are shown for the target ‘Laser’. Adapted from [176]

A genetic algorithm (GA) is a model free approach to decomposing data. To briefly explain the concept of GA, an example problem is shown in **Figure 3.6**. We aim to reconstruct a target, such as a string or vector, through the random generation of values. A large initial population of randomly generated attempts (or, to liken to biology, chromosomes) are made, and each ranked according to their performance. Results from the initial population are bred together to generate a new population. Mutations are applied to both induce randomness avoid minimisation to local minima, but also to make poorly performing chromosomes more likely to perform better in the next generation. This new population of attempts is again ranked, with the pair of highest scoring guesses passing through directly to the next generation without cross-breeding or mutation. This process of breeding, mutating, and ranking, is repeated until either the number of prescribed generations has elapsed, or until a condition for the score of the highest ranking attempt is met. An example for finding the string ‘Laser’ can be seen in **Figure 3.6**, where successive generations score better and better until the target is reached.

The same principles can be applied to TA data. The target can be a vector of numbers which defines the spectra of each component. Randomly generated populations can be achieved by taking a number of Gaussians with added noise. From the guessed spectra, kinetics can be found through division of the data by the spectra. As we determine that the kinetics can only be positive, we can add a term to the fitness function that penalises spectra that give negative kinetics. The GA used in this thesis was written by Gelinas *et al.*, reported elsewhere [177, 178]. To assess the goodness of fit for each spectrum, the fitness function is defined as

$$f = \sum_{i=t_i}^{t_f} \sum_{j=\lambda_i}^{\lambda_f} \left(\frac{(data_{i,j} - fit_{i,j})^2}{\sigma_{i,j}^2} (1 + kn) \right)^{-1}, \quad (3.9)$$

which can be surmised as the sum of the squared residuals of the data and modelled data, regularised by the uncertainty/variance of the data, with the inclusion of a negative kinetic penalty kn , reciprocated, such that a large fitness score indicates a better fit.

This approach also has a number of advantages and disadvantages. The approach is model free, which removes any user bias, and often performs well to decompose the data, being less prone to finding a linear combination of species than SVD. To an unwitting user, however, the GA is a black box, and can give unsuitable results. Exploration of initial guess parameters, wavelength/time ranges selected, and data downsampling should be conducted by the user. Through this, one can ensure the GA results are reproducible under different starting conditions, and that the data is not being skewed by oversampling of data equal to zero, or high $\Delta T/T$ values due to artefacts in the raw data. To achieve this, many runs of GA should be performed, which is both time and computationally demanding. However, GA can afford interesting results, that can then be fitted with exponential decays to establish kinetic information in the data.

GA and SVD serve well as complementary methods. SVD is fast, and can indicate to the user a suitable number of species to consider. GA requires minimal user input, and can help guide the kinetic model one could use in the SVD approach. Comparisons of the kinetics and spectra obtained from both methods does well to validate either analysis, as well as comparison to the raw data.

3.7.3 Defining Errors

When we fit data, we assign an error to the characteristic value, such as the rate constant. For fitting an exponential decay, this was relatively straightforward, as the function `scipy.optimize.curve_fit` returns the 2D covariance matrix for the optimal parameters, `pcov`. The error in the parameters can then be defined as

$$\text{perr} = \text{numpy.sqrt}(\text{numpy.diag}(\text{pcov}))$$

[179]. When using `scipy.optimize.minimize`, defining the error can be more complex. To approach this, two methods were taken. The first, if the minimization algorithm ‘BFGS’ is selected, the inverse Hessian matrix is outputted, which describes the curvature of the cost function for the minimisation. From the inverse Hessian, an approximation of the error can be defined as

$$\sqrt{\sigma_{res}^2 \times \text{diag}(H^{-1})},$$

where σ_{res}^2 is the variance of the residuals [180]. However, not all minimization methods output the inverse Hessian, or may over estimate the error. Another approach is to bootstrap the residuals. This method is computationally expensive, as it requires resampling the residuals (with replacement) and performing the optimization at least 100 n times, where n is the number of parameters being fitted. The standard deviation of the parameters from the 100 n evaluations then signifies the error in the fit. If the residuals are typically small, this will give a very small error. Within this thesis, both methods were typically employed. Furthermore, examining the residuals of the fit with a 2D map should not be underestimated for its usefulness, as this gives overall the best interpretation of where your model has performed well, and where sources of large error may be originating from.

Chapter 4

Modulated Magnetic Field Effects:

A Highly Sensitive Method for Examining Singlet Fission in Thin Films

Modulated magnetic field effects offer a fantastic tool for understanding the behaviour of singlet fission materials. The technique itself is fast with low degradation, as a result of its high sensitivity. It also probes the very low field values, < 100 mT, a region that is often inaccessible due to signal-to-noise. In this chapter, we apply modulated magnetic field effects to the ‘fruit fly’ of the singlet fission community: TIPS-Tetracene. We are able to reveal subtle changes in the singlet fission dynamics as a result of thin film morphology, and shed light on the controversial TT-emission. Furthermore, we show the capabilities of modulated magnetic field effects as a tool for screening thin films of singlet fission materials, and propose it as an excellent tool for studies alongside TA and ESR.

This project was a collaboration with Dr Olivier Paré-Labrosse and Prof. Christianne Timmel at the University of Oxford. Samples were prepared and measured by the author using apparatus in the Timmel Lab. All data processing and analysis was performed by the author.

4.1 Introduction

The performance of singlet fission in a material is often investigated with transient absorption (TA) spectroscopy, magnetic field effects in photoluminescence (magPL), and electron spin resonance (ESR). However, each of these techniques has their own complexities. They are often limited by signal-to-noise (S:N), which is often a direct impact of the thin film preparation and resultant morphology. For TA, we desire thin films with low absorbance for maximal probe transmission, and often highly homogeneous films for two beam detection. By comparison, for magPL, thin films will give poor S:N, and may photodegrade throughout the measurement of one field sweep. For magPL, a thicker film is desirable, as it offers better S:N, and PL techniques are impervious to low transmission; the more absorbing, often the better. For ESR, the thin films have their own requirement of being only 2 mm wide, meaning new and separate samples are required for ESR than all other measurements. Furthermore, ESR is a very difficult and expensive technique, requiring liquid helium and liquid nitrogen, and can often fail to yield results due to rapid spin relaxation of the triplet states.

These techniques are often used complementarily. However, with each demanding different thin film preparations, it is difficult to know whether we are examining behaviours in the films that is universally true, or rather behaviour that is sample, and so by extension, technique specific. Overall, quantifying singlet fission performance of a material in the solid state is highly complex, time consuming, and difficult to reproduce.

To add to this dilemma, the singlet fission performance of a material is highly dependent on the film morphology and preparation method. Experiments such as comparing thin films spin coated from different solvents on the same apparatus in rapid succession, without exponentially increasing the time required to examine the material, are highly desirable.

With all this in mind, it is clear that there is a need for a technique, that would be rapid (so many film preparations can be compared), concise (able to quickly identify singlet fission behaviour), have low degradation (so that samples could be reused for further measurements), and impervious to film thickness/scattering. To address these shortcomings, we employed modulated magnetic field effects in photoluminescence, modMPL. ModMPL is a technique

that has been used to study spin-correlated radical pairs [17, 18, 181]. Due to the lock-in detection method, modMPL boasts very high signal to noise (S:N). This high S:N has many impacts:

- Low field values can be examined in great detail, meaning sweeping the field values themselves is relatively fast compared to magPL (2-3 minutes per sweep *cf.* > 20 minutes per sweep in magPL);
- Lower fluences can be used, meaning reduced sample degradation;
- Due to low degradation, ‘difficult’ or low signal samples can be averaged for a long time, as the sample should be stable over time.

This leaves some questions to determine: can modMPL give a definitive answer as to whether a sample is undergoing singlet fission, and can it measure samples of different morphologies/thicknesses/scattering?

In this chapter, we use modMPL to examine TIPS-tetracene (TIPS-Tc), an archetypal singlet fission material, to ascertain whether modMPL gives lineshapes that inform us of the singlet fission dynamics. We complement our modMPL results with sample characterisation techniques to explore whether the signal is impervious to film thickness and morphology, and even if we can decipher subtle changes in the singlet fission dynamics as a result of thin film preparation.

4.2 TIPS-Tetracene: Molecule of Interest

First, we begin by characterising our molecule of interest. TIPS-Tc can be seen inset in **Figure 4.1 (a)**, alongside the excitation and emission spectra of three different thin films with differing morphologies. The ‘amorphous’ film is prepared by spin coating from toluene solution. The ‘spherulites’ film is also prepared through spin coating, but is aged such that new crystallites, called spherulites, have formed. This phenomenon of aged spin coated TIPS-Tc films forming spherulites has been reported for many systems, including TIPS-Tc [106, 182]. The ‘polycrystalline’ film is prepared by drop casting from chloroform. Examples of

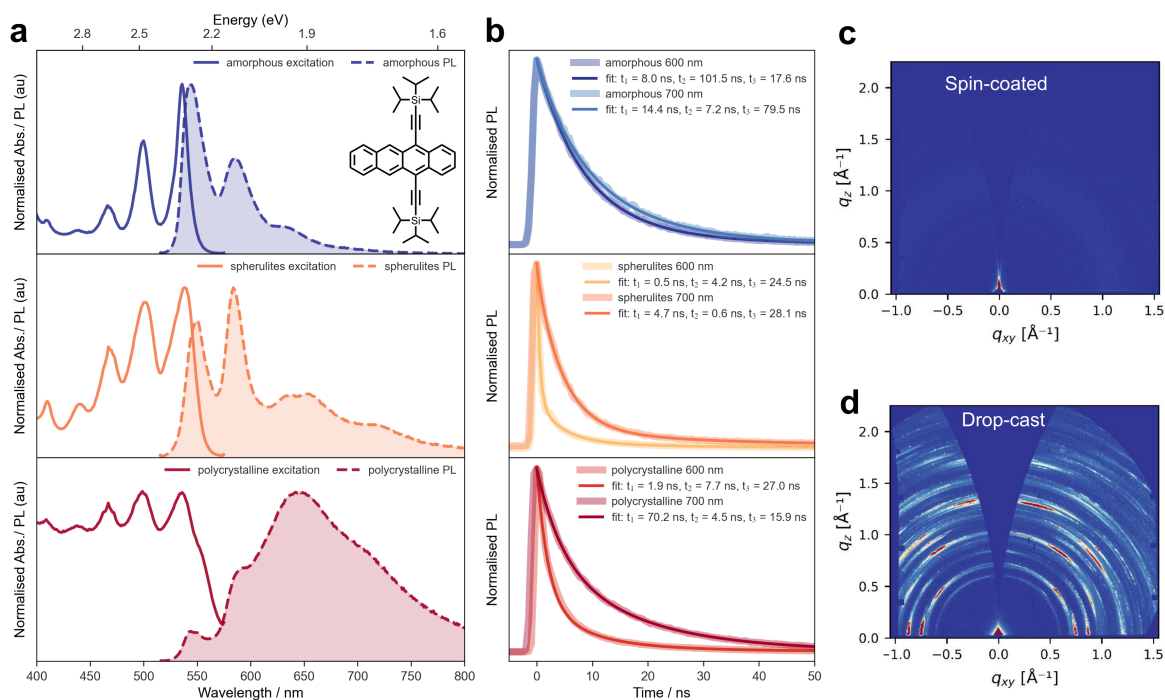


Figure 4.1: TIPS-Tetracene characterised by morphology: **(a)** excitation and emission spectra of TIPS-Tc films with three morphologies: amorphous, prepared by spin coating; film with spherulites, prepared through spin coating with ageing; and polycrystalline, prepared through drop casting. **(b)** TCSPC decays of PL for each film in two regions, 600 nm and 700 nm, indicative of S_1 PL and TT PL regions. **(c)** GIWAXS of an amorphous film prepared by spin coating with lack of crystalline features. **(d)** GIWAXS of polycrystalline film prepared by drop casting. Arcs indicate large crystalline grains with some preferential orientation. Excitation, emission, and TCSPC spectra collected by Lars Van Turnhout. GIWAXS measured and analysed by Dr Rachel Kilbride, University of Sheffield.

the GIWAXS of the spin coated film and drop cast film are shown in **Figure 4.1 (c)** and **(d)**. **(c)** shows a highly amorphous film, with very few features, whereas **(d)** shows a highly crystalline film, with arcs indicating many large, randomly orientated crystal grains.

Examining the excitation spectra in **(a)** (excitation spectra rather than direct absorption spectra are selected here due to high scattering and high film absorbances), the amorphous spectrum closely resembles the solution spectrum of TIPS-Tc found in literature [41]. The spherulites film is somewhat broadened, while the polycrystalline spectrum has clearly been deformed due to high sample scattering and overly high absorbances. Overall, the peaks of the vibronic progression for each film remain unchanged, with relative intensities of the peaks changing due to a scattering background as opposed to any effects from molecular aggregation. The emission spectra, however, begin to show profound differences in the vibronic progressions.

The amorphous film is a close mirror image of the excitation spectrum, close to the solution emission spectrum. The amorphous environment of the film is similar to the environment in solution. The polycrystalline film, by contrast, shows a highly suppressed 0-0 emission peak, and an intense, featureless emission centred at 650 nm that extends to 800 nm. The spherulitic film is somewhere between the two cases, where the amorphous-like vibronic progression is still present, while the increase in this redder emission between 650-700 nm is more apparent than in the amorphous film.

This red emission has been something of a controversy in the singlet fission community for the past decade. The discussion is summarised in a review by Musser and Clark [35], and has been further discussed in a recent preprint by Feng *et al.*[85]. Previously, this red, featureless emission was identified as the TT state emission, an intermediate of singlet fission [41, 42, 74]. Others identified this as a excimer emission, a loss pathway directly from the singlet state [76]. However, work by Bossanyi *et al.* confirmed the emission of TT pairs in pentacene single crystals with a red-shifted emission, different to the excimeric emission [45]. Feng *et al.* show evidence that the emission from both the excimer and the TT state are resolvable for solutions of 12-bis(noctyldiisopropylsilylethynyl) tetracene (NODIPS-Tc), [85] and that the emission from the TT state can be enhanced with a magnetic field [78, 90].

In **Figure 4.1 (b)**, the decay kinetics of these two regions, the ‘singlet’ emission and the ‘TT’/‘excimer’ emission are examined. TCSPC decays are shown at 600 nm and 700 nm for each of the three films. Each trace can be fitted to the sum of three exponential decays, summarised in **Table 4.1**. For the amorphous film, the decay is the longest, with the longest decay constant of 80-100 ns, with minimal difference between the two wavelength regions. For both the polycrystalline and spherulites film, the decay is much quicker, with the 600 nm region decaying faster than the 700 nm region. This suggests that the 700 nm TT emission is longer living compared to the 600 nm region. This would agree with the iCCD data reported in the literature [42].

Overall, the data shown in **Figure 4.1** suggests we are able to create a ‘sliding scale’ of morphologies through different film preparation methods. Generally, drop casted films will create

Sample	Wavelength / nm	τ_1 / ns	τ_2 / ns	τ_3 / ns
Amorphous	600	8.01 ± 0.07	17.6 ± 0.8	101 ± 23
	700	7.2 ± 0.3	14.4 ± 0.6	80 ± 14
Spherulites	600	0.50 ± 0.04	4.22 ± 0.08	24.5 ± 0.9
	700	0.57 ± 0.08	4.68 ± 0.03	28.1 ± 0.5
Polycrystalline	600	1.95 ± 0.05	7.7 ± 0.8	27.0 ± 4.5
	700	4.46 ± 0.03	15.9 ± 0.1	70.2 ± 4.3

Table 4.1: A summary of TCSPC decay lifetimes from **Figure 4.1 (b)**

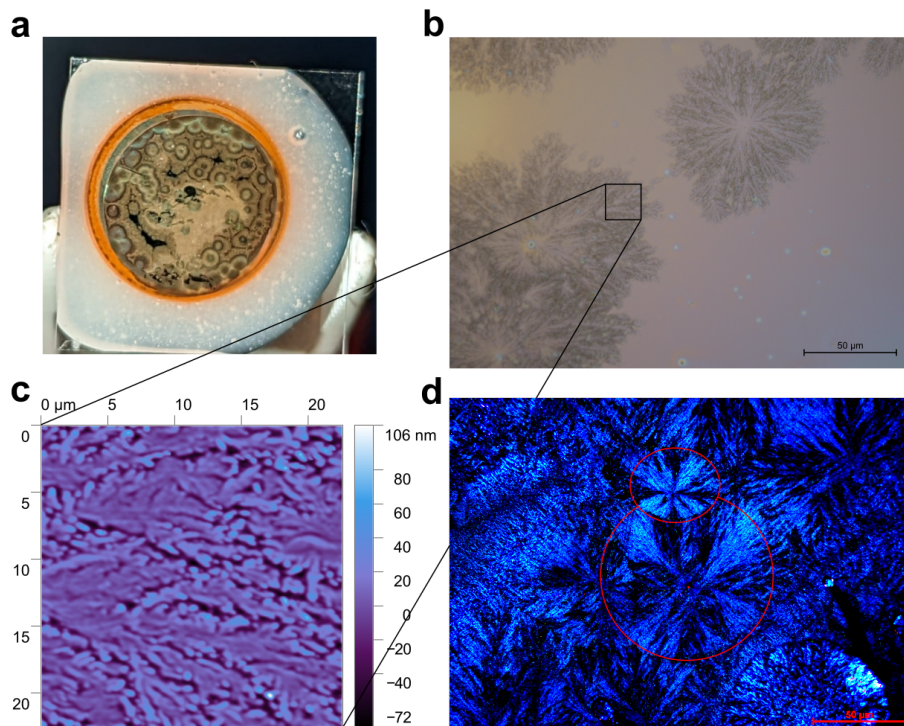


Figure 4.2: Spherulites in TIPS-Tc films: **(a)** photograph of encapsulated film with spherulites visible to the eye. **(b)** View of spherulite as from film measured in **(c)** with optical microscopy. **(c)** Atomic force microscope image of a region of a spherulite. False colour map highlights the changes in height across the region. Atomic force microscopy was performed with Dr Nicolas Gauriot. **(d)** Image of the spherulites with crossed polarisers under an optical microscope. Red circles highlight two spherulites where the hallmark maltese-cross is visible.

polycrystalline environments, spin coated films will initially create amorphous environments that may then form spherulites, or polycrystalline domains, whereas films prepared by rapid thermal evaporation will form amorphous films that are stable over the timescales of interest (days-months), and will not form new crystallites.

To expand upon the description of spherulites, **Figure 4.2 (a)** shows an image of a 13 mm circular substrate with spherulites clearly visible by eye. Under a visible microscope, shown

in panel (b), the spherulites appear snowflake-like, with a dark central spot known as the nucleation site. The representative region highlighted in (b) was examined with atomic force microscopy in panel (c), showing how the spherulites are made up of small crystallites that are randomly ordered, but form regions of local order. One characteristic of spherulites is the Maltese-cross, that can be observed with pairs of polarisers under optical microscopy, as shown in panel (d) [106]. As spherulites are visible to the eye, assignment of the presence of spherulites was verified through visual inspection.

4.3 Morphology and Magnetic Field Effects

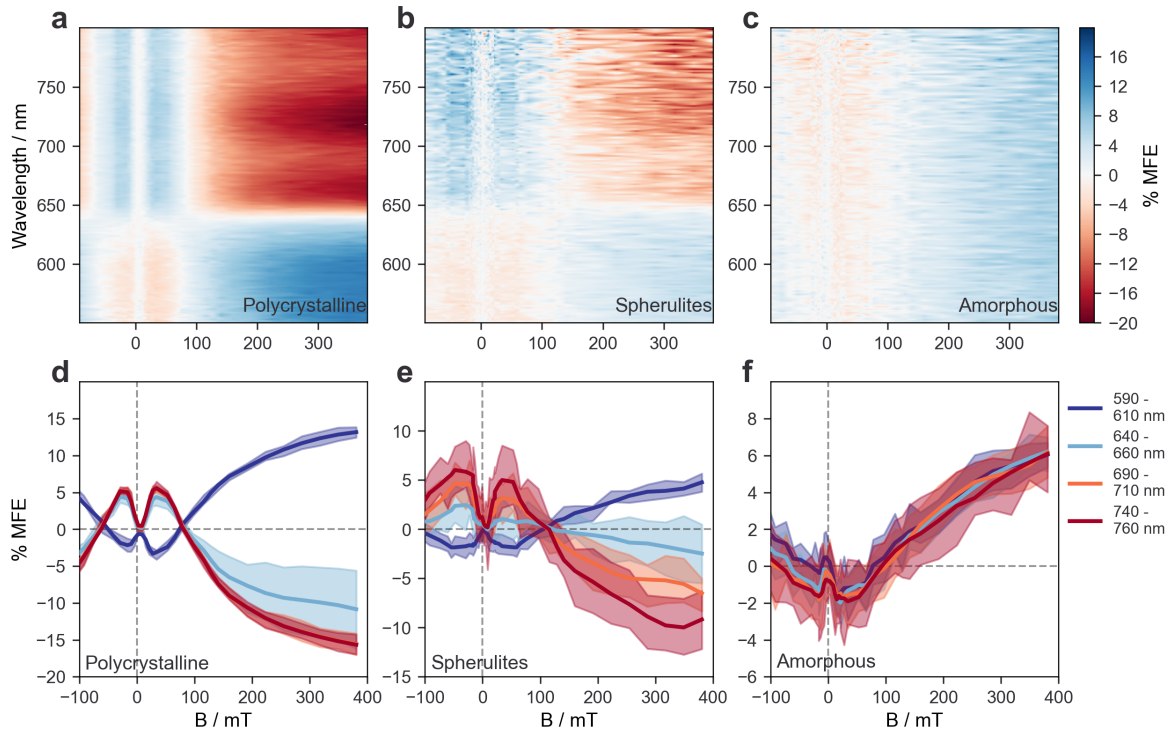


Figure 4.3: Morphology impact on magnetic field effects: magPL of three films: drop cast (polycrystalline, (a) & (d)), spherulitic (spin coated and aged, (b) & (e)), and amorphous (spin coated, (c) & (f)). A 2D of MFE over field strength and wavelength in (a), (b) & (c), are averaged for different wavelength regions in (d), (e) & (f). For the drop cast film in (d), the region from 550 - 650 nm gives the typical lineshape for singlet fission, whereas at wavelengths greater than 650 nm, the lineshape is inverted. This is not the case for the amorphous film in (f), where the lineshape does not change with wavelength.

Before we investigate the films with modulated magnetic field effects, we characterised the films with standard magnetic field effects in photoluminescence (magPL). MagPL captures the linear PL spectrum of the sample with a silicon camera under different field strengths. The signal to noise (S:N) of magPL is limited by laser power fluctuations and sample degradation.

As the S:N is generally poor with weakly emitting samples, field values >100 mT are typically employed to induced a larger, more easily detected, sample response. The time taken for field ramping to these values is on the order of minutes. One single field ‘sweep’ takes in the excess of 20 minutes. To increase S:N, the exposure time and number of accumulation for the linear PL spectrum can be increased, however if the sample is highly unstable this may increase the variance of the signal. In this apparatus, the field value is determined by a pre-selected voltage value, which is then calibrated for in a separate measurement. Small fluctuations in the field values are probable, with some hysteresis in the field value throughout the measurement.

The magPL spectra for three films are shown in **Figure 4.3**. The 2D maps in (a), (b) & (c) show the sample response at different wavelengths (y -axis) for the different field values (x -axis). The MFE is then averaged across wavelength windows in (d), (e) & (f), giving the typical two-Lorentzian lineshape for the MFE. The spectrum for the polycrystalline film ((a) & (d)) gives the strongest signal, as expected for a thick, drop cast film. The polycrystalline film shows two distinct behaviours at different wavelength regions. We first consider the region at $\lambda < 650$ nm. As shown in (d), the MFE initially causes a decrease in the PL at low fields < 100 mT, and then at higher fields an increase in the PL. This is as expected for a singlet fission system, as explained in **Section 2.4.1**. As the lineshape is as expected, and the wavelength region aligns well with the singlet emission in **Figure 4.1 (a)**, we assign this behaviour as a result of the MFE on the fluorescence from the singlet state.

When we consider the behaviour at the wavelengths above 650 nm, we observe an inverted MFE signal of comparable, if slightly greater, intensity. Time dependent MFE signs have been reported previously for other systems [45, 183]. The inverted sign of an MFE for SF systems is indicative of non-geminate TTA [93]. We therefore assert that this inverted lineshape, which we will refer to throughout as the *700 nm lineshape*, is most likely coming from a recombination pathway. While the lineshape is flipped in sign, the shape is highly similar between the two wavelength regions. This may suggest that the MFEs are being born from the same photocycle or kinetic scheme (as opposed to being the result of a competing side reaction).

By examining the comparative lineshapes for the spherulitic film in **Figure 4.1 (b)**, we can perhaps identify that the same, biphasic behaviour is occurring. The signal for this thinner film suffers from poor signal to noise. When we consider the amorphous film in **(c)**, we do not see any evidence for this *700 nm lineshape*. It appears that the typical lineshape, which we refer to as the *600 nm lineshape*, persists at all wavelengths. This suggests that this non-geminate *700 nm lineshape* is morphology dependent, with the effect of the spherulites being similar to large polycrystalline domains.

Now that we have made a preliminary assessment of the magnetic field effects in TIPS-Tc films, we move on to discuss the results of modulated magnetic field effects.

4.4 Modulated Magnetic Field Effects: Studying Thin Films

The modulated magnetic field effects, modMPL, were obtained using apparatus described in **Section 3.4.4**. The wavelength ‘resolution’ was achieved through the use of 40 nm FWHM bandpass filters at 50 nm intervals. For each measurement, the modulation depth was fixed at 1 mT, as discussed in Section 4.9.3, and modulation frequency fixed at 67 Hz. Unless stated otherwise, the samples were excited at 505 nm with a fluence of 100 mW cm^{-2} . The LIA signal is rephased and normalised to the PMT voltage at zero-field, as discussed in **Section 3.4.4**.

We begin by inspecting an amorphous film, prepared through thermal evaporation, presented in **Figure 4.4**. Panel **(a)** shows the modMPL responses at different wavelengths, which are integrated in panel **(b)** to show a representation of the typical magPL lineshape. ModMPL lineshapes with two different excitation densities are shown for 600 nm in **(c)** and 700 nm in **(d)**. The solid lines are representing the average lineshape for N repeats, with the shading representing the standard deviation of these N averages. A photograph of the encapsulated sample is shown as an inset to panel **(c)**.

Across each panel, there is minimal variation between the different lineshapes presented. Each shows a lineshape with a sharp peak at $\pm 1.25 \text{ mT}$ and zero point crossing at 0 and

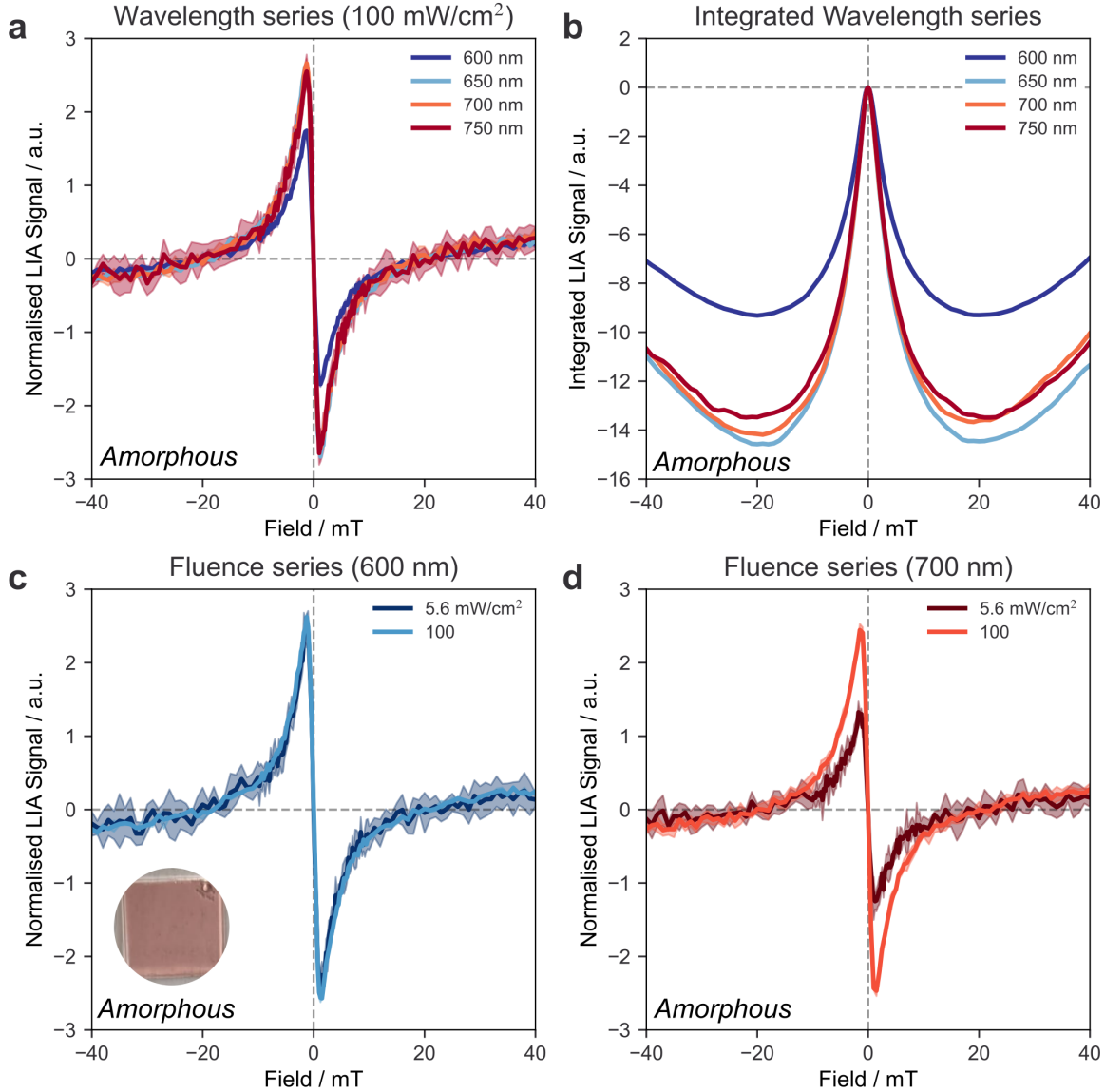


Figure 4.4: modMPL of amorphous film: **(a)** modMPL signal (lock-in amplifier output signal, R , normalised to the PMT voltage at $B=0$) for different wavelengths. **(b)** Integrated signals from **(a)**, proportional to the conventional magPL signal. The signal at 600 nm **(c)** and 700 nm **(d)** at two excitation densities, 5.6 and 100 mW cm^{-2} . In each figure **(a)**, **(c)** & **(d)**, the solid line represents the average of N repeats, with the shading representing the standard deviation of the N averages.

± 20 mT. As the modMPL is proportional to the derivative of the MFE lineshape, this corresponds to a minimum at both ± 20 mT, as seen in panel **(b)**. This lineshape is consistent at each wavelength interval, and at high and low fluences. There is perhaps a smaller signal intensity at 600 nm, and at the lower 700 nm fluence measurement, but generally the magnetic field effect for the amorphous film is invariant under wavelength and excitation density.

Overall, these observations agree with the linear magPL of amorphous TIPS-Tc films as measured in **Figure 4.3 (c)**. From the magPL, the initial minimum is hard to approximate due to low S:N, but lies between 20-60 mT. Thus, the value of 20 mT from the modMPL aligns with the expected value. We can therefore similarly assign the lineshape as the MFE of the S_1 fluorescence, as in the magPL. The modMPL has reproduced the expected results from magPL with far superior signal to noise, allowing for new measurements with low fluence to be performed.

The low fluence measurements required only 8 averages, taking less than 20 minutes total measurement time. This compares favourably to the > 20 minute per average measurement time of the magPL. The lowest fluence measurement at 600 nm, which has the poorest S:N of the measurements, has a maximum standard deviation of 0.36 mV, which corresponds to a maximum standard error of 0.046 mV for the 8 averages. As a percentage of the maximum LIA signal (2.48 mV), the maximal standard deviation is 15% of the signal, and the maximal standard error is 1.8% of the signal. When compared to the very poor S:N for the linear magPL measurement of a thin, amorphous film, it is clear that modMPL is a very sensitive and powerful technique.

We now examine the spherulitic film with the same methodology as for the amorphous film. In a stark contrast to the amorphous film, **Figure 4.5** shows a rich variety in the lineshapes at different wavelengths and fluences.

For panel **(a)**, we observe that the MFE is wavelength dependent for the spherulitic film. The lineshape at 600 nm features a sharp peak, now slightly narrower, at ± 1 mT, and a zero point crossing at ± 27 mT. The 600 nm lineshape is independent of fluence (panel **(c)**), as for the amorphous film.

Let us now consider the 750 nm lineshape in **(a)**. The sharp feature at ± 1 mT is present, but inverted in sign. The outermost zero point crossing is broadened slightly to ± 31 mT. In contrast to the *600 nm lineshape*, two new extrema are present: a minimum at -11 mT, and a maximum at -3 mT. These two features ‘grow in’ as we step through the wavelengths. These changes are exaggerated in the integrated spectra in panel **(b)**. The minimum of the 600 nm

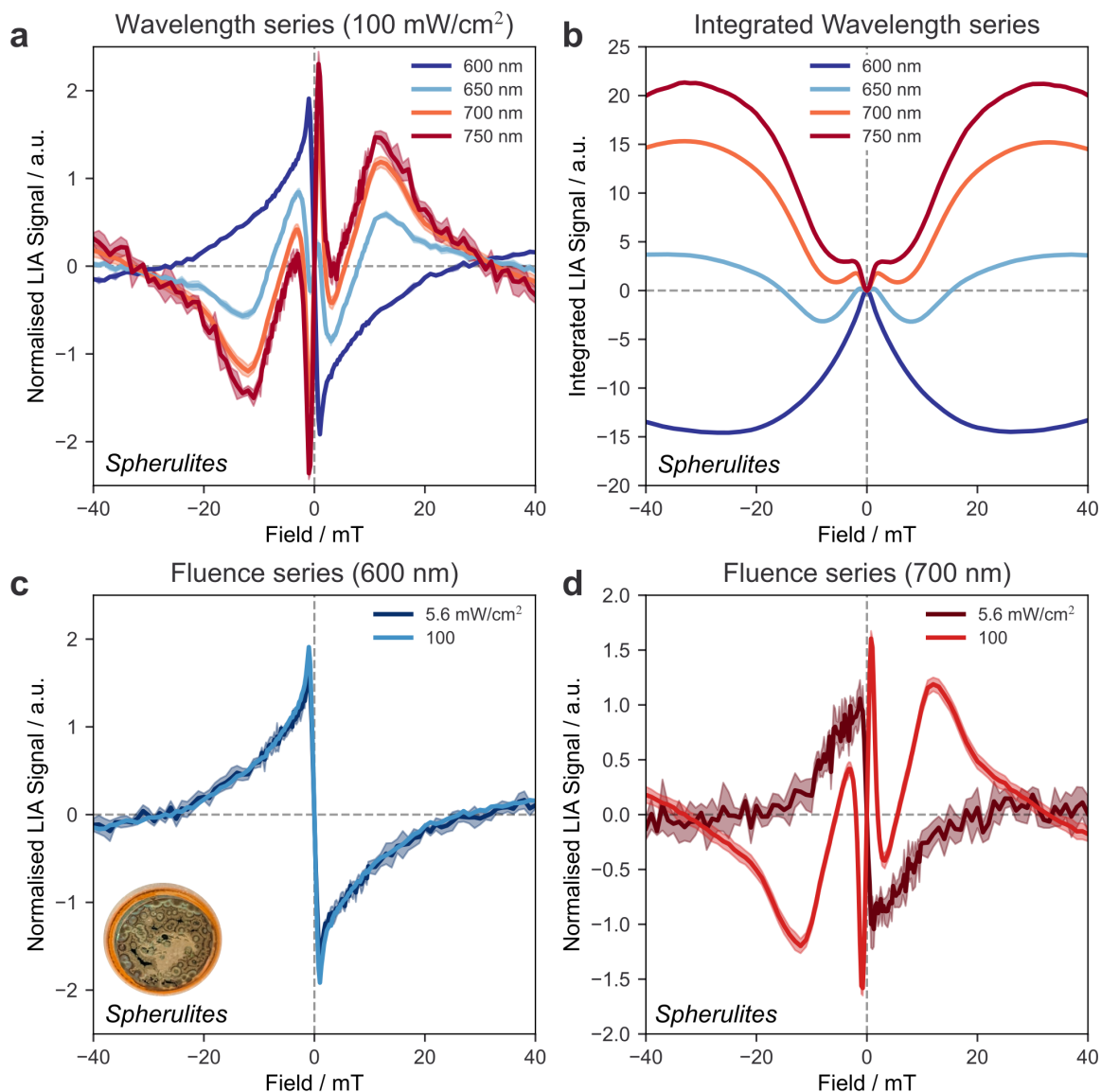


Figure 4.5: modMPL of spherulitic film: **(a)** modMPL signal (lock-in amplifier output signal, R , normalised to the PMT voltage at $B=0$) for different wavelengths. **(b)** Integrated signals from **(a)**, proportional to the conventional magPL signal. The signal at 600 nm **(c)** and 700 nm **(d)** at two excitation densities, 5.6 and 100 mW cm^{-2} . In each figure **(a)**, **(c)** & **(d)**, the solid line represents the average of N repeats, with the shading representing the STD of the N averages.

lineshape at ~ 30 mT is replaced by a sharper maximum at the same field value in the 750 nm lineshape. This is in accordance with the magPL (**Figure 4.3 (d) & (e)**). Two new extrema are present at wavelength region 650-750 nm at decreasing field strengths: a very low field, small intensity maximum, and an intermediary minimum. These are perhaps most visible in the 700 nm lineshape in both **(a)** and **(b)**. These new features have not been previously reported, nor were they detectable with the magPL experiment. These features appear to be unique to the

redder wavelengths, and are not present at the 600 nm region.

We further probe this new 700 nm lineshape at different fluences in **(d)**. At low fluence, the new features disappear, and the signal appears to revert to something closely resembling the 600 nm lineshape. This may suggest that the 700 nm lineshape arises from a non-geminate or a bimolecular interaction, and which reduces in yield at lower fluence. There may be some contribution from the 600 nm lineshape at 700 nm due to the presence of singlet state emission at 700 nm, seen in **Figure 4.1 (a)**. This ‘trace’ amount of 600 nm emission and subsequent MFE lineshape is unveiled when the bimolecular emission disappears at low fluence.

Similar behaviour was also observed for drop cast polycrystalline films. To confirm our suspicions that this was a property of polycrystalline TIPS-Tc, we performed modMPL on a polycrystal of TIPS-Tc. The polycrystal was grown by evaporation of a saturated solution as previously reported [49, 50]. ModMPL of the crystal is presented in **Figure 4.6**.

An image of a section of the crystal, collected with a microscope (300 μm field of view), is shown inset to panel **(c)**. The crystal shows dark lines or striations, likely due to the different crystal regions. We hence confirm this sample was a crystal of polycrystallites, rather than a single crystal. At first inspection, the results of the polycrystal are highly similar to the spherulitic film. The MFE is again wavelength dependent, with the 600 nm lineshape and 700 nm lineshape closely resembling those from the spherulites, respectively. The 650 nm lineshape differs a little, which may be a result of differing contributions between the 600 nm and 700 nm lineshapes.

At 700 nm, the low fluence lineshape again resembles the 600 nm lineshape, but is perhaps slightly broadened, with the peak aligning more with the ‘new’ maximum of the high fluence measurement. However, within noise, it is difficult to ascertain if the sharp peak at narrow fields is missing, or just lower in intensity compared to the shoulder.

For the convenience of the reader, the data in **Figures 4.4- 4.6** are displayed again side-by-side in **Appendix A Figure A.1**. Further fluence measurements for each sample and data of a drop cast polycrystalline film are included. The integrated forms of the lineshapes are also shown in **Figure A.2**. Side-by-side inspection of the integrated lineshapes shows clearly

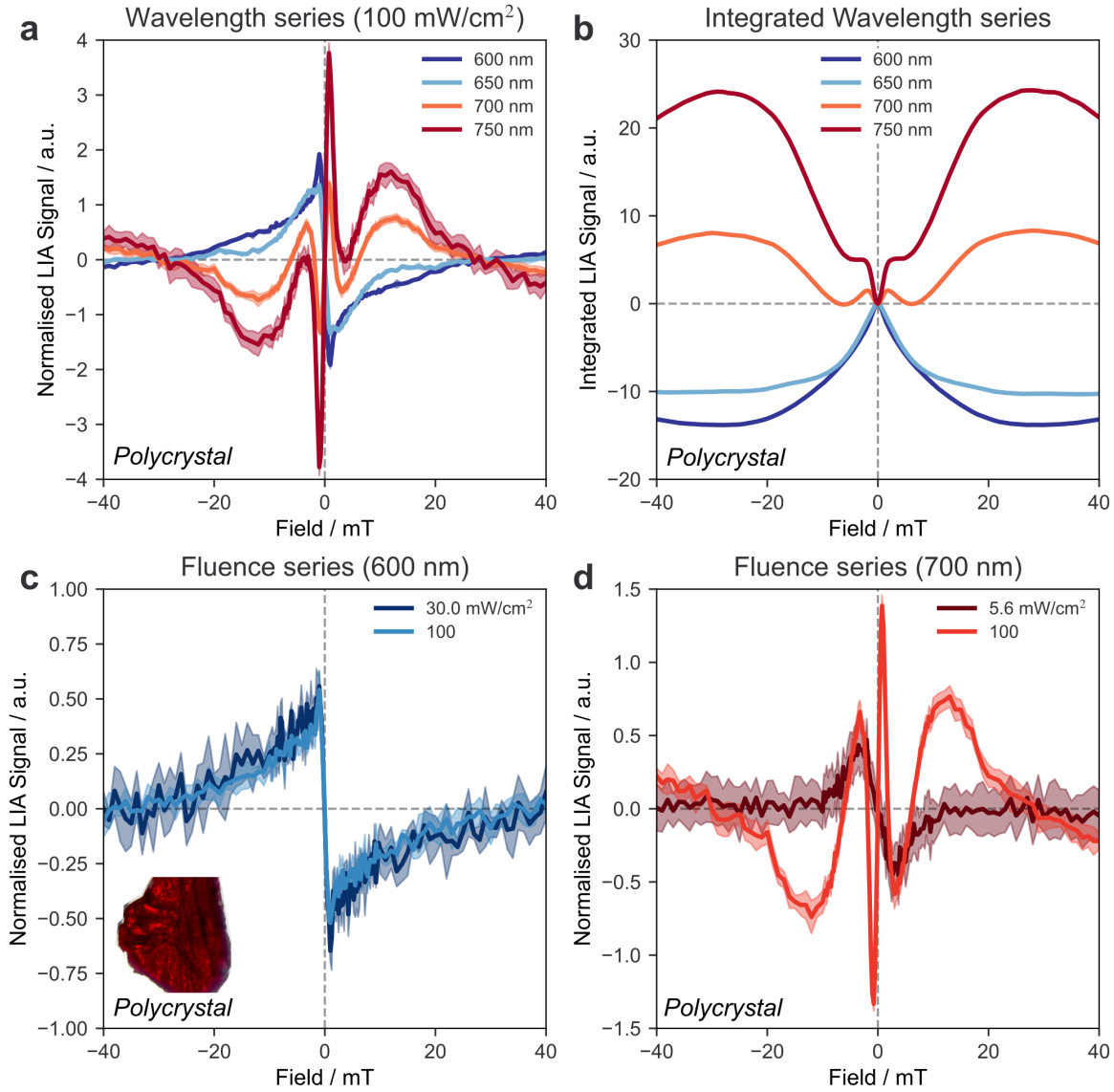


Figure 4.6: modMPL of a polycrystal: **(a)** modMPL signal (lock-in amplifier output signal, R , normalised to the PMT voltage at $B=0$) for different wavelengths. **(b)** Integrated signals from **(a)**, proportional to the conventional magPL signal. The signal at 600 nm **(c)** and 700 nm **(d)** at two excitation densities, 5.6 and 100 mW cm⁻². In each figure **(a)**, **(c)** & **(d)**, the solid line represents the average of N repeats, with the shading representing the STD of the N averages. An image of a section of the polycrystal, measured with an optical microscope ($300 \times 300 \mu\text{m}$), shows the difference crystal regions.

that, for each sample, there is a similarity between the 600 nm lineshape, and the low fluence lineshape at 700 nm. A more detailed comparison of the lineshapes is presented in the next section.

4.5 Modulated Magnetic Field Effects: Comparison of Results

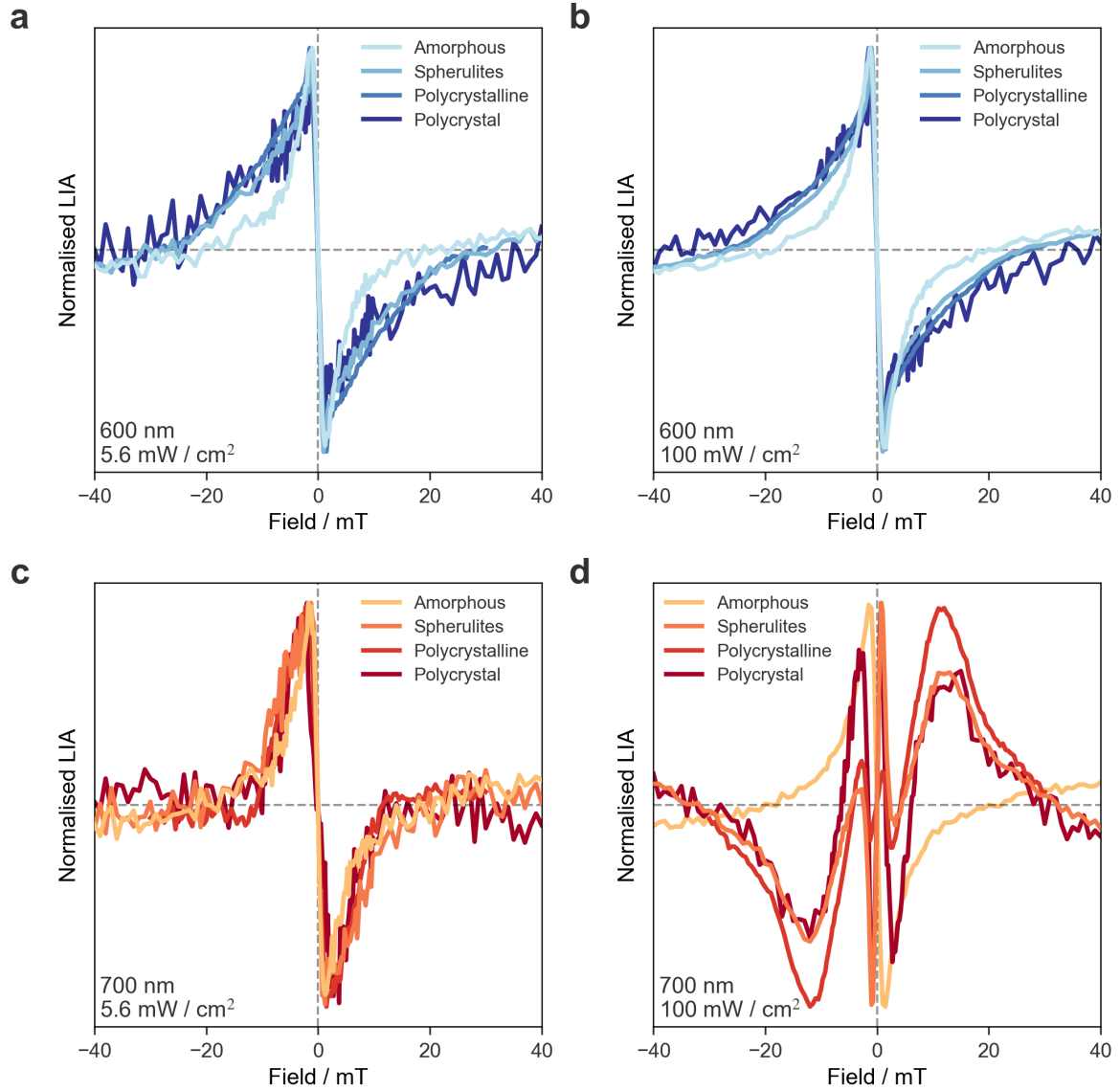


Figure 4.7: Comparing key modMPL results for different morphologies: **(a)** Low fluence lineshapes at 600 nm for each morphology: amorphous film, film with spherulites, polycrystalline film, and a polycrystal. **(b)** Higher fluence lineshape at 600 nm. **(c)** Low fluence lineshapes at 700 nm. **(d)** Higher fluence lineshapes at 700 nm, showing large differences between morphologies.

To more clearly compare the results of each sample, we present the low and high fluence lineshapes (left-to-right) at 600 and 700 nm (top-to-bottom) in **Figure 4.7**. Each lineshape is normalised to the maximum of the signal for more direct comparison of the lineshapes. For panels **(a)**, **(b)** & **(c)**, the lineshape is highly similar throughout, resembling the earlier described *600 nm lineshape*. The amorphous sample consistently gives rise to a far narrower lineshape, but the maximal peak position remains mostly unchanged between samples. In

panel (c), the low fluence 700 nm measurement, it is hard to distinguish if the lineshape is simply broadened, or if the peak position is slightly shifted to higher fields.

The main difference between the samples in panels (a) & (b) is the ‘shoulder’ of the lineshape, between the x -axis crossing and the peak. In the integrated lineshapes (**Figure A.2 (e)-(h)**), this shoulder makes very little impact to the overall shape of the MFE. What appears more significant is the subtle shifting integrated MFE maximum, which corresponds to the x -axis crossing in the modMPL signals. The amorphous sample crosses the x -axis at lower field values, giving rise to a narrower MFE curve. This broadening of the lineshape for polycrystalline environments could be a result of many factors. As this is not a resonance technique, this is unlikely to be due to effects such as lifetime broadening. More likely, it may be the results of different molecular orientations of crystal grains with respect to the field, giving rise to a greater range of dipolar interactions experience by the molecule. This is somewhat contradictory to expectation, as one might expect the amorphous film to ‘experience’ the greatest possible molecular orientations with respect to the external field. However, as this is an inhomogeneous broadening phenomenon, the amorphous film may sufficiently average out [32].

For panel (d), the lineshapes at high fluence 700 nm are very interesting. The amorphous lineshape is the ‘odd one out’, with its lineshape unchanging from 600 nm. For the remaining three, polycrystalline samples, the lineshapes are remarkably similar to each other in terms of peak positioning and x -axis crossings. The only difference is the relative peak heights. While the ratios of the peak heights can be affected by the modulation amplitude (explored in **Figure 4.15**), as the modulation depth is fixed for all samples, it is likely due to another effect.

The polycrystal and spherulites each have a maximum peak height at the narrowest peak, whereas for the drop cast polycrystalline film, the narrowest peak is far lower in intensity compared to the outermost peak at ~ 13 mT. As a first observation, the changes in peak ratios for the different samples at 700 nm indicate that there is more than one magnetically sensitive

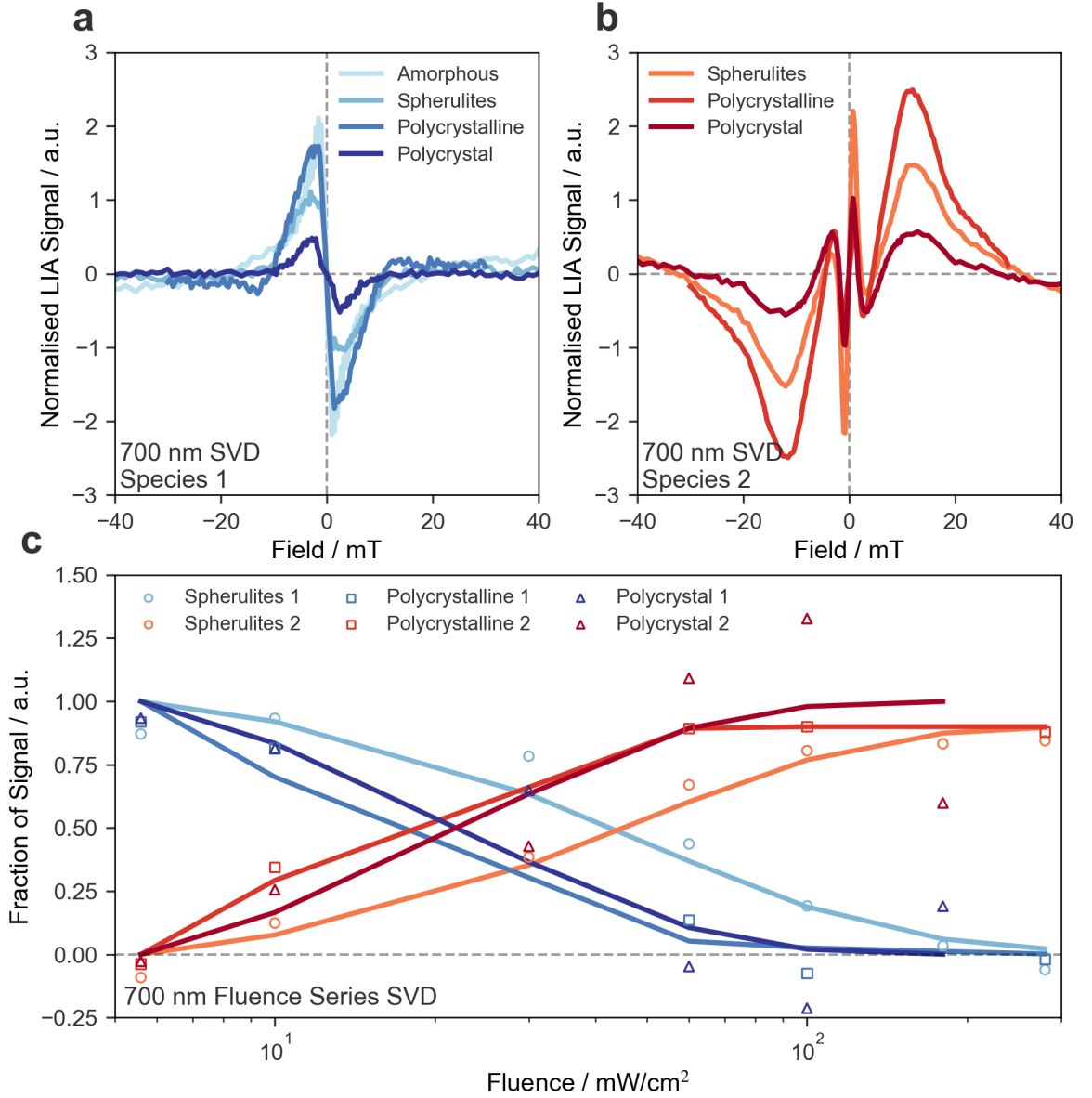


Figure 4.8: Decomposition of 700 nm fluence series for each morphology: Results of SVD decomposition for a two species model, where the low fluence lineshape transforms into the high fluence lineshape. The lineshapes of Species 1 and Species 2 are shown in (a) and (b). The amorphous film is fitted to a one species model. The Species 2 represents the high fluence 700 nm lineshape, which is well matched for each morphology. The fractional contributions of each species at each fluence is shown in (c).

species giving rise to the lineshape, otherwise the peak ratios should be broadly similar for each sample.

To further understand the number of species, or the number of lineshapes present, we perform a decomposition of the data through singular value decomposition (SVD). We firstly consider the 700 nm fluence series data. At low fluence, we observe a distinctly different

lineshape to the higher fluences. We assume that there are two lineshapes that are present as a linear combination for each fluence. If we assume that at the lowest fluence measurement only lineshape 1 is present, we can then decompose the data such that as the fluence increases, the signal gains increasing contribution from lineshape 2. We present the result of this decomposition in **Figure 4.8**.

Figure 4.8 shows the two ‘species’ or lineshapes present in the data in (a) and (b), where linear combination of the two species reproduces the data at each fluence point. The ratios of the two lineshapes for each fluence is shown in (c). For the amorphous film, only one species was present at each fluence. The lineshape of Species 1, the low fluence lineshape, for each sample is shown in (a). For the polycrystal, the sharp low field peak is noticeably less pronounced. Each of the polycrystalline samples shows a broader lineshape than the amorphous film.

The lineshapes for Species 2 are highly similar for each sample (excluding the amorphous film). The peak positions are matched for each sample to within 1 mT. The differences in the peak ratios for the different samples at very low fields compared to ~ 11 mT are still visible. Again, this may indicate there are two different species behind the *700 nm lineshape*. Different populations of the two species could give rise to different ratios of the peak heights at 1 mT and 11 mT.

A similar treatment is applied to the wavelength series at 100 mWcm^{-2} . As there is no fluence dependence at 600 nm for any of the samples, we assume that only one lineshape is present at 600 nm. At longer wavelengths, there is a linear combination of two lineshapes, 1 and 2. In comparison to the decomposition of the 700 nm fluence series in **Figure 4.8**, **Figure 4.9** shows greater similarities for the lineshape 2 for each sample. The lineshape 1 is much narrower now for each sample. From panel (c), it is clear that there is some contribution from lineshape 1 remaining at redder wavelengths. At 700 nm, it appears the ratio of the two lineshapes is around 50:50. This is not well matched in **Figure 4.8** (c), where at 100 mWcm^{-2} the ratio is almost 0:1. This further confirms that the lineshape 2 of the 700 nm fluence decomposition is made up of more than one component.

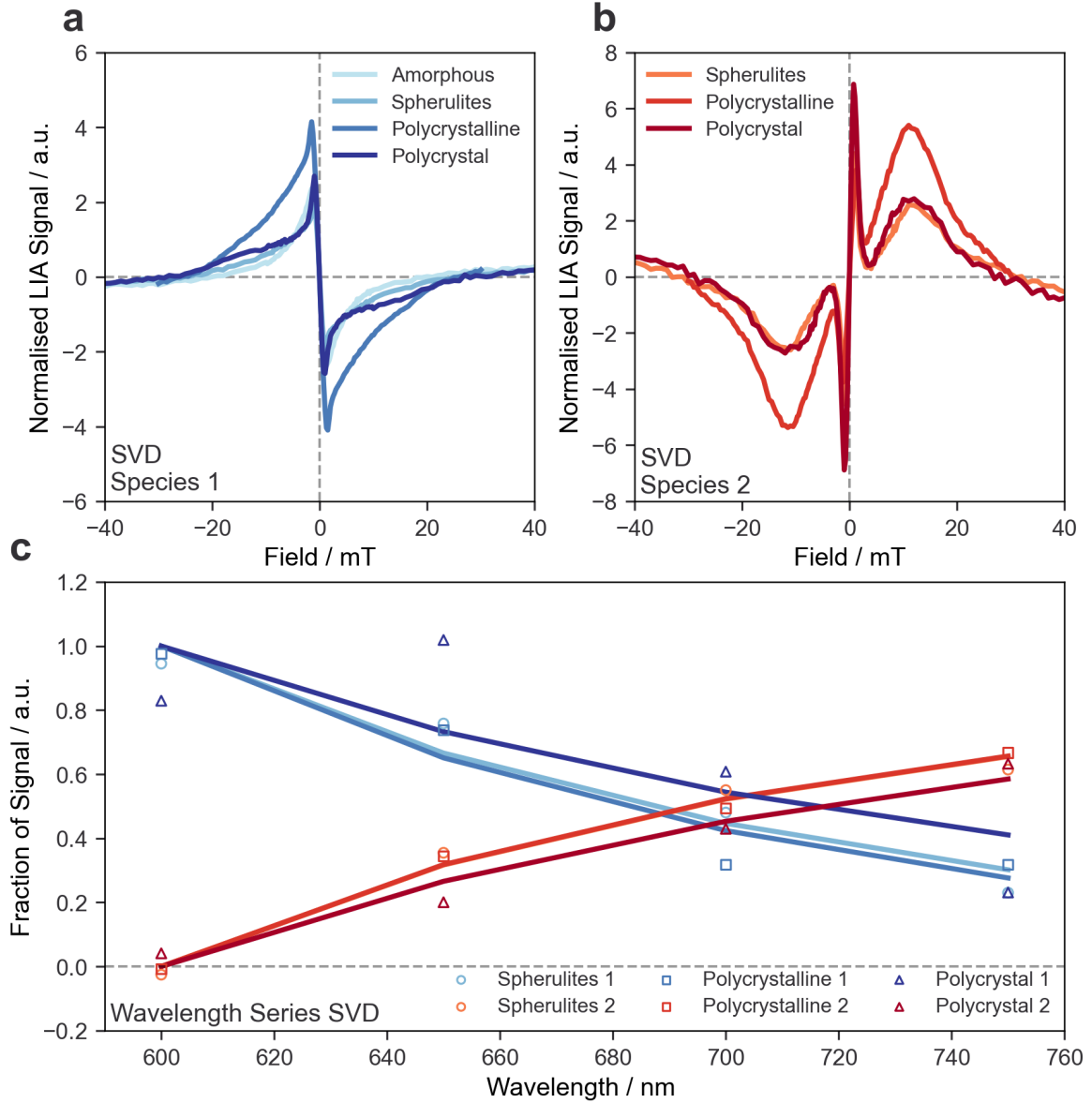


Figure 4.9: Decomposition of wavelength series for each morphology: Results of SVD decomposition for a two species model, where the 600 nm lineshape transforms into the 700 nm lineshape. The lineshapes of Species 1 and Species 2 are shown in (a) and (b). The amorphous film is fitted to a one species model. The Species 2 represents the 700 nm lineshape, which is well matched for each morphology. The fractional contributions of each species at each wavelength is shown in (c).

If we compare the ratios of lineshapes 1 & 2 in **Figure 4.9** to the PL spectra in **Figure 4.1**, we notice that the emission from the singlet state, seen in the amorphous film spectrum, has negligible intensity at 750 nm. However, in panel **Figure 4.9 (c)**, at 750 nm there is still considerable contribution from the lineshape 1. It is possible that the decomposition has not fully separated the two lineshapes. However, it might also be the case that lineshape 1 is not solely coming from the singlet state. We might expect that the strongly coupled $^1(\text{TT})$ state

to have a similar MFE lineshape to the S_1 , whilst slightly red-shifted [85]. It is therefore possible that lineshape 1 may capture both the MFE lineshape from emission from the S_1 and $^1(TT)$. If this is the case, then the lineshape 2 could arise from a third species, rather than from the $^1(TT)$.

4.6 Qualitative Assignment of Lineshapes

In assigning the lineshapes of the modMPL curves, it is worthwhile examining the previous work from the literature of spin correlated radical pairs (SCRPs). For SCRPs, it is typical to assign importance to the $B_{1/2}$, the field value of the FWHM of the lorentzian lineshape. The $B_{1/2}$ is empirically related to the magnitude of the hyperfine interaction tensors through the Weller formula [184, 185]:

$$B_{1/2} = 2\sqrt{3} \frac{(a_A^2 + a_B^2)}{a_A + a_B}, \quad (4.1)$$

where a_A and a_B are the hyperfine couplings for the two radicals, A and B. Conveniently in modMPL this can be approximated as

$$B_{1/2} = \sqrt{3}B_P \quad (4.2)$$

where B_P is the peak of the modMPL lineshape [181]. However, a similar treatment of relation between $B_{1/2}$ and the ZFS parameters has not yet been formulated. Therefore, to find a first understanding of the lineshape, we focus on the number of peaks and their field values, similarly to how one might approach an ESR spectrum on first inspection.

We have so far identified at least two important lineshapes, as shown in **Figures 4.8 & 4.9**: the narrow *600 nm lineshape*, and the more complex *700 nm lineshape*.

The *700 nm lineshape* is reminiscent of those observed by Justinek *et al.* in a SCR system of pyrene and dicyanobenzene in solution [181]. However, the lineshapes observed by Justinek had a total of 4 peaks, whereas the *700 nm lineshapes* we observe have a total of 6. Furthermore, the scale of the lineshape is far smaller than that observed here for the SF systems (5 mT range *cf.* 40 mT range). This is to be expected, as the ZFS parameters are > 10 times that of the hyperfine interactions. We can therefore rule out the presence of competing SCR

mechanism to singlet fission, as the scale of the interaction we observe is too large, and the lineshape is more complex.

As discussed in **Chapter 2**, the energy levels of the free triplet states are split by $|D_T|$, and the upper two eigenstates are further split by $2|E_T|$. For TIPS-Tc, D_T and E_T are previously reported as 1414 MHz and 14 MHz respectively [50, 168, 186]. Converting to mT [187], this corresponds to 50.5 mT and 0.5 mT accordingly. The energy splittings between the three triplet sublevels are thus $D_T \pm E_T = 50/51$ mT, and $2E_T = 1$ mT. We expect to observe strong features at field strengths directly comparable to the energy level splittings. The value of $2E_T$ matches well with the strong, narrow peak observed throughout the modMPL spectra at both 600 nm and 700 nm. We therefore tentatively assign this peak as the $2E_T$ energy splitting of the free triplets, T_1 .

For the 700 nm lineshape, we observe more extrema at 3 mT and 11 mT for the spherulites film. From Yunusova *et al.* [50], they predict that D_Q and E_Q are 17 mT and 0.8 mT respectively (474 / 22.5 MHz). The lowest three quintet sublevels are split by $D_Q \pm 3E_Q$, and $3E_Q$, corresponding to energy level splittings of 14.5/19 mT and 2.4 mT. These values arising from the energy splittings of the quintet align well, to a first approximation, with the values of the new extrema in the 700 nm lineshape. It is possible that the new features observed at 700 nm are evidence of quintet states with peaks aligning well with the values of $|D_Q|$ and $3|E_Q|$. However, it is not immediately explainable as to why the ZFS parameters of the quintet state, relating to the triplet pair, rather than the ZFS parameters of the free triplets, are relevant to this data, particularly as this is not a spin-resonance technique. Further work must be carried out to rationalise and understand this observation.

One further piece of information is that, as observed and predicted by Yunusova *et al.*, there is a quintet avoided level crossing at ~ 18 -20 mT, as shown in **Figure 4.10 (a) & (d)**. This may explain why the peak at 11 mT is significantly broader than the peak at 1 mT, due to overlap with the quintet avoided level crossing.

An empirical observation is that the x -axis crossings, around 27 mT for 600 nm and 31 mT for 700 nm, are of the same order as $D_T/2$ (25.25 mT). If we suppose that the x -axis crossing

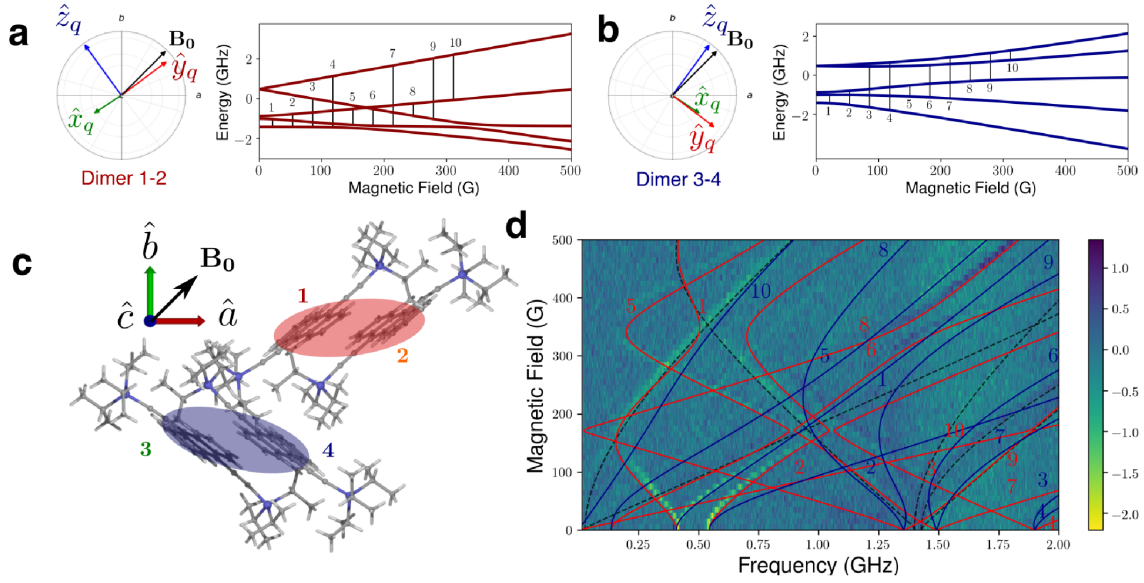


Figure 4.10: TIPS-Tc quintets from literature: reproduced from Yunusova *et al.*. Quintet bi-exciton ODMR with $B_0 \perp \hat{c}$. **(a,b)** Energy levels and ZFS tensor orientations for dimer 1-2 (red) in **(a)** and dimer 3-4 (blue) in **(b)** with $B_0 \parallel \hat{a}$. **(c)** Crystal structure with labelled molecules underlying dimer 1-2 highlighted in red and dimer 3-4 highlighted in blue. **(d)** X-channel ODMR with y-channel subtracted and corresponding resonant frequencies overlaid and labelled as in **(a,b)** for dimer 1-2 in red and dimer 3-4 in blue. ([50], supplementary material.)

of the *conventional* magPL lineshape will be when $B \approx D_T$, or the size of the Zeeman interaction is approximately the size of the ZFS, then the peak of the magPL lineshape will be at $\sim D_T/2$, corresponding with the x -axis crossing of the derivative modMPL.

4.7 A Summary of Initial Findings

To summarise our results thus far, we have examined different samples of TIPS-Tc with different morphologies. We have identified two distinct lineshapes, which are dependent on wavelength, morphology, and fluence. The *600 nm lineshape* is present for all samples, and we tentatively assign that this is the MFE of the singlet state due to its wavelength and fluence independence. The lineshape features a narrow peak, the value of which aligns well with the $2E_T$ energy level splitting of the free triplets. We also assert that this lineshape is the ‘typical’ sign for the MFE of singlet fission, rather than a non-geminate TTA lineshape.

For polycrystalline samples, we also observe a *700 nm lineshape*, that is only present at higher

fluences, suggesting a bimolecular origin. It is inverted in lineshape, further suggesting a non-geminate, TTA-like mechanism. The lineshape is more complex, with 6 extrema. The peak positions perhaps show evidence of the quintet ZFS parameters of the TT state, suggesting it is intimately related to the TT pair (although rationalisation of this observation requires further consideration). Due to its appearance at redder wavelengths, and distinct lineshape to the *600 nm lineshape*, we hypothesise that this lineshape is appearing due to the emission of a secondary species, that must in some way be related to the TT pair, but may not be directly related to the singlet state. If the two emissive species were directly related, such that one species was populated from the other, we would expect the lineshape of both emissions to share the same features.

In the following section, we explore further the relationship between morphology and the *700 nm lineshape*.

4.8 Observing the Growth of Spherulites

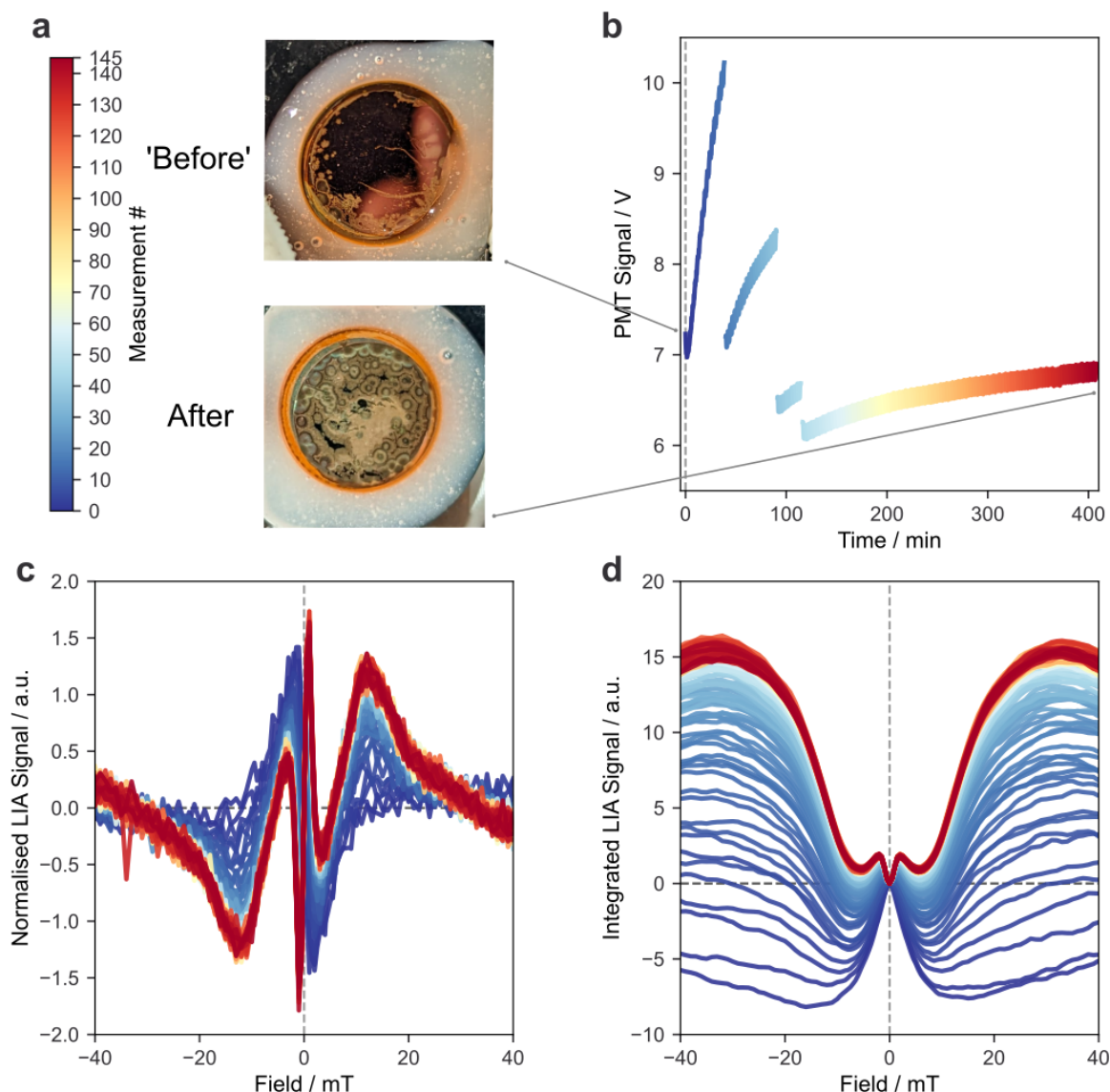


Figure 4.11: Growth of spherulites captured with modMPL: **(a)** shows the images of the film after measurement, and a corresponding unmeasured film as the 'before'. **(b)** The PMT trace over time, showing a large increase. Jumps in PMT signal correspond to gain changes. **(c)** modMPL signals over time, showing the evolution from the '600 nm lineshape' to the '700 nm lineshape' over 145 measurements. **(d)** Integrated lineshapes to highlight the change in MFE lineshape sign.

The impact of spherulites, or highly polycrystalline regions, compared to an amorphous film was captured by modMPL in real time. A highly amorphous spin coated film, with minimal formation of spherulites, was measured over a period of 6 hours. The measurement was at 700 nm, with 100 mWcm^{-2} excitation density (high fluence). During this time, spherulites formed, and the modMPL signal evolved.

The evolution of the modMPL signal is shown in **Figure 4.11**. Each sweep of the field is considered one ‘average’, and is colour-coded throughout each panel. Over the time period of 400 minutes, 145 averages were made. The changes in the sample appearance were recorded with images, shown in panel (a).

The PMT voltage at 700 nm, proportional to the intensity of fluorescence, greatly increased during the measurement, as shown in panel (b). Changes in the PMT gain were made on 3 occasions, giving rise to the discontinuities in the PMT signal over time. The breadth of the PMT signal is indicating how large a change in PMT voltage is induced by the field for each sweep. This increase in 700 nm emission intensity with the formation of spherulites agrees with the previous PL spectra in **Figure 4.1**. We previously attributed this increased 700 nm PL intensity as being due to TT emission or excimeric emission.

Panel (c) shows how the lineshape at 700 nm changes, from the *600 nm lineshape* to the *700 nm lineshape*. The lineshape rapidly changes, but then remains stable throughout the remaining averages. Over time, the 700 nm emission intensity increased, and the *700 nm lineshape* grew in. Seen most clearly in the integrated lineshapes in panel (d), the lineshape starts with the ‘typical’ sign, and inverts as the spherulites form. This suggests that the presence of spherulites, or crystal grains, allows for a non-geminate or bimolecular process to occur, resulting in a sign flip.

Recent work published by Shi *et al.* quantified that larger crystal grains result in longer triplet lifetimes and diffusion lengths for singlet fission systems [72]. They further observed that smaller grains lead to more grain boundaries, and increased exciton quenching. It is therefore possible that the presence of many small crystal grains allows for greater non-geminate triplet-triplet annihilation. In the amorphous case, as there are not any significant regions of crystallinity, the triplet diffusion length is very small, and so the triplets are more likely to recombine geminately.

This modMPL data as a function of time can be similarly decomposed with SVD, as shown in **Figure 4.12**. Panel (a) shows the modMPL lineshapes of the two decomposed species, compared to the raw signal at the first and last time points. The fractional contribution of each

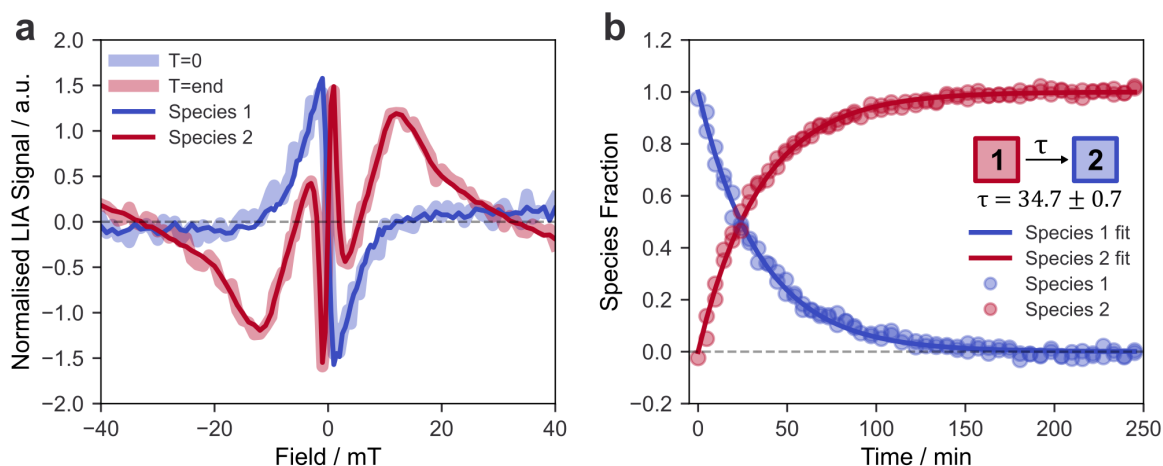


Figure 4.12: SVD spectra of spherulite evolution: **(a)** Comparison of spectra of Species 1 and 2 to the modMPL spectra of the first and last measurement, showing good agreement. **(b)** the change of the fractional contributions of the species spectra overtime. The growth of spherulites occurred in under 100 minutes, with a lifetime of 35 minutes.

of these lineshapes is shown in panel **(b)**. Only two ‘species’ or lineshapes are present. The straightforward evolution of one lineshape to another with one ‘rate constant’ fits extremely well, with low residuals. The ‘rate constant’ suggests the spherulite growth happened with a lifetime of around 35 minutes.

The two lineshapes in **(a)** reproduce very well the two lineshapes from the decomposition of the 700 nm fluence series in **Figure 4.8**. The lack of crystal grains reproduces similar conditions to a low fluence measurement; fewer crystal grains means less TTA at the grain boundaries, similar to an effective reduction in triplet concentration due to low fluences. This further confirms that the 700 nm lineshape is likely the result of a TTA pathway.

The spherulites grew most likely due to heating of the sample. The samples were prepared in a particularly cold week of late November. The warmth from the LED irradiation and gentle warmth of the electromagnetic field coils provided the thermal energy required for molecules in the film to reorganise, with the help of residual solvent. This was a particularly fortunate sequence of events. This *in situ* solvent-thermal annealing could require fine tuning to reproduce.

Before moving on to the final discussion, we present some further validations of the modMPL as a suitable apparatus for measuring and understanding singlet fission materials.

4.9 Further Supporting Evidence

Further experiments were conducted to validate the results observed above. This included investigating the impact of oxygen, a signal stability measurement, and understanding the impact of modulation depth. The measurement of a blank sample (an encapsulated clean substrate) was performed, giving no signal as expected. Measurement at an alternative modulation frequency (167 Hz) was also performed, showing no change from the measurements at 67 Hz. Further measurements with an alternative molecular system, diphenyl hexatriene (DPH) were also performed.

4.9.1 Impact of Oxygen

To understand the impact of oxygen on modMPL signals, we examined a sample where the encapsulation was damaged. This is shown in **Figure 4.13 (a)**, with damage to encapsulation highlighted with an arrow. The degraded sample post-measurement is compared to an unmeasured analogous sample (a sample prepared in the same way at the same time) with good encapsulation. The degraded sample bears the hallmark of TIPS-Tc degradation: the characteristic red-orange sample has become transparent. The outer ring of the sample, which is typically thicker due to ‘coffee-ringing’, still remains [188, 189]. This acts as a visual confirmation that the sample has been degraded through photo-oxidation [14, 190].

We examine the behaviour of the modMPL response throughout this oxidation process in **Figure 4.13**. Panel **(b)** shows the PMT voltage output, which is indicative of the intensity of fluorescence (at 600 nm in this case). Each modMPL ‘sweep’ of is highlighted by different colours. The initial few sweeps (time < 15 minutes) each show a marked peak, which corresponds with the zero field point. This is matched by the integrated LIA signal in panel **(d)**. As successive sweeps are made, the height of this peak in the PMT signal for each measurement is reduced, which is again mirrored in panel **(d)**. As the sample is degraded by the photo-oxidation, the magnitude of the magnetic field effect is reduced. However, the shape of the MFE lineshape remains the same breadth, which can be seen in both panel **(c)** and **(d)**. We therefore assert the impact of oxygen degradation is to minimise the MFE signal, rather than change its shape.

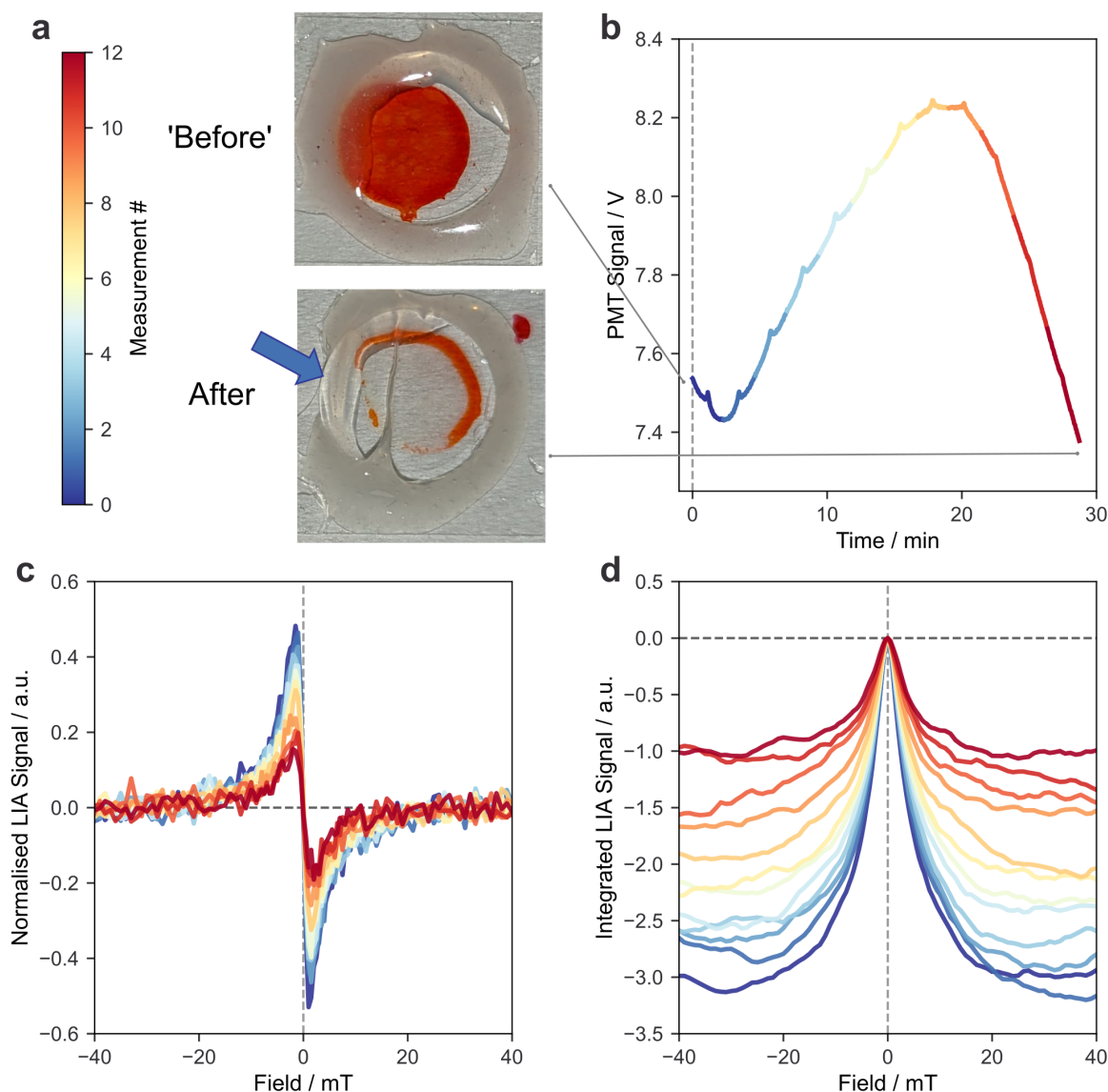


Figure 4.13: Oxygen degradation captured with modMagPL: **(a)** each of the 12 averages is colour-coded throughout. Images of the sample post-measurement are shown, with the arrow indicating broken encapsulation and a path for oxygen. The sample has photooxidised to become transparent, leaving only the thicker coffee-ring of sample. **(b)** The PMT signal shows an initial increase in PL intensity, as the molecules in the sample begin to behave monomerically. The PL sharply drops as the sample is fully degraded. **(c)** The modMPL signal, normalised to the zero-field PMT voltage, decreases in intensity. **(d)** Integrated modMPL signals in **(c)** highlight the reduction in MFE signal amplitude as the sample is photooxidised.

Another characteristic signature of the degradation is again shown in panel **(b)**. The PMT intensity increases, then sharply decreases. This indicates that the fluorescence is increasing as the chromophores are degrading; once the nearest neighbours have degraded, the chromophore is effectively monomolecular and free to fluoresce with high PLQE without competition from singlet fission. Beyond a limit of degradation, overall sample degradation takes

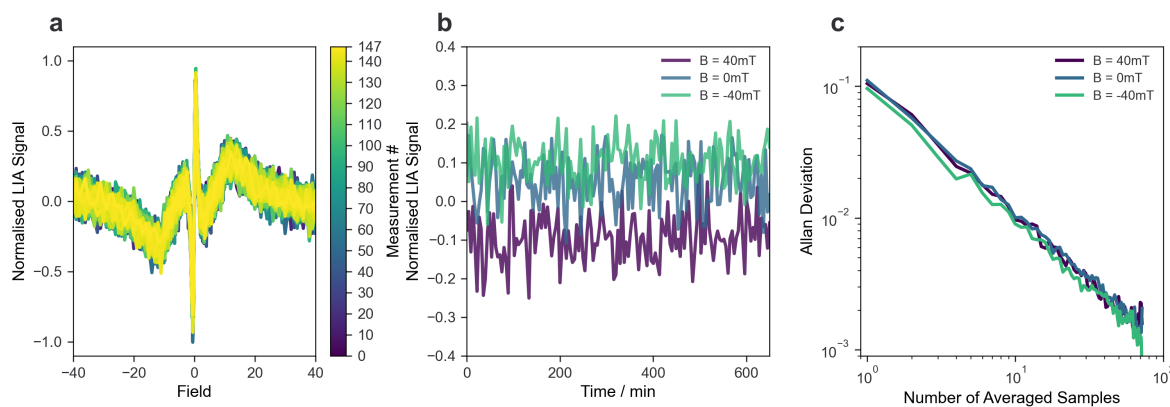


Figure 4.14: Stability of modMPL Signals: **(a)** modMPL signal of a TIPS-Tc film (spherulites, 700 nm, 100 mWcm⁻²) for 147 sweeps or averages. **(b)** the signal stability at low, high, and zero field values. While the average-to-average noise is 10-50%, the mean value stays constant throughout the 10 hour measurement. **(c)** The Allan Variance of the three signals in **(c)**, suggesting that averaging over a sampling window of up to 70 averages still improves the signal variance. This highlights the good signal stability of the modMPL.

over and the fluorescence intensity plummets as the whole sample is degraded. This experiment confirms the three signs to watch for when considering a modMPL time evolution: a visual inspection of the sample to confirm colour change, the gradual decrease in LIA signal intensity, and the increase then sharp decrease in PMT voltage. The lack of these three features in **Figure 4.11** confirms that the results were not due to the presence of oxygen.

4.9.2 Signal Stability

To ensure that features such as lineshape broadness at low fluences, where more averages were taken, were not a feature of fluctuations in field or irradiance, we examined the signal stability. **Figure 4.14** examines the stability of the modMPL signal over a long time and many averages. In one measurement, the spherulitic TIPS-Tc sample was measured for 147 sweeps, in over 600 minutes. Each consecutive LIA signal is plotted in panel **(a)**, with the signal intensity at high, low and zero field shown in panel **(b)**. This is included to examine whether there was any instability in the field at the extreme values, and that zero field was repeatably zero over time. Any inconsistency at these regions could be caused by heating of the field coils or any hysteresis.

The Allan deviation of the three signals in panel **(b)** are shown in panel **(c)**. Allan deviation represents how averaging over a larger and larger sampling window will improve the signal

to noise, to a point, and then subsequently reduced the quality of the signal by averaging in more sources of noise. **Figure 4.14 (c)** shows how the Allan deviation is still decreasing without a change in gradient up to a sampling window of 70 samples. This indicates it is still appropriate to average together the 147 averages. It also implies LIA detection technique is immune to any fluctuations in the field ramping or LED power intensity over the 10 hour time frame, giving a signal that is consistent and reproducible. This adds to the techniques sensitivity and reproducibility.

The modMPL signal shows high stability, and also does not show evidence of sample degradation over a 10 hour period. This validates that averaging more signals together should not impact the lineshape; by the opposite argument, any changes in signal are due to a sample effect, such as changes in morphology, and not due to field value or LED power drifts. This also further demonstrates how modMPL is a ‘gentle’ experiment, and does not cause significant sample damage with appropriate encapsulation. ModMPL therefore makes for an excellent measurement to be performed before other subsequent measurements such as ESR or TA.

4.9.3 Modulation Amplitude Distortion

The impact of the modulation amplitude, or modulation depth, is to increase the signal intensity with increasing amplitude. The amplitude can be thought of as a window over which the signal is summed. Konowalczyk *et al.* [18] formulated that the effect of a modulation experiment is to convolve the derivative of the signal, in this case the derivative of the MFE on PL ($\frac{dM}{dB}$), with a Chebyshev polynomial, K_h :

$$S(B) = (C \cdot K_h) \otimes \frac{dM}{dB} \quad (4.3)$$

$$K_h = \frac{\sqrt{2}}{h\pi} \sin(h \cdot \arccos(m)) \quad m \in [-1, 1] \quad (4.4)$$

$$C = \frac{1}{\sqrt{2}b_m \sum(K_h)} \quad (4.5)$$

This is applicable for the higher harmonics of the modulated signal, characterised by h . In the case of this study, $h = 1$. The first order Chebyshev polynomial scaled for different modulation depths, b_m , as formulated by Konowalczyk, are shown in **Figure 4.15 (b)** [18].

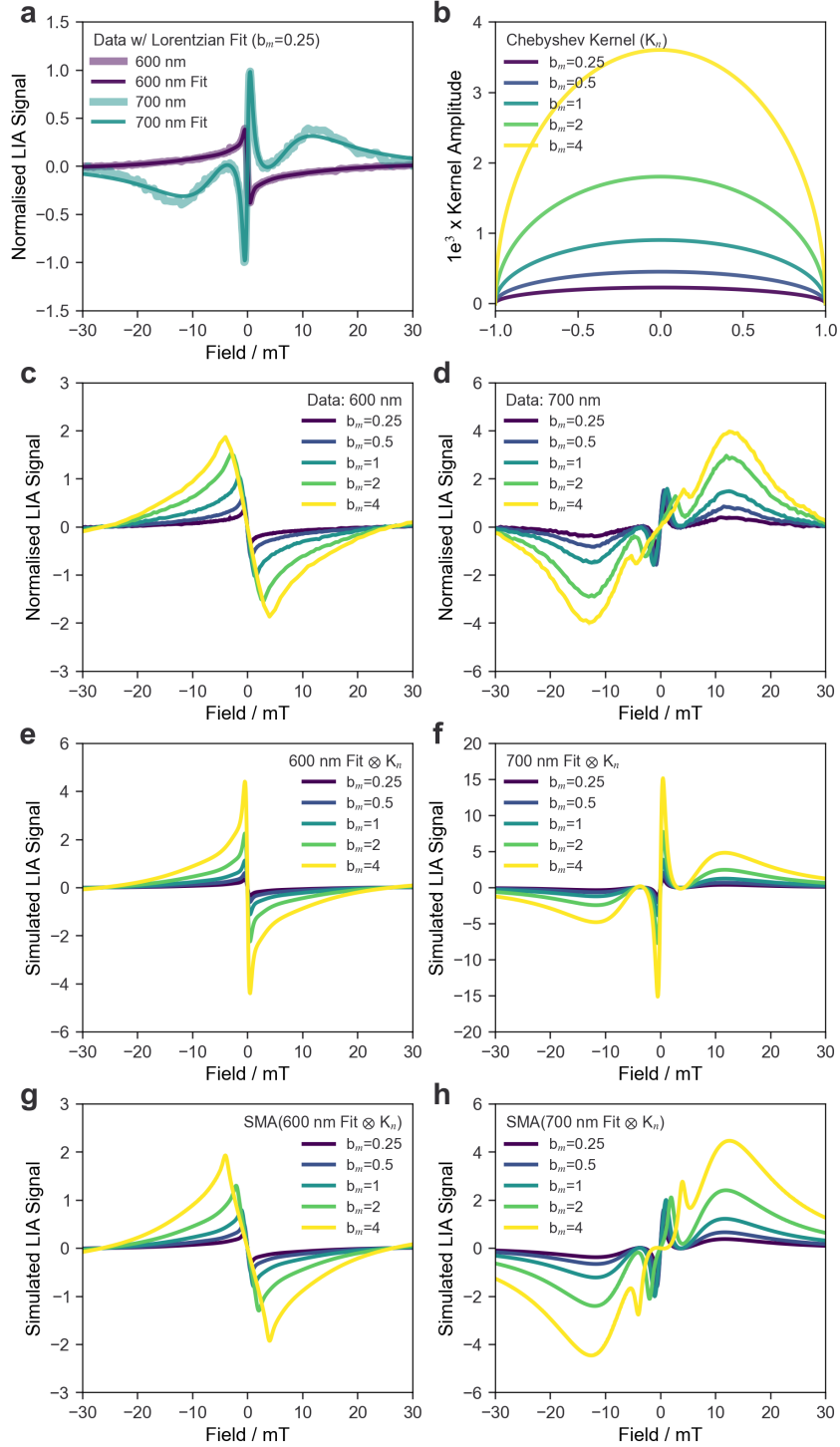


Figure 4.15: Understanding modulation amplitude distortion: **(a)** example data of TIPS–Tc films with modMPL spectra at 600 and 700 nm at low modulation amplitude (0.25 mT), fitted to arbitrary differentiated lorentzians. **(b)** The Chebyshev kernels, scaled according to 5 different modulation amplitudes, proposed to be the mathematical representation of the modulation experiment. **(c) & (d)** modMPL data at 600 nm and 700 nm at different modulation amplitudes, from 0.25 mT to 4 mT, normalised to the PMT voltage at zero-field. **(e) & (f)** The result of convolving the Chebyshev kernel for each modulation depth with the lorentzian fits for the 600 and 700 nm lineshapes. **(g) & (h)** The result of the convolutions in **(e) & (f)** with a simple moving average filter. These simulated lineshapes reproduce the equivalent data in **(c) & (d)**.

The effect of modulation amplitude was examined at 600 nm and 700 nm for 5 different amplitudes. The data normalised to the PMT voltage at $B=0$ is shown in **Figure 4.15 (c)** and **(d)**. The signal increases in intensity for larger modulation amplitudes, and appears to be broadened in x , as expected. The signals at the smallest b_m amplitude (0.25 mT) for 600 nm and 700 nm are shown in panel **(a)**, and fitted to the sum of four Lorentzians, differentiated. These fits are then used to simulate the effect of increasing modulation depth through the convolution of the fit with the accordingly scaled Chebyshev kernel. The direct result of this convolution is shown in panels **(e)** and **(f)**. While this convolution does well to show how the signal intensity will scale with b_m , it does not include the effective downsampling, or boxcar smoothing, that the modulation amplitude will cause. By applying simple mean averaging (SMA) with a window of $2 \times b_m$, shown in panels **(g)** and **(h)**, the lineshapes and magnitudes of the data in **(c)** and **(d)** are found to be similar.

The importance of this study of modulation amplitude is to rationalise the choice of $b_m = 1$ mT throughout the study. This value was chosen as it fulfilled a good compromise of a high signal intensity, requiring fewer averages, without compromising the lineshape through modulation distortion. This was most important due to the change in peak position of the very low field peaks (<1 mT). As most clearly seen in panel **(d)**, the innermost peak position is minimally impacted by increasing the modulation depth from 0.25 mT to 1 mT.

4.9.4 Testing an Alternative Molecular System

To examine how generally applicable the results from TIPS-Tc are to other SF systems, we performed modMPL measurements on another SF archetype: diphenyl-hexatriene (DPH) [89, 90, 95, 117, 191]. Two variants of DPH were measured, with results presented in **Figure 4.16**. The samples were prepared by Dr Ashish Sharma, who measured linear magPL of the films, shown in panels **(a)** and **(b)**. The two variants are dubbed DEH, ethyl-hexyl-DPH (panel **(a)**-**(c)**), and SM82 (panel **(d)**-**(f)**), an unpublished structure that will be reported elsewhere [192].

The linear magPL shows stark differences between the MFE lineshapes, despite them having similar ZFS parameters (obtained through ESR). The two lineshapes are remarkably similar

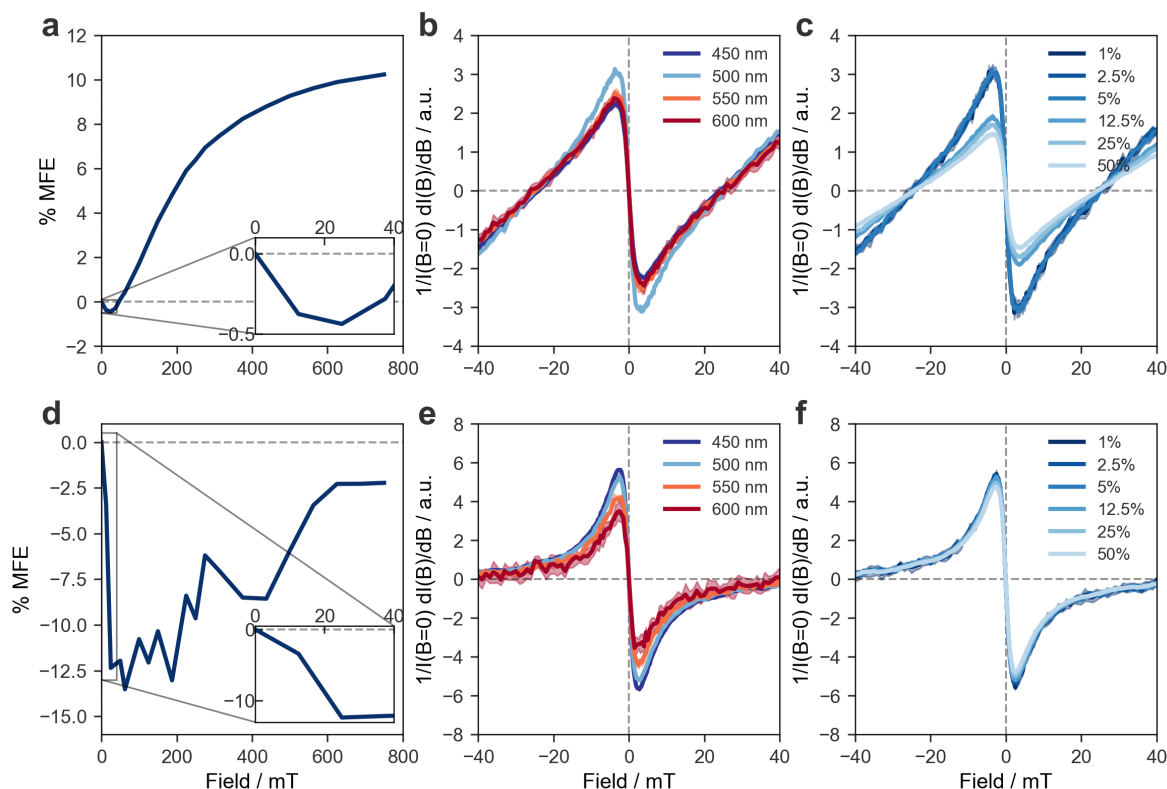


Figure 4.16: ModMPL signals from two diphenyl-hexatriene (DPH) derivatives, compared to conventional magPL. Linear magPL of DEH and SM82 are shown in (a) and (d), measured by Dr Ashish Sharma. ModMPL at different wavelengths are shown in (b) and (e) with 385 nm excitation. Different fluences at 500 nm emission are shown in (c) and (f), with fluence shown as % power of the LED, equating to an approximate range of 20-720 mWcm^{-2} .

to those observed by Tarasov *et al.* in 1997 [88]. Here, Tarasov attributed the two lineshapes to different triplet relaxation mechanisms due to morphology. Polycrystalline morphology in rubrene films gave a result similar to SM82 in panel (d), which they attributed to spin-lattice relaxation (SLR) of the triplet excitons being modulated by librations. The lineshape for DEH in (a) is similar to the lineshapes for the amorphous rubrene films, where the SLR is modulated by triplet hopping over many different molecular orientations with respect to the applied field.

The modMPL spectra from excitation at 385 nm is shown at different wavelengths in (b) & (e), and different fluences in (c) & (f). Unfortunately conversion between the % input of the LED driver to an irradiance was not achievable. However, from the technical specifications from Thorlabs [193], the typical irradiance should be approximately $4\times$ that of the 505 nm

excitation used for TIPS-Tc. Thus, 1% power - 50% power should be approximately 20 - 720 mWcm^{-2} 385 nm (*c.f.* 5.6 - 180 mWcm^{-2} 505 nm).

The modMPL spectra for both materials appear mostly invariant at different wavelengths and fluences. This perhaps confirms that the DPH systems have a simpler kinetic scheme than TIPS-Tc, with no apparent evidence of a second emissive species. The lineshapes for each molecule align well with the magPL. For DEH in), there is an x -axis crossing at 25 mT, which agrees well with the minimum of the MFE shown in panel (a). Similarly, for SM82 in (e), the modMPL lineshape appears to asymptotically approach the x -axis, matching the very broad minimum at higher field strengths shown in (d).

Applying the same logic as our earlier discussion of the TIPS-Tc lineshapes, one might suggest that the peak of the modMPL may align with the $2|E_T|$ for the DPHs. However, the peak appears at 3.75 mT and 2.25 mT for DEH and SM82 respectively. The value of D_T and E_T obtained from ESR are -2350 MHz (84 mT) and 230 MHz (8 mT) respectively. Thus, the energy splitting of $2|E_T|$ is 16 mT, which does not agree with the values of the peak position. However, the peak is at a higher field value for the DPHs than for TIPS-Tc, which would qualitatively align with the trend of DPHs having a higher value of E_T .

We might also suggest that the x -axis crossing of the modMPL for DEH could align with $D_T/2$. However, in this case, with $D_T = 84$ mT, the x -axis crossing of 25 mT is closer to $D_T/4$.

Overall, the measurements of the DPHs confirms the reproducibility of the modMPL results compared to the results of linear magPL. While it questions some of our empirical, qualitative assignments of the peaks in the TIPS-Tc spectra, it does well to confirm the modMPL as a suitable experiment for thin films of singlet fission materials.

4.10 Discussion and Conclusion

Application of modMPL on thin films of singlet fission materials has shown great feasibility for application of the technique as a screening tool. We have presented changes in the sub 100 mT region of the lineshapes of TIPS-Tc films as a result of film morphology. Superior S:N of the modMPL technique has allowed for investigation at very low field strengths and low fluences.

For TIPS-Tc, we have observed two clear, distinct MFE behaviours as a function of wavelength. The behaviour at wavelengths relevant to the singlet emission, 600 nm, are different to those relevant to the controversial TT/excimeric emission at 700 nm. The lineshape at 700 nm is inverted and fluence dependent, indicating a bimolecular or non-geminate origin. Conversely, the fluence independence of the 600 nm ‘singlet’ lineshape, and ‘correct’ MFE sign, indicate a geminate origin. We tentatively suggest that the features of the *600 nm lineshape* show peak positions relevant to the ZFS of the free triplets, whereas the *700 nm lineshape* may have peak positions relevant to the TT quintet ZFS parameters. Further work is required to understand why the TT pair ZFS are relevant to the lineshape of a non-resonance technique.

We further assert that this *700 nm lineshape* is morphology dependent, and requires a degree of strong polycrystallinity. This again confirms that the lineshape is most likely originating from the TTA of triplets meeting at the grain boundaries of the polycrystalline regions. The amorphous films do not exhibit this ‘TTA’ lineshape due to low triplet diffusion lengths, and only show the geminate lineshapes. We were able to confirm that increasing the polycrystallinity of a sample gives rise to this *700 nm lineshape* through observing the changes in modMPL lineshapes as spherulites grew, in real time.

Further validation of the modMPL as a suitable tool for singlet fission screening was performed. ModMPL is a rapid, low-degradation technique, with excellent S:N and signal stability. The lineshapes of modMPL make good agreement with conventional linear magPL for both TIPS-Tc and DPH systems. The superior S:N compared to the linear magPL makes interpretation of the data more concise, such as comparing modMPL *x*-axis crossings rather than linear magPL peak positions.

The intriguing lineshapes uncovered for TIPS-Tc are clearly indicative of different spin physics between the two emission regions. Further exploration of the origins of the two lineshapes will be performed through simulations in the next chapter.

Overall, this examination of modMPL has been highly interesting. Not only has it uncovered novel lineshapes of TIPS-Tc, adding further evidence to the long standing debate of the 700 nm emission, but it has also shown to be a very capable technique for examining singlet fission materials. We believe that modMPL has great potential for use in the singlet fission community, as its speed and S:N proffers an excellent resource for high throughput assessment of thin film behaviours. Furthermore, its tolerance to any sample preparation method would allow any sample to be measured before complementary experiments, such as ESR and TA, for a more unified and holistic understanding of the sample behaviour.

To establish modMPL as a technique for singlet fission screening, we must answer some remaining questions:

- Is the modMPL signature unarguably proof of singlet fission? This would need to be verified with an extensive ESR study.
- Is the modMPL signature similar for most singlet fission materials? Does it mostly change depending on the materials D and E value? And if so, can we use modMPL to estimate the ZFS parameters directly, avoiding the use of ESR altogether?
- Can we relate the modMPL signal to the singlet fission performance or yield? To establish this, an in depth comparison to TA must be conducted.

Once these queries are addressed, modMPL would be an invaluable resource in studying the performance of singlet fission materials.

Chapter 5

Simulating ModMPL Lineshapes with Kinetic Modelling

“With four parameters I can fit an elephant, and with five I can make him wiggle his trunk”

John von Neumann (1903-1957) [194, 195]

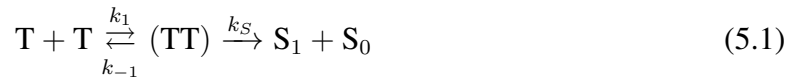
In this chapter, we provide an initial exploration of simulating the modMPL results from **Chapter 4**. Application of modMPL to thin films of TIPS-Tc revealed two distinct lineshapes at two different wavelength regions: the *600 nm lineshape*, and the *700 nm lineshape*. The *600 nm lineshape* was common to all samples, and featured a narrow peak at a field value relevant to the $2E_T$ triplet splitting. The *700 nm lineshape*, however, appeared only in samples with polycrystalline morphology, and was fluence dependent. It was inverted in sign with respect to the *600 nm lineshape*, and featured a total of 6 extrema at peak positions perhaps relevant to the $^5(\text{TT})$ state. To further understand how both these lineshapes arise, why there is a wavelength dependence to the lineshape, and why morphology plays a key role, it is important to model the results. We attempt two approaches to simulate the lineshapes with kinetic modelling. While this does not provide a full, comprehensive study of the spin physics at play, it serves as an important first approximation and assessment of the data. We attempt to explain the system in the simplest description, with the fewest possible parameters.

The simulations in this chapter have been the product of discussion with many scientists. Miles Collins, Prof. Murad Tayebjee, Prof. Dane McCamey from UNSW gave great insight, working on separate simulations in tandem and sharing findings. Phillip Benjamin and Prof.

Peter Hore from the University of Oxford gave excellent advice of how to simulate singlet fission behaviour with the density matrix formalism in the early stages. Dr Ashish Sharma gave input in kinetic modelling. In particular, discussion and code from Dr David Bossanyi from the University of Sheffield was instrumentally helpful to the simulations in this chapter, and we assumed a similar approach as they reported in the literature [45, 52]. All simulations in this chapter were performed by the author in python.

5.1 Introduction

Modelling singlet fission, and its magnetic field effects, has been contemplated by many throughout the decades [40, 45, 52, 54, 78, 88, 90, 91, 196–198]. Merrifield’s work in 1971 [40] inspired much further work over the following 50 years. Merrifield proposed a kinetic model for singlet fission, and its reverse process, TTA. Ignoring the proposed pathway of $(TT) \xrightarrow{k_T} T + S_0$, Merrifield proposed the following :



The kinetic equation for the steady-state population of the n^{th} pair states, P_n , is:

$$\frac{1}{9}k_1 [T]^2 = (k_{-1} + k_S |S_n|^2) P_n \quad (5.2)$$

where

$$|S_n|^2 = | \langle S | \psi_n \rangle |^2 \quad (5.3)$$

is the overlap integral of the n^{th} TT state and the singlet wavefunction. This relatively straightforward approach makes use of the overlaps between the wavefunctions of the TT pair ψ_n and the singlet state to find the ‘singlet character’ of each of the TT spin states. This degree of singlet character can then be used to modulate the kinetic rates. As the wavefunctions ψ_n are the eigenvectors of the Hamiltonian describing the TT pair, any impact on the spin physics will impart an effect on the kinetics. From this, one could consider the total rates of triplet fusion and also predict the impact of the application of a magnetic field. This approach of

kinetic modelling has featured in work by Piland *et al.* [91], which was subsequently revised by Tapping and Huang [54]. This was further continued by Bossanyi *et al.* [45, 52] who extended this model to include the strongly coupled TT pair in addition to the weakly coupled $^1(\text{T}\dots\text{T})$ pair.

Merrifield noted that a more complete treatment of the dynamics involves the consideration of the density matrix of the pair spin states, which was published in their earlier paper with Johnson [81]. Much work has been undertaken in the community to understand singlet fission with the density matrix approach, particularly for simulating resonance technique results such as ESR and ODMR [48, 50, 168, 186]. The density matrix formulation allows for modelling time dependent evolution of the spin density of the triplet pair, including processes such as resonances and relaxation. This is particularly important when considering transient data from experiments such as trESR. However, as we consider only steady state data, we elect to use a kinetic modelling approach. As such, any effects of spin relaxation are neglected.

Using the kinetic modelling, we consider two approaches to understanding the modMPL lineshapes. The first approach is to suppose that the resulting lineshapes come from changes in the kinetics that are a result of mixed morphologies. We assume that these morphology driven changes are independent and separable, and so a linear combination of lineshapes can be taken. The second approach is to suggest that the modMPL lineshape is the observation of one ‘true’ photocycle, and that the two lineshapes are originating from two separate species within one photocycle.

We firstly address the methodology of taking linear combinations of lineshapes from a simple model, then search for one single photocycle to unite both lineshapes. In both methods, the Hamiltonian is described in the same way, as we now explain.

5.2 Defining the Hamiltonian

To construct a simulation of the modMPL lineshapes, we define the Hamiltonian for the triplet pair state as described in the literature [45, 52–54]. We divide the Hamiltonian into four separable parts: the Zeeman interaction, the zero-field splitting (ZFS) for each of the two

triplets, the intertriplet dipole-dipole interaction, and the exchange interaction:

$$\hat{H} = \hat{H}_{Zee} + \hat{H}_{ZFS,A} + \hat{H}_{ZFS,B} + \hat{H}_{dipole-dipole} + \hat{H}_{exchange}. \quad (5.4)$$

We define the Zeeman interaction as

$$H_{Zee} = ig_e\mu_B B \begin{bmatrix} 0 & -H_z & H_y & -H_z & 0 & 0 & H_y & 0 & 0 \\ H_z & 0 & -H_x & 0 & -H_z & 0 & 0 & H_y & 0 \\ -H_y & H_x & 0 & 0 & 0 & -H_z & 0 & 0 & H_y \\ H_z & 0 & 0 & 0 & -H_z & H_y & -H_x & 0 & 0 \\ 0 & H_z & 0 & H_z & 0 & -H_x & 0 & -H_x & 0 \\ 0 & 0 & H_z & -H_y & H_x & 0 & 0 & 0 & -H_x \\ -H_y & 0 & 0 & H_x & 0 & 0 & 0 & -H_z & H_y \\ 0 & -H_y & 0 & 0 & H_x & 0 & H_z & 0 & -H_x \\ 0 & 0 & -H_y & 0 & 0 & H_x & -H_y & H_x & 0 \end{bmatrix} \quad (5.5)$$

where B is the strength of the magnetic field, g_e is the electron g -factor, μ_B the Bohr magneton, and

$$H_x = \sin(\theta) \cos(\phi) \quad (5.6)$$

$$H_y = \sin(\theta) \sin(\phi) \quad (5.7)$$

$$H_z = \cos(\theta) \quad (5.8)$$

where θ and ϕ describe the angle of the molecular axis of triplet A with respect to the magnetic field, as demonstrated in **Figure 5.1 (a)**.

To define the ZFS Hamiltonian, we first consider the Hamiltonian for a single molecule with molecular axes x, y, z ,

$$\hat{H}_{ZFS,SM} = \begin{bmatrix} \frac{D}{3} - E & 0 & 0 \\ 0 & \frac{D}{3} + E & 0 \\ 0 & 0 & -\frac{2D}{3} \end{bmatrix}. \quad (5.9)$$

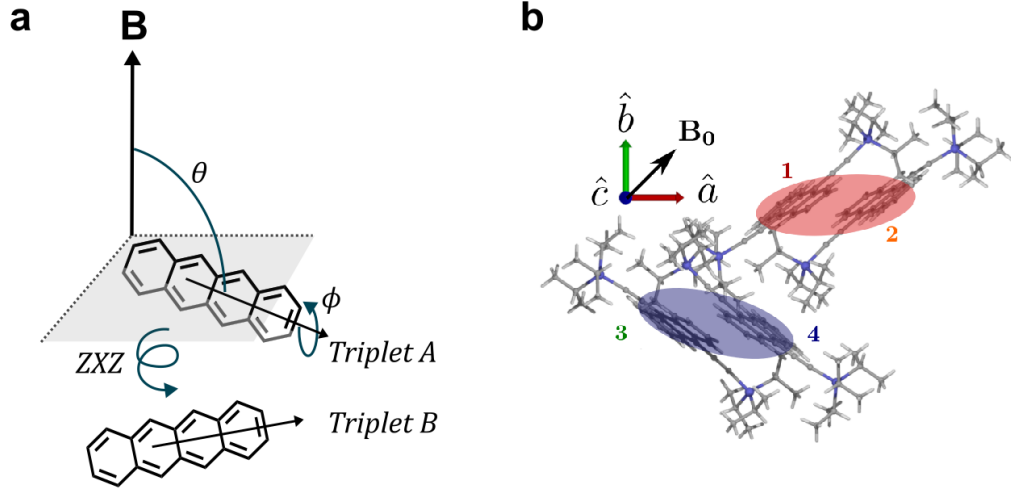


Figure 5.1: Angles defined within the Hamiltonian: **(a)** θ and ϕ describe the angle of the molecular axis of triplet A with respect to the magnetic field. Triplet B is then defined with respect to triplet A through a $ZX'Z''$ Euler rotation, defined by three angles, α , β and γ , as described by Tapping and Huang [54]. **(b)** Crystal structure of TIPS-Tc with labelled triplet pair 1-2 highlighted in red and triplet pair 3-4 highlighted in blue, reproduced from Yunusova *et al.* ([50], supplementary material.).

As according to Tapping and Huang [54], the ZFS Hamiltonian for molecule A is described as

$$\hat{H}_{ZFS,A} = \begin{bmatrix} \frac{D}{3} - E & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{D}{3} - E & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{D}{3} - E & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{D}{3} + E & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{D}{3} + E & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{D}{3} + E & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{2D}{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{2D}{3} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{2D}{3} \end{bmatrix} \quad (5.10)$$

while for molecule B, we must perform a rotation of the single-molecule ZFS Hamiltonian:

$$\hat{H}_{ZFS,B} = (\hat{R}^T \hat{H}_{ZFS,SM} \hat{R}) \otimes I_3, \quad (5.11)$$

where $\hat{R}$ is the rotation matrix

$$\hat{R} = \begin{bmatrix} \cos(\alpha) \cos(\gamma) - \sin(\alpha) \cos(\beta) \sin(\gamma) & \sin(\alpha) \cos(\gamma) + \cos(\alpha) \cos(\beta) \sin(\gamma) & \sin(\beta) \sin(\gamma) \\ -\cos(\alpha) \sin(\gamma) - \sin(\alpha) \cos(\beta) \cos(\gamma) & -\sin(\alpha) \sin(\gamma) + \cos(\alpha) \cos(\beta) \cos(\gamma) & \sin(\beta) \cos(\gamma) \\ \sin(\alpha) \sin(\beta) & -\cos(\alpha) \sin(\beta) & \cos(\beta) \end{bmatrix} \quad (5.12)$$

defining three angles, α , β and γ , that rotate molecule A onto molecule B through a $ZX'Z''$ Euler rotation.

The intertriplet dipole-dipole Hamiltonian, previously defined as

$$\hat{H}_{\text{dipole-dipole}} = X[3(\hat{\mathbf{S}}_A \cdot \hat{\mathbf{r}})(\hat{\mathbf{S}}_B \cdot \hat{\mathbf{r}}) - \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B], \quad (5.13)$$

can be expanded as

$$\hat{H}_{\text{dipole-dipole}} = -X \begin{bmatrix} 0 & 0 & 0 & 0 & 1 - 3w^2 & 3vw & 0 & 3vw & 1 - 3v^2 \\ 0 & 0 & 0 & -1 + 3w^2 & 0 & -3uw & -3vw & 0 & 3uv \\ 0 & 0 & 0 & -3vw & 3uw & 0 & -1 + 3v^2 & -3uv & 0 \\ 0 & -1 + 3w^2 & -3vw & 0 & 0 & 0 & 0 & -3uw & 3uv \\ 1 - 3w^2 & 0 & 3uw & 0 & 0 & 0 & 3uw & 0 & 1 - 3u^2 \\ 3vw & -3uw & 0 & 0 & 0 & 0 & -3uv & -1 + 3u^2 & 0 \\ 0 & -3vw & -1 + 3v^2 & 0 & 3uw & -3uv & 0 & 0 & 0 \\ 3vw & 0 & -3uv & -3uw & 0 & -1 + 3u^2 & 0 & 0 & 0 \\ 1 - 3v^2 & 3uv & 0 & 3uv & 1 - 3u^2 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (5.14)$$

where u, v, w are the x, y, z components of the vector $\hat{\mathbf{r}}$. X is dependent on distance r , and is of a magnitude $\sim X = D/100$.

Finally, we define the exchange coupling Hamiltonian as

$$\hat{H}_{exchange} = J \begin{bmatrix} 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{bmatrix}. \quad (5.15)$$

Using the Python function

```
eigenvalues, eigenstates = numpy.linalg.eigh(H),
```

we can find the 9 eigenstates for the Hamiltonian describing the TT state. We can then define the overlap coefficients for each spin state, to define the amount of spin character each eigenstate has, as $|C_S|_i^2 = |\langle S|\psi_i\rangle|^2$ for singlet character, $|C_T|_i^2 = \sum_{m=x,y,z} |\langle T_m|\psi_i\rangle|^2$ for triplet character, and $|C_Q|_i^2 = \sum_{m=a,b,x,y,z} |\langle Q_m|\psi_i\rangle|^2$ for quintet character, where S, T_m and Q_m are the 3×3 spin matrices.¹ Within the code, we calculate the overlap coefficients as

```
numpy.abs(M @ eigenstates)**2,
```

¹

$$S = \frac{1}{\sqrt{3}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$T_x = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix} \quad T_y = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} \quad T_z = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$Q_a = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad Q_b = \frac{1}{\sqrt{6}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{bmatrix} \quad Q_x = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \quad Q_y = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} \quad Q_z = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

where M is the flattened spin matrix. Once the Hamiltonian is defined and the overlap coefficients with each spin state calculated, the coefficients can be used within the definition of the kinetic model.

We make a key assumption that the kinetics observed are linearly dependent, and do not include bimolecular terms. We consider rate constant for TTA, k_{TTA} , which is a bimolecular process, to be an effective rate constant that takes into account some scaling for the effective concentration of triplet states. Put simply, we take k_{TTA} to be relatively small. This is an oversimplification, but is one that allows more straightforward calculation. As we assume the system to be linear rather than quadratic, and in a steady state, we can devise a set of rate equations and set them to zero to solve for the effective concentration of each species. We can approach the model as an $Ax = b$ problem, where A is the matrix of rate constants defining the kinetic model, x is the vector of N states included in the model, and b is a vector of zeros. To find x , we use

$$\text{numpy.linalg.solve}(A, b).$$

We solve for x at each of the field values. From our allocation of the S_1 state within the model in A , we can identify the population of the S_1 state in x at each of the fields. We then calculate the MFE as the percentage change in S_1 population from the zero-field value. We can also identify the PLQE of the S_1 emission as

$$\text{PLQE} = 100\% \frac{S_1 \times k_S}{G_S} \quad (5.16)$$

where k_S is the rate of fluorescence and G_S is the rate of generation of the S_1 state (excitation density). PLQE was a helpful heuristic to ensure that the results of the simulations were reasonable. To find the shape of the modMPL signal, we then apply `numpy.gradient` to the MFE.

5.3 Approach 1: Linear Combinations of Independent Lineshapes

In this approach, we consider one, simple photocycle. We change the triplet pair separation rate to free triplets, giving two instances: *slow* and *fast* separation of the triplet pair. This is valid, as the separation of the triplet pair to free triplets is dependent on morphology. If we assumed that different local areas of morphology result in differences in triplet separation rates, we can sum the two resulting lineshapes together to approximate the ensemble photophysics. To achieve this we make an assumption: if a photocycle is being initially populated from the triplets, *i.e.*, through the TTA of triplet excitons, we assume that the lineshape is multiplied by -1. This is a crude oversimplification, and yet is empirically true.

We then assume that two or more lineshapes can be considered as independent, and can be summed together. This approach has been reported in the literature [197], and was suggested by Miles Collins *et al.*, who assisted in identifying successful kinetic values for an early iteration of a kinetic model. The model we consider is adapted from the Merrifield model [78], as shown in **Figure 5.2**.

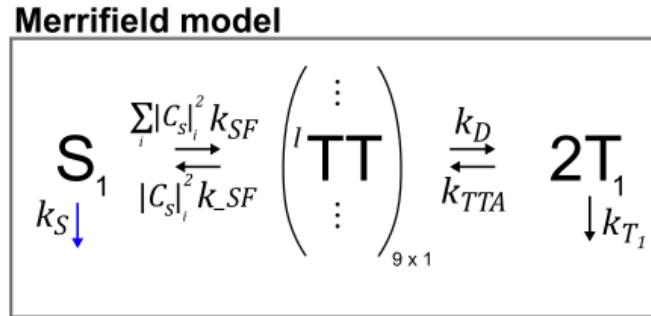


Figure 5.2: The Merrifield model

In this *simplest description*, we consider only 10 states: the S_1 , the 9 lTT states, and the T_1 state. We consider the MFE to be originating from changes in the singlet fluorescence, marked as a blue arrow, defined by the rate constant k_S . We include the overlap of the 9 lTT states with the singlet spin state, $|C_{S_i}|^2$, to impart that the transition from S_1 to lTT preferentially populates the singlet states, and the reverse process is modulated by the amount of singlet character possessed by the lTT states. The triplet states T_1 are reversibly populated, and decay with a constant k_{T_1} through processes such as relaxation.

In this simplest possible model, we have neglected to separate between the strongly coupled and weakly coupled TT states; an approximation that is not uncommon within the literature. We chose to do this for two main reasons. Firstly, we desired fast computation, and a straightforward kinetic model. The second, is that the interconversion between the strongly and weakly coupled states is something of a black box. We are, to some extent, assuming that the TT state is weakly coupled throughout. This may be an oversimplification. However, we are confident that we can learn enough from this simplistic model to lay the foundations for future work to be conducted by theoreticians.

From this simplest model, we can now define our ODEs. Shortening $|C_S|^2$ as c_i^2 for convenience, and including a generation term G_S , we can describe the matrix of rate constants, A , for our simulation as

$$A = \begin{bmatrix} G_S - k_S - k_{sf} \sum_{i=1}^9 c_i^2 & k_{sf} c_1^2 & k_{sf} c_2^2 & \dots & k_{sf} c_9^2 & 0 \\ k_{sf} c_1^2 & -k_d - k_{sf} c_1^2 & 0 & \dots & 0 & \frac{1}{9} k_{TTA} \\ k_{sf} c_2^2 & 0 & -k_d - k_{sf} c_2^2 & \dots & 0 & \frac{1}{9} k_{TTA} \\ \vdots & \ddots & \ddots & \dots & \ddots & \vdots \\ k_{sf} c_9^2 & 0 & 0 & \dots & -k_d - k_{sf} c_9^2 & \frac{1}{9} k_{TTA} \\ 0 & 2k_d & 2k_d & \dots & 2k_d & -k_T - 2k_{TTA} \end{bmatrix}. \quad (5.17)$$

We take the values of each parameter as stated in **Table 5.1**.

	Hamiltonian, $\hat{H}$	Kinetics, A / ns^{-1}
D, E	1414 MHz, 14 MHz	G_S 10
θ, ϕ	91.6°, 30.6°	k_S 10
X	0.001 μeV	k_{sf}, k_{sf} 100, 50
J	0.01 μeV	k_{TTA} 0.06022
α, β, γ	0°, 0°, 0°	k_D 2 (0.1-100)
r_{AB}	[0,0,1]	k_{T_1} 1

Table 5.1: Default parameters taken for modelling MFEs.

The parameters selected are relatively arbitrary, as we will soon discuss that very few have a direct impact on the modMPL lineshape. However, the selected values empirically work well. The D and E values and θ, ϕ are taken from the ESR and ODMR of TIPS-Tc in the

literature [50]. J and X are taken to be very small, as we expect the triplet pair to be weakly exchange coupled in order to observe low-field MFEs. Such small values of exchange coupling are consistent with other accounts of modelling low-field magnetic field effects [52, 53, 93]. However, there is a discrepancy between the observations of J between the low-field measurements, and experiments such as high-field magnetic measurements or spin-resonance experiments, where higher values of J are selected [48, 49]. This discrepancy between observations of high values of J in resonance measurements and low values of J for MFE measurements is well known within the singlet fission community, and yet a rationalisation of this has yet been made.

The rates were selected, based on values in the literature [52, 197], with k_{sf} taken to be relatively fast compared to the other kinetic processes. k_{TTA} , the effective bimolecular constant, was taken to be small compared to the remaining values. Overall, a balance of values was chosen such that the PLQE from the singlet state was high yet feasible (50% PLQE, indicating that the singlet state was successfully maintaining some level of population), and an MFE saturation value of 15-20 %. It is worthwhile again highlighting at this point that due to our kinetic modelling approach, as opposed to a spin density approach, we have neglected to include any spin relaxation rates.

With these default values, we varied each parameter of the Hamiltonian, and each rate constant in the photocycle, independently. The results of these parameter-by-parameter explorations are shown in **Figures 5.3** and **5.4**.

We first consider the impacts of the Hamiltonian on the modMPL lineshapes in **Figures 5.3**. Each curve is normalised to the maximum for a more detailed assessment of changes to the lineshape, rather than the magnitudes. The unnormalised, integrated lineshapes (comparable to magPL) for each panel are given in **Appendix Figures B.1** and **B.2**.

The ZFS parameters, D and E , are varied in **(a)** (varying D , with E fixed as $D/100$) and **(b)** (value of D fixed at 1414 MHz). The ZFS parameters are yielded from ESR, and are assumed to stay constant over a sample. However, the impact of increasing D and E shows

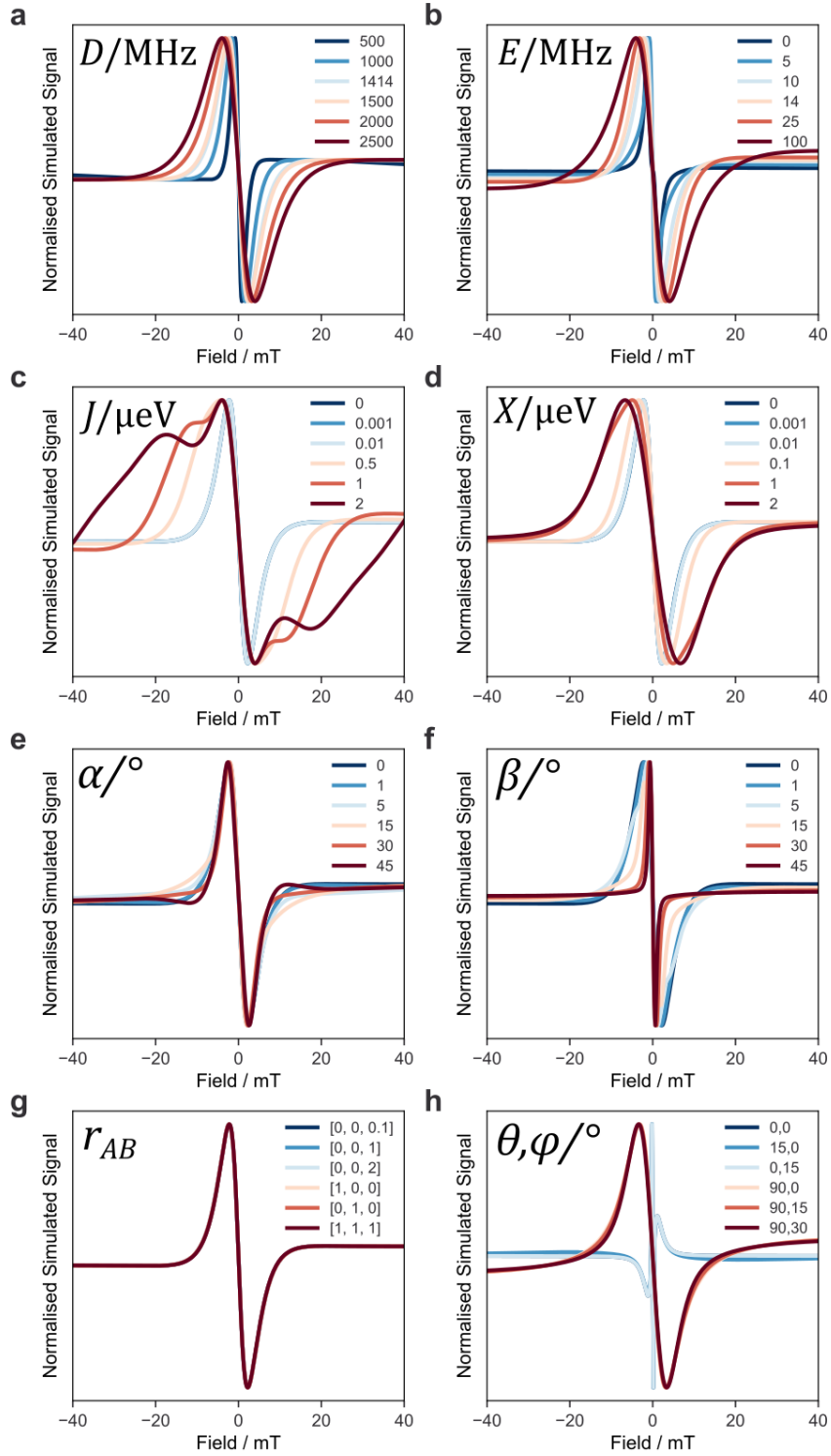


Figure 5.3: Effects of the Hamiltonian on a simple model: each parameter of the Hamiltonian is varied independently, with the the remaining parameters as listed in **Table 5.1**. Normalised to maximum.

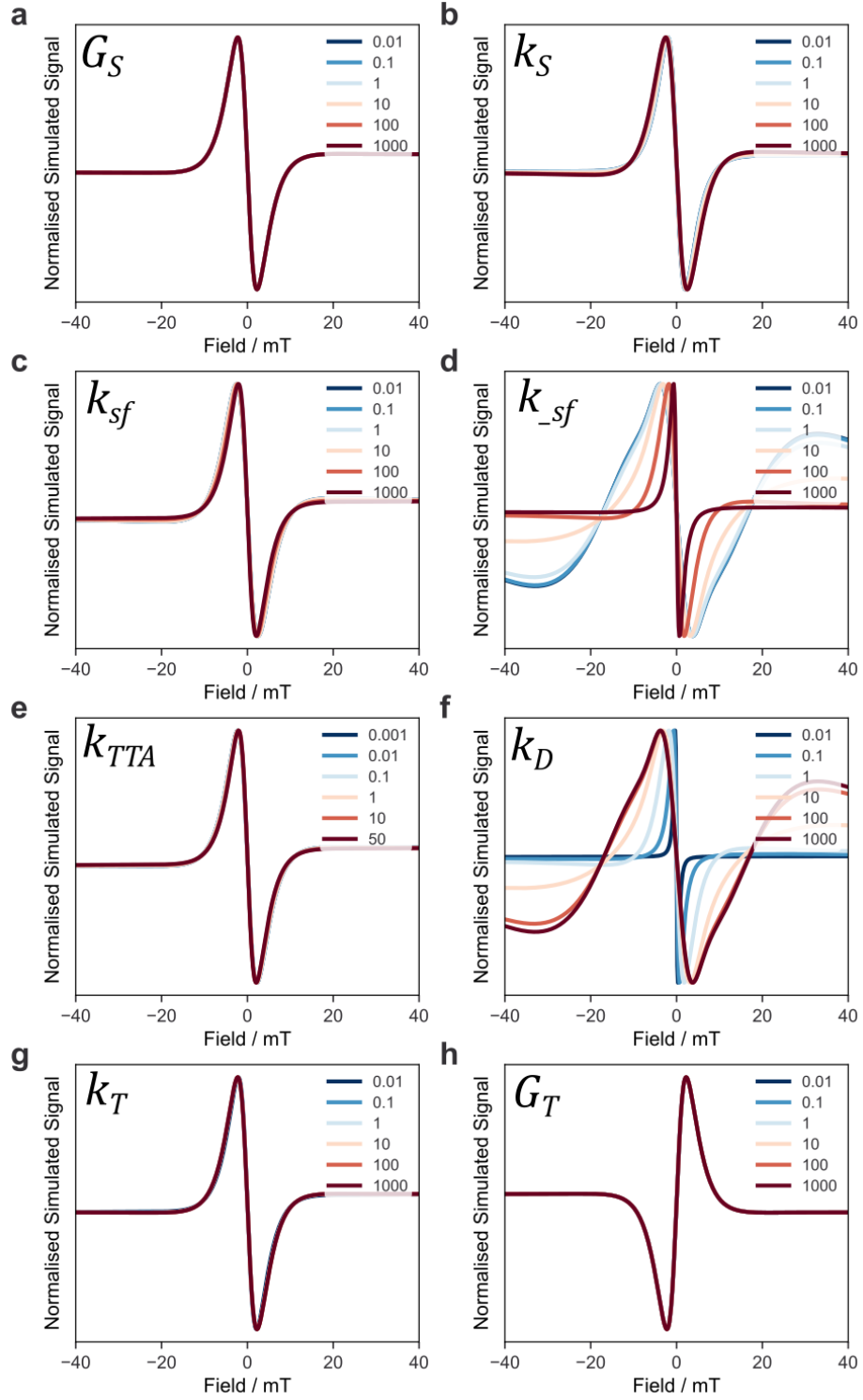


Figure 5.4: Effects of kinetics on a simple model: each parameter of the kinetic matrix is varied independently, with the the remaining parameters as listed in **Table 5.1**. Normalised to maximum.

a broadening of the lineshape and peak positions. This is as we predicted from the measurements of DPHs in **Section 4.9.4**, where the DPHs have a larger D value than TIPS-Tc, and a comparatively broadened modMPL lineshape.

For the exchange coupling and intertriplet dipolar coupling, described by J and X respectively (panels **(c)** and **(d)**), we observe a similar lineshape broadening when increasing the strength of the interaction. For the exchange coupling, however, we observed an increase in the shoulder of the peak. This may have some role in the *600 nm lineshape*.

Changing the intertriplet angles, α and β , have minimal impact on the lineshape, with β again appearing to impact the breadth of the lineshape, and α impacting the approach toward the x -axis. Changing r_{AB} changes only the magnitude of the derivative signal, not its shape.

θ and ϕ , the angle of the triplet pair with respect to the applied field, has a considerable impact on the lineshape, with smaller values of θ causing an inversion in sign and a sharp peak close to $B = 0$. Comparatively, ϕ causes very minimal change to the lineshape. As the value of $\theta = 90^\circ$ gives a lineshape with the correct sign and breadth, we select this angle for modelling going forward. This agrees with angles used within literature for modelling TIPS-Tc lineshapes in ODMR, where Yunusova *et al.* selected θ and ϕ to be 90° and 30° respectively [50].

Notably, while many of the lineshapes look similar to the *600 nm lineshape*, none look similar to the *700 nm lineshape*. This may suggest that changes to the Hamiltonian alone are insufficient to explain the differences between the two lineshapes from this initial approximation of parameters.

When we consider each of the rate constants parameter-wise (**Figure 5.4**), we find most do not impact the lineshape. This is true for the generation term of the singlet (G_S), the fluorescence (k_S), rate of singlet fission (k_{sf}), and the rate of triplet decay (k_T). For the rate of TTA (k_{TTA}), the lineshape does not change, but the linear solver is unstable for large values of k_{TTA} , so a suitably small value must be selected. If we set G_S to zero, and instead instantiate the model such that the triplets are being generated with rate G_T (through a hypothetical sensitisation), we now see the lineshape is inverted, as expected.

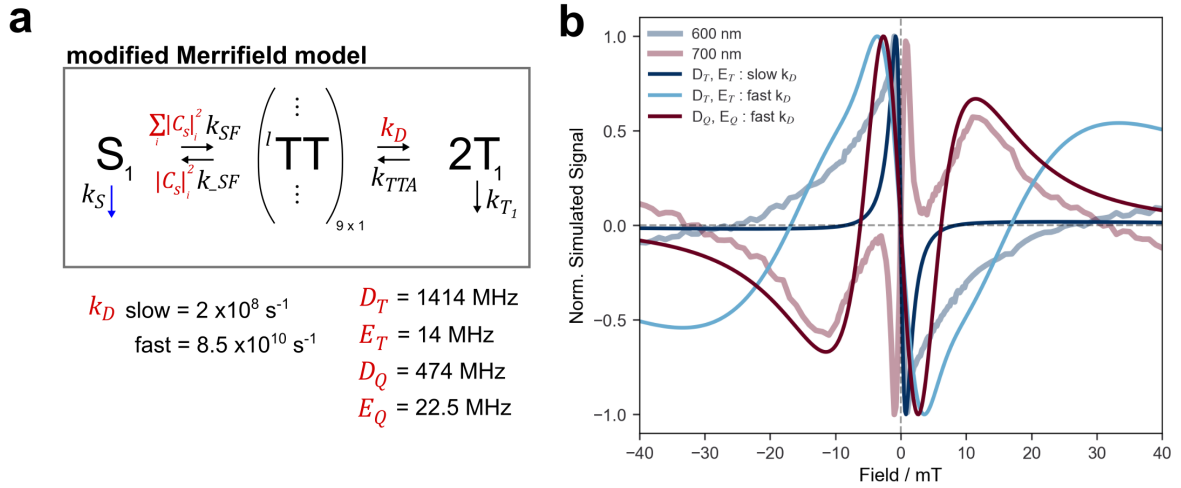


Figure 5.5: Three lineshapes from a simple kinetic model **(a)** for different values of triplet pair dissociation, and values of ZFS parameters for the triplet state and quintet state **(b)**. Kinetic parameters changed are marked in red, with values stated in **(a)**.

When we now change the rate of reverse singlet fission, k_{sf} and dissociation of the TT state to free triplets, k_D , we now observe that the lineshape is altered. From a qualitative argument, this is logical that the two rate constants that lead away from the TT state will be the most likely to impact the lineshape, as (although we are considering a steady state) they impact the population of the TT manifold most significantly, and from a physical argument, will impact how *long* the TT state is populated for. This would impact how long the spins have to evolve and mix within the TT manifold.

For slow k_{sf} or fast k_D , or in other words, greater drive toward the free triplets as opposed to returning to the singlet state, we now observe a broader lineshape, and a new extremum at values $>20 \text{ mT}$. While the *700 nm lineshape* is not perfectly reproduced, we can assert that fast formation of free triplets may be related to the new lineshape.

To examine this more closely, in **Figure 5.5** we overlay lineshapes for fast and slow k_D with the *600 nm* and *700 nm lineshapes* derived from the SVD analysis described previously for the spherulite film (**Figure 4.9**).

Three simulated lineshapes are shown in **Figure 5.5**. By varying the separation/dissociation rate of the triplet pair, k_D , between two cases (fast, 85 ns^{-1} and slow, 0.2 ns^{-1}) we were able to find a narrow lineshape that aligned with the *600 nm lineshape* for slow separation, and

a broader lineshape that perhaps aligned with the shoulder of the *600 nm lineshape* for fast separation. However, in either case, alignment with the extrema at ± 10 mT for the *700 nm lineshape* were not obtained.

When we instead take the ZFS parameters of the quintet state, as defined by Yunusova *et al.* [50], for fast separation we found a lineshape that aligned very well with the *700 nm lineshape*. While perhaps this may not have a good physical meaning, it does go some way to confirm our earlier suspicions that the *700 nm lineshape* has features related to the quintet TT state. This surprising alignment with the exact parameters for D_Q and E_Q seems unlikely to be coincidental. A heat map of the differences in peak positions, shown in **Appendix B Figure B.3**, shows that the peak positions for the simulated lineshapes are very sensitive to the values of D_Q and E_Q .

From **Figure 5.5**, one may conjecture that the *600 nm* and *700 nm lineshapes* could be well reproduced by taking a linear combination of these independent lineshapes, $a_1y_1 + a_2y_2 + a_3y_3$. We optimise for the values of the coefficients, a_n , with `scipy.optimize.curve_fit`. Results of such combination of lineshapes are shown in **Figure 5.6**.

The results of the linear combination are interesting. We consider the two lineshapes of fast and slow k_D for the triplet ZFS parameters, D_T and E_T , in **Figure 5.6 i**. A relatively good ‘fit’ is made for the *600 nm lineshape* (**a**), but these two lineshapes are not sufficient to fit the *700 nm lineshape* (**b**). We can then add more lineshapes to the combination, adding firstly the lineshape for fast k_D with ZFS parameters D_Q and E_Q in (**ii**), which gives a much better ‘fit’ to the *700 nm lineshape*. Adding the quintet lineshape with slow k_D in (**iii**) gives the best fit for both the *600 nm* and *700 nm lineshapes*. However, we advise caution in this approach; adding more lineshapes to a linear combination will make the approximation better, as even an elephant can be approximated with 4 parameters [194, 195]. However, interesting observations can still be made about the linear combinations.

In this thought experiment of combining lineshapes, it is clear that taking the lineshapes with ZFS parameters of D_T and E_T is not sufficient. To describe both the *600 nm* and *700 nm* behaviours, including D_Q and E_Q makes a vast improvement to the lineshape. This once

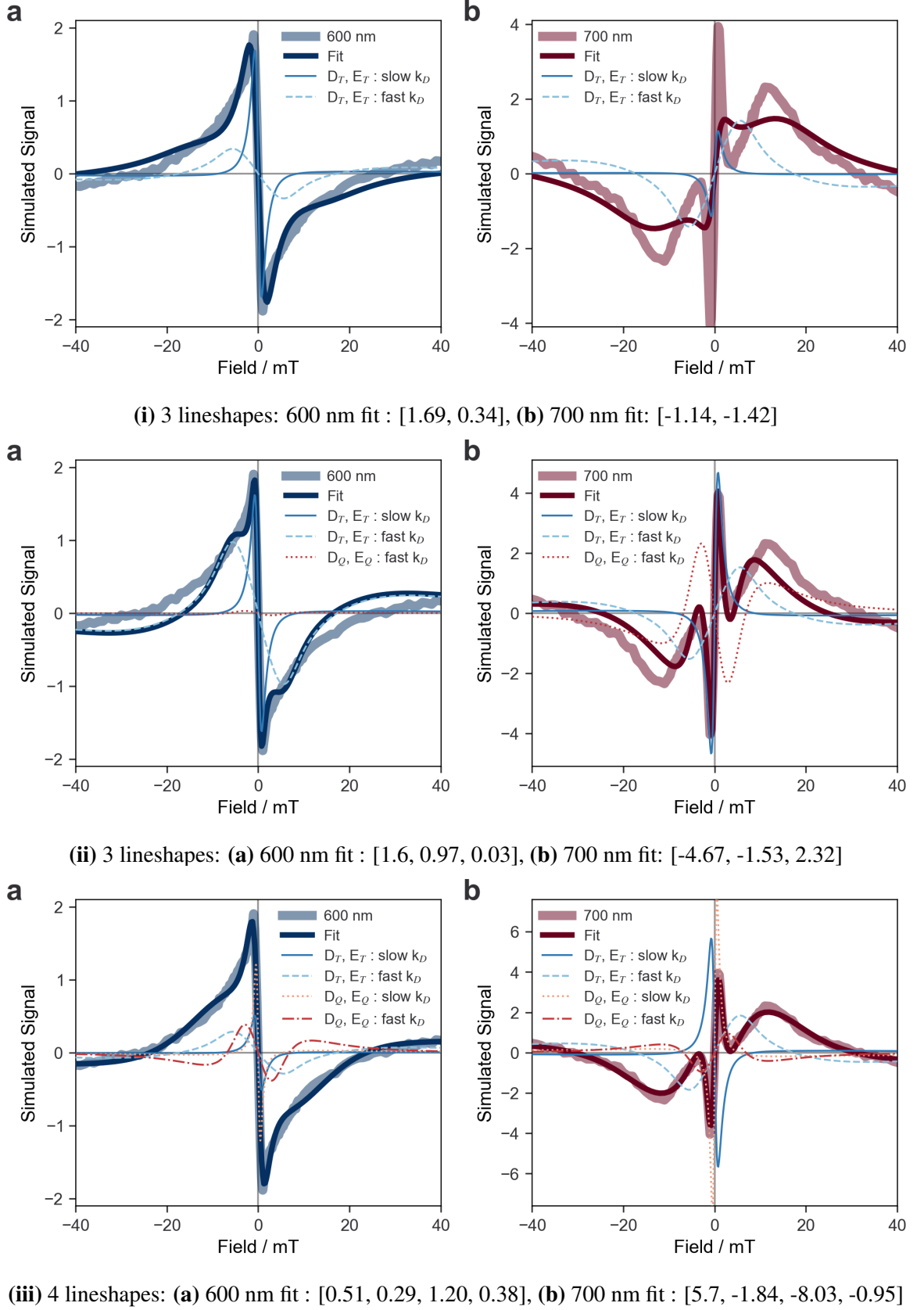


Figure 5.6: Fitting a linear combination of independent lineshapes: fitting the 600 nm and 700 nm lineshapes with a linear combination of lines simulated from values of k_D and ZFS parameters identified in **Figure 5.5**. Coefficients for linear combination are given in each subcaption, with the order matching the legend entries.

again may confirm that the *700 nm lineshape* is connected to the quintet state of the TT pair. However, it may not only be influencing the *700 nm lineshape*, but from **(iii-a)** it may also indicate there is some contribution from the D_Q/E_Q lineshapes at *600 nm*.

One of the main uncertainties in this methodology is the sign of the coefficients. For each of the ‘fits’, the *600 nm lineshape* contains only positive coefficients, such that each lineshape is added together. This is in line with expectations; a positive lineshape in this sense is one generated from a ‘forward’ or ‘geminate’ process (rather than a non-geminate recombination process), due to how we defined our simulation. When we consider the ‘fit’ to the *700 nm lineshape*, for the two-lineshape combination in **(i-b)**, both coefficients are negative, which is necessary as the *700 nm* line is inverted in sign relative to the *600 nm*. We may then suggest that the *700 nm lineshape* is due to a non-geminate triplet recombination process. One might try to ascribe some physical explanation to this.

We could postulate that there are two particular morphologies in the film, where the morphology defines k_D to be either fast or slow. The forward pathway, from a photoexcited singlet through to free triplets, and the reverse pathway, where free triplets diffuse through the solid to this morphology region and fuse back to the singlet, are both governed by the value of k_D as dictated by the morphology. The forward pathway features emission at 600 nm, which gives rise to the *600 nm lineshape*. The reverse pathway, where free triplets have fused, result in some red-emission, through the population of an energetically stabilised species ². If we continue on this hypothesis, another possible explanation for the two regimes of k_D could be the formation of different TT pairs within the unit cell of TIPS-Tc. There are four TIPS-Tc molecules per unit cell, allowing a possible 6 TT pairs to form. Examination of the possible TT pairs is described in **Section 5.4**. However, in either case, the explanation as to why the non-geminate or reverse process results in a lineshape present only at redder wavelengths is still not clear. Why, if the forward and reverse processes are directly related and governed by the same kinetics, are the modMPL lineshape features not common to both wavelength regions?

²or, a species with a destabilised ground state.

When we come to consider the addition of the further lineshapes with the quintet ZFS parameters, the ability to assimilate meaningful physical interpretation becomes limited. If we consider in (ii) where three lineshapes are added in combination, we note that there is a positive or geminate contribution from the quintet ZFS lineshape, that is only present at 700 nm and not 600 nm . Why this would be the case is unclear. It is clear that this approach of taking linear combinations of lineshapes to understand the 600 nm and 700 nm has its limitations in terms of physical interpretation.

Overall, the approach of taking a linear combination of independent lineshapes gave qualitatively good reproduction of the lineshapes, and was grounded in a reasonable approximation that changes in morphology may cause the different lineshapes. However, the lack of physical interpretability indicates an alternative method should be adopted to understand the TIPS-Tc modMPL lineshapes. It is possible, therefore, that these regions of different morphologies result in entirely different photophysics in the regions. This methodology could be extended so that two different photocycles are considered in combination. For example, morphology region A could exhibit one kinetic scheme, while morphology region B could exhibit a different kinetic scheme, or even the combination of two kinetic models. It is clear that this might be a valuable avenue to explore in future investigations.

While this model could be made more and more complex, an alternative approach would be to describe both lineshapes simultaneously with one photocycle, with a possible explanation for the origin of this redder emission and its distinct lineshape to the singlet emission. Before we adopt this approach, however, we consider the 6 possible triplet pairs within the TIPS-Tc unit cell, as it is important to determine if this may be the cause of the different lineshapes. Deciding their role within the lineshapes could impact the photocycle we adopt for the model.

5.4 The Possible TT Pairs

One possible explanation for the inclusion of different ZFS parameters is that different TT pairs are forming within the unit cell. As discussed by Yunusova [50], the 6 possible pair states will give rise to different couplings, which impacts the quintet states most. The summary of the triplet pair parameters are found in **Table 5.2**. Using the parameters **Table 5.2**,

	$ D_Q $ / MHz	$ E_Q $ / MHz	θ_q / deg.	ϕ_q /deg.	r_{ab} / Å
$TT_{1,2}$	474.0	22.5	91.6	30.6	10.0
$TT_{1,3}$	227.5	72.4	13.5	77.8	10.5
$TT_{1,4}$	250.4	42.7	15.5	84.7	9.7
$TT_{2,3}$	234.8	62.0	13.8	90.8	15.7
$TT_{2,4}$	245.5	69.7	11.0	78.9	17.7
$TT_{3,4}$	474.0	22.5	88.4	30.6	10.0
Obs.	477	22	90	30	-

Table 5.2: Reproduced from Yunusova *et al.* [50]. Predicted fine structure parameters from distances in TIPS-Tc crystal structure with $|D_T| = 1414$ MHz and $|E_T| = 14$ MHz from the measured zero-field values with angles given between B_0 and $\hat{z}_q(\theta_q)$ and $\hat{x}_q(\phi_q)$ for $B_0 \parallel \hat{c}$. The final row shows the corresponding experimental observations, consistent with the predicted values of $TT_{1,2}$ and $TT_{3,4}$.

but keeping the kinetic parameters the same, we replot the results of **Figure 5.5** for each possible triplet pair in **Figure 5.7**. There are two triplet pairs that are most likely to contribute to the lineshape due to their cofacial alignment, as shown previously in **Figure 4.10**, which are pair 1-2 and 3-4. The results of these two pairs are shown in **Figure 5.7 (a)** and **(b)**. Panel **(a)** includes the *600 nm* and *700 nm lineshapes* for comparison. The four simulated lineshapes, arising from fast and slow k_D (85 ns^{-1} and 0.2 ns^{-1}) and the D and E values for the triplet and quintet states, are shown for each possible triplet pair. Pairs 1-2 and 3-4 are surprisingly similar, indicating that the subtle changes in the parameters, as described in **Table 5.2**, have minimal impact on the modMPL lineshape in this region. When we consider the other pairs, however, they all appear somewhat similar to each other, but highly dissimilar to pairs 1-2 and 3-4. The overly complex lineshapes of the remaining pairs rule them as unlikely to contribute significantly to the lineshapes observed. We therefore only consider pairs 1-2 and 3-4. However, as the changes between these two pairs are so subtle, we progress by considering the parameters of pair 1-2 only. We do not suggest that pair 3-4 does not play a role in the lineshapes, but that its contribution is inseparable from that of pair 1-2 within these simulations.

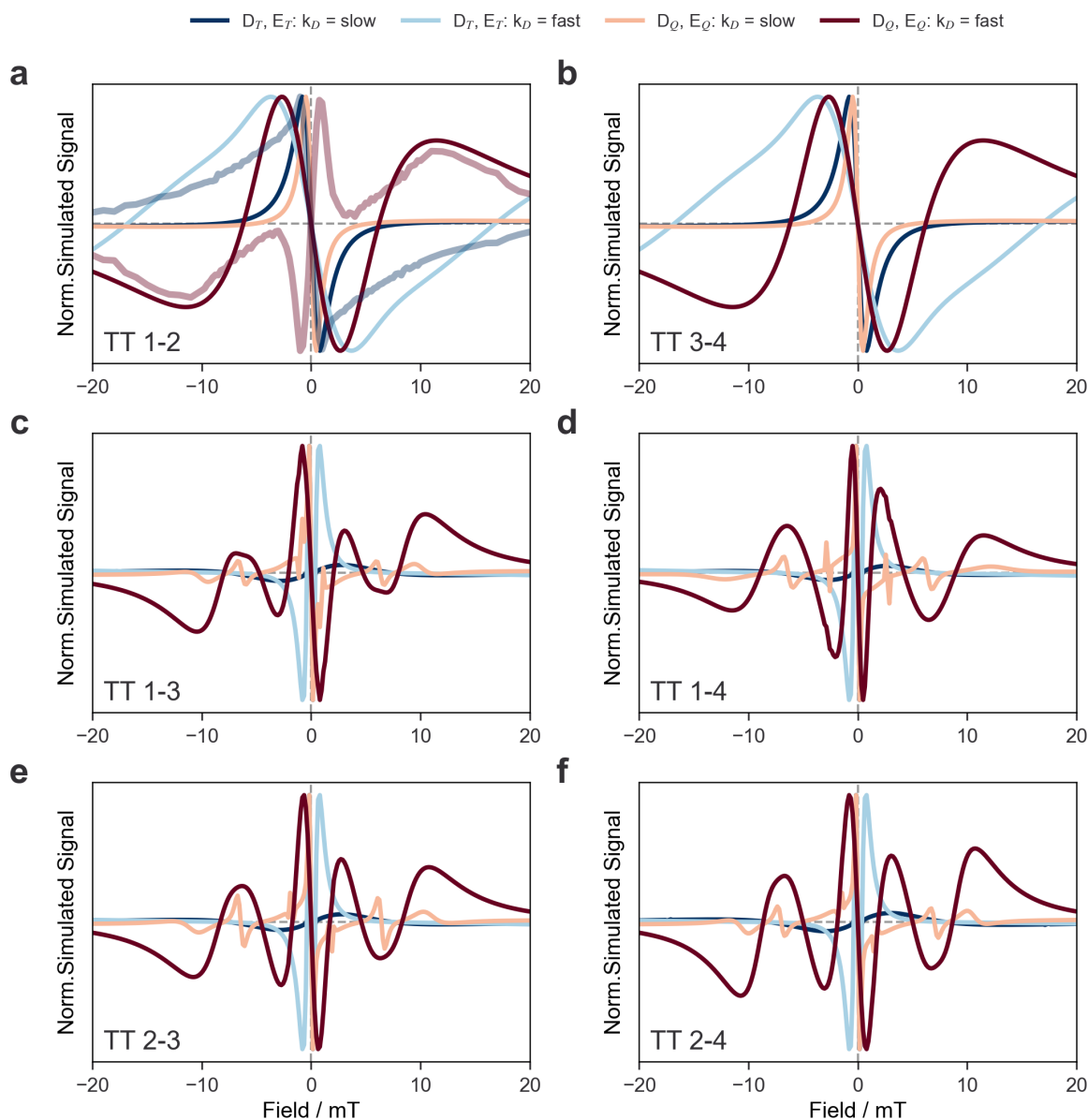


Figure 5.7: Lineshapes arising from the possible TT pair parameters. Pairs 1-2 and 3-4 are of most interest due to their cofacial arrangement, whose lineshapes are highly similar. The lineshapes for the remaining pairs are highly dissimilar to pair 1-2/3-4, and to the 600 nm and 700 nm lineshapes, therefore suggesting they do not make meaningful contribution to the lineshapes. The 600 nm and 700 nm lineshapes are shown in (a) for reference.

5.5 Approach 2: One photocycle

*“One [photocycle] to rule them all,
One [photocycle] to find them,
One [photocycle] to bring them all
and in the darkness bind them.”*

J.R.R. Tolkien (1892-1973)

The Fellowship of the Ring (edited)

We now consider an alternative approach, such that both lineshapes are being generated by one underlying photocycle. To achieve this, we consider the two lineshapes generated from the SVD of the wavelength series for the spherulitic film. We consider the high fluence wavelength series, as we assume that the fluence was high enough that the triplet triplet annihilation can be approximated as monomeric, agreeing with our earlier simplification of the TTA process.

We aimed to optimise select parameters of the suggested photocycles, such that the residuals to both the *600 nm* and *700 nm lineshapes* were considered simultaneously. This was achieved through creating a bespoke error function, which summarised the sum-squared residuals to the two lineshapes together. This was then minimised in Python with `scipy.optimize.minimize` and an Nelder-Mead minimisation algorithm.

We have a number of observations that must be rationalised within one model. This creates the following requirements for the model:

- There must be a wavelength dependence to the lineshape, which we assume means two distinct species are behind the two lineshapes.
- There may be two distinct spin dependent steps, otherwise the shapes of the two lineshapes would be the same.
- The *700 nm lineshape* is probably generated through a bimolecular process, while the *600 nm lineshape* is probably generated by an effectively unimolecular process.

- The two lineshapes must be inverted with respect to each other.

We assume that the *600 nm lineshape* originates from the singlet excited state. We therefore must find the identity behind the *700 nm lineshape*, and how it relates to the photocycle. From the stipulations above, it is most likely for the second emissive species to be related to the triplet pair state, to be formed *after* an initial spin mixing step (to ensure an inverted sign compared to the S_1 lineshape). It is also unlikely to be directly generated from the singlet state, as otherwise the features of one lineshape would be reproduced by the other; their populations would be too intimately related to allow for differences in lineshapes.

The Hamiltonian parameters may not necessarily be the same for each process of the photocycle, for example, a new spin sensitive species with different ZFS parameters may be generated. However, as we have already established that the ZFS parameters for the free triplet and the quintet 1-2/ 3-4 TT pair can reproduce the lineshapes well through linear combination, it is unlikely for different Hamiltonian parameters to be involved.

We attempted numerous kinetic models, taking some inspiration from the literature. We consider the simplest cases possible. To rule out some of the more, perhaps intuitive photocycles, we attempt to fit both lineshapes, as shown in **Figure 5.8**.

The three models we try initially, shown in (a), (c), and (e), all contain two emissive species, and all give highly similar results. The first model in (a) is the simplest possible: the second emissive species is the TT pair directly. When fitting this model, we allowed the dissociation of the TT pair, k_D , and the emission rate, k_{TT} , to vary. As can be seen in (b), the most optimal fit, such that the S_1 reproduces the *600 nm lineshape*, and the TT emission reproduces the *700 nm lineshape*, is one where the two narrow peaks are well described. The inversion of sign between the two lineshapes is represented. However, the ± 11 mT peaks for the *700 nm* are not captured. This is not entirely unexpected, as the S_1 population and TT population are very intimately connected. While there is a secondary spin selection in place (the TT emission depends on the singlet state character), it is insufficient to allow for the *700 nm lineshape* to be ‘fitted’ without compromising the ‘fit’ of the *600 nm lineshape*.

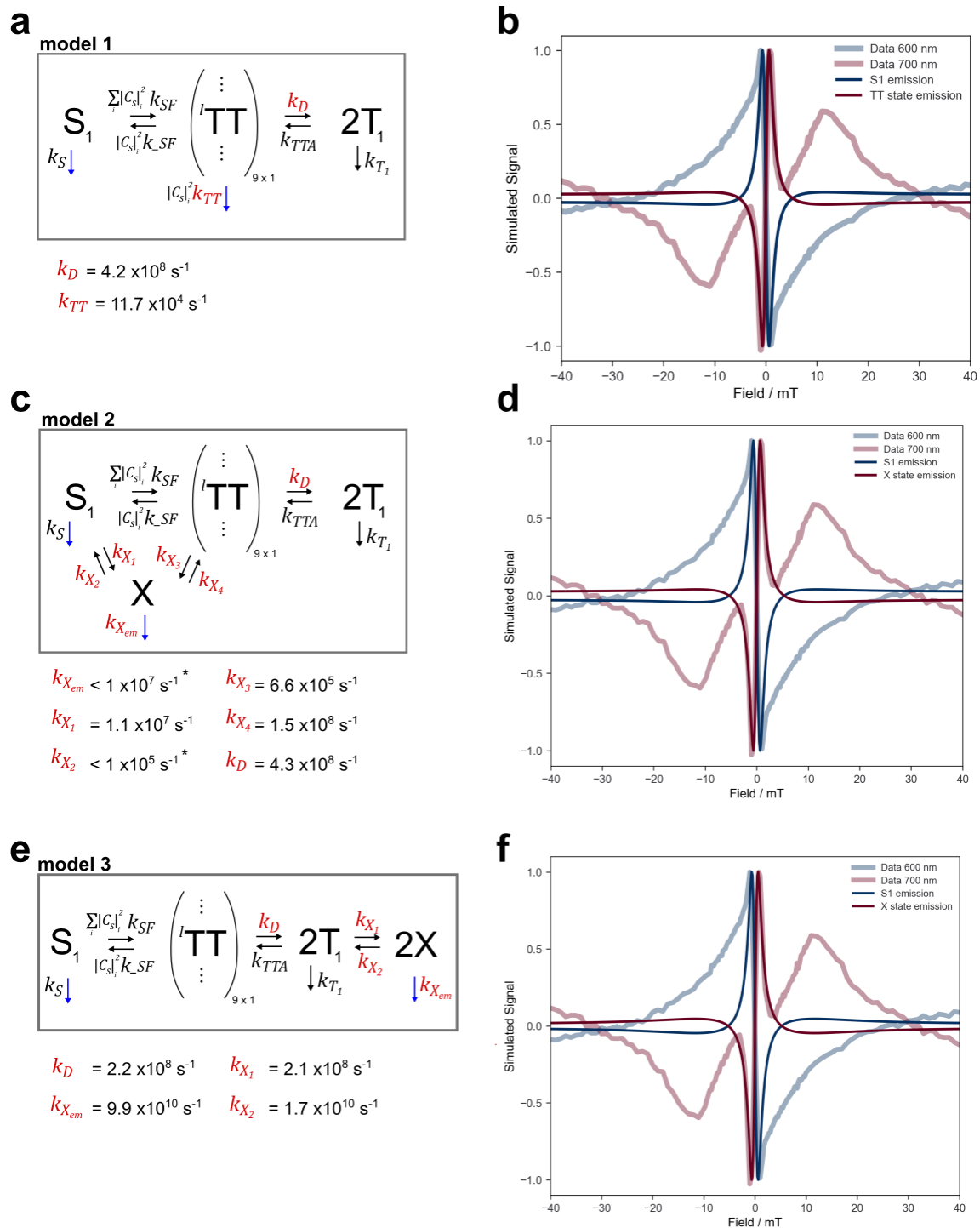


Figure 5.8: Ruling out three potential models, featuring emission directly from TT in (a), an excimer from the singlet and TT states in (c), and an emissive species from the free T₁ states in (e). The kinetic parameters allowed to change under optimisation are highlighted in red. Results of the optimisation are shown in (b), (d) and (f), where the S₁ emission is fitted to the 600 nm lineshape, and the secondary emissive species is fitted to the 700 nm lineshape.

The second model we consider in (c) is that as suggested by Feng *et al.* [85], where an excimer is populated from either the S_1 or from the TT pair. This excimer, X, then can emit at 700 nm. This model was highly unstable within this parameter space, with $k_{X_{em}}$ and k_{X_2} unable to converge. From an energetic standpoint, a broad emission at redder wavelengths is most likely to be explained by an excimer formed from the S_1 state. However, as with the previous model, this model is not sufficient to explain both the 600 nm and 700 nm lineshapes simultaneously. Also, as suggested by Feng *et al.*, we would expect a singlet excimer to have the same sign of MFE as the singlet state. This may explain why the optimisation to the 700 nm lineshape is unstable. From these two initial tests, we hypothesise that the emissive species must be further removed from the S_1 state.

We attempt another model, which is perhaps more unconventional, but important to rule out. Model 3 in (e) considers that the triplet states go on to form an emissive species. The hypothesis is that the triplet, which is more mobile, finds a defect in the morphology which then allows for emission. This is rather unlikely from an energetic standpoint, as the wavelength would be much closer to that of the triplet energy in the near-IR, rather than at 700 nm, close to the singlet energy. Nonetheless, we test this model to rule out such processes. Again, we observed the same results, that the lineshapes fit the innermost peak, but do not capture the additional extrema for the 700 nm lineshape. This is again perhaps expected, as there is not a secondary spin mixing step.

From these three simulations, we perhaps can rule out some of the more ‘obvious’ models. Another model that could be considered in future work is the possibility of triplet-charge annihilation, as seen in organic photovoltaic materials [199, 200]. However, this phenomenon may be more appropriate when considering MFEs in electroluminescence.

To reiterate, with this methodology, we do not suggest that the 700 nm lineshape could not be reproduced by these models, but rather that these models cannot *simultaneously* reproduce the 600 nm and 700 nm lineshapes within this parameter space from our initial investigation. Now that these models have been addressed, we consider another model.

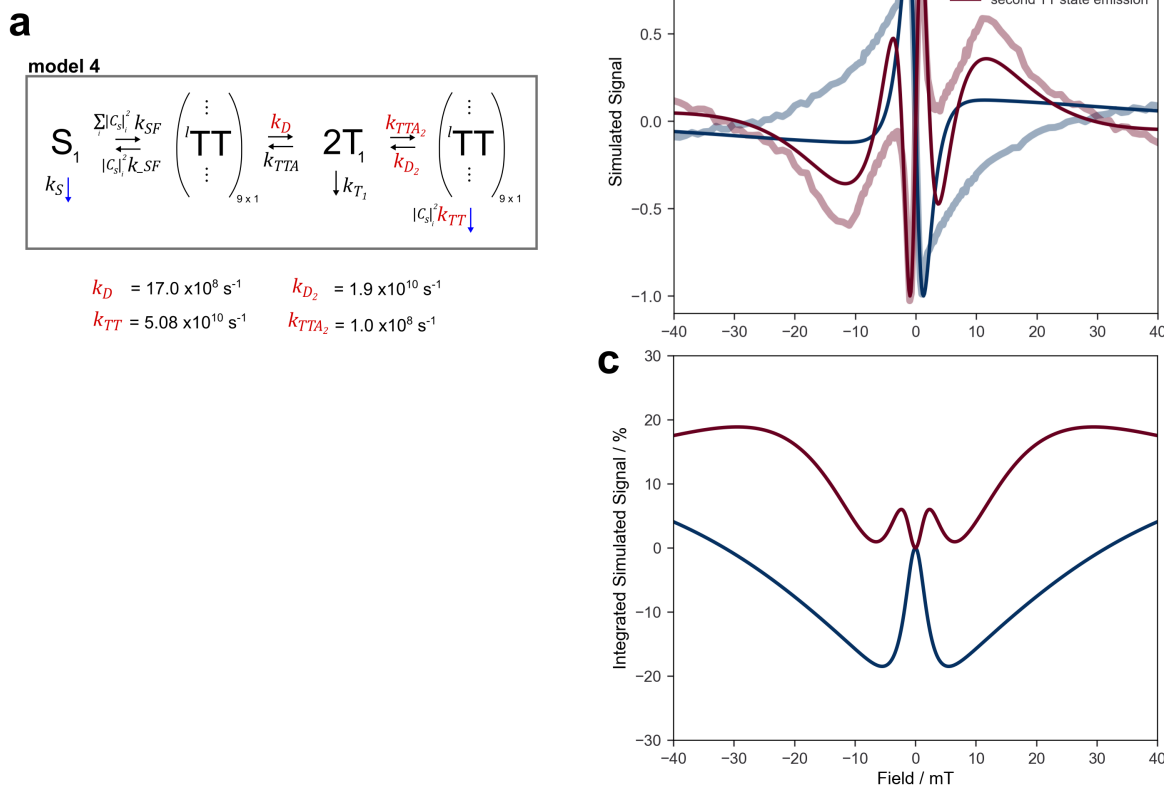


Figure 5.9: A potential model for understanding the two modMPL lineshapes, including the reformation of a triplet pair which emits, but cannot return to the S_1 state. The kinetic parameters allowed to change under optimisation are highlighted in red. Results of the optimisation are shown in **(b)** and **(c)** where the S_1 emission is fitted to the *600 nm lineshape*, and the second TT pair emission is fitted to the *700 nm lineshape*. The unnormalised, integrated lineshapes are shown in **(c)**.

In **Figure 5.9** we consider a model where the free triplets recombine to form a triplet pair state, that can either emit or dissociate into free triplets, but crucially cannot return to the singlet state. We will postulate on the physicality of this model momentarily, but we will first consider the results and their relation to our earlier stipulations for a kinetic model. The rate equation matrix for model 4 is given in **Appendix B Equation B.1**.

The lineshapes for the S_1 emission and secondarily formed TT pair emission are shown in **Figure 5.9 (b)**, with very good alignment to *both* the *600 nm* and *700 nm lineshapes* simultaneously. The peak positions of the *700 nm lineshape* in particular are well captured, with only discrepancy between the ratios of the peak heights. The shoulder of the *600 nm lineshape* is not well reproduced. However, as the shoulder could be a result of many processes, such as

broadening due to many angles being averaged over within the film, larger values of J being exhibited, or even perhaps some degree of modulation amplitude distortion in the data, we deem that good alignment with the peak position is satisfactory for the meanwhile.

When we consider the integrated, unnormalised lineshapes in (c), we note that the MFE values of $\sim 20\%$ are not unreasonable when compared to the values of 5% MFE at low field with magPL experiments (**Figure 4.3**).

We postulate that this model was most successful for a number of reasons. The reformation of a secondary triplet pair through TTA satisfies the ‘bimolecular’ nature of the *700 nm lineshape*, and would necessarily give a lineshape that is inverted in sign with respect to the S_1 lineshape. We included a second spin selection process, whereby the emission of the TT pair depended on the degree of singlet character. This perhaps allows for a change in the lineshape and the inclusion of more extrema for the second modMPL lineshape. Overall, this model 4 is not entirely dissimilar to model 1, *except* that by considering two distinct populations of TT pairs in model 4, it necessitates that the emission can only occur when the TT pair is formed from TTA, and not from SF from the S_1 state, as is possible in model 1.

This model suggests that TTA forms two subpopulations of the TT pair, one population that can continue to the S_1 state, and one population that undergoes some degree of energetic change, whether relaxation of the excited state, or destabilisation of the ground state, such that it can emit at a wavelength redder than the S_1 fluorescence. The formation of either TT pair population from free triplets is governed by k_{TTA}/k_{TTA_2} , which are $6 \times 10^7 \text{ s}^{-1}$ and $1 \times 10^8 \text{ s}^{-1}$ respectively. This indicates the emitting TT pair forms faster, and thus has significant emission intensity, as observed. The physical difference between the two TT populations is not established, but as we earlier noted that TT pairs 1-2 and 3-4 are indistinguishable in modMPL lineshape, it remains a plausible explanation that one of the pairs can reform the singlet, whilst the other leads to emission. Further examination of the two pairs with theoretical methods such as DFT would be needed to support this hypothesis further.

For kinetic model 4, variation of each term, parameter-by-parameter, is included in **Appendix B**, with the impact on the *600 nm lineshape* in **Figure B.4** and the *700 nm lineshape* in

Figure B.5. Unnormalised, integrated lineshapes of both are given in **Figures B.6** and **B.7** respectively.

Overall, model 4 works well to describe both lineshapes, and to some degree has physical interpretation. There remain some unanswered questions, such as why the secondary population of the TT state cannot reform the singlet, how it gains oscillator strength for emission, and why this emission is redder. It is also possible that the secondary population of the TT state goes on to form an emissive species, such as an excimer or a trap, that is the origin of this red emission.

From the simulated lineshapes from model 4, we applied the SVD coefficients for each of the two lineshapes to reconstruct the raw data for the spherulite film. Taking the wavelength series, with coefficients shown previously in **Figure 4.9**, we simulated four lineshapes for the different wavelength measurements. Comparison to the raw data for each measurement is shown in **Figure 5.10**.

With the exception of the 600 nm data in **(a)**, data for each wavelength is very well reproduced in peak position and x -axis crossings. The ratios of the peaks are not as well reproduced, and finding the origin behind this discrepancy is of interest. However, as previously stated, there are a number of possible reasons behind this discrepancy. The data for the 600 nm reproduces the peak position well, but not the peak shoulder or x -axis crossing. A deeper assessment of factors such as exchange coupling, angle averaging, and modulation amplitude distortion is required to further understand this discrepancy.

Using the SVD coefficients for the fluence series at 700 nm from **Figure 4.8**, the raw data for four low fluence measurements are simulated in **Figure 5.11**. Again, for the lineshape most similar to the *600 nm lineshape*, the data at 5.6 mW cm^{-2} , the simulated data does not reproduce the shoulder or x -axis crossing. However, for the remaining fluences, the reconstructed data performs well.

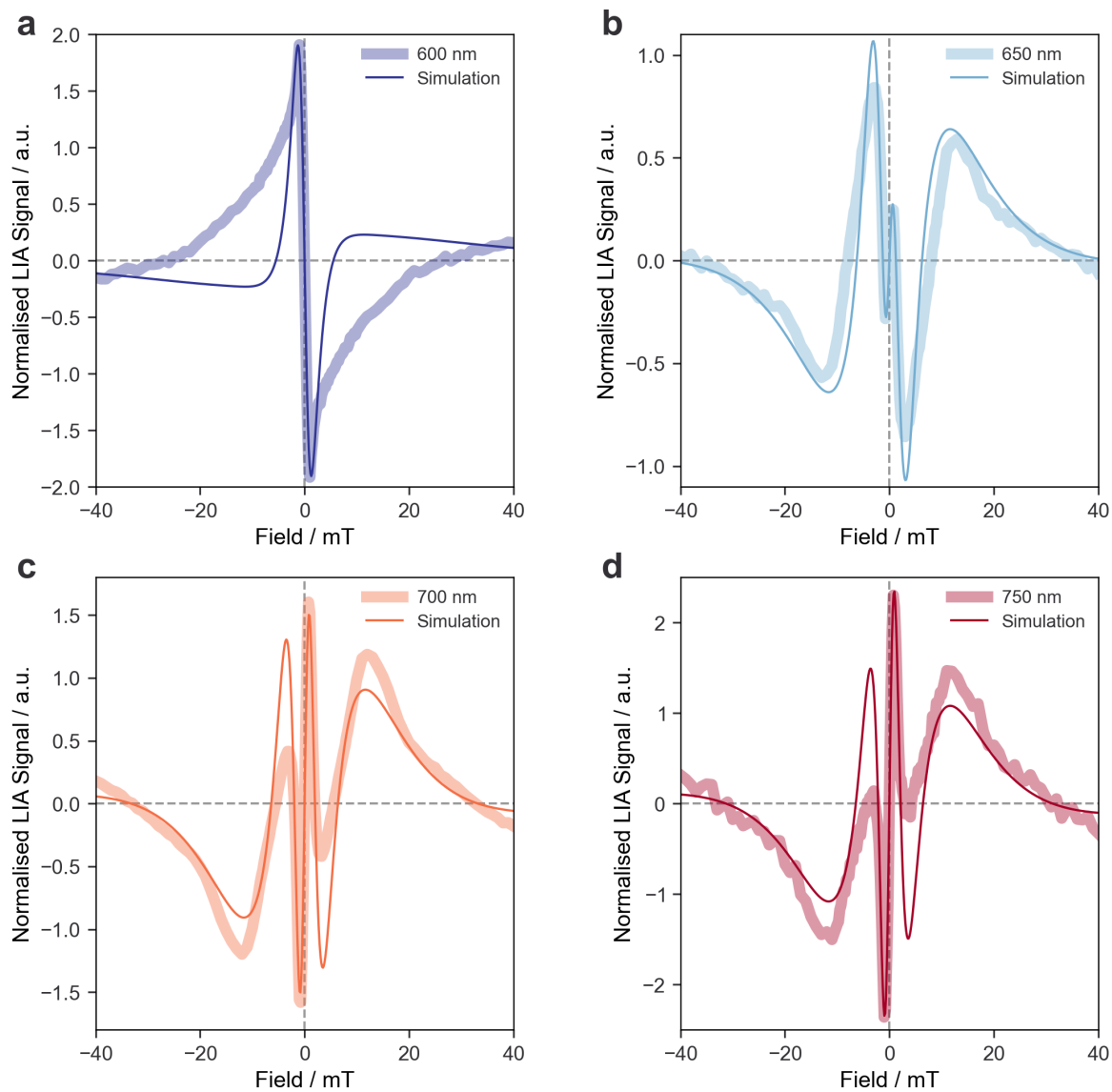


Figure 5.10: Reconstructing the raw wavelength series data for the spherulitic film, using the simulated lineshapes from **Figure 5.9** and SVD coefficients obtained in **Figure 4.9**.

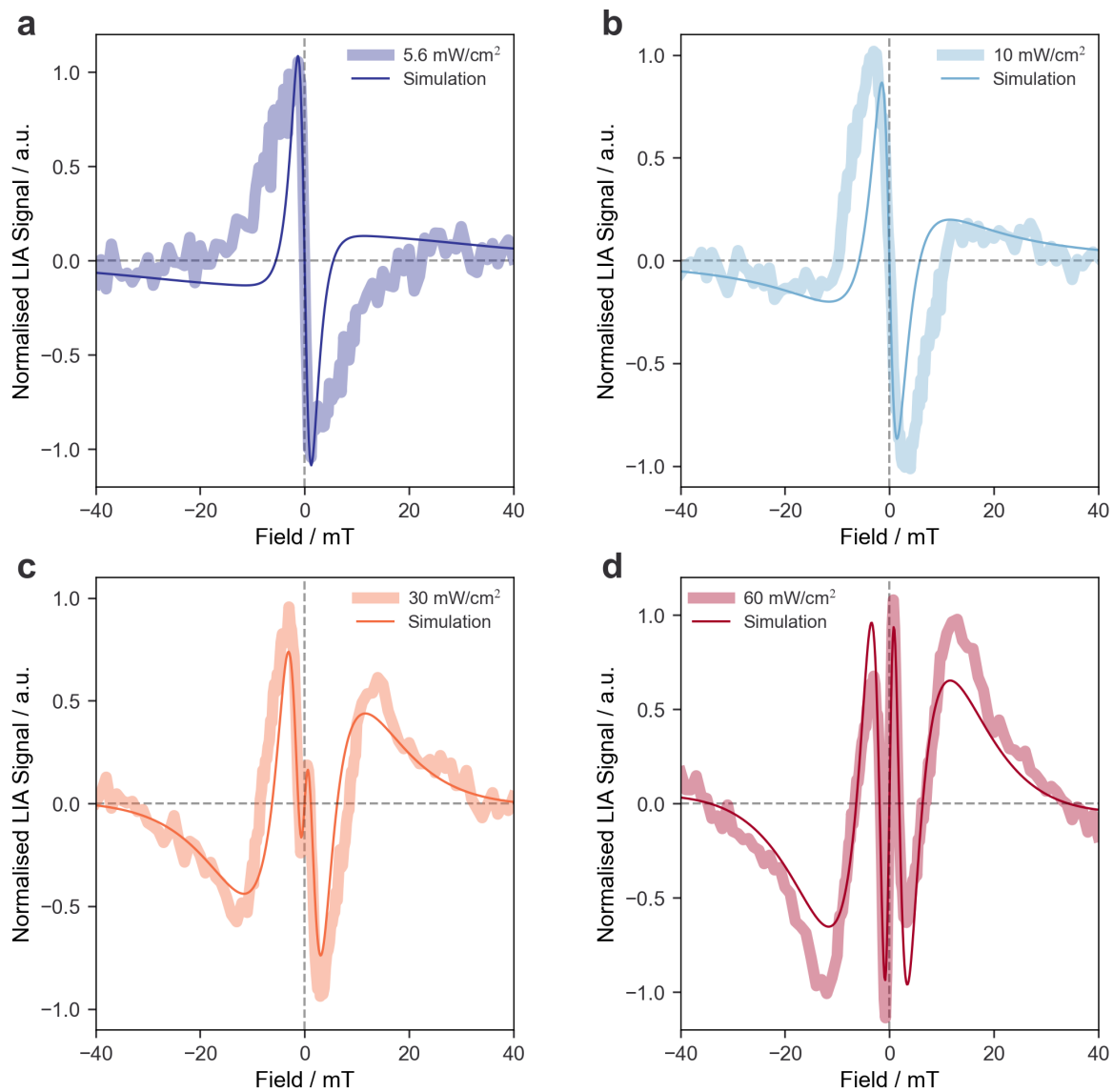


Figure 5.11: Reconstructing the raw 700 nm fluence series data for the spherulitic film, using the simulated lineshapes from **Figure 5.9** and SVD coefficients obtained in **Figure 4.8**.

5.6 Discussion and Conclusion

In this chapter, we have explored a number of different kinetic models to understand the *600 nm* and *700 nm* lineshapes from modMPL. We took two approaches, firstly to fit the lineshapes to linear combinations of simulated lineshapes with different parameters, and secondly to find a photocycle that could simultaneously simulate the two lineshapes with one model. Each approach has its own successes, limitations, and points of interest.

The first approach of taking a linear combination of lineshapes did well to identify possible component lineshapes using only a simple model, which depended on the rate of dissociation of the TT pair, and used the ZFS parameters of the triplet and quintet states, D_T and D_Q as identified by Yunusova *et al.* [50]. The linear combinations did well to reproduce the two desired lineshapes, but were limited in their physical interpretability. We rationalised, though, that this approach could have a clear explainability, as different regions of morphology could result in different kinetics, for which we observe an ensemble average of the regions. In future work, this method could be expanded to consider that not only do the regions have different rate constants, but they could also exhibit completely distinct photophysics, with more than one kinetic model being considered.

We then considered a number of possible photocycles to model both lineshapes simultaneously. We tentatively rule out a number of possible cases, such as the *700 nm lineshape* originating from an excimer of the S_1 state. Models for future consideration could invoke triplet-charge annihilation, but was not considered here [199, 200]. We instead find that a photocycle which invokes a sub-population of the TT pair, formed only *via* TTA and unable to return directly back to the S_1 , reproduces both lineshapes well. With this model, we were able to reconstruct the raw data at different wavelengths and fluences very well from the SVD coefficients previously identified. While discrepancy between the simulations and the shoulder of the *600 nm lineshape*, and peak ratios for the *700 nm lineshape*, requires further investigation, the reconstruction of the peak positions across each wavelength and fluence was well matched.

This simple model performed very well. To some degree, it confirms our earlier suspicions that the *700 nm lineshape* was originating from TTA of diffusing triplets. This would qualitatively explain both the fluence dependence of the lineshape, and the appearance only for polycrystalline samples where triplet diffusion lengths are long enough for annihilation events to occur in substantial yield. However, the model still leaves some open questions:

- Why would a sub-population of TT states form, and what could prevent them from reforming the S_1 state?
- Why would this sub-population give rise to a red emission? Has the state somehow been energetically stabilised? Is a new emissive species, such as a trap or an excimer, formed from this TT sub-population?
- Is this red emission ultimately a loss pathway, and can we quantify its impact on singlet fission performance?

As we earlier identified, these simulations are unable to distinguish between the subtle changes between the triplet pairs 1-2 and 3-4 within the unit cell. It is therefore possible that the formation of different TT pairs within the unit cell may result in these populations. However, this hypothesis is speculative and would require further investigation to understand how the different TT pairs may impact the energetic landscape to give rise to a red emission, or the preferential formation of a new emissive species.

Future work for this promising study takes two outlooks. Firstly, it is of interest to seek the *700 nm lineshape* in other material systems. Confirming the origin of this lineshape and assessing the applicability of our kinetic model beyond TIPS-Tc would enhance the robustness of our findings in the context of singlet fission systems. The second avenue is to develop a more holistic and sophisticated model. In particular, including a bimolecular rate term would be important to further understand the fluence dependence. Inclusion of spin relaxation effects through the use of spin density matrix modelling could also prove insightful. Furthermore, distinction between the strongly and weakly coupled triplet pair would be of interest to further unify these findings within the existing literature.

To gain a deeper understanding of the weak and strong exchange coupling of the triplet pair, it is important to contextualise the results of modMPL with other experimental methods. The simulations in this thesis relied on very small values of J , which align with expectations for low-field magnetic field effects (which depend on small J values to facilitate spin mixing in the triplet pair state). However, a noticeable discrepancy persists between low-field measurements, and the high J values observed in high-field or resonance measurements. The broader question of why we observe two distinct regimes of J coupling in singlet fission systems remains unsolved. Nevertheless, the versatility and sensitivity of modMPL position it as a valuable tool to bridge gaps in our understanding of the underlying spin physics, warranting further investigation.

As to the future directions of the simulations themselves, developing a simulation routine akin to EasySpin for ESR simulations would accelerate the progression of modMPL as a screening tool for singlet fission. This would facilitate a more in-depth exploration of new materials using modMPL, potentially allowing for a rough estimation of zero-field splitting parameters through the application of a simple kinetic model. Such a tool would serve as a valuable asset to the singlet fission community.

Chapter 6

Aza-Cibalackrot: Altering Molecular Design for Singlet Fission

Finding new, stable singlet fission chromophores is a key goal within the community. The search for new molecules relies on design principles and criteria such as energetics. However, molecules identified as candidates may not undergo singlet fission due to morphology. In this chapter, we consider previously identified and highly stable cibalackrot, and offer a simple molecular alteration, rationalised from crystal structures, to induce singlet fission behaviour. We return to conventional techniques, and employ ultrafast spectroscopy to investigate thin films of a novel molecule, aza-cibalackrot, to assess whether singlet fission has been “turned on”.

This project was conceptualised by Prof. Hugo Bronstein. The materials in this Chapter were synthesised by Dr Michael Purdy. Single crystal growth and XRD was performed by Merina Corpinot. GIWAXS of thin films was performed by Dr Daniel Toolan. TCSPC was performed by Lars Van Turnhout. Thin film preparation and spectroscopic investigation was performed by the author.

This content of this chapter is adapted from the resulting publication *Aza-Cibalackrot: Turning on Singlet Fission Through Crystal Engineering*, available from <https://pubs.acs.org/doi/10.1021/jacs.3c00971> [21]. This publication is the result of collaboration with Michael Purdy^a (joint first author), Kealan Fallon^a, Daniel Toolan^d, Peter Budden^b, Weixuan Zeng^a, Merina

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6.1 Introduction

The design of singlet fission candidates is non-trivial and requires careful optimisation of two key criteria: correct energetic alignment, and appropriate intermolecular coupling. Meanwhile, this optimisation must not come at the cost of molecular stability or feasibility for device applications.

In the search for new singlet fission materials, most studies are considered from an energetic standpoint. With density functional theory (DFT), vast computational studies have been undertaken to predict whether a material should undergo fission by meeting the $E(S_1) \approx 2E(T_1)$ requirement, and whether it would be suitable for silicon device applications from $E(T_1) > 1.1\text{eV}$ [19, 97, 134]. In one such study in recent work by our group, Fallon *et al.* investigated indolonaphthyridine thiophene (INDT) [19, 20].

INDT, an annulated indigo derivative with thiophene groups flanking an aromatic core, has singlet fission propensity when substituted with electron withdrawing groups (such as Br or CN). INDTs also boast superior photo- and ambient stability compared to other popular SF systems. They presented a versatile molecule, where the substitutions of the core impacted the singlet fission properties and triplet energies. This is a great example of how one might consider adapting or changing a molecular structure to impact the energetics for singlet fission. However, the triplet excitons produced in INDT variants are below the 1.1 eV benchmark required for silicon photovoltaics. Replacing the thiophene groups of INDT with phenyl groups hypsochromically shifts the triplet state to above 1.1 eV, giving a molecule known as cibalackrot [201].

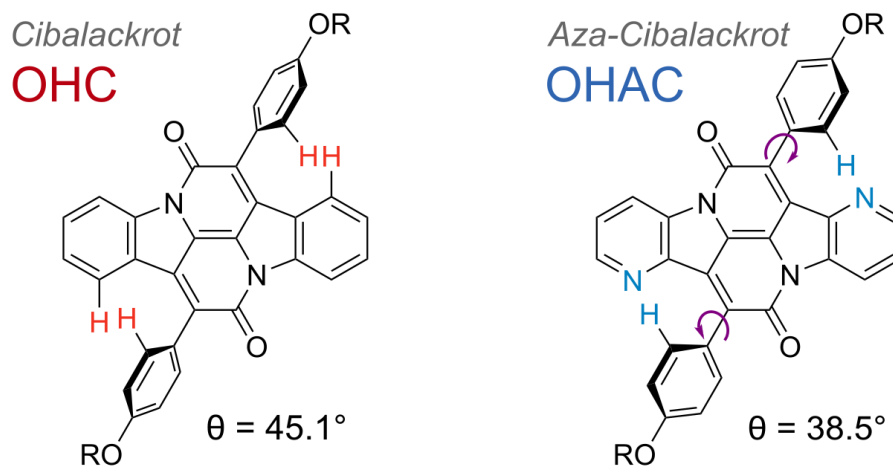


Figure 6.1: Molecular structures of cibalackrot (R = octyl-hexyl, OHC, shown in red) and novel aza-cibalackrot (OHAC, blue). Inclusion of nitrogen atoms in the aromatic core reduces torsion of the peripheral phenoxy rings while maintaining a favourable $T_1:S_1$ energy ratio. Increased planarity of the phenoxy rings with respect to the aromatic core from $\theta = 45.1^\circ$ (taken from the crystal structure) to $\theta = 38.5^\circ$ (DFT calculated ground state optimized structure at the M062X/G** level by Dr Michael Purdy) in OHAC is postulated to improve intermolecular orbital overlap efficiency required for singlet fission.

Cibalackrot is a historic and stable organic dye, and highly attractive singlet fission candidate [13, 20]. Previous calculations have been reported which suggest it to have ideal energetics for singlet fission [13]. However, a recent study by Ryerson *et al.* confirmed that cibalackrot does not undergo efficient singlet fission due to non-optimal molecular packing [132]. Thus, while the energetic alignment is satisfied, the molecule does not have the desired intermolecular coupling due to morphology.

The solid-state packing of singlet fission materials can be determined via X-ray crystallography of molecular single crystals. Short interchromophore distances and a slip-stacked orientation (along with others) have been shown to facilitate sufficient intermolecular coupling for rapid SF [202–205]. Studies have been previously made to try invoking the desired crystal packing for singlet fission, through changing side groups or solubilising chains [95, 130, 142, 143]. Here, we offer an alternative approach.

Through analysis of the crystal structure of cibalackrot, we hypothesise that a protic clash in the aromatic core creates an intramolecular twist that is disrupting the intermolecular coupling, and prohibiting singlet fission. We therefore replace a carbon in the aromatic core for a nitrogen to remove the protic clash and enhance the intermolecular coupling, whilst aiming

to cause minimal impact on the energetic landscape of the material. This inclusion of the aza-indole moiety is shown in **Figure 6.1**, highlighting the reduction of the intramolecular twist. We present the first synthesis of an aza-cibalackrot, and aim to “turn on” singlet fission with this crystal engineering approach. This differs from conventional molecular design approaches, such as altering the energetics with electron donating/withdrawing groups, or side chain engineering. We assess the success of our crystal engineering with structural methods and ultrafast spectroscopy of thin films of the novel aza-cibalackrot in comparison to the parent molecule cibalackrot.

6.2 Crystal Structure Engineering

The molecular structures of cibalackrot (octyl-hexyl-cibalackrot, OHC) and modified aza-cibalackrot (octyl-hexyl-aza-cibalackrot, OHAC) are shown in **Figure 6.1**. In both OHC and OHAC, the central aromatic core is flanked by phenoxy rings. For OHC, these phenoxy rings are twisted out of plane by 45.1° due to a protic clash with the aromatic core. By substituting the associated C-H on the aromatic core with a nitrogen atom, which is sterically smaller. Through DFT calculations performed by Dr Michael Purdy, the dihedral angle of the phenoxy rings is predicted to decrease to 38.5° . This has important consequences on the crystal structure, as explained with **Figure 6.2**.

The single crystal X-ray diffraction (XRD) of octyl-cibalackrot (OC, **Figure 6.2 (a)**) yielded a crystal structure as shown in **Figure 6.2 (b)**. Crystal growth and X-ray crystallography performed and analysed by Dr Merina Corpinot at University College London. The crystal structure of OC highlights the disruption the flanking phenoxy rings has on the intermolecular interactions. Short contact interactions (yellow lines) are found between the aromatic cores and the phenoxy rings, rather than being found between the two cores of the neighbouring molecules. The phenoxy rings are interrupting the desired $\pi - \pi$ interactions between the two aromatic cores. Unfortunately, similar examination of the novel aza-cibalackrot was unsuccessful due to difficulties with single crystal growth. However, from the DFT results, we predict that the aza-substitution will twist the phenoxy rings in plane, and facilitate the desirable close contact interactions between the two aromatic cores.

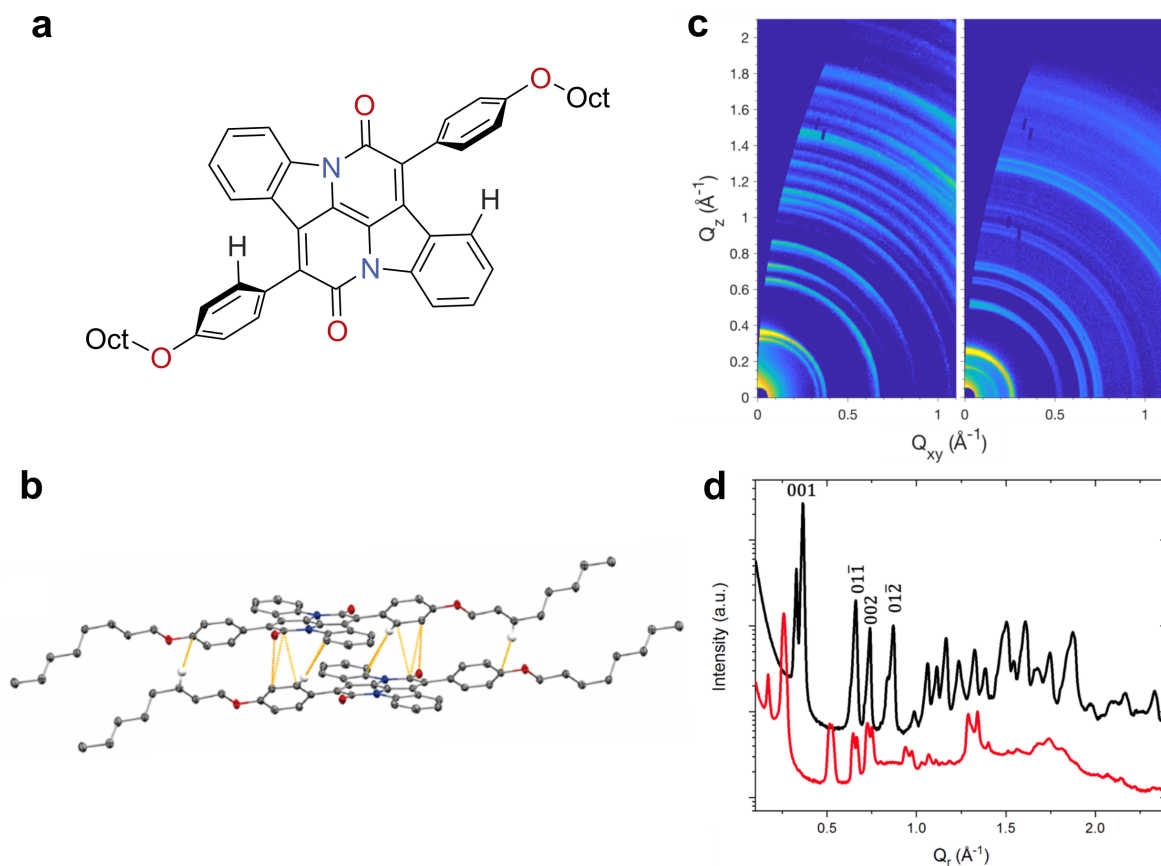


Figure 6.2: Understanding cibalackrot crystal packing: **(a)** Molecular structure of octyl-cibalackrot (OC) with corresponding atomic colour coding as in **(b)**. **(b)** Perspective views of stacked cibalackrot molecules in the crystal structure of OC highlighting: short contacts between the twisted outer phenoxy groups and chromophore cores of neighbouring cibalackrot molecules (yellow lines), and the lack of short intermolecular contacts between the cibalackrot chromophore within the OC stacks. Crystallography performed by Dr Merina Corpinot. **(c)** Two-dimension grazing incidence scattering data for OC (left) and OAC (right) drop cast from chlorobenzene, with corresponding radial integrated data in **(d)** (OC = black line, OAC = red line), performed by Dr Daniel Toolan.

In lieu of single crystal information, we present grazing incidence wide angle X-ray scattering (GIWAXS) of thin films, performed by Dr Daniel Toolan. The GIWAXS data (**Figure 6.2 (c) & (d)**) of OC and OAC (octyl-aza-cibalackrot) thin films drop cast from chlorobenzene indicate both are highly crystalline, with many large, randomly oriented crystal grains. For OC, the thin film packing is comparable to the single crystal packing, allowing assignment of the radially integrated data in **(d)**. For OAC, the molecular modification has had a considerable impact on the crystal packing. We speculate that reducing the torsion of the flanking phenoxy rings impacts how the solubilising octyl chains arrange within the unit cell. For OC, the octyl chains are interdigitated (like locking fingers), while for OAC they are not interdigitated. This

	OC unit cell parameters (obtained via single crystal X-ray diffraction)	OAC unit cell parameters (estimated from GIWAXS data)
$a / \text{\AA}$	5.3	5.3
$b / \text{\AA}$	10.4	13.4
$c / \text{\AA}$	17.1	26.0

Table 6.1: Unit cell parameters of octyl-cibalackrot (OC) and octyl-aza-cibalackrot (OAC) from single crystal XRD and GIWAXS respectively. Increase in parameters b and c for OAC are likely due to changes in interdigitation of octyl packing groups.

was repeated for OHC and OHAC, however the GIWAXS showed highly amorphous films with lamellar stacking. The unit cell parameters for OAC were estimated through simulation of the GIWAXS data, as presented in **Table 6.1**. The increase in unit cell parameters b and c are representative of the changes in the octyl group interdigitation.

6.3 Steady State Characterisation

The steady state absorbance of OHC and OHAC are presented in **Figure 6.3**. The solution state absorption spectra (solid line) of OHC and OHAC share similar vibrational progressions, with OHAC red shifted with respect to OHC. Despite the red-shift, OHAC still boasts a bluer absorbance than the previously reported INDTs [19]. To investigate the cause of this red shift, time-dependent density functional theory (TD-DFT) calculations were performed by Dr Michael Purdy, shown in **Table 6.2**. The increased planarity of OHAC appears to increase the delocalisation of the spin density over the outer phenoxy rings, and the energies of the singlet and triplet excited states are stabilised compared to OHC, giving rise to a redder absorption.

Comparing the absorbance of solution and thin films (**Figure 6.3**, solid and dashed lines respectively), a hypsochromic shift of the λ_{max} is seen for both OHC and OHAC in the thin film. This is indicative of preferential slipped stack H-aggregate formations in the films [63, 64, 206]. Measurements of photoluminescence quantum efficiency (PLQE) at 520 nm excitation showed highly emissive solutions for OHAC (74%) and OHC (86%) and a large quenching of photoluminescence (PL) in thin film for both, with PLQEs of 0.5% and 4% respectively, as summarised in **Table 6.3**. This quenching of PL in the thin film can be attributed to both

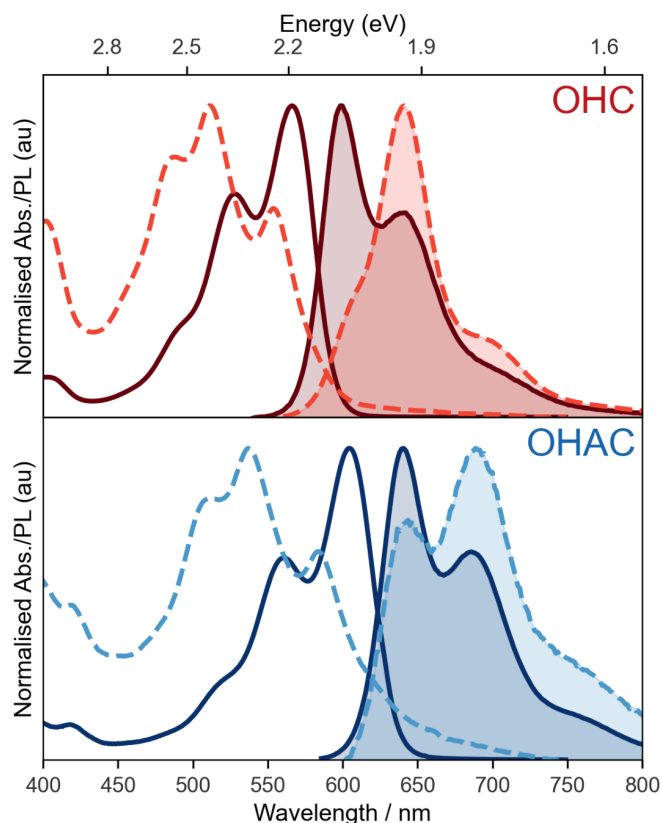


Figure 6.3: Absorbance (line) and photoluminescence (shaded) spectra of OHC (red) and OHAC (blue) in chlorobenzene solution (darker, solid line) and thin films (dashed line) prepared by drop casting.

subradiance potentially due to H-aggregation [63], and new non-radiative pathways becoming active in the solid state, such as singlet fission. The PL spectra obtained by PLQE measurements in **Figure 6.3** show a suppressed 0-0 emission peak in thin film, which is attributed to both H-aggregation effects and self-reabsorption.

Time-resolved PL measurements of OHAC, shown in **Figure 6.4** indicate a rapid PL decay of 7.5 ± 0.5 ns in solution, which is reduced to 2.53 ± 0.03 ns in thin film. Due to the very low PLQE of the OHAC thin film (0.5%), it is likely that most photogenerated singlet excitons have a different, non-radiative fate. The quenching of the singlet emission lifetime in the thin film suggests that new pathways from the singlet state are being accessed in the thin film.

Molecule	Torsional Twist	S ₁ Energy	T ₁ Energy	T ₁ :S ₁ ratio	ηPh
	/ °	/ eV	/ eV	/ eV	/ %
OHC	45.1	2.30	1.24	0.53	12
OHAC	38.5	2.13	1.07	0.50	18

Table 6.2: Summary of data extracted from theoretical calculations performed on OHC and OHAC by Michael Purdy. Torsional twist take from DFT optimized ground state structures. The S₁ and T₁ energies are slightly reduced for OHAC, whilst a favourable T₁:S₁ ratio is maintained. The spin population density of the delocalised diradical on the outer phenoxy groups, ηPh, is increased for OHAC, which may account for the stabilisation of the singlet and triplet states.

		PLQE	Absorbance at 520 nm	0-0 transition	0-0 transition
		/ %	/ OD	/ nm	/ eV
OHAC	Solution	74	0.1	624	1.99
	Film	0.5	0.24	620	2.00
OHC	Solution	86	0.1	584	2.12
	Film	4.0	0.95	589	2.11

Table 6.3: Photoluminescence quantum yield, sample absorbance at laser excitation, and 0-0 transitions of aza- cibalackrot OHAC and cibalackrot OHC obtained from PQLE and UV-Vis measurements in thin film and solution (0.1 mg ml⁻¹, 1mm path length).

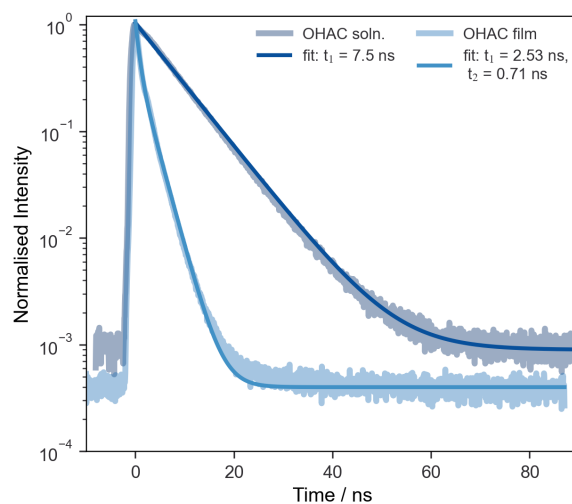


Figure 6.4: Time correlated single photon counting (TCSPC) traces of OHAC in both solution and thin film, demonstrating a quenching in the film compared to solution, indicating the presence of non-radiative processes in the thin film. (OHAC solution: $t_1 = 7.5 \pm 0.5$ ns, OHAC film: $t_1 = 0.71 \pm 0.01$ ns (from instrument response), $t_2 = 2.53 \pm 0.03$ ns). Excitation wavelength 510 nm, emission wavelength 645 nm.

6.4 Solution Transient Absorption

We investigate the dynamics of OHAC with transient absorption spectroscopy (TA). We begin by considering the dilute solution state dynamics, and perform triplet sensitisation experiments to assign the regions of interest for triplet state photoinduced absorption. We then examine the thin film dynamics to find evidence for singlet fission.

Nanosecond transient absorption spectroscopy (nsTA) was applied to OHAC in dilute solutions of two concentrations, as shown in **Figure 6.5**. Negative signals correspond to the PIA of the excited states, and positive signals correspond to GSB or stimulated emission. The spectra feature two positive features at 690 nm, attributed to stimulated emission (SE), and 630-650nm, which we assign as a combination of the SE and ground state bleach (GSB). A strong photoinduced absorbance (PIA) is centred at 910 nm, which we assign at the $S_1 \rightarrow S_n$ absorption. At both concentrations (3 mg ml^{-1} and 0.06 mg ml^{-1} , approximately 3 mM and 0.06 mM), there is negligible spectral evolution over the nanosecond timescale. We therefore rule out that intersystem crossing, a slow monomolecular process, is happening within OHAC in solution. This is confirmed by triplet sensitisation in the following section, which highlights the absence of triplet spectral features in this data. The singlet state decays rapidly with a lifetime of $5.8 \pm 0.1 \text{ ns}$, which is close to the S_1 fluorescence lifetime as recorded with TCSPC.

To further rule out any spectral evolution on the picosecond timescale, we performed psTA on the OHAC solution. The spectra at 1-2 ps is shown as a dashed line in **Figure 6.5 (a)**. A small artefact is present at 660 nm. Otherwise, the spectra at ps and ns match well, further confirming that only the photoexcited S_1 forms in solution.

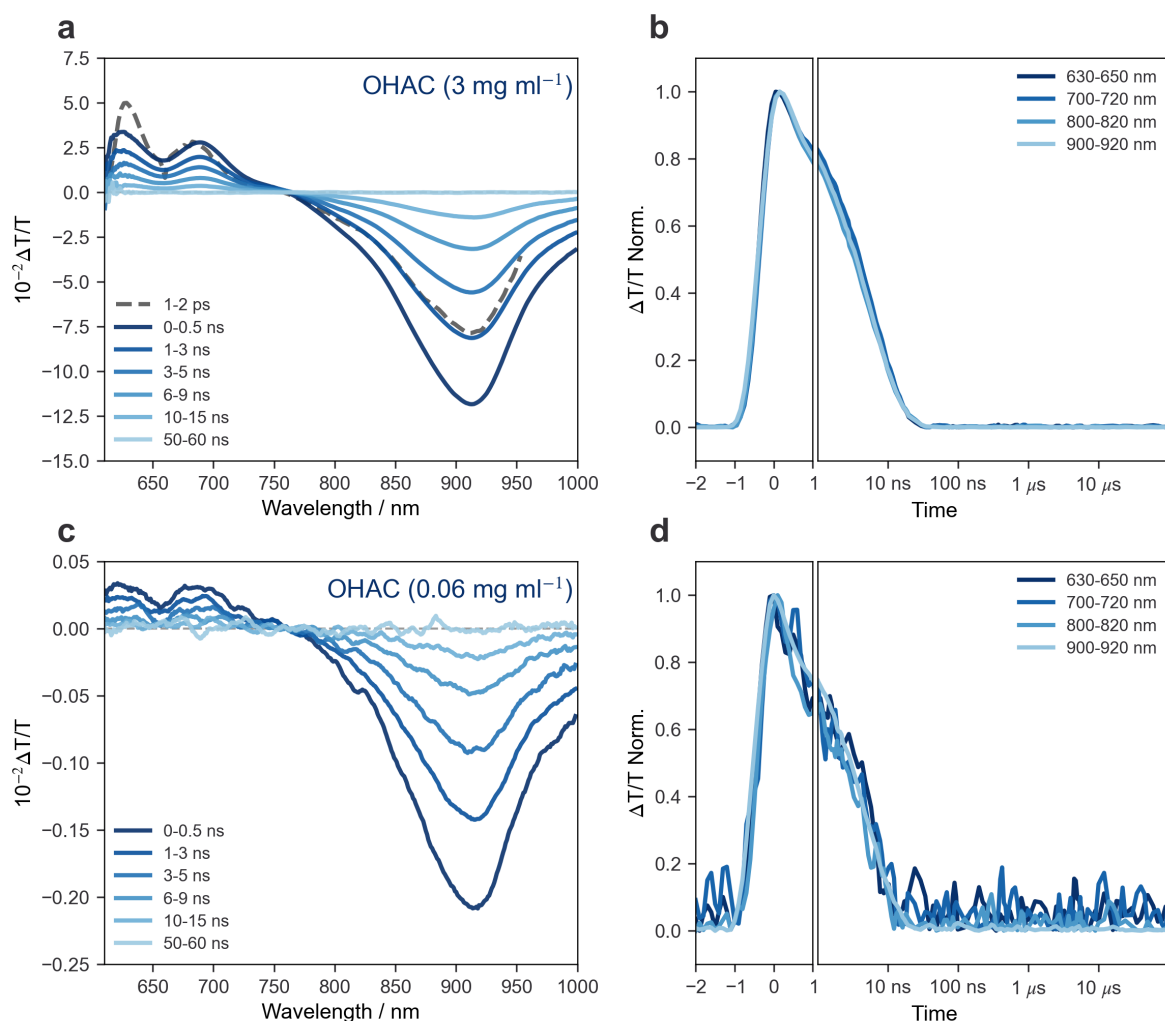


Figure 6.5: OHAC solution at two concentrations ((a) & (b), 3 mgml⁻¹, (c) & (d) 0.06 mgml⁻¹ (50x dilution), 2:1 toluene:THF, 200 μ m path length) transient absorption spectra on a nanosecond timescale. No spectral evolution indicated only one state present (S_1), ruling out intersystem crossing. There is rapid decay of S_1 state at both concentrations. (2.9×10^{-4} J cm⁻² excitation density at 630 nm). Spectrum at 1-2 ps (5.9×10^{-5} J cm⁻² excitation density at 550 nm) is shown in (a) (dashed line).

6.5 Triplet Sensitisation in Solution

To identify the spectral features of the triplet state, we performed triplet sensitisation in solution with two sensitisers: anthracene and meso-tetraphenyl-tetrabenzoporphine palladium complex, PdTPTBP.

Figure 6.6 shows the triplet sensitisation of OHC and OHAC with anthracene ($E(T_1)$ = 1.78-1.8 eV [98, 207]), chosen due to its high absorbance in the UV (355 nm), high transmission in the visible, and high triplet yield [208, 209]. Excitation at 355 nm causes some initial

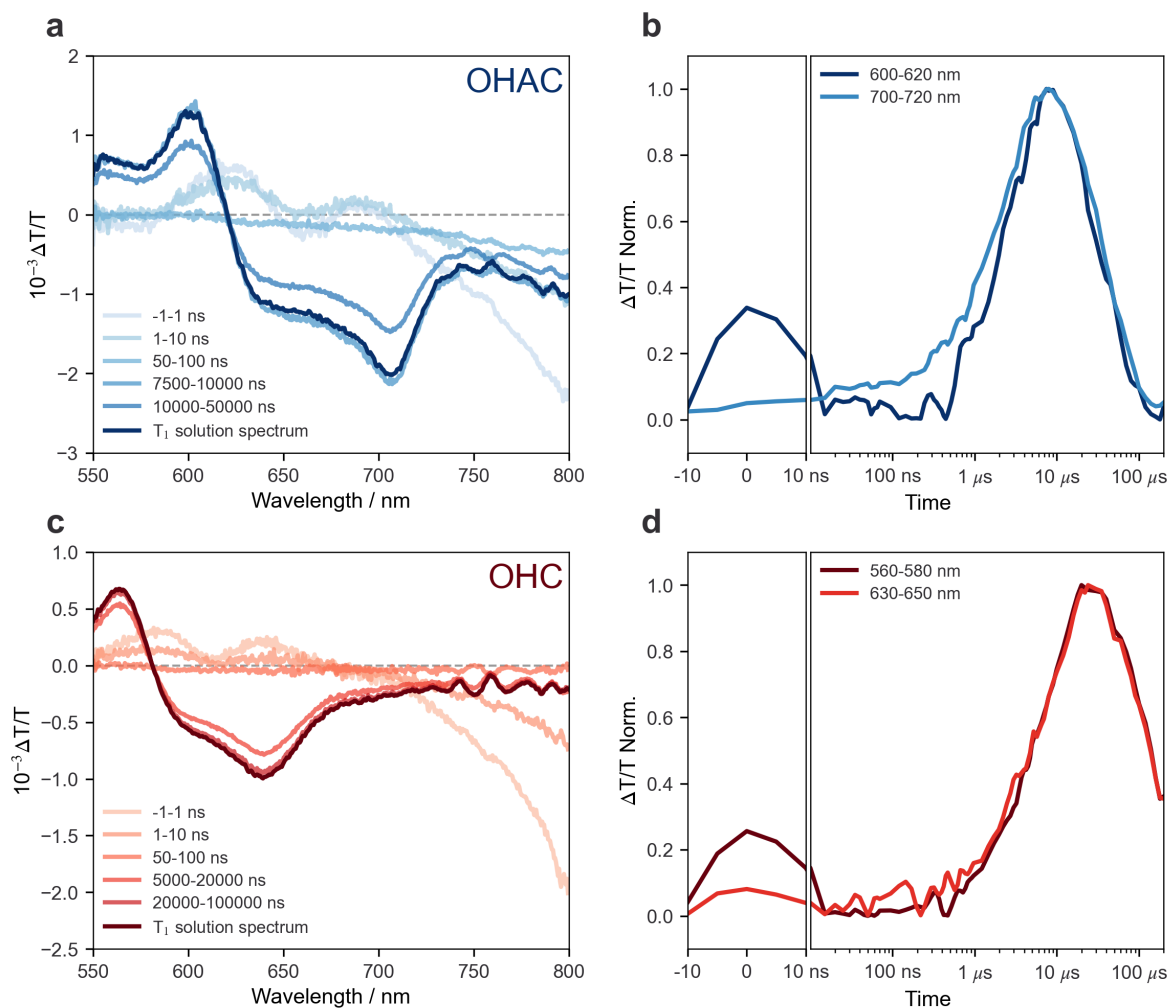


Figure 6.6: Triplet sensitization measurements in solution of OHAC (a & b) and OHC (c & d), using anthracene as a sensitizer with 355 nm photoexcitation. Measured with TA on a ns timescale. Excitation density $1.88 \times 10^{-4} \text{ J cm}^{-2}$ at 355 nm.

photoexcitation of the cibalackrots, seen at early times ($< 10 \text{ ns}$), giving spectra highly reminiscent of the solution state spectra in **Figure 6.5**. This singlet spectrum for OHC and OHAC decays rapidly, as before, and at late times ($> 1 \mu\text{s}$) the solution triplet spectrum is observed. The triplet PIA is visible between 630-730 nm for OHAC and 580-670 nm for OHC. The GSB is clearly visible for each, with OHAC redshifted with respect to OHC as expected from the UV-Vis spectra. The triplet signal persists for tens of microseconds. There are no visible signatures from the anthracene sensitizer throughout. The late time signal is averaged over a $20 \mu\text{s}$ window and recorded as the T_1 solution spectrum.

Sensitisation is repeated for OHAC in solution with PdTPTBP ($E(T_1) = 1.54\text{--}1.56 \text{ eV}$ [210, 211]), shown in **Figure 6.7**, excited at 633 nm [212, 213]. This is to confirm that PdTPTBP

is a suitable sensitiser for OHAC for thin film sensitisation.

Here, the PdTPPTBP has overlapping signatures with the OHAC. The solution spectra of OHAC are shown in (a) & (b), as shown in **Figure 6.5**. The PdTPPTBP sensitiser is shown in solution in **Figure 6.7 (c) & (d)**, and a 10:1 mix (3 mM: 0.3 mM) of OHAC:PdTPPTBP shown in (e) & (f). The spectra of PdTPPTBP in (c) & (d) show the GSB of the porphyrin Q-band at 630-650 nm [210], and a broad PIA from 650-950 nm that shows negligible spectral evolution over the nanosecond timescale. The PdTPPTBP signal decays with a lifetime on the order of 10 μ s. In the 10:1 mix, the spectra and kinetics are colour coded to the relevant species, with OHAC initial photoexcitation in blue, the PdTPPTBP in green, and the new species assigned as the OHAC triplet in purple.

The initially excited OHAC singlet state decays rapidly, and is outlived by the PdTPPTBP signal. The PdTPPTBP signal is then quenched, giving rise to the OHAC triplet signal as observed in **Figure 6.6**. These spectra are decomposed in **Figure 6.8** using SVD and kinetic modelling with an N=3 model. The lifetime of the initially excited OHAC S_1 state is 3.2 ± 0.3 ns, with the PdTPPTBP co-excited. The PdTPPTBP then transfers the triplet energy to the OHAC with a lifetime of 323 ± 67 ns, and the OHAC triplet then decays with a lifetime of 23 ± 1 μ s.

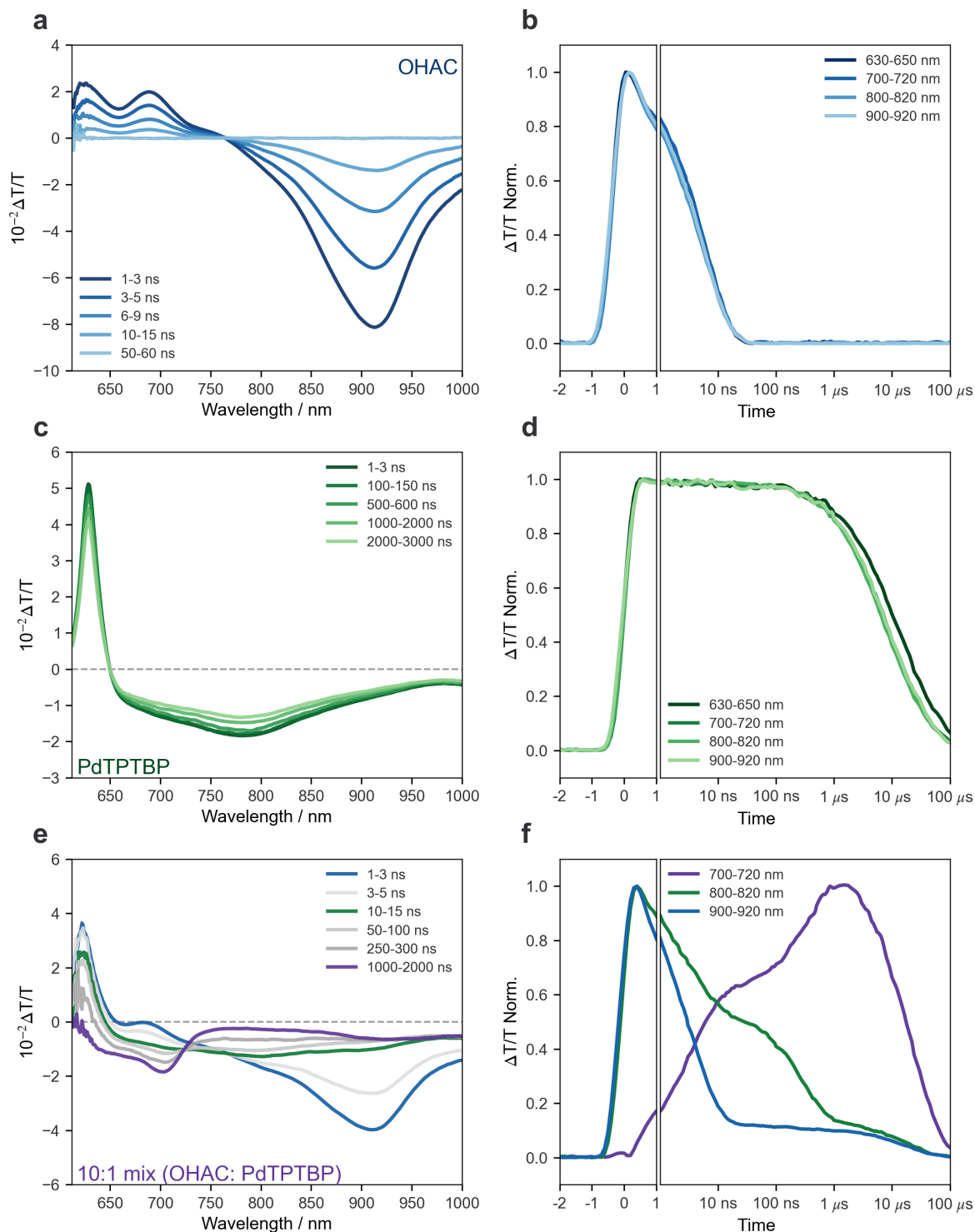


Figure 6.7: Triplet sensitization measurements in solution (200 μm path length) of OHAC using meso-tetraphenyl-tetrabenzoporphine palladium complex (PdTPTBP) as a sensitizer with 632 nm photoexcitation with a 10:1 OHAC:PdTPTBP ratio (3mM OHAC : 0.3 mM PdTPTBP). Excitation density $2.9 \times 10^{-4} \text{ J cm}^{-2}$

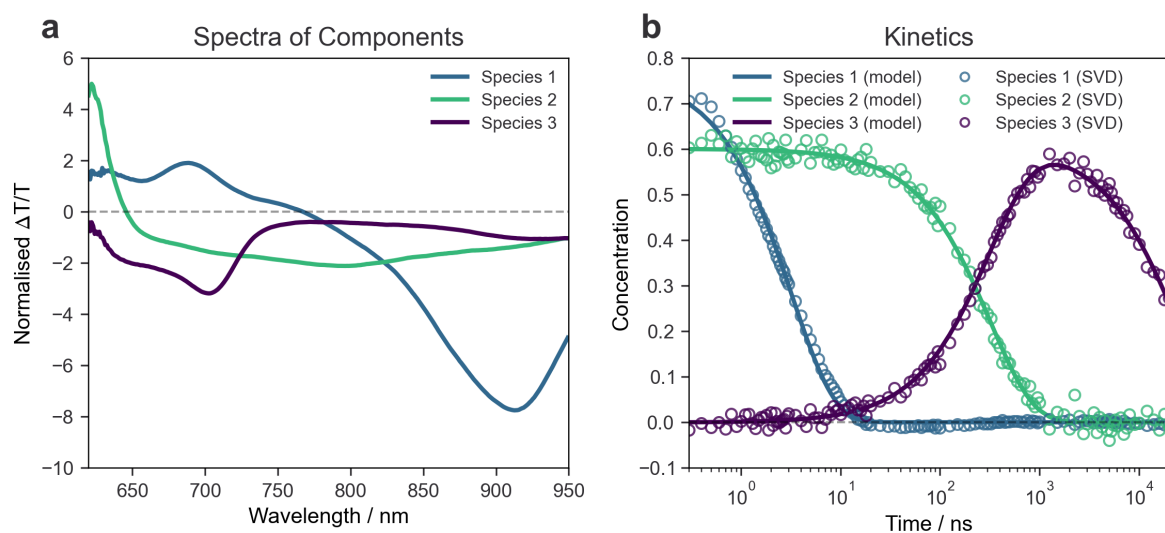


Figure 6.8: Decomposition of PdTPPTBP/OHAC sensitisation data using SVD and kinetic modelling (N=3 model, $A \rightarrow$; $B \rightarrow C \rightarrow$). Model scaled such that the spectral $\Delta T/T$ in (a) matches that of the neat solutions of the PdTPPTBP and OHAC respectively, so that the initial ‘concentration’ in (b) represents the fractional excitation of the solution in the mix compared to the neat solution, *i.e.* the PdTPPTBP is only 60% excited compared to the neat solution.

6.6 Triplet Sensitisation in Thin Film

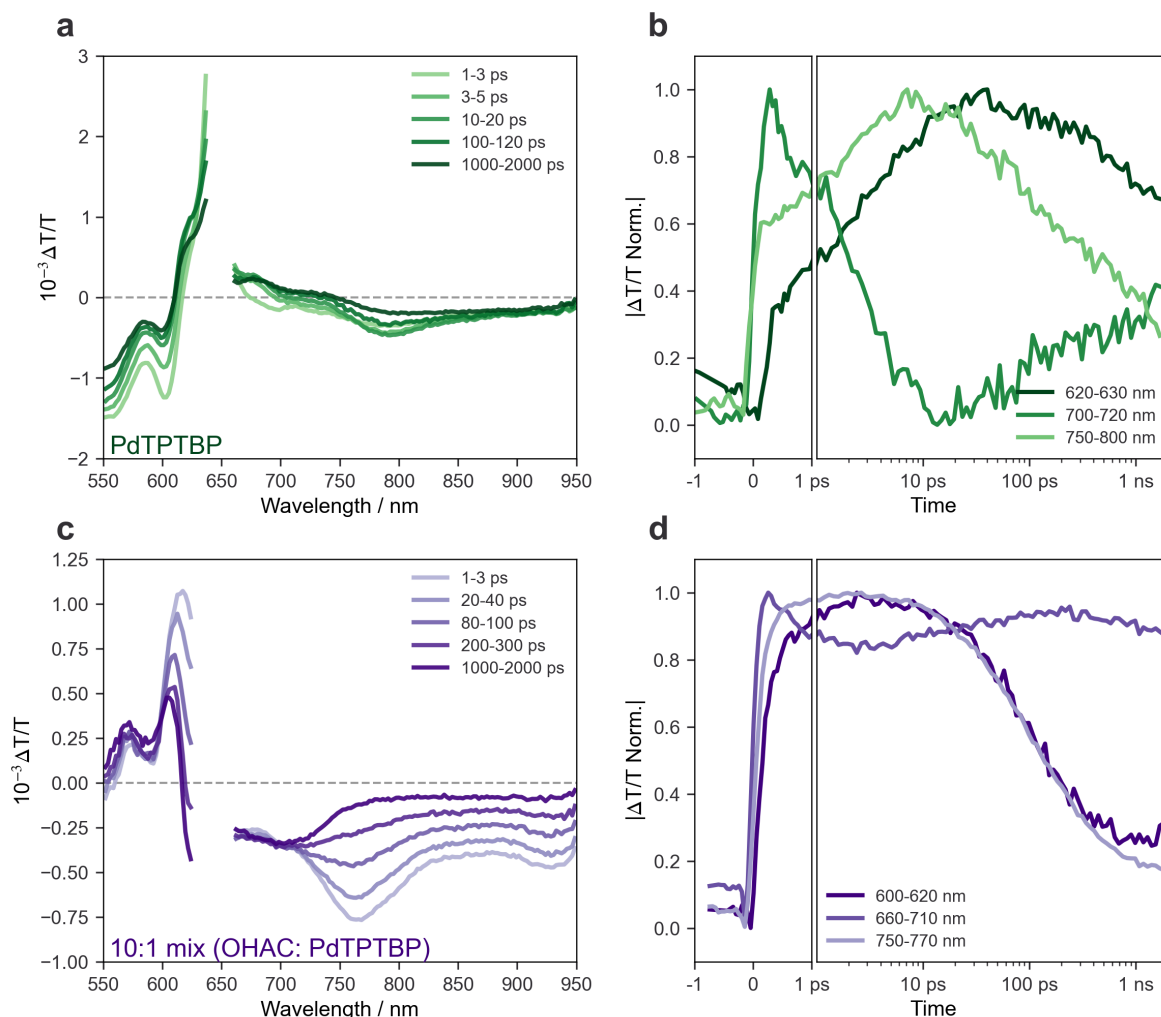
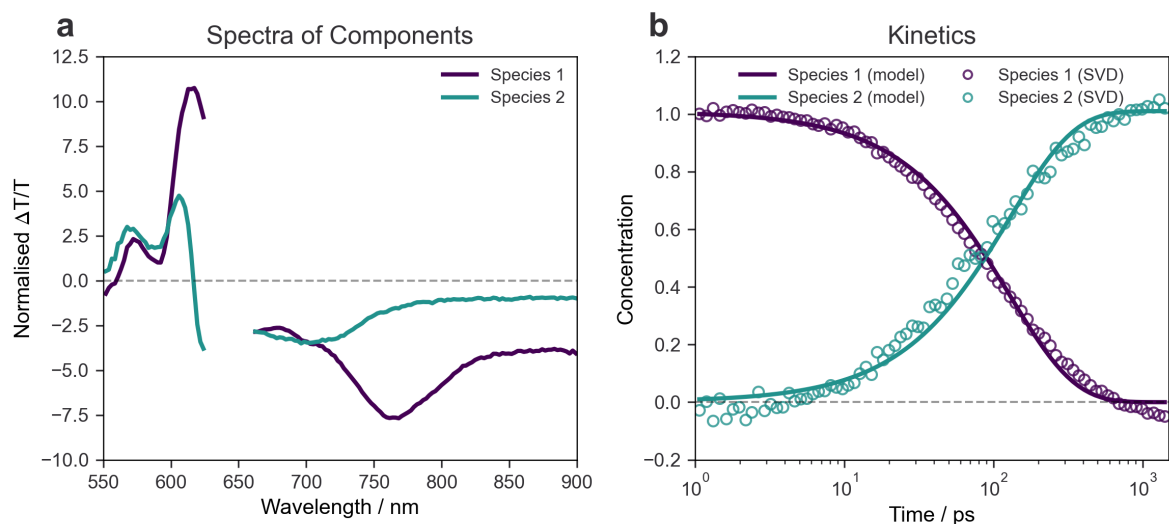


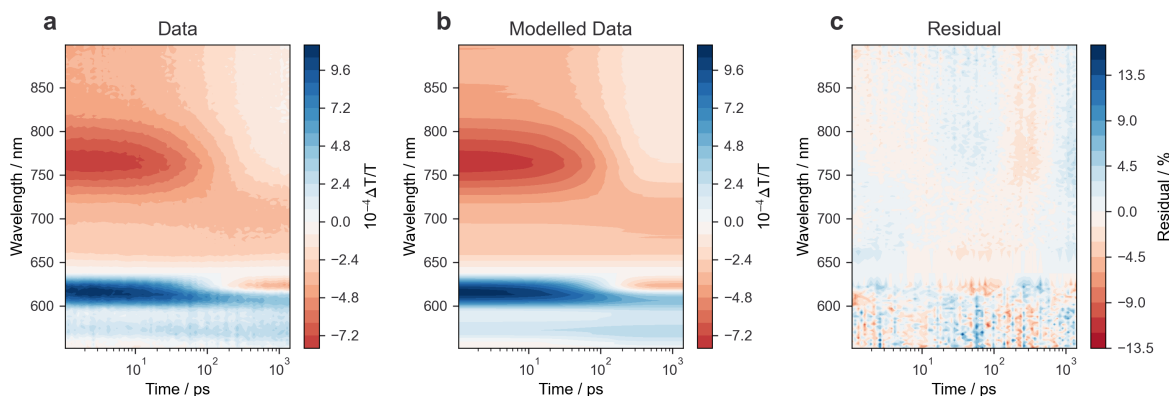
Figure 6.9: Triplet sensitization measurements in thin film of OHAC using meso-Tetraphenyl-tetrabenzoporphine Palladium Complex (PdTPTBP) as a sensitizer with 650 nm photoexcitation. Measured with TA on a picosecond timescale. Excitation density $3.86 \times 10^{-5} \text{ J cm}^{-2}$ at 650 nm.

To attain the triplet spectrum of OHAC in the thin film environment, a thin film sensitisation experiment was performed with PdTPTBP. The films were dropcast from a 2:1 vol/vol ratio of toluene:THF with a 10:1 mixture of OHAC:PdTPTBP (3 mM: 0.3 mM).

To verify that the two materials were sufficiently mixed in the thin film to enable triplet transfer, we observed the quenching of the PdTPTBP phosphorescence at 800 nm with TCSPC. A pristine film of PdTPTBP had a phosphorescence lifetime of $321 \pm 2 \mu\text{s}$, which was quenched to $204 \pm 17 \mu\text{s}$ in the 10:1 mix film. This confirms that the triplet lifetime of the PdTPTBP is being quenched to some degree in the mix-film, most likely due to triplet energy transfer to



(i) Spectral decomposition of 10:1 OHAC:PtTPTBP mix thin film on picosecond timescale.



(ii) Residuals of modelled data.

Figure 6.10: (i) Spectral decomposition (with SVD and a kinetic model) of 10:1 OHAC:PtTPTBP mix thin film on picosecond timescale. Species 1 is assigned as PtTPTBP T_1 , and Species 2 is assigned as OHAC T_1 . The model illustrates how the PtTPTBP T_1 transfers triplet energy to the OHAC with a lifetime of 130 ± 3 ps. Fitted with a simple kinetic model ($A \rightarrow B$), with one rate constant. Residuals of the global fit are shown in (ii)

the OHAC. As the film was drop cast, and so inhomogeneous, it is possible that some regions had efficient triplet transfer, while others exhibited poor transfer.

The films were interrogated on the picosecond timescale with 650 nm excitation, as presented in **Figure 6.9**. (a) & (b) show the behaviour of a pristine PtTPTBP film, while (c) & (d) show the 10:1 mix film of OHAC:PtTPTBP. Due to the hypsochromic shift of the OHAC film absorbance compared to solution, the excitation at 650 nm did not excite a pristine OHAC film.

The spectra of PtTPTBP in (a) show a blue PIA, a narrow GSB close to the laser scattering

peak, and a PIA between 750-800 nm, which aligns well with the nsTA spectra of PdTPPTBP in solution. There appears to be some spectral evolution between 650-750 nm at early time (< 10 ps), which is either due to the intersystem crossing of the Pd complex from the S_1 to T_1 state on the ps timescale ($\tau = 2.8 \pm 0.1$ ps), or a thermal artefact. The spectrum at late times (1000-2000ps) is reminiscent of the solution PdTPPTBP spectra in **Figure 6.7**, with a GSB of the Q band between 630-650 nm, obscured by the pump scatter at 650 nm, and a broad PIA with a small peak centred at 800 nm.

The mix-film in (c) & (d) by comparison shows far greater spectral evolution. The blue PdTPPTBP PIA has been replaced by a positive feature. The PdTPPTBP triplet PIA at 750-800 nm is present at early times, and is replaced by a new PIA 650-700 nm. The GSB of the PdTPPTBP at 620-650 nm is replaced at later times with GSB feature closely resembling the UV-Vis spectrum of OHAC in solution. Considering there is some increased PIA intensity at early times at 900 nm, and a positive feature at 550 nm throughout, it is possible that some OHAC has been co-excited with the PdTPPTBP. This is possibly due to monomeric behaviour of OHAC due to disrupted crystal packing in the presence of the large PdTPPTBP complex.

Overall, the spectra suggest that the PdTPPTBP triplet PIA is replaced with a new PIA related to OHAC, which is spectrally different to the OHAC singlet PIA in solution, and is in a region that overlaps with the OHAC solution triplet spectrum. We therefore suggest that triplet transfer from PdTPPTBP has been successful. These dynamics are captured through decomposition, as shown in **Figure 6.10**.

The mix-film fitted well to a simple two-species model ($A \rightarrow B$). The lifetime of the triplet transfer from the PdTPPTBP to the OHAC was found to be 128 ± 3 ps. This is somewhat faster than expected from the quenching of the PdTPPTBP phosphorescence, suggesting we perhaps interrogated a 'hot spot' within the inhomogeneous sample where triplet transfer was rapid and efficient. The spectra of Species 1, shown in **Figure 6.10 (a)**, agree well with the PdTPPTBP GSB at 640 nm and broad PIA centered around 750 nm as observed in solution. Species 1 may also bear some features of singlet OHAC, with a positive feature between 550-590 nm and some PIA intensity at 900 nm. Further separation of the PdTPPTBP and

OHAC S_1 spectrum was not possible or relevant. Species 2 has a GSB that matches well with the *solution* OHAC steady-state absorbance. Similarly, the PIA of the OHAC triplet state aligns well with the triplet PIA in solution. This implies that, while triplet transfer from the PdTPTBP was successful in the film, the crystal packing of the OHAC has been severely disrupted. We assert that otherwise, we would see a similar effect of H-aggregation in the GSB. Thus, the triplet spectrum of OHAC in film collected is typical of an amorphous environment, and not a polycrystalline environment. Nonetheless, the region between 650-750 nm is still of interest for expected triplet PIAs.

6.7 ps-Transient Absorption of Films

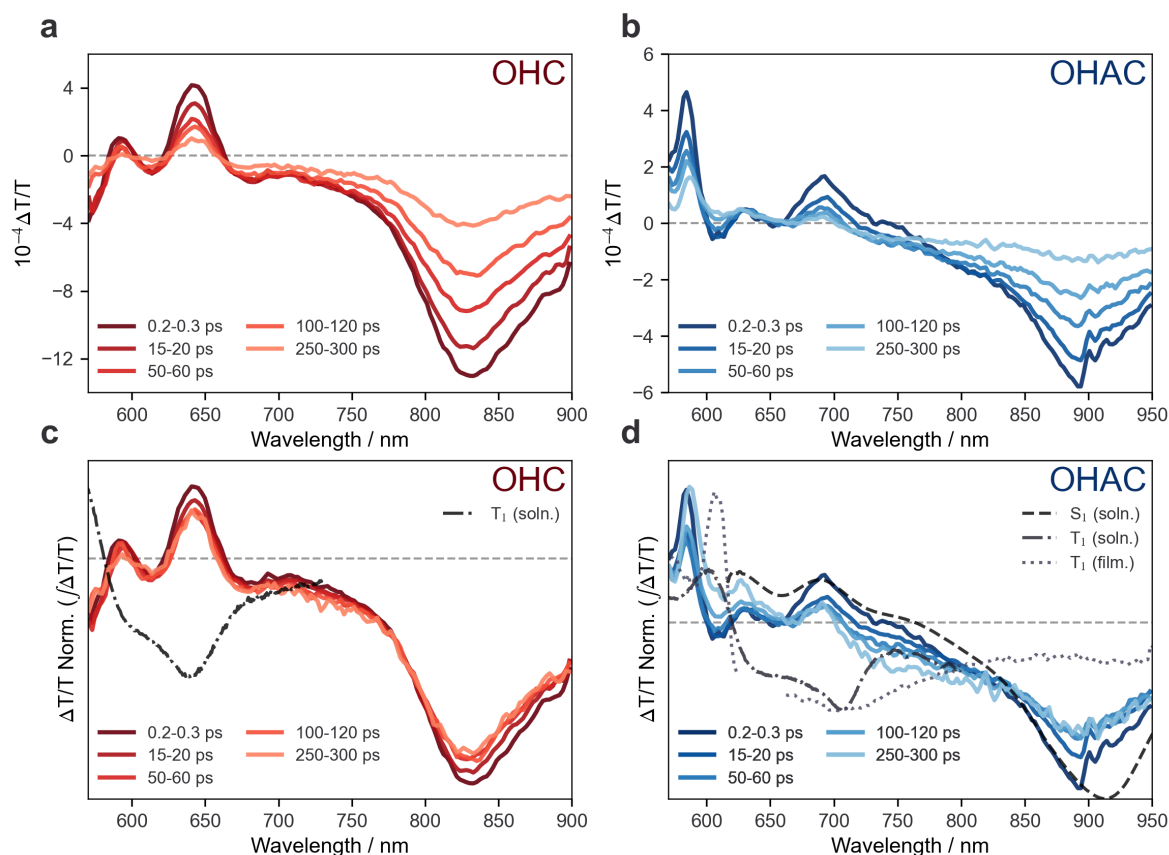


Figure 6.11: Ultrafast dynamics of OHC (red, (a)) and OHAC (blue, (b)), performed in thin films (transient absorption spectroscopy, 550 nm excitation, $9.9 \times 10^{-6} \text{ J cm}^{-2}$). Spectra normalised to integral $\Delta T/T$ shown in (c) and (d). The OHC signal is indicative of single species, whereas OHAC indicates the presence of two species. Results concordant with those seen by Fallon *et al.* [19], attributed to formation of a geminate TT state, indicative of singlet fission. Solution singlet, triplet sensitisation spectra (dot-dashed/dotted) attributed to free triplets in solution (anthracene sensitiser, 355 nm excitation) and free triplets in thin film (PdTPBP sensitiser, 650 nm excitation) are added for reference (Figures 6.6-6.10).

We investigated the singlet fission capability of OHAC in comparison with OHC, known to be singlet fission inactive [132], using picosecond transient absorption (TA) spectroscopy of thin films. **Figure 6.11** shows $\Delta T/T$ spectra for OHC (a) and OHAC (b) measured in thin films under 550 nm photoexcitation. The spectra of both materials are dominated by a strong PIA from the singlet states, with a maximum at 840 nm and 890 nm for OHC and OHAC, respectively. In **Figure 6.11** (c) & (d) we normalise the TA spectra shown in (a) & (b) respectively, such that the integrated area under the curves is equivalent. This allows for changes in spectral shapes to be better visualised. As can be seen in (c), the spectra of OHC

showed little spectral evolution in the first 300 ps, indicating that no new species are formed from the singlet state. This is consistent with previous reports that singlet fission does not occur in these systems.

In contrast, the normalised spectra of OHAC (**Figure 6.11 (d)**) show pronounced spectral shifts in the first 300 ps. A new PIA is seen to grow in, centred at 740 nm, concomitant with a decay of the PIA at 890 nm. For comparison, we overlay the singlet spectra measured in dilute solutions (black dashed line), the triplet spectra measured via sensitisation in solution (black dot-dashed line) and the triplet spectra measured in thin film blends with a triplet sensitizer (black dotted line) from the previous sections.

Comparison with these spectra show that the early time OHAC spectrum, which we label Species 1, is well matched with the singlet spectrum from dilute solutions, with a PIA centred at 900 nm and stimulated emission band at 700 nm. We hence assign Species 1 to the singlet exciton, S_1 , in OHAC. The S_1 state is then quenched, and a new species, which we label Species 2, grows in with a broad PIA in the region relevant to triplet species, as seen from the comparison to TA spectra of free triplets in OHAC solution and sensitised film blend. Thus, we conjecture that Species 2 must be connected either with free triplets or the intermediate $^1(TT)$. We note that the spectra of free triplets in solution and film sensitisation closely resemble each other in both GSB and PIA, while the pristine OHAC film exhibits both a blue shifted GSB and a red-shifted triplet region. This indicates that the triplet sensitisation experiments yielded free triplets in amorphous environments in the film (resembling free triplets in solution) and are not representative of free triplets in a highly crystalline region, such as the pristine film. Thus, the apparent red-shift of the Species 2 PIA in OHAC film is consistent with greater aggregation in the pristine film, resulting in broadening as observed in other organic systems [19, 46]. Similar PIAs and apparent red- shifting of the triplet regions were observed in our previous measurements of INDТ systems, where triplets formed rapidly via singlet fission, which we summarise in **Table 6.4**.

The INDТs showed very similar triplet spectra from sensitisation compared to the cibalackrots. Each of the INDТs that had clear evidence of triplet formation in the TA data, verified

Molecule	Peak of T ₁ PIA from sensitization / nm	Peak of T ₁ PIA from SF in films / nm	Apparent Shift / nm	Red-
Cl-INDT	650	680	30	
F-INDT	635	635	0	
H-INDT	635	n/a	n/a	
CN/Br-INDT	680	720	50	
Br-INDT	655	695	40	
CN-INDT	700	740	40	

Table 6.4: Reproduced from pages S35 - S36 of Supplementary Information from Fallon *et al.*[19]. INDTs are similar systems to the cibalackrots, and were confirmed to have high yields of singlet fission. Most INDT systems investigated exhibited a strong red-shifting of the triplet photoinduced absorption (PIA) in the pristine films, when compared to the free triplets generated by sensitisation experiments.

by electron spin resonance (ESR) as originating from SF, showed spectral shifts of the triplet PIAs by up to 50 nm. Therefore, our observed shift for OHAC is not unreasonable, particularly as the triplet-related PIA is obscured by the stimulated emission for this system. Similar verification of the triplet state through ESR was attempted on numerous occasion, but the spin lifetime was too short to be captured with ESR.

The decay kinetics of the singlet PIA and triplet relevant PIA are shown at different fluences in **Figure 6.12**. Within noise, there is no evidence of a fluence dependence for either sample. There is some greater noise at very low fluence for both samples, as expected. The kinetics of the triplet-related region in OHAC is very noisy at the different fluences, but overall each of the kinetic traces share a maximum at the same time region, which indicates the kinetics are fluence independent. This suggests a geminate decay pathway, rather than bimolecular decay processes such as TTA.

To gain further insight into the data, we performed spectral decomposition with two methods: a model free genetic algorithm, and a combination of singular value decomposition and kinetic modelling.

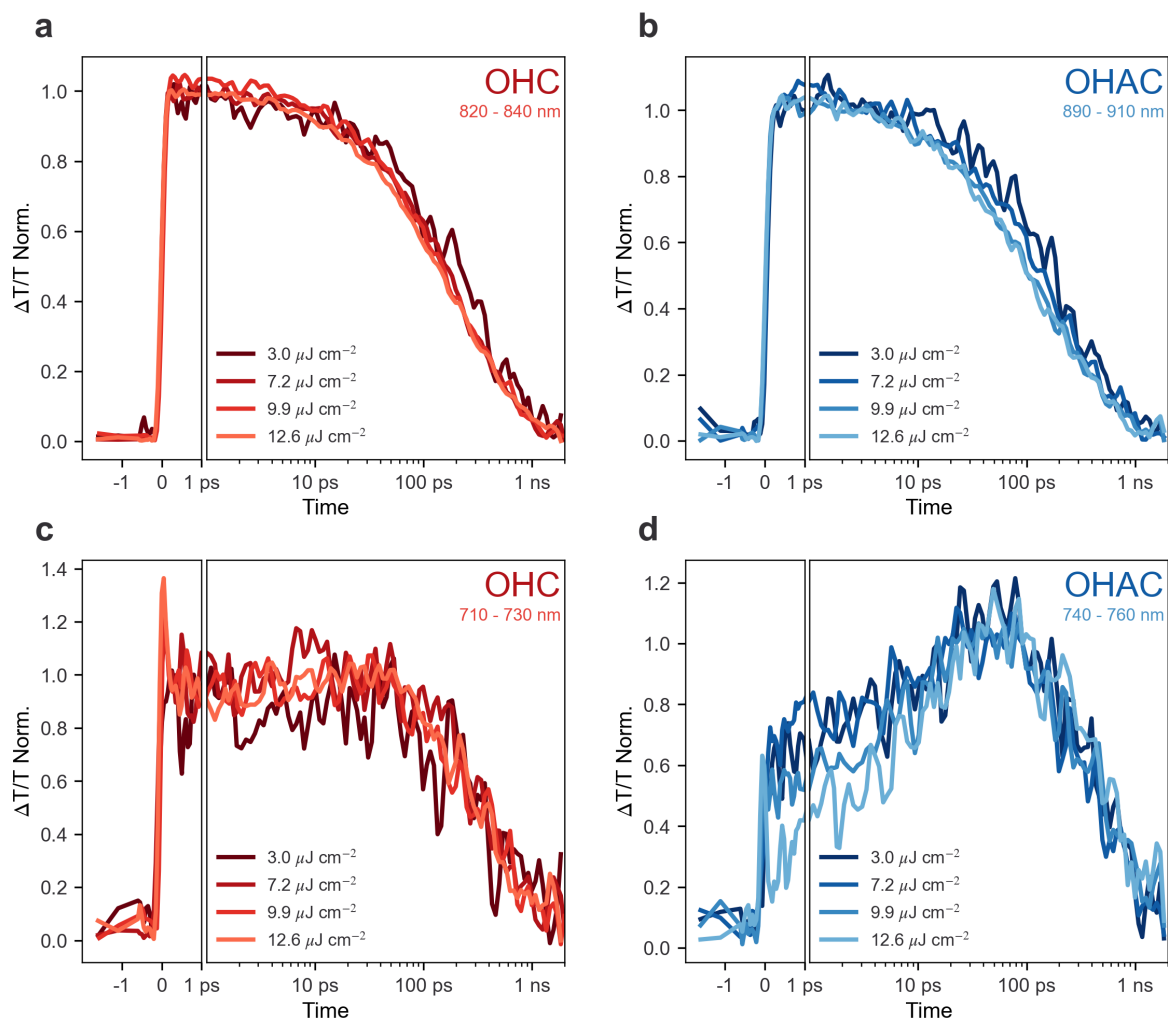
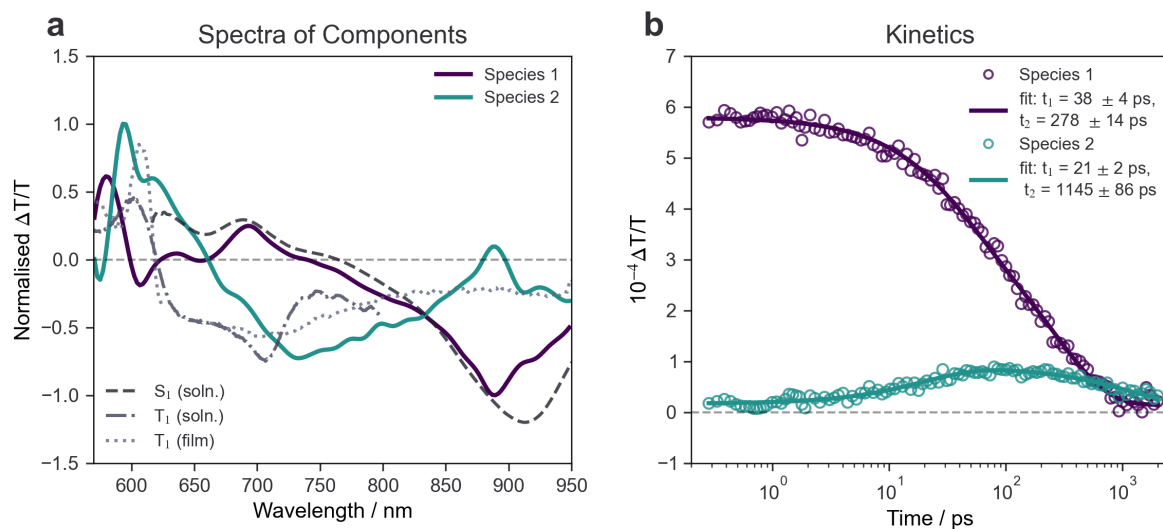
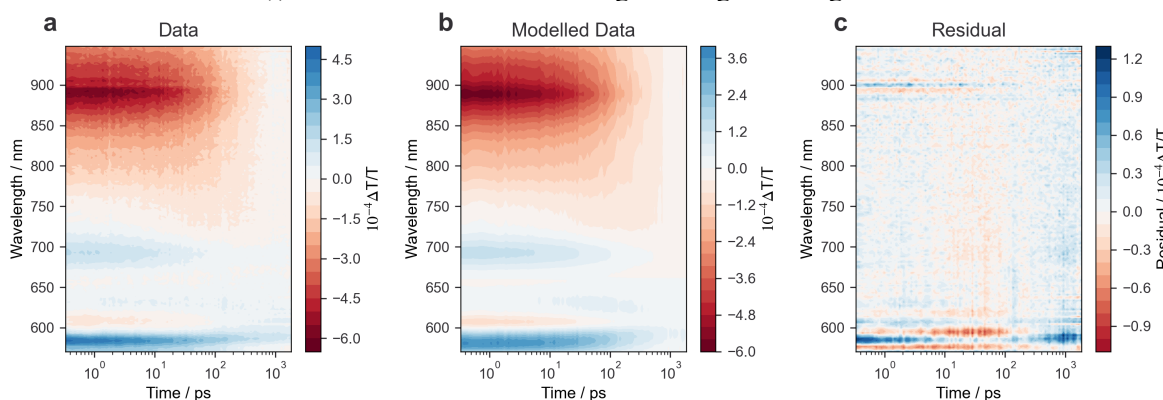


Figure 6.12: Fluence dependence of psTA on kinetics over wavelength ranges for OHC ((a) & (c)) and OHAC ((b) & (d)). The singlet PIA region ((a), OHC, (b), OHAC) and TT state region ((c), OHC, (d), OHAC) are shown at increasing excitation power. Absence of change in the decay profile of the TT state in OHAC with fluence indicates the decay pathway is exciton density independent, suggesting geminate TT annihilation. Minimal singlet-singlet annihilation (SSA) is observed in either film at these excitation densities, as seen by little change in the S_1 decay rate. Excitation density 3.0×10^{-6} - 1.26×10^{-5} J cm^{-2} at 550 nm.

6.8 Spectral Decomposition



(i) Reconstruction of data using a N=2 genetic algorithm



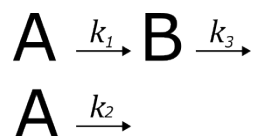
(ii) Residuals

Figure 6.13: (i) 2-species spectral decomposition of OHAC ps-TA data (from **Figure 6.11 (b)**), using a genetic algorithm. Spectra in (a) are compared the spectra of OHAC solution S_1 (**Figure 6.5**), solution T_1 (**Figure 6.6**), and film T_1 (**Figure 6.10**). The kinetics in (b) are fitted to independent exponential decays. Species 1 is assigned as the S_1 state and Species 2 the TT state. Species 2 spectrum shows good comparison to the solution T_1 spectrum of OHAC. In the kinetics, Species 1 decay of 38 ps matches well with the growth of Species 2 of 21ps, so we can say this is concomitant. Species 1 also has a non-radiative decay (280 ps). The absorption cross section of Species 2 is lower than Species 1. From the ratios of PIA intensities in **Table 6.5**, we can approximate the yield of Species 2 to be 29-32%. Residuals shown in (ii).

To gain further insights into the timescale for the growth of Species 2 in OHAC, a spectral decomposition was performed with a genetic algorithm (GA). An N=2 species model was found to be most appropriate. **Figure 6.13** shows the spectra of the two species retrieved from the GA. (b) shows the normalised decomposed kinetics associated with Species 1 and 2 (data points), fitted to exponential decays (solid line). Species 1 (S_1) rapidly decays with a

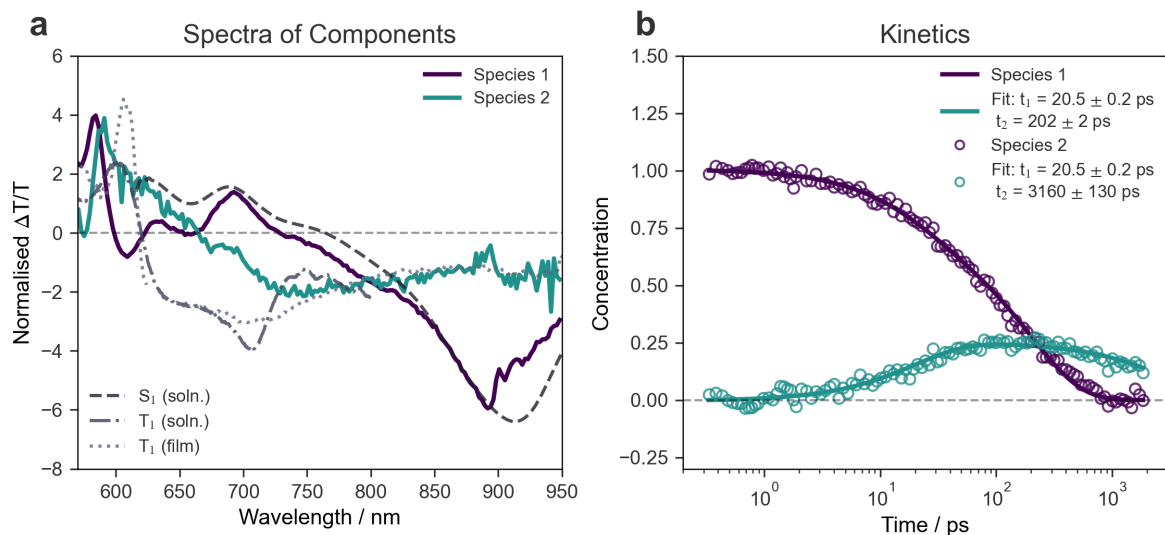
lifetime of 38 ± 4 ps, with approximately concomitant growth Species 2 (21 ± 2 ps). Species 1 transforms into Species 2 with an approximate yield of 29-32%; a value that is concurrent with additional methods to determine the yield (24-51%, **Table 6.6**).

The biexponential decay of Species 1 indicates the presence of at least two sub-populations. The remaining Species 1 sub-population, that does not convert to Species 2, undergoes non-radiative decay, with a lifetime of 278 ± 14 ps. Species 2 decays with a longer lifetime of 1145 ± 86 ps. This lifetime is possibly limited by the apparatus, and is examined with nsTA in the following section. The GA results were compared to a decomposition with SVD and kinetic modelling in **Figure 6.14**.

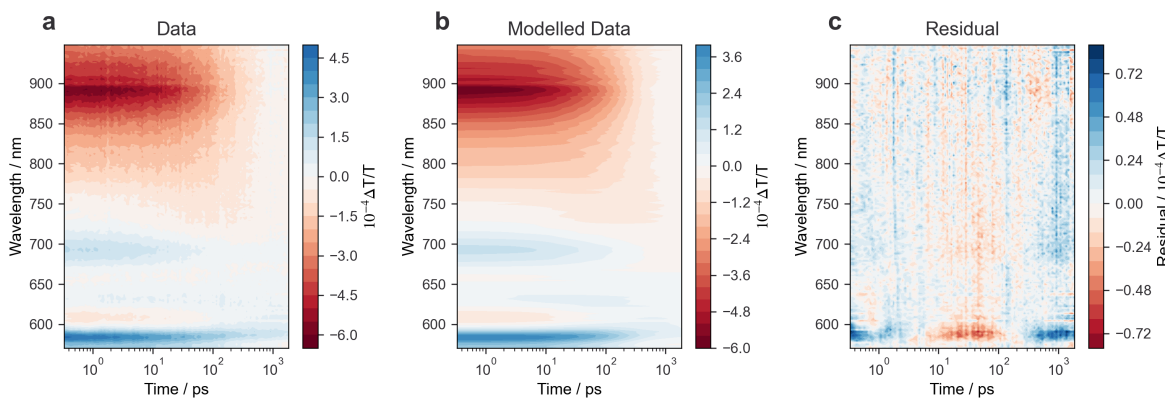


A branching kinetic model aligns well with the kinetics fitted to the GA model. Again, an N=2 model was selected as the most suitable. The spectra shown in **(a)** match very well with those resulting from the GA model. Again, the spectrum of Species 1 matches the solution state S_1 very well, with a blue shifted GSB. The spectrum of Species 2 shows a slightly shifted PIA, comparable to the T_1 PIA in solution and in film.

The lifetimes extracted in **(b)** (20.5 ± 0.2 , 202 ± 2 , and 3160 ± 130 ps) align well with those extracted from the GA. The SVD may even suggest that Species 2 lives slightly longer than in the GA. The effective yield of Species 2 from Species 1 is estimated as 24-30%.



(i) Reconstruction of data using a N=2 SVD



(ii) Reconstruction of data using a N=2 genetic algorithm

Figure 6.14: (i) 2-species spectral decomposition of OHAC ps-TA data (from **Figure 6.11 (b)**), using SVD and a kinetic model. Spectra in (a) are compared the spectra of OHAC solution S_1 (**Figure 6.5**), solution T_1 (**Figure 6.6**), and film T_1 (**Figure 6.10**). The kinetics in (b) are fitted to a branching kinetic model, as shown in the main text. Species 1 is assigned as the S_1 state and Species 2 the TT state. Species 2 spectrum shows good comparison to the solution T_1 spectrum of OHAC. Species 1 transforms to Species 2 with a yield of 24-30%, and a lifetimes of 20.5 ± 0.2 ps. Both Species 1 and 2 decay non-radiatively with respective lifetimes of 202 ± 2 ps and 3160 ± 130 ps. The decomposition from SVD aligns well with the model free GA approach. Residuals shown in (ii).

6.9 ns-Transient Absorption of Films

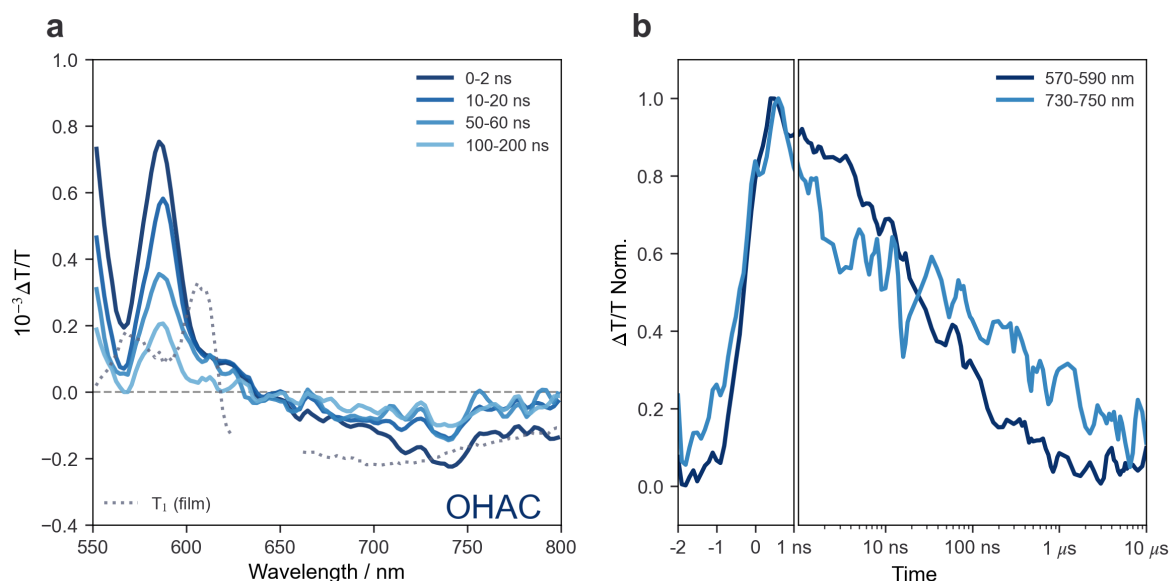


Figure 6.15: nsTA of OHAC thin film. Spectra in (a) are compared to the film T_1 spectrum (Figure 6.10). The kinetics in (b) indicate the 750 nm PIA persists for hundreds of nanoseconds, with a lifetime of 270 ± 49 ns. (5.61×10^{-5} J cm $^{-2}$ excitation density at 532 nm)

To further investigate Species 2, we performed nsTA on the OHAC film. Spectra in Figure 6.15 (a) agree well with the Species 2 spectra extracted from the psTA data from SVD. The broad PIA at 650-800 nm persists for hundreds of nanoseconds, and decays with a lifetime of 270 ± 49 ns.

Overall, short lifetime and fluence independence indicate that Species 2 is unlikely to be free triplets. However, its overlap with the spectral region relevant to triplets, and similarity to the behaviour for the INDts, could suggest that Species 2 is a geminate TT state. We thus tentatively assign Species 2 as TT moving forward. The rapid decay of Species 2 meant we were unable to confirm its identity with electron spin resonance. However, we rule out that Species 2 is formed from intersystem crossing due to the clear absence of a triplet signature in the TA of OHAC solution (Figure 6.5).

Following our hypothesis that Species 2 is the geminate TT state, the fast decay and lack of evidence for free triplets suggests the TT pair cannot dissociate with the current film preparation and subsequent morphology. Further optimisation of OHAC would be required to confirm

this hypothesis. However, the suspected presence of TT states indicates greater propensity for singlet fission in OHAC than the OHC.

6.10 Yield Estimation

We estimated the yield of Species 2 through a number of methods previously reported [19], summarised in **Figure 6.16** and **Tables 6.5-6.6**. At this stage, we have ruled out that Species 2 is T_1 state. However, we can still attempt to confirm this through estimating the yield of the state. While these yields are only approximate, a yield of $> 100\%$ would be a strong indicator of free triplets produced from singlet fission. However, the yields we estimate are all $< 100\%$. This does not necessarily mean that Species 2 is not being formed from singlet fission, but that the yield of the SF process is low, or more likely, the species formed has not fully separated into two free triplet excitons.

In **Figure 6.16 (a) & (b)**, we compared the ratios of the PIA intensities of the S_1 and T_1 with normalised absorbance. We then apply these ratios, calculated from both solution and film spectra, to the TA data and estimate the yield of the TT species. This assumes that the extinction of the TT PIA is the same as the extinction of the free T_1 . It also neglects the effect of aggregation and crystal packing occurring for the OHAC films, as both T_1 spectra were only appropriate for highly amorphous environments. Aggregation will likely have an impact on the extinction coefficient of the T_1 PIA. However, we choose to ignore this for the sake of a simple approximation. Applying the two ratios, one from the solution spectra and one from the film spectra, to the kinetics shown in panel **(d)**, we estimate that Species 2 is formed with 31-34% yield in the OHAC film. The calculations are summarised in **Table 6.5**.

Method		Max S_1	Max TT	Max TT / Ratio		Yield	
				Solution	Film	Solution	Film
Raw Data	TA	-5.22	-0.85	-1.77	-1.63	0.34	0.31
GA (N=2)		5.94	0.90	1.8754	1.731	0.32	0.29

Table 6.5: Estimating the TT yield, using the ratio of the maximal intensities of the S_1 and TT regions from the TA data. The ratios, defined from **Figure 6.16 (a) & (b)** for solution and film, are used to calculate the yields from the maximal PIA values from the raw data and the GA simulated data.

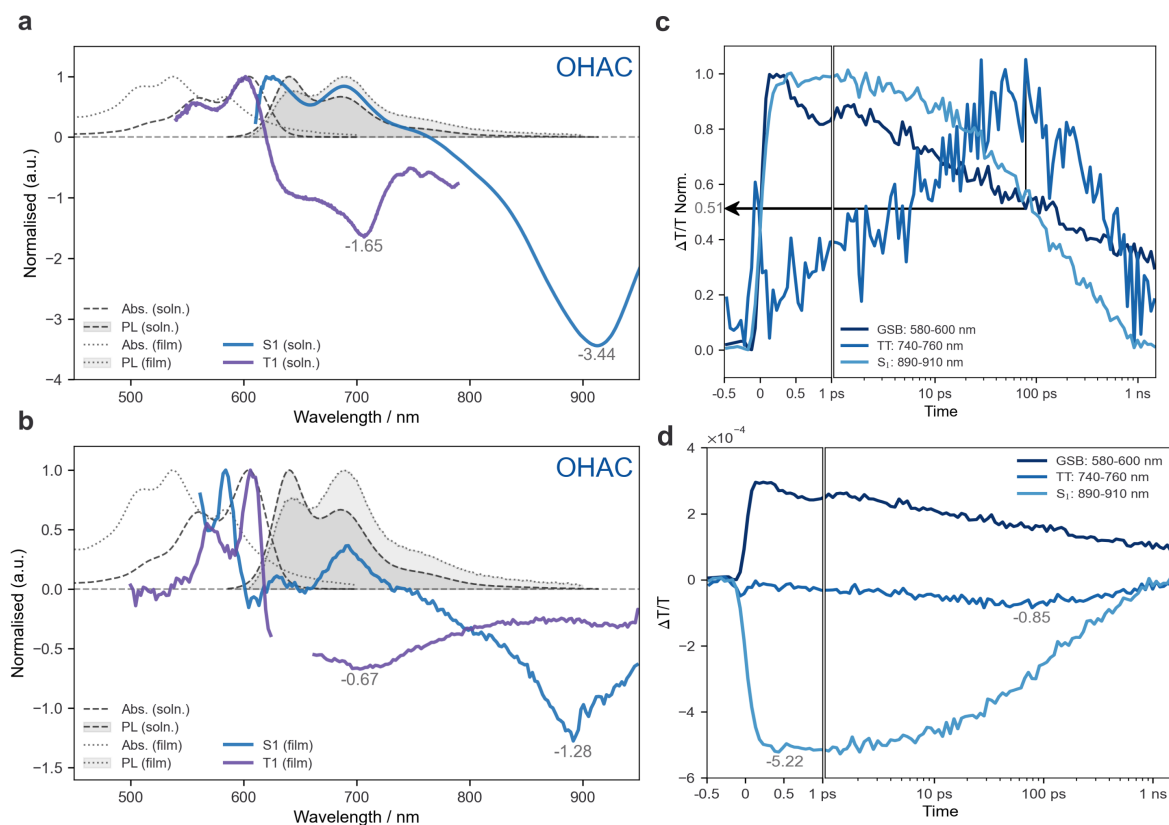


Figure 6.16: Yield calculations: (a) the ratios of the PIA intensities of the S_1 and T_1 in solution are taken, as normalised to the GSB. (b) The ratios of the PIA intensities of the S_1 and T_1 in film are taken, as normalised to the GSB. (c) The fractional value of the GSB when the TT PIA is at its maximum is taken as the uppermost bound for the possible TT yield. (d) The raw kinetics of the S_1 and TT kinetics from the film psTA data, from **Figure 6.11**.

Another method for estimating the yield is to examine what fraction of the GSB is remaining at the maximum of the Species 2 PIA intensity, as shown in panel (c). This method assumes that the only photoproduct present is the Species 2. This will likely over estimate the yield, giving an uppermost bound. Here, we estimate that 48-54 % of the GSB is remaining, putting the maximum yield of Species 2 at 51 ± 3 %.

The final method of approximating the yield is from the spectral decompositions achieved with GA and SVD. For GA, we still must apply the ratios from the S_1 and T_1 spectra. This gave an estimated yield of 29-32%. For SVD, because we apply a kinetic model, we can normalise to the intensity of the GSB and then find effective ‘concentrations’ from the kinetics. Here, the SVD estimated the yield as 24-30%.

A more rigorous approach would have been to directly calculate the extinction coefficient

Method	Approximate TT Yield (%)
Ratio solution (Table 6.5)	34
Ratio film (Table 6.5)	31
Decay of GSB population (Figure 6.16)	48-54*
Genetic Algorithm (Table 6.5)	29-32
SVD (Figure 6.14)	24-30

Table 6.6: Summary of approximate TT yields from the various methods discussed. * The yield calculated from the decay of the GSB is taken as an upper bound of the possible yield.

of the T_1 PIA from the sensitisation experiments. However, due to the simultaneous photo-excitation of the OHAC along with the sensitizer, these calculations would have been similarly approximate. A summary of the approximate yields of the Species 2/TT state is presented in **Table 6.6**.

6.11 Discussion and Conclusion

In this work, we have explored how crystal structure engineering strategies could be employed to search for new singlet fission chromophores. We suggested a molecular alteration, beyond the scope of side-chain engineering, to potentially enhance intermolecular couplings based on analysis of the crystal structure of cibalackrot. These strategies could be applied to materials previously identified as SF candidates through DFT, that did not fulfil the potential of their favourable energetic alignments in practice.

We introduce a novel molecule, aza-cibalackrot (OHAC), and examined it in comparison to its parent species, cibalackrot (OHC). We applied ultrafast spectroscopy to examine if singlet fission behaviour is enhanced due to our change in molecular design. For our novel compound, OHAC, we observed a new spectroscopic signal in a region relevant to the triplet state, that we tentatively assign as the formation of a geminate TT pair. This formation of a new species is not present in the parent OHC. We confirmed this through triplet sensitisation measurements. More conclusive experiments, such as magPL or ESR, were unfortunately unsuccessful due to the low PLQE of the material, and short lifetime of the triplet-relevant species. However, within the context of comparable INDT systems in the literature, we believe the results to be consistent with those previously reported [19]. DFT confirmed that our energy level alignment has not been significantly altered, indicating our change in singlet fission activity is a direct result of changes to crystal structure and intermolecular coupling.

For future investigation, certain issues must be addressed for aza-cibalackrot to be a suitable chromophore for singlet fission. The synthetic yield of OHAC must be improved, as it currently is very low (0.6% reaction yield). Generation of more material would allow a more in depth exploration into sample preparations and morphology, such as through use of different solvent and annealing processes. By optimising the sample morphologies, it may allow more efficient separation of the TT state, longer lifetimes, and higher yields. With greater yield and longer lifetime, we may have more success in concretely identifying Species 2 to be the TT pair, through techniques such as ESR, magPL, and modMPL.

Overall, this investigation of OHAC has yielded interesting results. The formation of Species 2 suggests we have taken a promising first step toward singlet fission ability in OHAC. Further optimisation of the system is required to identify aza-cibalackrot as a potential suitable material. As to our reflections on molecular design principles, applying the same crystal engineering strategies to another organic chromophore system would be highly interesting, to observe if similar results could be replicated with other material systems.

Chapter 7

Thienoisindigos: A Polyene-Like Singlet Fission Candidate?

In this chapter, we consider a derivative of indigo, thienoisindigo, as a candidate for singlet fission. This content of this chapter is the result of collaboration with Anastasia Klimash^a, Anastasia Leventis^b, Hugo Bronstein^a, Rachel Kilbride^c, Daniel Toolan^c, Pratyush Ghosh^d, Simon Dowland^b, and Jurjen Winkel^b.

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7.1 Introduction

One of the oldest known dyes [121, 123], indigo, and its derivatives have been of interest for singlet fission applications for over a decade. Michl and co-workers suggested in 2010 that indigo itself may have a favourable structure for singlet fission, as biradical character of the triplet state may be stabilized by planarization and captodative resonance [11]. They also note that the triplet energy satisfies the $E(S_1) > 2E(T_1)$ criteria required for singlet fission. Annulated derivatives of indigo, such as cibalackrot and indolonaphthyridine thiophene have been investigated for singlet fission potential [19, 21, 132]. Fallon *et al.* further identified that a thiophene derivative of isoindigo, thienoisindigo, follows similar molecular design

principles as the INDs, and has favourable energetics according to theoretical calculations ($E(T_1) = 1.04$ eV, $E(T_1)/E(S_1) = 0.45$) [19].

Thienoisindigo (TIIG) has previously been reported for application in organic field effect transistors, OFETs, [23–25], but not yet considered as a potential singlet fission chromophore. Here, we investigate thienoisindigo, in solution and thin films, with steady-state and ultrafast spectroscopy, to assess its potential to undergo singlet fission. We compare and contrast thienoisindigo molecules with two packing chains, octyl and ethyl-hexyl, as they present altered photophysics.

A recent paper from Wang *et al.* considered a similar isoindigo with a thiophene functionalization, which was suggested to undergo intramolecular singlet fission (iSF) [214]. Their justification relied on TDDFT which suggested that the triplet wavefunction could be localized on one half of the isoindigo core. They also observed spectral similarities to Hu *et al.* who observed intramolecular singlet fission within a polymer of a functionalized isoindigo [215]. A summary of their key findings, relevant to this chapter, is shown in **Figure 7.1**. They noted a triplet signature, which they verified through triplet sensitisation, that formed within 100 ps, which featured a ground state bleach and a blue PIA. The origin of triplets from either intermolecular or intramolecular singlet fission is yet to be satisfactorily determined. The results reported within this investigation share similarities to those reported by Wang *et al.*, although we consider alternative reasoning to explain the photophysics of TIIG.

The parent molecule of TIIG, indigo itself, is well known for rapid internal conversion to a dark state that efficiently decays non-radiatively. For indigo, there has been discussion of the role of cis-trans photoisomerization as a mechanism for its photostability. However, it was later discussed that excited state intramolecular proton transfer (ESIPT) was more likely due to the energetic barrier of the cis-trans rotation [124, 125, 216]. We therefore also rule out the role of cis-trans photoisomerization within the TIIG. However, due to the molecular structure of TIIG, ESIPT would no longer be possible. Instead, we argue that TIIG behaves more like a polyene, sharing behaviour with carotenoids. Carotenoids are known to undergo rapid internal conversion from the bright 1Bu state to the dark 2Ag state in monomer, but in

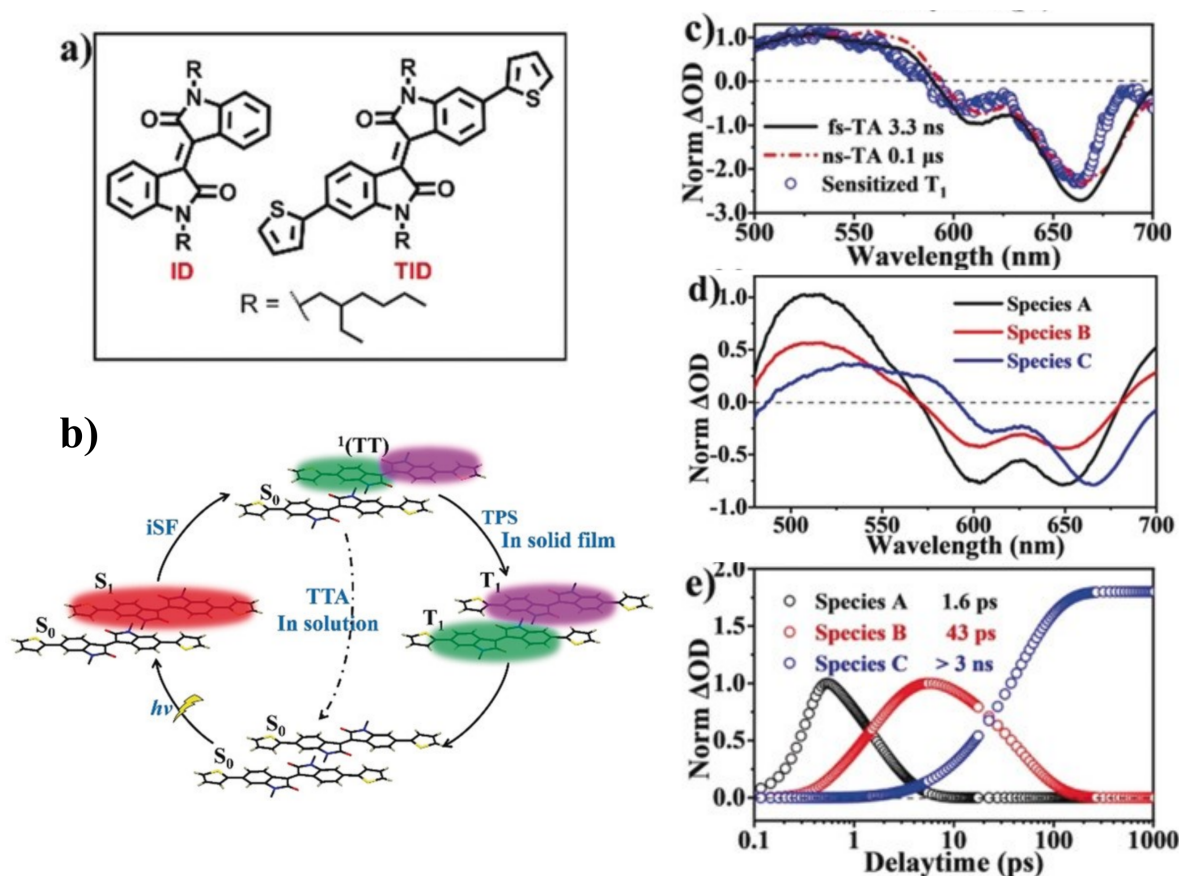


Figure 7.1: Results of thiophene functionalised isoindigo (TID) from Wang *et al.* [214]. Signals of free triplets, confirmed through sensitisation studies, were hypothesised to be generated from intramolecular singlet fission. (a) The molecular structure of isoindigo and thiophene functionalised isoindigo. (b) The proposed intramolecular mechanism for singlet fission. (c) Early and late time TA signals of the thiophene isoindigo thin films with signal from triplet sensitisation. (d) Decomposed spectra from the TA of thiophene isoindigo, with corresponding modelled kinetics in (e).

aggregates was able to undergo singlet fission to two free triplets directly from the 1Bu state [46, 114, 217, 218]. The lower energy 2Ag state then offers a pathway for recombination to the ground state. A similar argument has been recently applied to singlet fission in stilbenes [219].

Within this chapter, we investigate TIIGs with two different side-chains, and employ ultrafast spectroscopy to uncover their photophysics in both solution and thin films.

7.2 Steady State Characterisation

TIIG with two packing groups, ethyl-hexyl, EH and octyl, Oct, were compared in thin film and solution. Molecular structures are shown in **Figure 7.2 (a)**, with corresponding steady

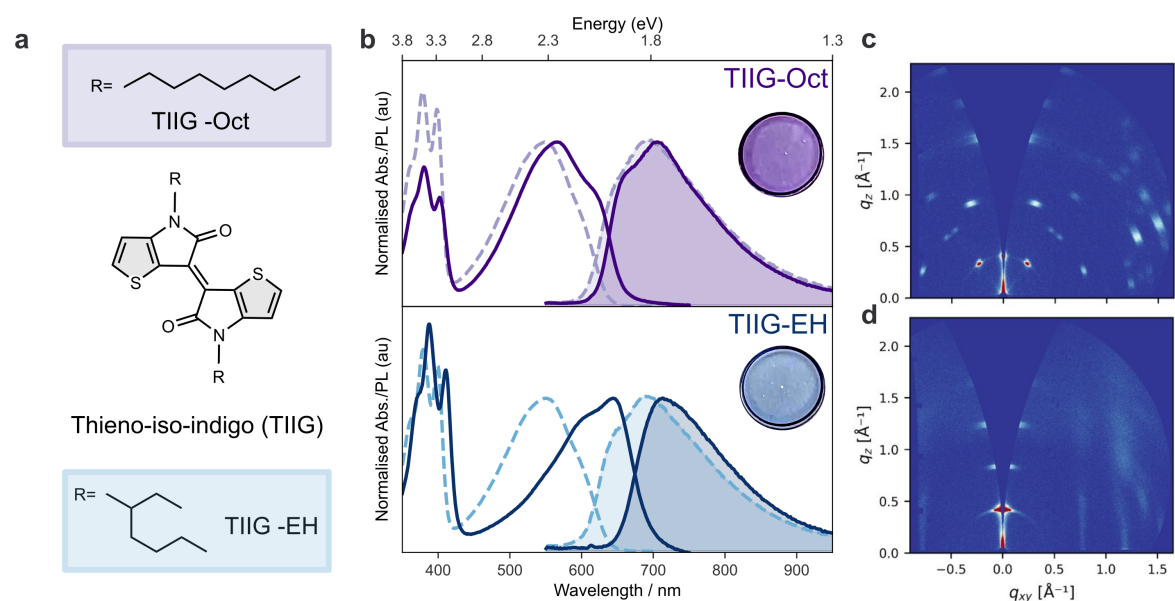


Figure 7.2: Thienoisindigo (TIIG) molecular structure (a) with two packing groups, octyl, TIIG-Oct, and ethyl-hexyl, TIIG-EH. (b) Steady state absorption and emission spectra in solution (dashed line, 1 mM toluene, 200 μm path length) and thin film (solid line, spin coated 2000 rpm). The appearance of a pronounced 0-0 peak and a strong red shift for TIIG-EH is characteristic of J-aggregation [46]. Thin films shown in (b) inset. Grazing incidence wide-angle X-ray scattering (GIWAXS) of TIIG-Oct (c) and TIIG-EH (d), measured and analysed by Dr Rachel Kilbride, show distinct packing behaviours for the two molecules.

state absorption and photoluminescence in toluene solution (dashed line) and thin film (solid line) shown in **Figure 7.2 (b)**. While TIIG-Oct shows minimal spectral changes from solution to thin film, TIIG-EH shows a pronounced apparent red shift and prominence of the 0-0 peak, suggesting J aggregation, as seen in carotenoid aggregates [46]. This red shift is apparent in the colour of the thin film, where TIIG-EH is distinctly blue, compared to the purple TIIG-Oct which matches the colour of the dilute solution.

GIWAXS shown in **Figure 7.2 (c) & (d)** also highlight the changes in molecular packing. Both exhibit strong preferential stacking with respect to the substrate, and show significant differences to each other. The differences in molecular packing are discussed in the next section.

Despite the differences between the aggregation of TIIG-EH and TIIG-Oct, both exhibit a very low PLQE of approximately 0 (<0.5%, within instrument limitations) in both solution and thin film. When dispersed in polystyrene, the PLQE of the thin films remained approximately zero at all weight percentages (**Table 7.1**). These low PLQEs in both dilute solution

	Molecule	PLQE
		%
TIIG-Oct	solution	0.014
	film	0.027 / 0.17
	50% w/w film	0.16
	5% w/w film	0.08
	1% w/w film	0.08
TIIG-EH	solution	0.016
	film	0.025 / 0.06
	50% w/w film	0.18
	5% w/w film	0.08
	1% w/w film	0.09

Table 7.1: PLQEs of TIIG in solution and thin film, and films diluted by w/w ratio of polystyrene, with 520 nm excitation. Pristine films were prepared by the author. Encapsulated solutions and polystyrene doped films were prepared and measured by Dr Jurjen Winkel and Dr Simon Dowland.

and dilute thin film indicate a strong, “dark” intramolecular process causing rapid relaxation. While this property of low emission intensity is shared with polyenes, suggesting similar photophysics, the absorption and emission spectra of the thienoisindigos are mirror-image-like, which is not a property common to polyenes.

7.3 Morphology: Impact of Side-Chains

The morphology of TIIG-Oct and TIIG-EH is examined further in **Figure 7.3**. Single crystals of both were successfully grown by Dr Anastasia Leventis, and single crystal structures obtained with X-ray diffraction (XRD), as shown in **(a) & (b)**. The crystal structures are quite different between the two. The ethyl-hexyl groups are raised in and out of the plane, which might be impacting the face-to-face packing between layers for the TIIG-EH. The octyl groups, however, lay flat, and appear to allow better face-to-face stacking of the isoindigos between layers. This may well impact the exciton diffusion lengths in the crystal structures.

The crystal structures allowed for simulation of the GIWAXS data, performed by Dr Rachel Kilbride. The TIIG-Oct experimental data was well reproduced through simulation, as shown in **(c) and (d)**. The simulation indicated that the TIIG-Oct molecules are preferentially forming layers with respect to the substrate, with the octyl groups laying flat on the substrate.

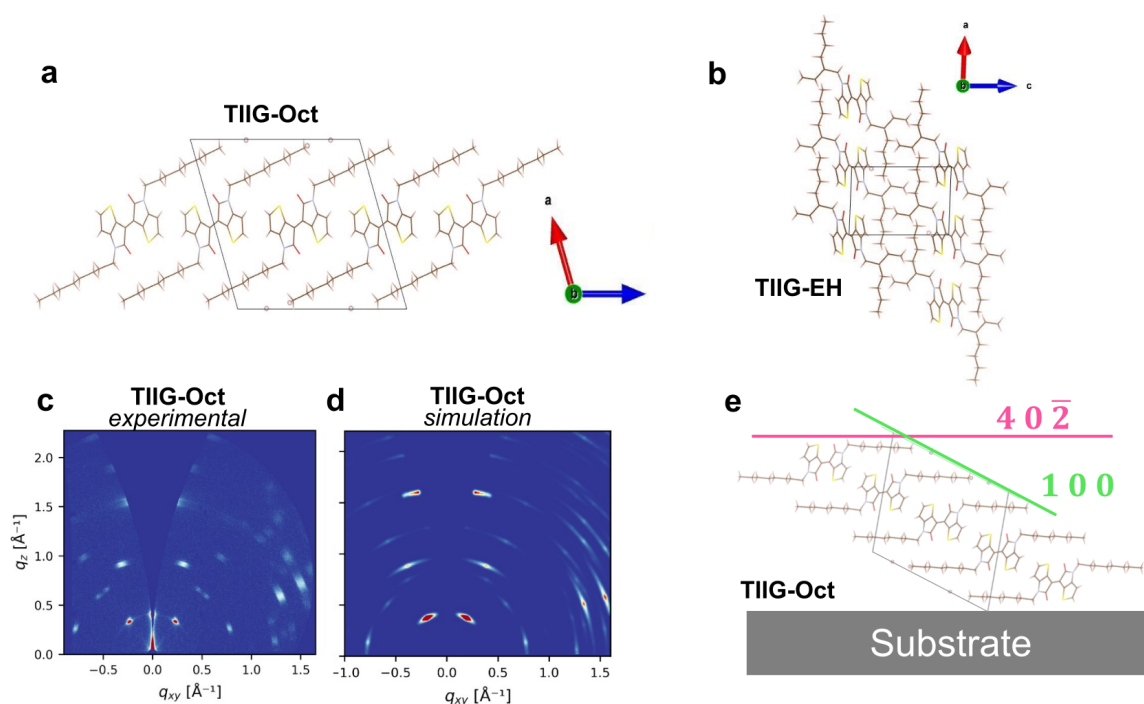


Figure 7.3: Crystal structures of TIIG-Oct (**a**) and TIIG-EH (**b**) are obtained from single crystal XRD. Crystals were grown and XRD performed by Anastasia Leventis. The single crystal structures show how the packing chains cause large changes to the unit cell structure. From the crystal structure, the GIWAXS from **Figure 7.2** can be simulated (performed by Dr Rachel Kilbride). For TIIG-Oct, the simulation (**d**) corresponded well with the experimental GIWAXS data (**c**), indicating preferential packing as demonstrated in (**e**). For TIIG-EH, the crystal structure did not yield a comparable simulation.

For the TIIG-EH GIWAXS data, however, simulation from the unit cell parameters was unable to replicate the data. This suggests that the TIIG-EH behaves differently in the thin film compared to the single crystal environment, unlike TIIG-Oct. However, from the steady state absorbance spectra, we can suggest that in the thin film, TIIG-EH exhibits preferential J aggregation, or slipped stack packing. Further investigation to more fully understand the morphology of TIIG-EH in thin film is required, but it is clear from a first assessment that the packing is highly different to the TIIG-Oct.

7.4 Ultrafast Polyene-Like Behaviour in Solution

To investigate the nature of the photophysical process in these molecules in solution we perform ultrafast transient spectroscopy. **Figure 7.4 (a & c)** shows the transient absorption spectra for the two molecules in dilute toluene solution (0.5 mg ml^{-1} , $200 \text{ }\mu\text{m}$ path length, 1 mM). The spectra are identical for the two compounds, as expected in solution where a change in the

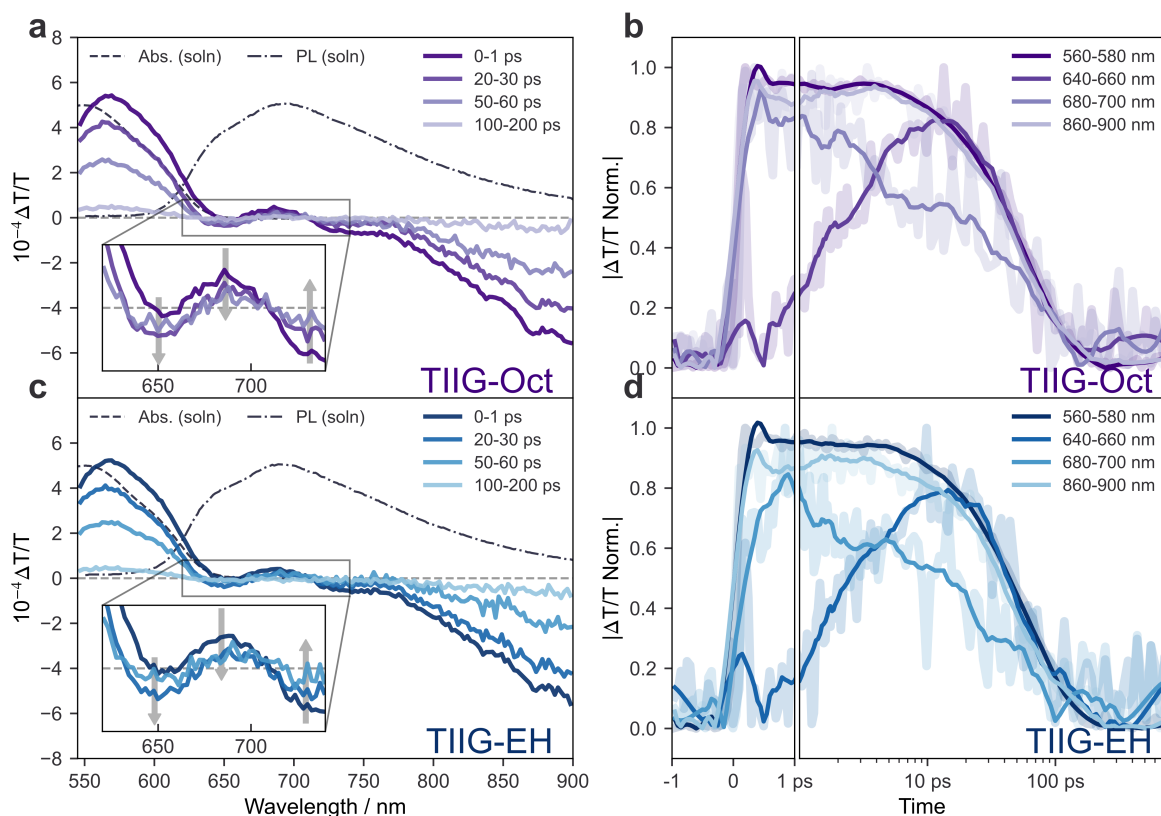


Figure 7.4: Ultrafast transient absorption spectroscopy on picosecond timescales for solutions of TIIG-Oct ((a), (b)) and TIIG-EH ((c), (d)), excited at 532 nm, with respective steady state absorbance (dashed) and photoluminescence (dot-dashed) spectra. Kinetic traces ((b), (d)) smoothed with 5 pt Savitzky-Golay filter. (532 nm, $2.86 \times 10^{-5} \text{ J cm}^{-2}$)

packing side chain will have negligible impact. The spectra are dominated by a ground state bleach (GSB) at 560 nm, aligning well with the steady state absorbance spectrum (dashed line). A photoinduced absorbance (PIA) from 800-900 nm is likely the $S_1 \rightarrow S_n$ transitions. There is some evidence of stimulated emission (SE) at very early times, being pulled down by a neighbouring PIA at 650 nm. In the kinetics, shown in **Figure 7.4 (b) & (c)**, there is a sharp feature at time zero, attributed to instrument response, which we explore further with fs-TA. Overall, despite the changing relative intensity of the SE and the PIA at 650 nm, the whole signal can be fitted well to a 1-species model, with a lifetime of $64 \pm 2 \text{ ps}$. The excitation in dilute solution is very short-lived, similar to the behaviour of carotenoids.

To further investigate this early time behaviour in solution, we used fs-TA to check for a clear transition, such as $1\text{Bu} \rightarrow 2\text{Ag}$ as in carotenoids. The fs-TA spectra and kinetics are shown in **Figure 7.5**. (a) & (c) show again that the spectra of TIIG-EH and TIIG-Oct are identical in solution. The kinetics in (b) & (d) also confirm that one species is formed in under 1 ps,

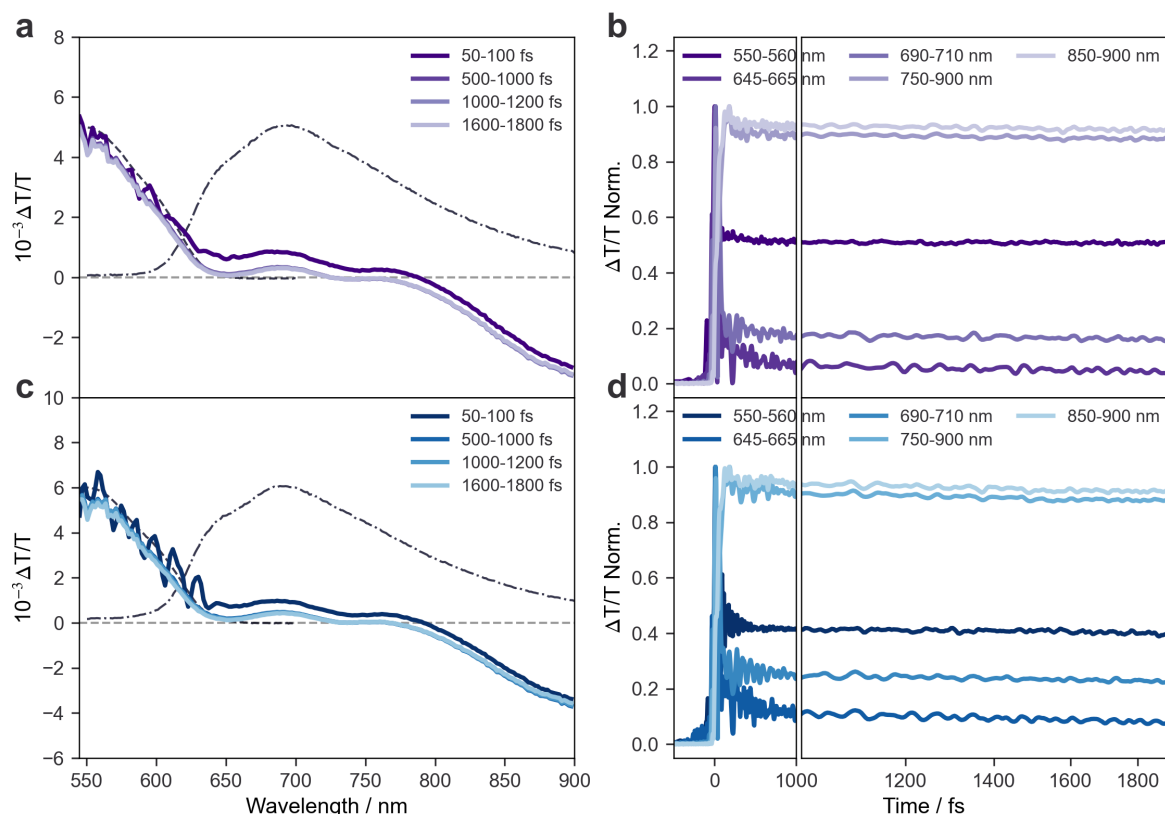


Figure 7.5: Ultrafast transient absorption spectroscopy on femtosecond timescales for solutions of TIIG-Oct (a, b) and TIIG-EH (c, d), with respective steady state absorbance (dashed) and photoluminescence (dot-dashed) spectra. 575 nm excitation, with a 12 fs pulse width, and excitation density of $1.20 \times 10^{-5} \text{ J cm}^{-2}$.

with no further evolution. Coherent oscillations are clearly visible, which with future work may shed light on the vibrational modes active in these molecules.

The behaviour of rapid deactivation for thienoisindigo in solution is reminiscent of the carotenoids and polyenes. There is weak, short lived stimulated emission, possibly from a $2A_g$ -like state. The state is very short lived, decaying rapidly, much like a $2A_g$ state. However, unlike polyenes, we do not observed a sub-picosecond transition from a bright $1B_u$ state to the dark $2A_g$ state. Furthermore, recalling the absorption and emission spectra in **Figure 7.2** as mirror-image-like for the thienoisindigos, this further suggests that only one excited state is involved, rather than the two states as observed in polyenes.

This ultrafast behaviour and rapid relaxation in solution contrasts with the photophysics of the thin films, shown in **Figure 7.8**. Before investigating the thin films, it is worthwhile examining the results of triplet sensitisation in solution.

7.5 Solution Triplet Sensitisation

Solution triplet sensitisation was performed with meso-tetraphenyl-tetrabenzoporphine palladium complex, PdTPTBP, in toluene. PdTPTBP was selected for its very red absorbance of the Q-band at ~ 640 nm [210–212]. As the absorption of TIIG is so broad, it was difficult finding a suitable sensitizer with an absorbance wavelength that would not simultaneously coexcite the TIIG.

The solution TA data are presented in **Figure 7.6**. Excitation at 640 nm with a pump NOPA at late times meant using the white-light DISCO probe, which has lower S:N than the standard probe NOPA for the late time apparatus. The spectra of PdTPTBP in neat solution, shown in **(a) & (b)**, show the expected Soret and Q-band GSB peaks for the porphyrin, with a broad PIA centred ~ 520 nm [212]. The triplet states of the PdTPTBP last a long time, with a lifetime $> 10 \mu\text{s}$. When mixed in a 10:1 ratio of TIIG:sensitizer (1 mM: 0.1 mM), the similar PdTPTBP features are present at early time, and quenched, giving rise to a new signal at $10 \mu\text{s}$. The new signal is very low in intensity, despite clearly efficient triplet energy transfer from the PdTPTBP to the organic. To inspect the new signal, we perform a spectral decomposition to more clearly observe the new spectrum.

The results of the spectral decomposition are shown in **Figure 7.7**. The quenching of the PdTPTBP triplet lifetime is highlighted well in the kinetics shown in **(b), (d) & (f)**. The new spectra for each TIIG-Oct and TIIG-EH are more visible in panels **(c) & (e)**. Both are very noisy traces, indicating low signal intensity. Both show a GSB that matches well to the solution steady-state absorbance spectra. This further confirms that the PdTPTBP was indeed transferring energy to the TIIG, rather than an impurity, or being quenched by oxygen. However, it does not rule out the possibility of a low-yield FRET from the PdTPTBP to the TIIG, rather than successful triplet transfer.

The triplet signal for TIIG shows signs of a PIA at the blue and red-edges of the GSB. This perhaps indicates that, as the GSB is so broad, the triplet PIA is underneath the GSB. This would explain why the signal is of such low intensity. In other singlet fission materials, particularly rylene and DPP derivatives, the most intense triplet-state PIA has been reported

to overlap with the GSB [158]. Further measurements with different organic:sensitiser ratios (1 mM: 0.5 mM, 1 mM: 0.1mM, 4 mM: 0.2 mM) were attempted without greater success of recording the T_1 spectrum.

The neat PdTPTBP solution fitted well to a $N=1$ model with a lifetime of the triplet as $\sim 80 \mu s$. For the mixed solutions, the data fitted well to a simple $A \rightarrow B \rightarrow$ model, indicating a triplet transfer lifetime of 500-600 ns, and a lifetime of the TIIG triplet state of 3000-4000 ns in solution.

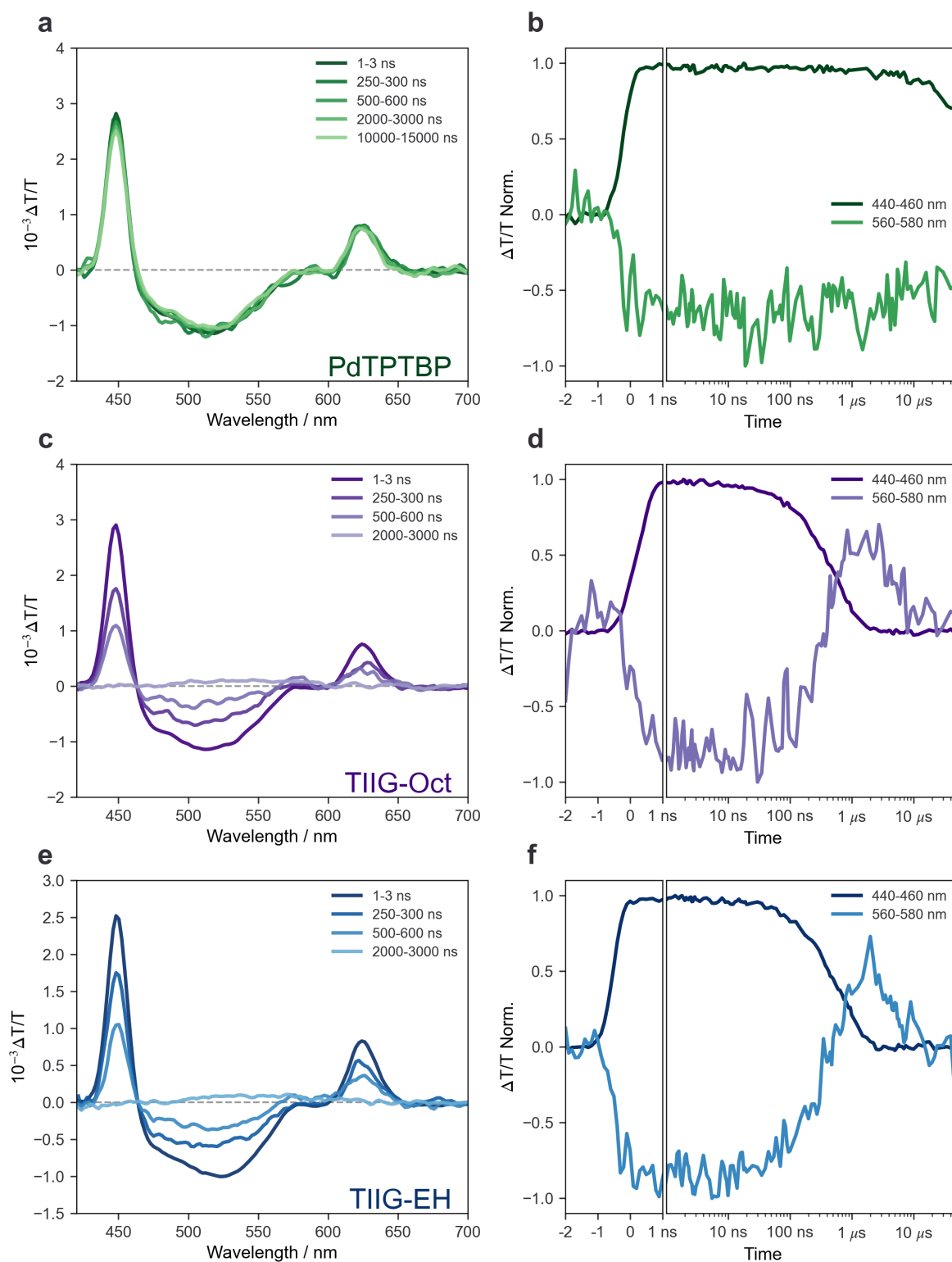


Figure 7.6: Solution triplet sensitisation with PdTPPTBP (10:1 ratio, 200 μ m pathlength). PdTPPTBP triplets are long lived in (a) & (b), and are successfully quenched by the presence of TIIGs. The TIIG triplet spectrum is remarkable low in intensity. Further examination of the TIIG T_1 spectrum is achieved with decomposition in **Figure 7.7**. ($6.52 \times 10^{-5} \text{ J cm}^{-2}$ excitation density at 640 nm)

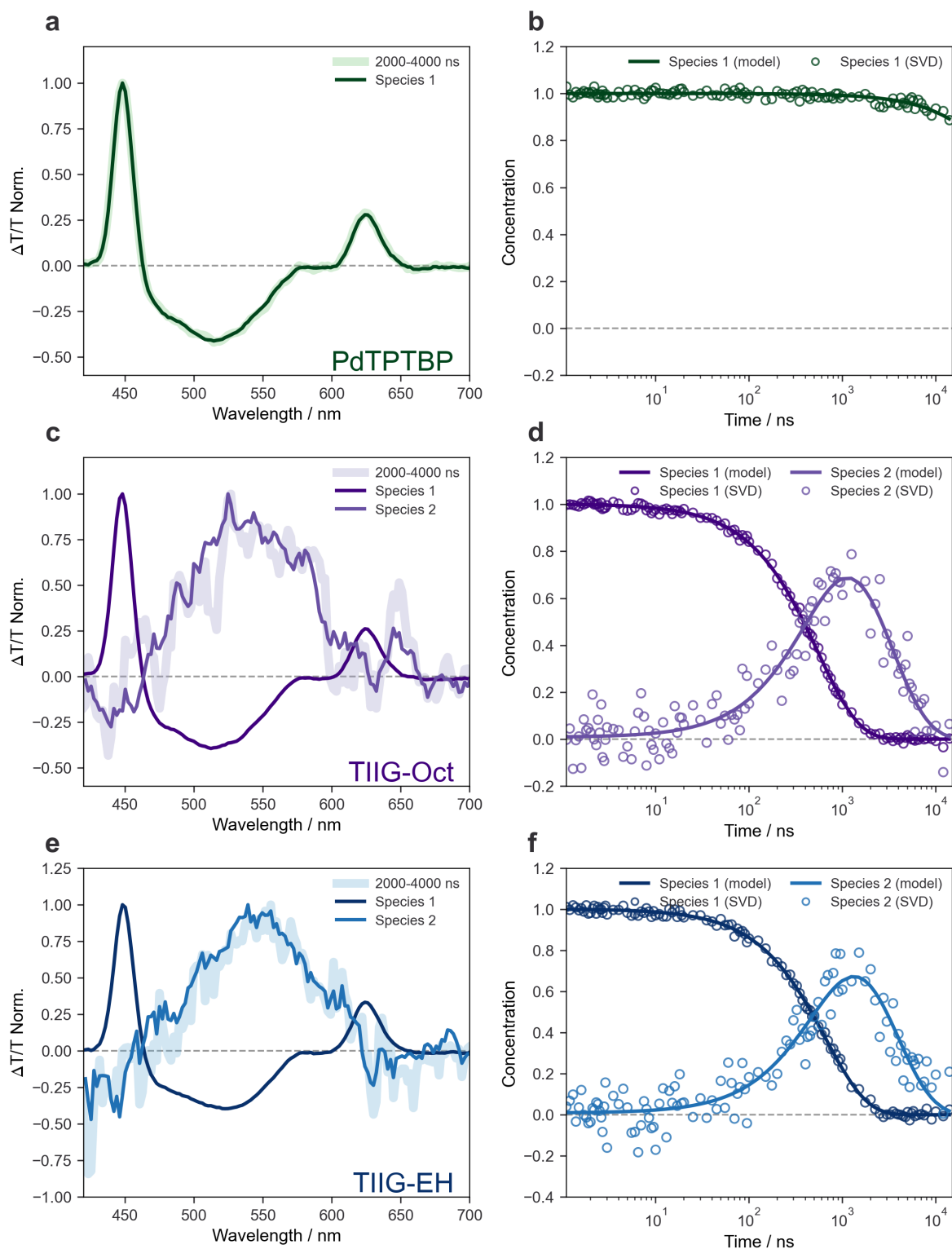


Figure 7.7: Decomposition of solution triplet sensitisation spectra with an N=2 SVD and kinetic model (A→B→). PdTPTBP: $87 \pm 8 \mu\text{s}$. TIIG-Oct: $554 \pm 8 \text{ ns}$, $2970 \pm 611 \text{ ns}$. TIIG-EH: $670 \pm 9 \text{ ns}$, $3950 \pm 890 \text{ ns}$.

7.6 Ultrafast TA of Thin Films

The transient absorption spectra of TIIG thin films are presented on picosecond and nanosecond timescales (**Figure 7.8 (a) & (c) and (b) & (d)** respectively). Both TIIG-Oct and TIIG-EH now show excited states persisting to μs timescales, a stark contrast to the 60 ps lifetime of the solution state.

In every spectrum, there is a strong GSB which matches well with the thin film steady-state absorption spectrum for each molecule. Accordingly, the features of the TIIG-EH spectra are red shifted by approximately 20nm with respect to TIIG-Oct. The increased intensity of the 0-0 peak for TIIG-EH is also captured in the GSB feature.

TIIG-EH appears to have a more prominent SE feature, centred at 770 nm, compared to TIIG-Oct. The very short lifetime of the SE signal is as expected from the very low PLQE measured under steady state conditions.

The PIAs are intriguing. We first consider TIIG-Oct. There is an early time (2 ps) PIA at 850-900 nm, which is reminiscent of the solution state PIA. This is likely a $S_1 \rightarrow S_n$ transition. This PIA loses intensity quickly. Meanwhile, a bluer PIA, centred at 660 nm, persists beyond the picosecond timescale with a slight blue shift to 650 nm. This 650 nm PIA is present in the nsTA and lasts until a microsecond. This PIA is present in the solution spectra, but is far more pronounced and longer living in the thin films. A third PIA, centred at 600 nm, must also be present, as observed from the pulling down of the GSB in this region. This is most clear in the nsTA data. A positive 'background' beyond 700nm at late times is likely a thermal artefact.

By comparison, TIIG-EH appears to show no PIAs at first glance. However, in the early time data, it is clear the 0-1 absorbance peak in the GSB is pulled down with respect to the 0-0 peak, suggesting a PIA is present at 600 nm, obscured underneath the GSB. This PIA is more visible in the nsTA data, with a negative feature at 550 nm. The presence of long living PIAs sitting underneath the GSB could be indicative of a triplet-related species. An interesting point to note is that TIIG-EH does not show a PIA that is similar to the solution state. From the solution spectra, we might expect a PIA from the S_1 from 850 nm onwards. Despite an

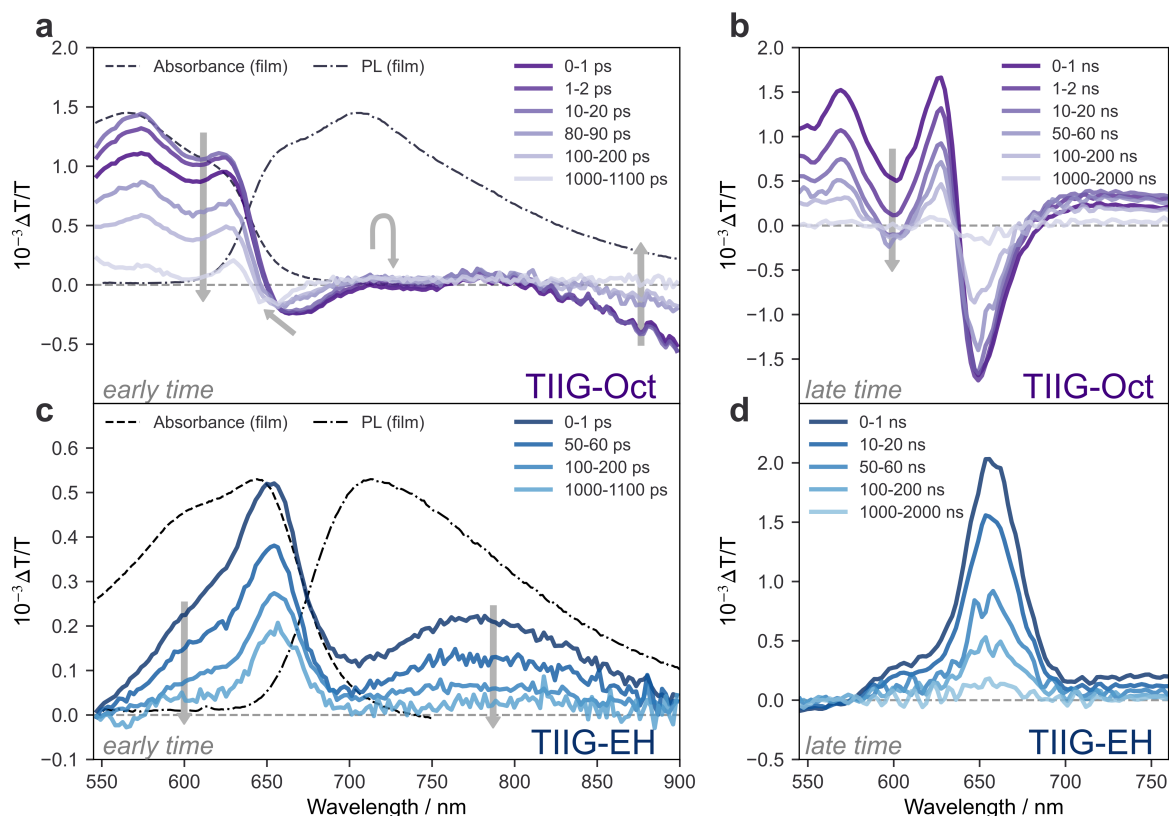


Figure 7.8: Ultrafast transient absorption spectroscopy on picosecond (**a, c**) and nanosecond (**b, d**) timescales for thin films of TIIG-Oct (**a, b**) and TIIG-EH (**c, d**), excited at 532 nm. Respective thin film steady state absorbance (dashed) and photoluminescence (dot-dashed) spectra are shown for reference. Late time spectra in (**b**) and (**d**) have a 5 pt Savitsky Goleay filter to reduce noise from thin film interference. (532 nm, psTA $2.38 \times 10^{-5} \text{ J cm}^{-2}$, nsTA $7.5 \times 10^{-5} \text{ J cm}^{-2}$)

absence of this red PIA, the presence of a clear SE may indicate a singlet-like ‘bright’ species at early times.

We now consider the late time kinetics shown in **Figure 7.9**. TIIG-Oct displays an inverse fluence dependence on the nanosecond timescale, whereby the signal at 620 nm, which is GSB with underlying PIA, decays more rapidly at lower fluence. This is contrary to the expected response for a system where triplets are generated, as they would recombine non-geminately more efficiently at higher fluence, and so have a shorter lifetime. Thus, this fluence dependence is more likely due to trap limited recombination at low fluence. More traps are occupied with increasing fluence, resulting in an apparent increase in lifetime of the GSB. TIIG-EH, however, does not show any indication of a fluence dependence, with the kinetics in (**c**) & (**d**) remaining invariant at different fluences. Both wavelength regions decay with

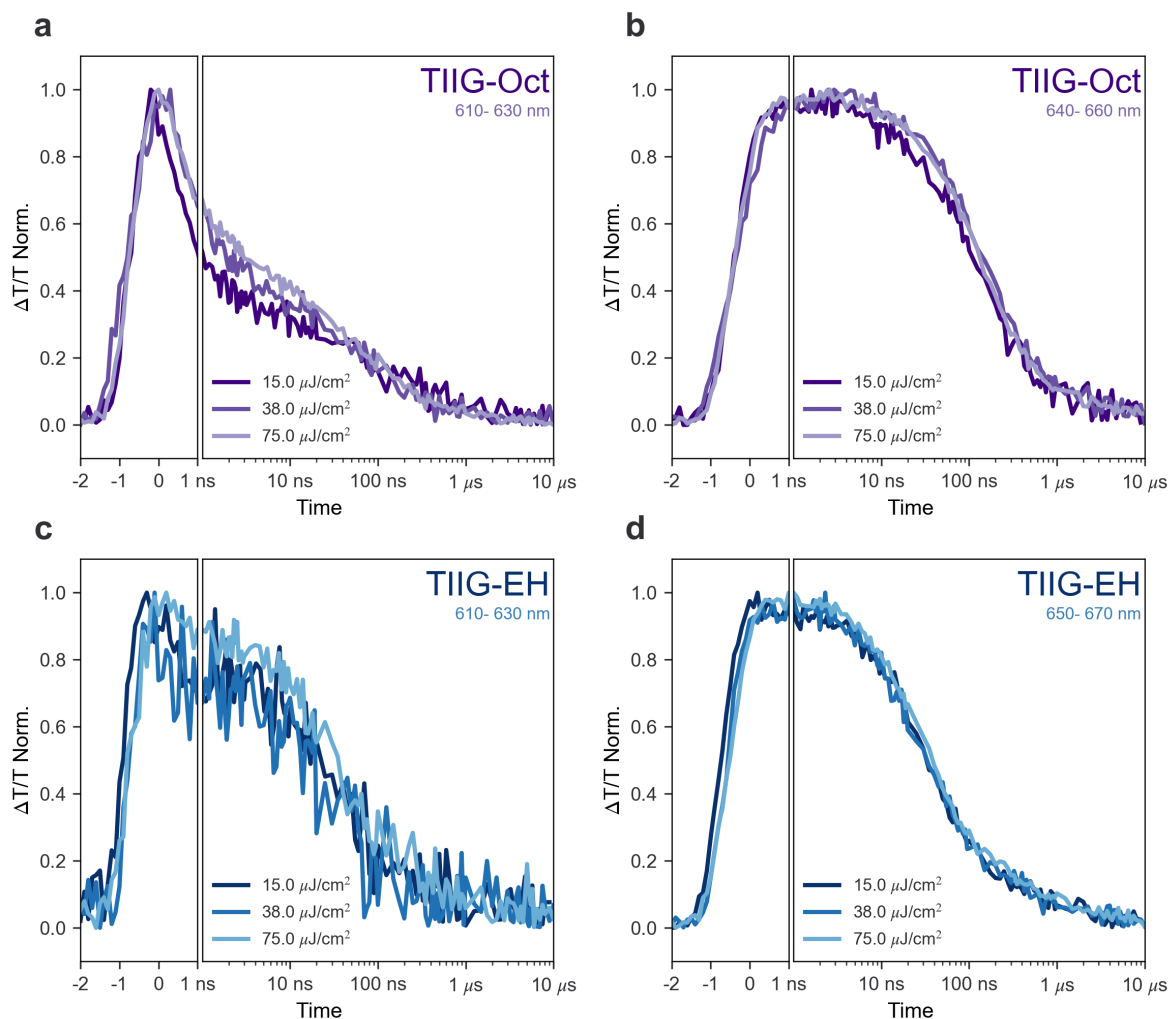


Figure 7.9: Late time fluence series for TIIG-Oct and TIIG-EH at two regions of the GSB. For TIIG-EH there is no apparent fluence dependence at either wavelength range. For the TIIG-Oct, there is an inverse fluence dependence at the bluer wavelength region. This perhaps indicates trap mediated decay pathways. The two kinetics for the two regions of GSB are different for TIIG-Oct, possibly suggesting more than one signal is present in the GSB region.

similar timescales, indicating perhaps only one species is present in TIIG-EH at late times. These dynamics for the two systems are explored further in **Section 7.7**.

Interestingly, these late time results were reproduced with different samples, prepared through blade coating by Dr Simon Dowland, and with 355 nm excitation. The results of nsTA are shown in **Figure 7.10**. The spectra are well reproduced compared to the spectra of **Figure 7.8**. The slightly bluer probe in **Figure 7.10** shows more clearly the blue PIA for TIIG-EH, which perhaps is now more convincing, particularly in comparison to the solution state triplet sensitisation spectra and the results of Wang *et al.* in **Figure 7.1**. This perhaps confirms that

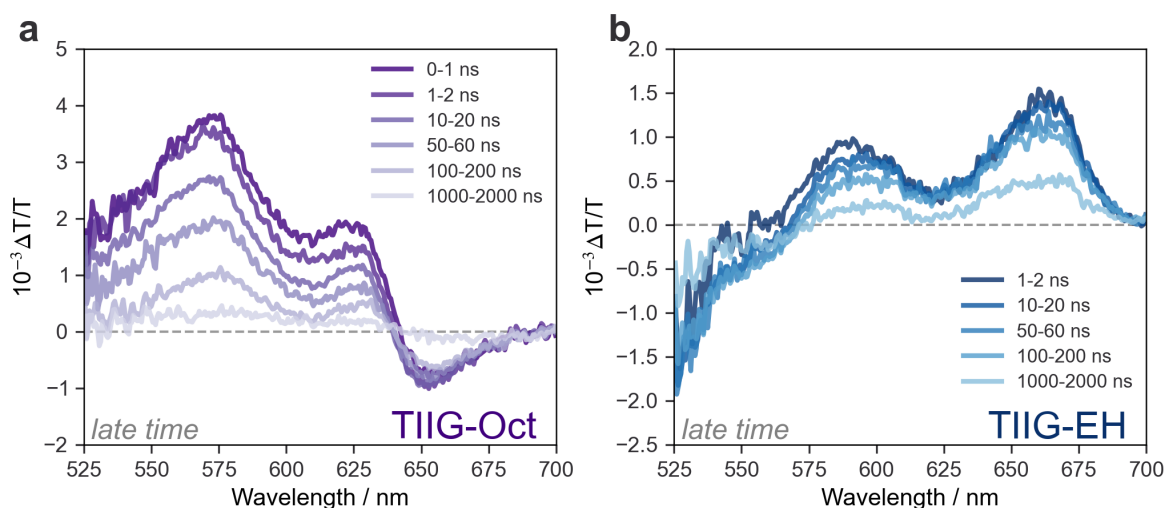


Figure 7.10: Late time nsTA of blade coated films, excited at 355 nm. Spectra match well with the spin coated samples measured at 532 nm in **Figure 7.8**, with the TIIG-EH PIA at 525-575 nm more clearly visible with this probe range. (Excitation density $1.41 \times 10^{-4} \text{ J cm}^{-2}$)

TIIG-EH may have long-lived triplets present on the ns timescale.

7.7 Decomposition and Modelling

Spectral decomposition of data in **Figure 7.8** is shown in **Figure 7.11**. This was achieved through singular value decomposition and globally fitting a kinetic model to reconstruct the data. This was performed for both the early time and late time TA data of the thin films independently, which are displayed together. The resulting spectra are shown in panels **(a)** and **(b)**, with comparisons to the steady state thin film absorbance and PL spectra, with the $\Delta T/T$ spectrum at 100 ns shown. The relevant kinetics are shown in **(d)** and **(e)**, with the ODE model (solid line) and the reconstructed kinetics (markers) for each species. The kinetics are summarized for both cases in panel **(c)**.

TIIG-EH fits well to, overall, a two species model. Species 1 is present within the instrument response, and transforms to Species 2 with a lifetime of 130 ps, as well as having an intrinsic decay with a lifetime of 215 ps due to two distinct sub-populations. Species 2 then persists for tens of nanoseconds, decaying dispersively with a multi-exponential decay, indicating multiple sub-populations, potentially due to inhomogeneous morphology. The lifetimes of Species 2 can be approximated as 30 ns and 200 ns, with a small fraction of the Species 2 population decaying slower with a lifetime >500 ns. To identify the species, we consider the related spectra. The spectrum for Species 2 agrees well between the ps and ns data, confirming that the same species is being observed. The differences between the spectra of Species 1 and 2 are subtle, yet significant. Species 1 has a stimulated emission, suggesting it cannot be related to the dark 2Ag state due to the symmetry requirements for emission. For Species 2, there is no longer a stimulated emission, and a PIA has pulled down the GSB between 550-600 nm.

The late time spectrum for TIIG-EH, with a GSB with a PIA to the bluer edge, is highly similar to the spectra of free triplets observed by Wang *et al.* in their thiophene functionalised isoindigos [214]. Furthermore, it qualitatively agrees with the spectra we observed from solution triplet sensitisation measurements, as seen in **Figure 7.7 (e)**. It is therefore possible that, for TIIG-EH, a bright state transforms directly into free triplets, or a triplet-related species such as $^1(TT)$, with a timescale of 130 ps. More conclusive evidence of free triplets would

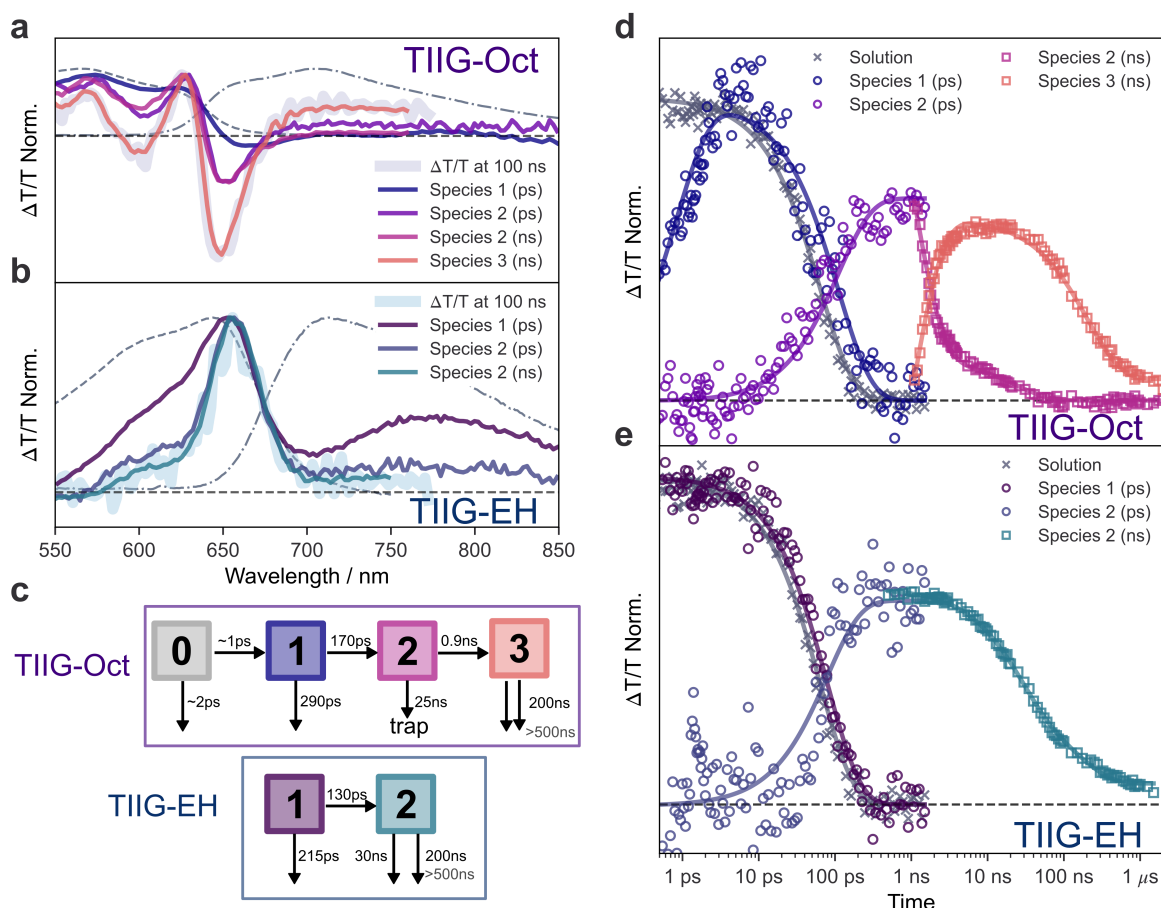


Figure 7.11: Combined spectral decomposition of the transient absorption data presented in **Figure 7.8**. Spectra are presented in (a) and (b), with late time raw data shown for reference (shaded line). Associated kinetics are shown in (d) and (e), with their relevant photoschemes and decay lifetimes shown in panel (c). The ps and ns data were analysed separately, with the spectra of the overlapping Species 2 aligning well. Over the two time regions, the TIIG-EH data fits well to a 2-species model, while the TIIG-Oct fits well to a 3-species model.

be required through methods such as ESR. However, within the context of the literature, it is not unreasonable that free triplets are being formed through singlet fission. This behaviour of rapid transformation of a bright state directly to triplets, which then decay with a multi-exponential, is highly similar to the results of Musser *et al.* for the carotenoid aggregates [46].

For TIIG-Oct, we again observe PIAs underneath the GSB. However, they appear in slightly different regions to the TIIG-EH, and are more intense. While the kinetics appear deceptively more complex, the rate constants compare well to those of TIIG-EH. TIIG-Oct requires the addition of a third species in the kinetic model. Species 1 grows in with a lifetime of ~ 1 ps,

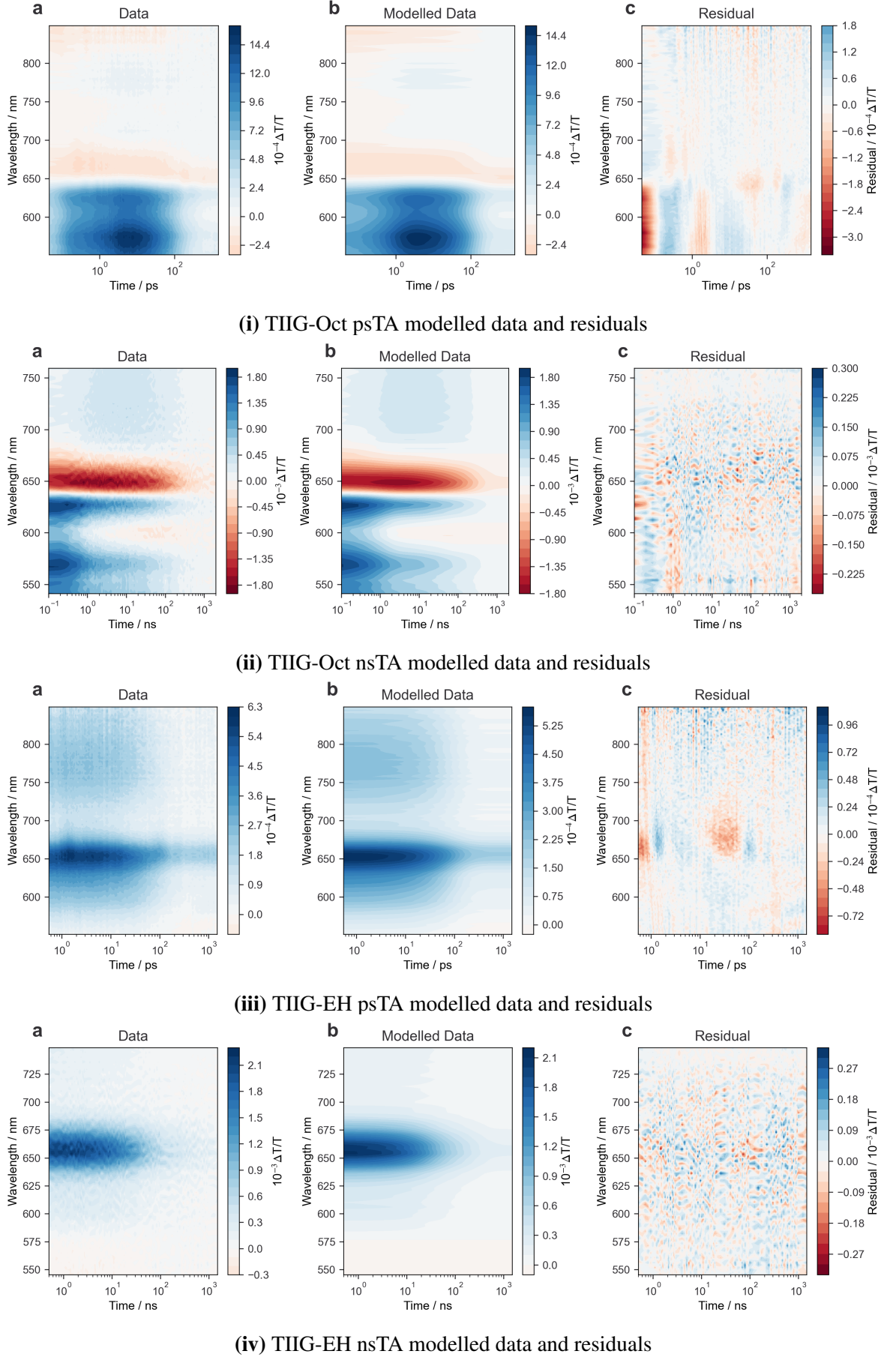


Figure 7.12: Residuals of early and late time data and modelled data for both TIIG-Oct and TIIG-EH.

as opposed to appearing from time zero as in the TIIG-EH. Species 1 transforms to Species 2 with a lifetime of 170 ps, as well as having an intrinsic decay with a lifetime of 290 ps due to different sub-populations. The spectrum for Species 2 agrees well between the early time and late time decompositions. Species 2 in the ns TA then goes on to form Species 3, which can be modelling as either a 1-to-1 or 1-to-2 process, and also has an intrinsic decay. As this intrinsic decay is on the same time scale as the inverse fluence dependence (**Figure 7.9**) then we assert that this decay pathway occurs via a trap state. Species 3 then decays with a lifetime of 200 ns, with a considerable population of states existing beyond 1 μ s, with a lifetime > 500 ns. In both the TIIG-EH and TIIG-Oct, the decays of Species 2/3 are complex, suggesting there is a distribution of available populations of the state in the thin films, possibly due to a range of morphologies.

Spectrally, Species 2 and 3 for TIIG-Oct are similar, with only a change in the relative amplitudes of the PIA compared to the GSB. This may suggest that Species 2 and 3 are spectrally the same, but with differing absorption cross sections of the PIA at 600 nm. However, the more likely explanation is that the attempts at decomposing the complex kinetics is somewhat limited.

As the kinetic model fitted to the data is somewhat complex, with many species invoked over the two timescales for the TIIG-Oct, the 2D plots of the data, the modelled data, and the residuals are presented in **Figure 7.12**. This is to emphasise the clear ‘growing in’ of Species 1 for TIIG-Oct on the ps timescale, and also highlight the apparent growth of a third species at later times. For TIIG-EH, it is more clear that over the two timescales, only two species are present.

Overall, both TIIG-Oct and TIIG-EH show long living species in the thin films, in contrast to their rapid deactivation in solution. For TIIG-EH, one may be convinced from the context of the literature and from attempts at triplet sensitisation in solution that triplets might be forming, due to the PIA to the blue edge of the GSB. From kinetic analysis, it appears that this possible triplet species forms directly from a bright state. For TIIG-Oct, the results are less convincing. The spectra for TIIG-Oct also feature PIAs under the GSB, but they are

dissimilar to those for TIIG-EH and in the literature. The kinetics for TIIG-Oct are more complex, perhaps indicating that more processes are at play, including the possibility of trap limited recombination.

For further confirmation of the presence of triplet species in TIIG-EH, we performed trESR on thin films of both samples. Unfortunately, a signal was unable to be obtained, possibly due to sub- μ s lifetimes of the possible-triplet species.

There is one further piece of information yet to consider, which is the presence of thermal artefacts. As the triplet PIAs are predicted to be obscured by the GSB, it is worth examining the possibility of wrong assignment of the PIAs.

7.8 Thermal Artefacts

Triplet PIAs obscured by the GSB are not uncommon for singlet fission systems. However, thermal artefacts can also appear in similar regions. One way to ‘test’ for thermal artefacts is to compare the spectra to the first derivative of the steady state absorption [158, 174, 220]. In **Figure 7.13**, we compare the spectra from the decompositions in **Figure 7.11** to the first derivative of the thin film absorbance spectra in **Figure 7.2**. Similarities between the PIAs and the derivative absorbance may indicate signatures of thermal artefacts.

For TIIG-EH in **(b)**, we fortunately do not see resemblance between the derivative absorbance and the TA signals. This suggests the data is relatively artefact free. However, for TIIG-Oct, there is a striking resemblance between the two PIAs at 600 nm and 650 nm and the derivative signal. The PIAs are perhaps red-shifted by ~ 10 nm. This suggests that the PIAs observed in TIIG-Oct are possibly thermal artefacts. This appears to be a material property, as it was observed on multiple different TA set-ups, different fluences, and between different samples. It is perhaps not surprising, as indigos are well-known for rapid internal conversion and ultimately loss of photoexcitation through heat-loss.

Surprisingly the derivative steady state absorbance for TIIG-Oct is almost identical to the signatures reported by Wang *et al.* as the spectrum for the free triplets. However, they reported their data as $\Delta A/A$, which would necessitate a sign flip of the signal.

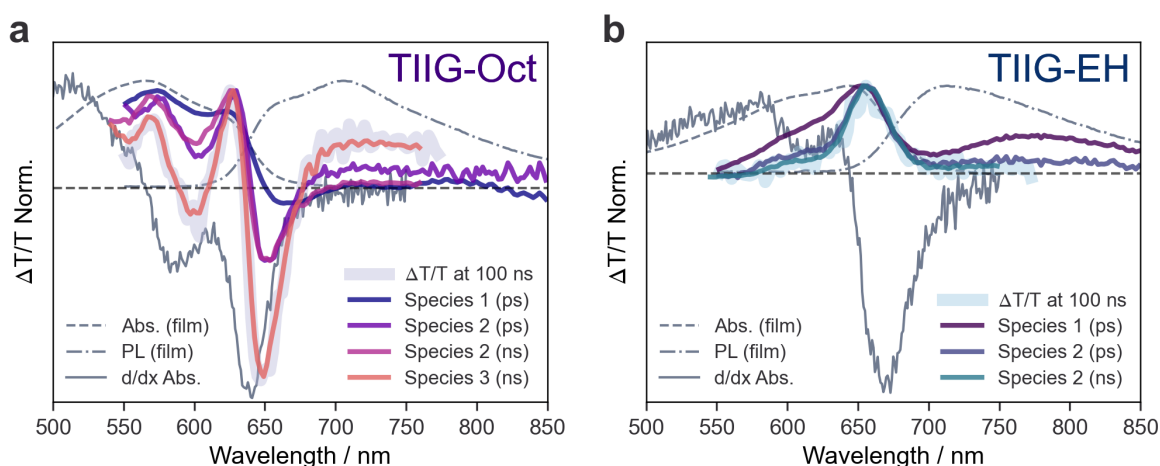


Figure 7.13: Considering thermal artefacts: comparisons of the spectra obtained from decomposition in **Figure 7.11** to the first derivative of the thin film absorbance spectra in **Figure 7.2**, as suggested in the literature [158, 174, 220].

Overall, the presence of thermal artefacts in TIIG-Oct is convincing. This would also explain the more complex TA kinetics for this sample. However, the presence of thermal artefacts and triplets from singlet fission are not mutually exclusive, but are far harder to distinguish. Similar results were observed by Maity *et al.* for HR-TDPP-TEG, a DPP derivative [158]. To avoid the confusion of the thermal artefacts, they examined regions in the NIR. In future work on thienoisindigos, it would be a worthy endeavour to search for possible NIR signatures for both samples. Further more, repeating the visible measurements with a sapphire substrate would also help to confirm that the signals for TIIG-Oct are the result of thermal artefacts.

7.9 Discussion and Conclusion

We have investigated two thienoisindigo derivatives with differing side-chains, in the aim of understanding if TIIG is a potential singlet fission chromophore. Prior literature suggests that TIIG should have satisfactory energetics for singlet fission, while others report intramolecular fission in a similar isoindigo derivative. The two side chains showed distinct molecular packing properties, with TIIG-EH showing more prominent aggregation than the TIIG-Oct.

Both materials were intensely absorbing and weakly emitting in solution, thin film, and films diluted with polystyrene, making them difficult materials to characterise. We employed ultrafast transient absorption which revealed a rapid decay in solution, but longer living dynamics in the thin film. This behaviour is reminiscent of the carotenoid aggregates from the literature, where a fast deactivation in the solution state is outcompeted by singlet fission in aggregates.

This ‘dark’ nature of the thienoisindigos and fast non-radiative decay in solution is similar to the behaviour of polyenes. However, the steady-state absorption and emission spectra are mirror-image-like, in contrast to polyenes, where the ‘bright’ $1B_u$ state decays non-radiatively through a ‘dark’ $2A_g$ state; it is unlikely that the thienoisindigos invoke such a two-state pathway. This was further confirmed with fs-TA, where there was no evidence of a sub-picosecond transition from a bright state to a dark state, as would be expected in a polyene system. So, while some properties of the thienoisindigos are similar to polyenes, they do not exhibit the same solution photophysics upon closer examination.

In thin films, we observed long-living species that featured PIAs underneath the GSB, consistent with solution state triplet sensitization and literature reports. The PIAs in TIIG-Oct were dominated by a thermal artefact, showing more complex decay dynamics, with an inverse-fluence dependence suggesting trap limited recombination of states. While thermal artefacts and singlet fission are not mutually exclusive, the artefact signatures obscured any evidence for triplets.

For TIIG-EH, the kinetics were more straightforward, with a simple conversion from a bright state to the triplet-related species on the timescale of 130 ps. The lack of an ESR signal makes

assignment of these signatures tentative, but in the balance of probability, it is not unlikely that they are triplets. However, we see no direct evidence for an intramolecular fission mechanism. It is clear that the 'triplet'-like signal is highly dependent on the side chains and morphology to outcompete deactivation and thermal pathways, which is not an indication of an inherently intramolecular process. In future work, establishing a clear triplet signature, either through further sensitisation experiments, or more ESR attempts, is a priority in understanding these materials further.

Overall, the thienoisindigos proved an interesting system to investigate. This competition between the rapid deactivation process, and a possible triplet formation pathway, is one of interest for further study. The relationship between the side chains and thermal artefacts is non-trivial, and again affirms the complex relationship between singlet fission and morphology, driven by molecular design.

Chapter 8

Conclusions and Outlook

8.1 Summary

This thesis aimed to study singlet fission, offering an innovative methodology for the study of singlet fission materials, suggesting an alternative approach to molecular design considerations, and examining two potential singlet fission candidates. This study carries significant relevance to the ongoing search for new singlet fission chromophores for application with photovoltaics to circumvent the Shockley-Queisser limit.

In **Chapter 4**, the utilization of modulated magnetic field effects (modMPL) for the investigation of thin films of TIPS-Tc has yielded invaluable insights. The study with modMPL proved to be highly sensitive, showing key differences in the spin physics of the films contingent upon changes in morphology. We uncovered detailed lineshapes for two emission regions of TIPS-Tc, contributing fresh observations to the longstanding debate of the assignment of TT or excimeric emission in TIPS-Tc. Furthermore, we observed in real-time the impact of polycrystallinity on the lineshapes. This body of work underscores the potential of modMPL as an excellent tool for screening singlet fission materials, particularly when confronted with the need to compare numerous sample preparation methods and morphologies.

In **Chapter 5**, we employed kinetic modelling to simulate and understand the lineshapes produced by modMPL. Our findings affirmed that the lineshape at 700 nm bears features relevant to the TT pair, and cannot be explained by direct excimeric emission originating from the singlet state alone. We have proposed a plausible explanation for this data, involving the

reformation of a triplet pair, incapable of reverting to the singlet state, that leads to emission at longer wavelengths. This exploration forms a solid foundation for future simulations by theoreticians.

In **Chapter 6** we investigated cibalackrot and a novel derivative, aza-cibalackrot, to explore whether our unconventional molecular design choices could invoke singlet fission behaviour. By employing transient absorption spectroscopy, we asserted that the molecular design changes had resulted in the formation of a new species, which we tentatively assign as a triplet-triplet pair that was unable to separate to free triplets.

In **Chapter 7** we inspect thienoisindigo for its singlet fission potential with two different side-chains, in the context of prior literature suggesting intramolecular fission in a similar isoindigo derivative. Despite the inherent challenges in working with this system, such as rapid deactivation in solution and lack of emission, we detected signals potentially linked to triplets for one of the side-chains, while the other exhibited a dominant thermal artefact. While we find no evidence for intramolecular fission, this observation hints at the existence of a delicate equilibrium required to surpass deactivation pathways leading to thermal artefacts, in order to generate triplet species through singlet fission.

8.2 Future Outlook

The most exciting outcome of this thesis lies in the discovery of modMPL's aptitude for studying thin films. Subsequent research should focus on extending the application of modMPL to other singlet fission systems. Exploring if lineshapes akin to the 700 nm feature observed in TIPS-Tc emerge in other systems, such as TIPS-pentacene, would validate the origin of the lineshape as the TT pair. Definitively determining if the 700 nm emission represents a loss pathway is also an avenue of research where modMPL may hold invaluable insight.

Furthermore, as more materials are screened, development of a cost-effective apparatus for routine screening of singlet fission films would facilitate the investigation and corroboration between the modMPL features and the singlet fission performance of a material.

With future simulations of modMPL lineshapes, exploring the estimation of D and E parameters of materials holds great potential in addressing material systems where electron spin resonance (ESR) proves challenging. Developing a simulation routine which implements simple kinetic models to analyse modMPL results would streamline future data interpretation and allow for the comparable analyses of different molecular systems. These future avenues of research could result in a deeper understanding of singlet fission dynamics and material systems, positioning modMPL as an invaluable tool in deciphering these processes.

For the cibalackrots, following optimization of synthetic yield and film morphology, further work to confirm the identity of the TT state is desired. A more comprehensive examination of the impact of morphology on the TT separation rate is also of interest. Such a study would be ideal for examination with modMPL upon generation of further material. Furthermore, we could extend the molecular design methodology to other systems for replication of similar results.

In the case of thienoisindigos, efforts should be directed towards establishing the existence of triplets, and proving or disproving the hypothesis of intramolecular singlet fission in these systems. This may necessitate further ESR studies. Understanding why one packing chain gives rise to thermal artefacts, and the other triplets, is of high interest. Moreover, simulating the morphology of the TIIG-EH film can provide deeper insights into its packing arrangement, and may illicit clues as to why thermal artefacts are minimised in this derivative.

In conclusion, this thesis has made a significant contribution to the field of singlet fission materials. It has particularly advanced our understanding of the modulated magnetic field effects, innovative molecular design approaches, and the intriguing potential of indigoids as candidates in this context. These findings share deeper insights into the complex world of singlet fission, and its intimate interplay with molecular design and sample morphology.

Bibliography

1. Fitzgerald Weaver, J. World has installed 1TW of solar capacity. *PV Magazine* (2022).
2. OurWorldInData. Solar PV cumulative capacity (2023).
3. Hallam, B., Kim, M., Zhang, Y., *et al.* The silver learning curve for photovoltaics and projected silver demand for net-zero emissions by 2050. *Progress in Photovoltaics: Research and Applications*, 598–606 (2022).
4. UNFCCC. The Paris Agreement (2015).
5. Verlinden, P. J. Future challenges for photovoltaic manufacturing at the terawatt level. *Journal of Renewable and Sustainable Energy* **12**, 053505 (2020).
6. Engel, E. & Engel, N. A Review on Machine Learning Applications for Solar Plants. *Sensors* **22**, 9060 (2022).
7. Alfari, F. E. A Sensorless Intelligent System to Detect Dust on PV Panels for Optimized Cleaning Units. *Energies* **16** (2023).
8. Shockley, W. & Queisser, H. J. Detailed balance limit of efficiency of p-n junction solar cells. *Journal of Applied Physics* **32**, 510–519 (1961).
9. Rao, A. & Friend, R. H. Harnessing singlet exciton fission to break the Shockley-Queisser limit. *Nature Reviews Materials* **2**, 17063 (2017).
10. NREL. Best Research-Cell Efficiency Chart (2023).
11. Smith, M. B. & Michl, J. Singlet fission. *Chemical Reviews* **110**, 6891–6936 (2010).
12. Daiber, B., van den Hoven, K., Futscher, M. H., *et al.* Realistic Efficiency Limits for Singlet-Fission Silicon Solar Cells. *ACS Energy Letters* **6**, 2800–2808 (2021).
13. Smith, M. B. & Michl, J. Recent advances in singlet fission. *Annual Review of Physical Chemistry* **64**, 361–386 (2013).
14. Jiang, Y., Nielsen, M. P., Baldacchino, A. J., *et al.* Singlet fission and tandem solar cells reduce thermal degradation and enhance lifespan. *Progress in Photovoltaics: Research and Applications* **29**, 899–906 (2021).

15. Dexter, D. L. Two ideas on energy transfer phenomena: Ion-pair effects involving the OH stretching mode, and sensitization of photovoltaic cells.
Journal of Luminescence **18-19**, 779–784 (1979).
16. Paci, I., Johnson, J. C., Chen, X., *et al.*
Singlet Fission for Dye-Sensitized Solar Cells : Can a Suitable Sensitizer Be Found ?,
16546–16553 (2006).
17. Grampp, G., Justinek, M. & Landgraf, S.
Magnetic field effects on the pyrene-dicyanobenzene system: Determination of electron self-exchange rates by MARY spectroscopy.
Molecular Physics **100**, 1063–1070 (2002).
18. Konowalczyk, M., Foster Vander Elst, O. & Storey, J. G.
Development of lock-in based overtone modulated MARY spectroscopy for detection of weak magnetic field effects. *Physical Chemistry Chemical Physics* **23**, 1273–1284 (2021).
19. Fallon, K. J., Budden, P., Salvadori, E., *et al.* Exploiting Excited-State Aromaticity to Design Highly Stable Singlet Fission Materials.
Journal of the American Chemical Society **141**, 13867–13876 (2019).
20. Fallon, K. J. & Bronstein, H. Indolonaphthyridine: A Versatile Chromophore for Organic Electronics Inspired by Natural Indigo Dye.
Accounts of Chemical Research **54**, 182–193 (2021).
21. Purdy, M., Walton, J. R., Fallon, K. J., *et al.*
Aza-Cibalackrot: Turning on Singlet Fission Through Crystal Engineering.
Journal of the American Chemical Society **145**, 10712–10720 (2023).
22. Zeng, W., El Bakouri, O., Szczepanik, D. W., *et al.*
Excited state character of Cibalackrot-type compounds interpreted in terms of Hückel-aromaticity: a rationale for singlet fission chromophore design.
Chemical Science **12**, 1–34 (2021).
23. Ashraf, R. S., Kronemeijer, A. J., James, D. I., *et al.* A new thiophene substituted isoindigo based copolymer for high performance ambipolar transistors.
Chemical Communications **48**, 3939–3941 (2012).
24. Hasegawa, T., Ashizawa, M. & Matsumoto, H. Design and structure-property relationship of benzothienoisindigo in organic field effect transistors.
RSC Advances **5**, 61035–61043 (2015).
25. Yoo, D., Hasegawa, T., Ashizawa, M., *et al.* N-Unsubstituted thienoisindigos: preparation, molecular packing and ambipolar organic field-effect transistors.
Journal of Materials Chemistry C **5**, 2509–2512 (2017).
26. Atkins, P. & Friedman, R. in. 5th, 110–118 (Oxford University Press, 2011).

27. Pazur, A., Schimek, C. & Galland, P. Magnetoreception in microorganisms and fungi. *Open Life Sciences* **2**, 597–659 (2007).
28. Hore, P. J. & Mouritsen, H. The Radical-Pair Mechanism of Magnetoreception (2016).
29. Steiner, U. E. & Ulrich, T.
Magnetic field effects in chemical kinetics and related phenomena.
Chemical Reviews **89**, 51–147 (1989).
30. McCamey, D. R., van Schooten, K. J., Baker, W. J., *et al.* Hyperfine-Field-Mediated Spin Beating in Electrostatically Bound Charge Carrier Pairs.
Physical Review Letters **104**, 017601 (2010).
31. Zarea, M., Carmieli, R., Ratner, M. A., *et al.*
Spin Dynamics of Radical Pairs with Restricted Geometries and Strong Exchange Coupling: The Role of Hyperfine Coupling.
The Journal of Physical Chemistry A **118**, 4249–4255 (2014).
32. Weil, J. A. & Bolton, J. R. Electron Paramagnetic Resonance.
<http://doi.wiley.com/10.1002/0470084987>
(John Wiley & Sons, Inc., Hoboken, NJ, USA, 2006).
33. Weiss, L. R. *Spin-sensitive probes of triplet excitons in organic semiconductors*.
PhD thesis (University of Cambridge, 2018).
34. Walton, J. R. Investigating Avian Magnetoreception Using Broadband Cavity-Enhanced Absorption Spectroscopy (MChem Thesis, University of Oxford). 2019.
35. Musser, A. J. & Clark, J. Triplet-Pair States in Organic Semiconductors.
Annual Review of Physical Chemistry **70**, 323–351 (2019).
36. Pope, M & Swenberg, C. E. Electronic Processes in Organic Solids.
Annual Review of Physical Chemistry **35**, 613–655 (1984).
37. Richert, S., Tait, C. E. & Timmel, C. R. Delocalisation of photoexcited triplet states probed by transient EPR and hyperfine spectroscopy.
Journal of Magnetic Resonance **280**, 103–116 (2017).
38. Kollmar, C. Electronic structure of diradical and dicarbene intermediates in short-chain polydiacetylene oligomers.
The Journal of Chemical Physics **98**, 7210–7228 (1993).
39. Scholes, G. D.
Correlated Pair States Formed by Singlet Fission and Exciton–Exciton Annihilation.
The Journal of Physical Chemistry A **119**, 12699–12705 (2015).

40. Merrifield, R. E. Magnetic effects on triplet exciton interactions.
Pure and Applied Chemistry **27**, 481–498 (1971).
41. Stern, H. L., Musser, A. J., Gelinas, S., *et al.*
Identification of a triplet pair intermediate in singlet exciton fission in solution.
Proceedings of the National Academy of Sciences of the United States of America **112**, 7656–7661 (2015).
42. Stern, H. L., Cheminal, A., Yost, S. R., *et al.*
Vibronically coherent ultrafast triplet-pair formation and subsequent thermally activated dissociation control efficient endothermic singlet fission.
Nature Chemistry **9**, 1205–1212 (2017).
43. Burdett, J. J., Gosztola, D. & Bardeen, C. J.
The dependence of singlet exciton relaxation on excitation density and temperature in polycrystalline tetracene thin films: Kinetic evidence for a dark intermediate state and implications for singlet fission. *The Journal of Chemical Physics* **135** (2011).
44. Tayebjee, M. J. Y., Clady, R. G. C. R. & Schmidt, T. W.
The exciton dynamics in tetracene thin films.
Physical Chemistry Chemical Physics **15**, 14797 (2013).
45. Bossanyi, D. G., Matthiesen, M., Wang, S., *et al.*
Emissive spin-0 triplet-pairs are a direct product of triplet–triplet annihilation in pentacene single crystals and anthradithiophene films. *Nature Chemistry* **13**, 163–171 (2021).
46. Musser, A. J., Maiuri, M., Brida, D., *et al.*
The nature of singlet exciton fission in carotenoid aggregates.
Journal of the American Chemical Society **137**, 5130–5139 (2015).
47. Bakulin, A. A., Silva, C. & Vella, E. Ultrafast Spectroscopy with Photocurrent Detection: Watching Excitonic Optoelectronic Systems at Work.
The Journal of Physical Chemistry Letters **7**, 250–258 (2016).
48. Bayliss, S. L., Weiss, L. R., Rao, A., *et al.*
Spin signatures of exchange-coupled triplet pairs formed by singlet fission.
Physical Review B **94**, 1–7 (2016).
49. Bayliss, S. L., Weiss, L. R., Mitiglu, A., *et al.*
Site-selective measurement of coupled spin pairs in an organic semiconductor.
Proceedings of the National Academy of Sciences **115**, 5077–5082 (2018).
50. Yunusova, K. M., Bayliss, S. L., Chaneière, T., *et al.*
Spin Fine Structure Reveals Biexciton Geometry in an Organic Semiconductor.
Physical Review Letters **125**, 1–6. arXiv: 1912.04191 (2020).

51. Yong, C. K., Musser, A. J., Bayliss, S. L., *et al.*
The entangled triplet pair state in acene and heteroacene materials.
Nature Communications **8** (2017).
52. Bossanyi, D. G., Sasaki, Y., Wang, S., *et al.*
Spin Statistics for Triplet–Triplet Annihilation Upconversion: Exchange Coupling, Intermolecular Orientation, and Reverse Intersystem Crossing.
JACS Au **1**, 2188–2201 (2021).
53. Bossanyi, D. *Triplet-Pair States in Exciton Fission and Fusion*.
PhD thesis (University of Sheffield, 2021).
54. Tapping, P. C. & Huang, D. M. Comment on "Magnetic field effects on singlet fission and fluorescence decay dynamics in amorphous rubrene".
Journal of Physical Chemistry C **120**, 25151–25157 (2016).
55. Burdett, J. J. & Bardeen, C. J. Quantum Beats in Crystalline Tetracene Delayed Fluorescence Due to Triplet Pair Coherences Produced by Direct Singlet Fission.
Journal of the American Chemical Society **134**, 8597–8607 (2012).
56. Wilkinson, F. & Abdel-Shafi, A. A. Mechanism of Quenching of Triplet States by Oxygen: Biphenyl Derivatives in Acetonitrile.
The Journal of Physical Chemistry A **101**, 5509–5516 (1997).
57. Hore, P. Nuclear Magnetic Resonance.
<https://books.google.co.uk/books?id=L9umCAAQBAJ>
(Oxford University Press, 2015).
58. Chabr, M., Wild, U., Fünfschilling, J., *et al.*
Quantum beats of prompt fluorescence in tetracene crystals.
Chemical Physics **57**, 425–430 (1981).
59. Atkins, P. & De Paula, J. *Atkins' Physical Chemistry* 9th
(Oxford University Press, Oxford, 2010).
60. Orlandi, G. & Siebrand, W. Theory of vibronic intensity borrowing. Comparison of Herzberg-Teller and Born-Oppenheimer coupling.
The Journal of Chemical Physics **58**, 4513–4523 (1973).
61. Allardice, J. *Spectroscopic Study of Triplet Exciton Dynamics at the Hybrid Organic-Inorganic Interface*. PhD thesis (University of Cambridge, 2020).
62. Lakowicz, J. R. *Principles of Fluorescence Spectroscopy* 3rd
(Springer, Baltimore, 2007).
63. Spano, F. C. The spectral signatures of frenkel polarons in H- And J-aggregates.
Accounts of Chemical Research **43**, 429–439 (2010).

64. Spano, F. C. & Silva, C. H- and J-aggregate behavior in polymeric semiconductors. *Annual Review of Physical Chemistry* **65**, 477–500 (2014).
65. Köhler, A. & Bässler, H. Electronic Processes in Organic Semiconductors: An Introduction (2015).
66. Majumdar, S., Majumdar, H. & Österbacka, R. Organic Spintronics, 109–142 (Elsevier, 2011).
67. Shen, L., Xie, B., Li, Z., *et al.* Role of Multistate Intersections in Photochemistry. *The Journal of Physical Chemistry Letters* **11**, 8490–8501 (2020).
68. Boeijs, Y. & Olivucci, M. From a one-mode to a multi-mode understanding of conical intersection mediated ultrafast organic photochemical reactions. *Chemical Society Reviews* **52**, 2643–2687 (2023).
69. Förster, T. Zwischenmolekulare Energiewanderung und Fluoreszenz. *Annalen der Physik* **437**, 55–75 (1948).
70. Dexter, D. L. A Theory of Sensitized Luminescence in Solids. *The Journal of Chemical Physics* **21**, 836–850 (1953).
71. Laquai, F., Park, Y.-S., Kim, J.-J., *et al.* Excitation Energy Transfer in Organic Materials: From Fundamentals to Optoelectronic Devices. *Macromolecular Rapid Communications* **30**, 1203–1231 (2009).
72. Shi, K., Healy, A. T., Curtin, I. J., *et al.* Impact of Grain Boundaries on Triplet Exciton Diffusion in Organic Singlet-Fission Materials. *The Journal of Physical Chemistry C* **126**, 4792–4798 (2022).
73. Huang, Y., Buyanova, I. A., Phansa, C., *et al.* Competition between triplet pair formation and excimer-like recombination controls singlet fission yield. *Cell Reports Physical Science* **2**, 100339 (2021).
74. Walker, B. J., Musser, A. J., Beljonne, D., *et al.* Singlet exciton fission in solution. *Nature Chemistry* **5**, 1019–1024 (2013).
75. Dron, P. I., Michl, J. & Johnson, J. C. Singlet Fission and Excimer Formation in Disordered Solids of Alkyl-Substituted 1,3-Diphenylisobenzofurans. *The Journal of Physical Chemistry A* **121**, 8596–8603 (2017).
76. Dover, C. B., Gallaher, J. K., Frazer, L., *et al.* Endothermic singlet fission is hindered by excimer formation. *Nature Chemistry* **10**, 305–310 (2018).
77. Singh, S., Jones, W. J., Siebrand, W., *et al.* Laser Generation of Excitons and Fluorescence in Anthracene Crystals. *The Journal of Chemical Physics* **42**, 330–342 (1965).

78. Merrifield, R. E., Avakian, P. & Groff, R. P.
Fission of singlet excitons into pairs of triplet excitons in tetracene crystals.
Chemical Physics Letters **3**, 386–388 (1969).
79. Geacintov, N., Pope, M. & Vogel, F.
Effect of Magnetic Field on the Fluorescence of Tetracene Crystals: Exciton Fission.
Physical Review Letters **22**, 593–596 (1969).
80. Groff, R. P., Avakian, P. & Merrifield, R. E.
Coexistence of exciton fission and fusion in tetracene crystals.
Physical Review B **1**, 815–817 (1970).
81. Johnson, R. C. & Merrifield, R. E. Effects of magnetic field effects on the mutual annihilation of triplet excitons in anthracene crystals.
The Journal of Chemical Physics **1**, 896–902 (1970).
82. Monahan, N. & Zhu, X.-Y. Charge Transfer–Mediated Singlet Fission.
Annual Review of Physical Chemistry **66**, 601–618 (2015).
83. Johnson, J. C., Nozik, A. J. & Michl, J.
The Role of Chromophore Coupling in Singlet Fission.
Accounts of Chemical Research **46**, 1290–1299 (2013).
84. Lukman, S., Richter, J. M., Yang, L., *et al.* Efficient Singlet Fission and Triplet-Pair Emission in a Family of Zethrene Diradicaloids.
Journal of the American Chemical Society **139**, 18376–18385 (2017).
85. Feng, J., Hosseinabadi, P., Clercq, D. M. D., *et al.* Observation of an emissive intermediate in a liquid singlet fission and triplet fusion system at room temperature.
eprint: chemrxiv-2023-vn492 (10.26434).
86. Kim, H. & Zimmerman, P. M. Coupled double triplet state in singlet fission.
Physical Chemistry Chemical Physics **20**, 30083–30094 (2018).
87. Xu, J., Jarocha, L. E., Zollitsch, T., *et al.*
Magnetic sensitivity of cryptochrome 4 from a migratory songbird.
Nature **594**, 535–540 (2021).
88. Tarasov, V. V., Zorinants, G. E., Shushin, A. I., *et al.*
The role of spin-lattice relaxation in magnetic field effects on the luminescence of amorphous and polycrystalline rubrene films. *Chemical Physics Letters* **267**, 58–64 (1997).
89. Wakasa, M., Yago, T., Sonoda, Y., *et al.* Structure and dynamics of triplet-exciton pairs generated from singlet fission studied via magnetic field effects.
Communications Chemistry **1**, 1–6 (2018).

90. Wakasa, M., Kaise, M., Yago, T., *et al.* What Can Be Learned from Magnetic Field Effects on Singlet Fission: Role of Exchange Interaction in Excited Triplet Pairs. *Journal of Physical Chemistry C* **119**, 25840–25844 (2015).
91. Piland, G. B., Burdett, J. J., Kurunthu, D., *et al.* Magnetic field effects on singlet fission and fluorescence decay dynamics in amorphous rubrene. *Journal of Physical Chemistry C* **117**, 1224–1236 (2013).
92. Budden, P.
Investigating the Photophysics of New and Stable Singlet Fission Materials.
PhD thesis (University of Cambridge, 2021).
93. Baldacchino, A. J., Collins, M. I., Nielsen, M. P., *et al.*
Singlet fission photovoltaics: Progress and promising pathways.
Chemical Physics Reviews **3**, 021304. eprint: 2202.01326 (2022).
94. Johnson, J. C., Nozik, A. J. & Michl, J.
High Triplet Yield from Singlet Fission in a Thin Film of 1,3-Diphenylisobenzofuran.
Journal of the American Chemical Society **132**, 16302–16303 (2010).
95. Fallon, K. J., Sawhney, N., Toolan, D. T. W., *et al.*
Quantitative Singlet Fission in Solution-Processable Dithienohexatrienes.
Journal of the American Chemical Society **144**, 23516–23521 (2022).
96. Allardice, J. R., Thampi, A., Dowland, S., *et al.*
Engineering Molecular Ligand Shells on Quantum Dots for Quantitative Harvesting of Triplet Excitons Generated by Singlet Fission.
Journal of the American Chemical Society **141**, 12907–12915 (2019).
97. Casillas, R., Papadopoulos, I., Ullrich, T., *et al.* Molecular Insights and Concepts to Engineer Singlet Fission Energy Conversion Devices.
Energy & Environmental Science (2020).
98. Pan, Y. Y., Huang, J., Wang, Z. M., *et al.* Computational investigation on the large energy gap between the triplet excited-states in acenes.
RSC Advances **7**, 26697–26703 (2017).
99. Burdett, J. J., Müller, A. M., Gosztola, D., *et al.* Excited state dynamics in solid and monomeric tetracene: The roles of superradiance and exciton fission.
The Journal of Chemical Physics **133** (2010).
100. Lee, J., Jadhav, P. & Baldo, M. A.
High efficiency organic multilayer photodetectors based on singlet exciton fission.
Applied Physics Letters **95** (2009).
101. Rao, A., Wilson, M. W. B., Hodgkiss, J. M., *et al.* Exciton Fission and Charge Generation via Triplet Excitons in Pentacene/C 60 Bilayers.
Journal of the American Chemical Society **132**, 12698–12703 (2010).

102. Wilson, M. W. B., Rao, A., Clark, J., *et al.*
Ultrafast Dynamics of Exciton Fission in Polycrystalline Pentacene.
Journal of the American Chemical Society **133**, 11830–11833 (2011).
103. Reddy, A. R. & Bendikov, M. Diels–Alder reaction of acenes with singlet and triplet oxygen – theoretical study of two-state reactivity. *Chemical Communications*, 1179 (2006).
104. Zade, S. S., Zamoshchik, N., Reddy, A. R., *et al.*
Products and Mechanism of Acene Dimerization. A Computational Study.
Journal of the American Chemical Society **133**, 10803–10816 (2011).
105. Matsui, Y., Kawaoka, S., Nagashima, H., *et al.* Exergonic Intramolecular Singlet Fission of an Adamantane-Linked Tetracene Dyad via Twin Quintet Multiexcitons.
The Journal of Physical Chemistry C **123**, 18813–18823 (2019).
106. Toolan, D. T., Weir, M. P., Dowland, S., *et al.* Linking microscale morphologies to localised performance in singlet fission quantum dot photon multiplier thin films.
Journal of Materials Chemistry C **10**, 11192–11198 (2022).
107. Bae, Y. J., Kang, G., Malliakas, C. D., *et al.*
Singlet Fission in 9,10-Bis(phenylethynyl)anthracene Thin Films.
Journal of the American Chemical Society **140**, 15140–15144 (2018).
108. Ma, L., Zhang, K., Kloc, C., *et al.* Singlet fission in rubrene single crystal: direct observation by femtosecond pump–probe spectroscopy.
Physical Chemistry Chemical Physics **14**, 8307 (2012).
109. Eaton, S. W., Shoer, L. E., Karlen, S. D., *et al.* Singlet Exciton Fission in Polycrystalline Thin Films of a Slip-Stacked Perylenediimide.
Journal of the American Chemical Society **135**, 14701–14712 (2013).
110. Lewis, P. A. in *Applied Polymer Science: 21st Century* 493–526 (Pergamon, Oxford, 2000).
111. Conrad-Burton, F. S., Liu, T., Geyer, F., *et al.*
Controlling Singlet Fission by Molecular Contortion.
Journal of the American Chemical Society **141**, 13143–13147 (2019).
112. Margulies, E. A., Miller, C. E., Wu, Y., *et al.* Enabling singlet fission by controlling intramolecular charge transfer in π -stacked covalent terrylenediimide dimers.
Nature Chemistry **8**, 1120–1125 (2016).
113. Zhao, X., Bae, Y. J., Chen, M., *et al.*
Singlet fission in core-linked terrylenediimide dimers.
The Journal of Chemical Physics **153** (2020).
114. Tavan, P. & Schulten, K. Electronic excitations in finite and infinite polyenes.
Physical Review B **36**, 4337–4358 (1987).

115. Barford, W. Singlet Fission in Lycopene H-Aggregates (2023).
116. Musser, A. J., Al-Hashimi, M., Maiuri, M., *et al.*
Activated Singlet Exciton Fission in a Semiconducting Polymer.
Journal of the American Chemical Society **135**, 12747–12754 (2013).
117. Millington, O., Montanaro, S., Leventis, A., *et al.* Soluble Diphenylhexatriene Dimers
for Intramolecular Singlet Fission with High Triplet Energy.
Journal of the American Chemical Society **145**, 2499–2510 (2023).
118. Wang, C. & Tauber, M. J. High-Yield Singlet Fission in a Zeaxanthin Aggregate
Observed by Picosecond Resonance Raman Spectroscopy.
Journal of the American Chemical Society **132**, 13988–13991 (2010).
119. Quaranta, A., Krieger-Liszkay, A., Pascal, A. A., *et al.*
Singlet fission in naturally-organized carotenoid molecules.
Physical Chemistry Chemical Physics **23**, 4768–4776 (2021).
120. Sonoda, Y. & Kamada, K. Synthesis, characterization, and fluorescence properties of
a series of trifluoromethylated diphenylhexatrienes.
Journal of Fluorine Chemistry **267**, 110110 (2023).
121. Splitstoser, J. C., Dillehay, T. D., Wouters, J., *et al.*
Early pre-Hispanic use of indigo blue in Peru. *Science Advances* **2** (2016).
122. Séquin, M. The Chemistry of Plants: Perfumes, Pigments and Poisons 2nd, 103,183
(Royal Society of Chemistry, 2021).
123. Yin, S. People Have Been Dyeing Fabric Indigo Blue for 6,000 Years. 2016.
<https://www.nytimes.com/2016/09/17/science/people-have-been-dying-fabric-indigo-blue-for-6000-years.html>.
124. Yamazaki, S., Sobolewski, A. L. & Domcke, W.
Molecular mechanisms of the photostability of indigo.
Physical Chemistry Chemical Physics **13**, 1618–1628 (2011).
125. Pina, J., Sarmiento, D., Accoto, M., *et al.* Excited-State Proton Transfer in Indigo.
Journal of Physical Chemistry B **121**, 2308–2318 (2017).
126. Stalder, R., Mei, J., Graham, K. R., *et al.* Isoindigo, a Versatile Electron-Deficient
Unit For High-Performance Organic Electronics. *Chemistry of Materials* **26**, 664–678
(2014).
127. Kolaczowski, M. A. & Liu, Y.
Functional Organic Semiconductors Based on Bay-Annulated Indigo (BAI).
Chemical Record **19**, 1062–1077 (2019).

128. Mauck, C. M., Bae, Y. J., Chen, M., *et al.* Charge-Transfer Character in a Covalent Diketopyrrolopyrrole Dimer: Implications for Singlet Fission. *ChemPhotoChem* **2**, 223–233 (2018).
129. Papadopoulos, I., Álvaro-Martins, M. J., Molina, D., *et al.* Solvent-Dependent Singlet Fission in Diketopyrrolopyrrole Dimers: A Mediating Charge Transfer versus a Trapping Symmetry-Breaking Charge Separation. *Advanced Energy Materials* **10**, 2001496 (2020).
130. Wang, L., Feng, C., Wu, C., *et al.* Efficient Singlet Fission in Loose Packing Benzodipyrrolidone Thin Films. *Journal of Physical Chemistry C* **125**, 22093–22099 (2021).
131. Wang, L., Zhang, T.-S., Fu, L., *et al.* High-Lying 3 1 A g Dark-State-Mediated Singlet Fission. *Journal of the American Chemical Society* **143**, 5691–5697 (2021).
132. Ryerson, J. L., Zaykov, A., Aguilar Suarez, L. E., *et al.* Structure and photophysics of indigoids for singlet fission: Cibalackrot. *Journal of Chemical Physics* **151** (2019).
133. Purdy, M., Fallon, K., Congrave, D. G., *et al.* Synthesis of asymmetric indolonaphthyridines with enhanced excited state charge-transfer character. *Journal of Materials Chemistry C* **10**, 10742–10747 (2022).
134. Nakano, M. Open-Shell-Character-Based Molecular Design Principles: Applications to Nonlinear Optics and Singlet Fission. *The Chemical Record* **17**, 27–62 (2017).
135. Ito, S., Nagami, T. & Nakano, M. Molecular design for efficient singlet fission. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **34**, 85–120 (2018).
136. Padula, D., Omar, Ö. H., Nematiram, T., *et al.* Singlet fission molecules among known compounds: finding a few needles in a haystack. *Energy & Environmental Science* **12**, 2412–2416 (2019).
137. El Bakouri, O., Smith, J. R. & Ottosson, H. Strategies for Design of Potential Singlet Fission Chromophores Utilizing a Combination of Ground-State and Excited-State Aromaticity Rules. *Journal of the American Chemical Society* **142**, 5602–5617 (2020).
138. Weber, F. & Mori, H. Machine-learning assisted design principle search for singlet fission: an example study of cibalackrot. *npj Computational Materials* **8**, 176 (2022).
139. Accomasso, D., Ben Amor, N., Persico, M., *et al.* Computational design of covalently bound dimers for singlet fission. *Journal of Photochemistry and Photobiology A: Chemistry* **443**, 114836 (2023).

140. Mathew, C. M., Varghese, A., Sugunan, S. K., *et al.*
Rapid Computational Approach Towards Designing Singlet-Fission Chromophores by Tuning the Diradical Character of Heteroatom-Doped Polycyclic Aromatic Hydrocarbons Using the Atom-Specific Fukui Function.
The Journal of Physical Chemistry A **126**, 1579–1590 (2022).
141. Budden, P. J., Weiss, L. R., Müller, M., *et al.* Singlet exciton fission in a modified acene with improved stability and high photoluminescence yield.
Nature Communications **12**, 1527 (2021).
142. Pensack, R. D., Tilley, A. J., Grieco, C., *et al.* Striking the right balance of intermolecular coupling for high-efficiency singlet fission.
Chemical Science **9**, 6240–6259 (2018).
143. Le, A. K., Bender, J. A., Arias, D. H., *et al.* Singlet Fission Involves an Interplay between Energetic Driving Force and Electronic Coupling in Perylenediimide Films.
Journal of the American Chemical Society **140**, 814–826 (2018).
144. Tabernig, S. W., Daiber, B., Wang, T., *et al.*
Enhancing silicon solar cells with singlet fission: the case for Förster resonant energy transfer using a quantum dot intermediate. *Journal of Photonics for Energy* **8**, 1 (2018).
145. Futscher, M. H., Rao, A. & Ehrler, B. The Potential of Singlet Fission Photon Multipliers as an Alternative to Silicon-Based Tandem Solar Cells.
ACS Energy Letters **3**, 2587–2592 (2018).
146. Ehrler, B. in *Emerging Strategies to Reduce Transmission and Thermalization Losses in Solar Cells* 313–339 (Springer International Publishing, Cham, 2022).
147. NREL. Reference Air Mass 1.5 Spectra.
<https://www.nrel.gov/grid/solar-resource/spectra-am1.5.html>.
148. Ehrler, B., Wilson, M. W., Rao, A., *et al.*
Singlet exciton fission-sensitized infrared quantum dot solar cells.
Nano Letters **12**, 1053–1057 (2012).
149. Ehrler, B., Alarcón-Lladó, E., Tabernig, S. W., *et al.*
Photovoltaics Reaching for the Shockley–Queisser Limit.
ACS Energy Letters **5**, 3029–3033 (2020).
150. Polman, A., Knight, M., Garnett, E. C., *et al.*
Photovoltaic materials: Present efficiencies and future challenges. *Science* **352** (2016).
151. Polman, A. & Atwater, H. A.
Photonic design principles for ultrahigh-efficiency photovoltaics.
Nature Materials **11**, 174–177 (2012).

-
152. Van den Boom, A. F. J., Ferro, S., Gelvez-Rueda, M., *et al.*
Toward Improving Triplet Energy Transfer from Tetracene to Silicon Using a Covalently Bound Tetracene Seed Layer.
The Journal of Physical Chemistry Letters **14**, 4454–4461 (2023).
153. Davis, N. J. L. K., Allardice, J. R., Xiao, J., *et al.* Singlet Fission and Triplet Transfer to PbS Quantum Dots in TIPS-Tetracene Carboxylic Acid Ligands.
The Journal of Physical Chemistry Letters **9**, 1454–1460 (2018).
154. Ehrler, B., Yanai, N. & Nienhaus, L.
Up- and down-conversion in molecules and materials.
The Journal of Chemical Physics **154** (2021).
155. Purdy, M. *Synthesis and Characterisation of Singlet Fission and Open-Shell Materials for Optoelectronic Application.*
PhD thesis (University of Cambridge, 2023).
156. Spooner, E., Hassan, H. & Griffin, J.
Spin Coating: Complete Guide to Theory and Techniques.
<https://www.ossila.com/pages/spin-coating>.
157. Yoo, H., Choi, H. H., Shin, T. J., *et al.* Self-Assembled, Millimeter-Sized TIPS-Pentacene Spherulites Grown on Partially Crosslinked Polymer Gate Dielectric.
Advanced Functional Materials **25**, 3658–3665 (2015).
158. Maity, N., Kim, W., Panjwani, N. A., *et al.*
Parallel triplet formation pathways in a singlet fission material.
Nature Communications **13**, 1–14 (2022).
159. Nogueira, B. A., Castiglioni, C. & Fausto, R. Color polymorphism in organic crystals.
Communications Chemistry **3**, 34 (2020).
160. Mattheus, C. C., de Wijs, G. A., de Groot, R. A., *et al.*
Modeling the Polymorphism of Pentacene.
Journal of the American Chemical Society **125**, 6323–6330 (2003).
161. Mahmood, A. & Wang, J. L.
A Review of Grazing Incidence Small- and Wide-Angle X-Ray Scattering Techniques for Exploring the Film Morphology of Organic Solar Cells. *Solar RRL* **4**, 1–39 (2020).
162. Greenham, N., Samuel, I., Hayes, G., *et al.* Measurement of absolute photoluminescence quantum efficiencies in conjugated polymers.
Chemical Physics Letters **241**, 89–96 (1995).
163. De Mello, J. C., Wittmann, H. F. & Friend, R. H. An improved experimental determination of external photoluminescence quantum efficiency.
Advanced Materials **9**, 230–232 (1997).

164. Ophir. Power Density Calculator. 2023.
<https://www.ophiropt.com/en/power-density-calculator>.
165. Ellis, G. Chapter 6 - Four Types of Controllers Fourth Edition, 111
(Butterworth-Heinemann, Boston, 2012).
166. Instruments, Z. Principles of Lock-in Detection. 2023.
<https://www.zhinst.com/europe/en/resources/principles-of-lock-in-detection>.
167. Harvie, A. J. & de Mello, J. C. OLIA: An open-source digital lock-in amplifier.
Frontiers in Sensors **4** (2023).
168. Weiss, L. R., Bayliss, S. L., Kraffert, F., *et al.*
Strongly exchange-coupled triplet pairs in an organic semiconductor.
Nature Physics **13**, 176–181 (2017).
169. Baikie, T. K., Kosmützký, D., Lawrence, J. M., *et al.*
Ultrafast In vivo Transient Absorption Spectroscopy. arXiv: 2307.09448 (2023).
170. Boyd, R. W. Nonlinear Optics (fourth ed.) (Elsevier, 2020).
171. Franken, P. A., Hill, A. E., Peters, C. W., *et al.* Generation of Optical Harmonics.
Physical Review Letters **7**, 118–119 (1961).
172. Li, A. & Liu, W. Optical properties of ferroelectric nanocrystal/polymer composites,
108–158 (Elsevier, 2010).
173. Grupp, A., Budweg, A., Fischer, M. P., *et al.*
Broadly tunable ultrafast pump-probe system operating at multi-kHz repetition rate.
Journal of Optics (United Kingdom) **20** (2018).
174. Rao, A., Wilson, M. W., Albert-Seifried, S., *et al.*
Photophysics of pentacene thin films: The role of exciton fission and heating effects.
Physical Review B - Condensed Matter and Materials Physics **84**, 1–8 (2011).
175. Shlens, J. A Tutorial on Principal Component Analysis. arXiv: 1404.1100 (2014).
176. Kumar, A. Genetic Algorithms. 2023.
<https://www.geeksforgeeks.org/genetic-algorithms/>.
177. Gélinas, S., Paré-Labrosse, O., Brosseau, C. N., *et al.* The binding energy of
charge-transfer excitons localized at polymeric semiconductor heterojunctions.
Journal of Physical Chemistry C **115**, 7114–7119 (2011).
178. Gélinas, S.
Spectroscopic Study of Charge-Separation Dynamics in π -Conjugated Systems.
PhD thesis (Univeristy of Cambridge, 2013).
179. Python. scipy.optimize.curve_fit documentation.
https://docs.scipy.org/doc/scipy/reference/generated/scipy.optimize.curve_fit.html.

180. Gill, J. & King, G. Numerical Issues Involved in Inverting Hessian Matrices, 143–176 (2003).
181. Justinek, M., Grampp, G., Landgraf, S., *et al.* Electron Self-Exchange Kinetics Determined by MARY Spectroscopy: Theory and Experiment. *Journal of the American Chemical Society* **126**, 5635–5646 (2004).
182. Shtukenberg, A. G., Punin, Y. O., Gunn, E., *et al.* Spherulites. *Chemical Reviews* **112**, 1805–1838 (2012).
183. Kerpál, C., Richert, S., Storey, J. G., *et al.* Chemical compass behaviour at microtesla magnetic fields strengthens the radical pair hypothesis of avian magnetoreception. *Nature Communications* **10**, 1–7 (2019).
184. Weller, A., Nolting, F. & Staerk, H. A quantitative interpretation of the magnetic field effect on hyperfine-coupling-induced triplet formation from radical ion pairs. *Chemical Physics Letters* **96**, 24–27 (1983).
185. Wong, S. Y., Benjamin, P. & Hore, P. J. Magnetic field effects on radical pair reactions: estimation of B_{1/2} for flavin-tryptophan radical pairs in cryptochromes. *Physical Chemistry Chemical Physics*, 975–982 (2022).
186. Bayliss, S. L., Chepelianskii, A. D., Sepe, A., *et al.* Geminate and nongeminate recombination of triplet excitons formed by singlet fission. *Physical Review Letters* **112**, 1–5 (2014).
187. EasySpin. mhz2mt. <https://easyspin.org/documentation/mhz2mt.html>.
188. Li, H., Buesen, D., Williams, R., *et al.* Preventing the coffee-ring effect and aggregate sedimentation by in situ gelation of monodisperse materials. *Chemical Science* **9**, 7596–7605 (2018).
189. Beating the Coffee Ring Effect. *Royal Society of Chemistry* (2018).
190. Dabestani, R., Nelson, M. & Sigman, M. E. Photochemistry of Tetracene Adsorbed on Dry Silica: Products and Mechanism. *Photochemistry and Photobiology* **64**, 80–86 (1996).
191. Sonoda, Y., Katoh, R., Tohnai, N., *et al.* Singlet Fission in Solid 1,6-Diphenyl-1,3,5-hexatriene Dicarboxylic Acids and Esters: Effects of Meta and Para Substitution. *Journal of Physical Chemistry C* **126**, 8742–8751 (2022).
192. Sharma, A. Private correspondence. 2023.
193. Thorlabs. Mounted LEDs. https://www.thorlabs.com/newgrouppage9.cfm?objectgroup{_}ID=2692.
194. Dyson, F. A meeting with Enrico Fermi. *Nature* **427**, 297–297 (2004).

195. Mayer, J., Khairy, K. & Howard, J.
Drawing an elephant with four complex parameters.
American Journal of Physics **78**, 648–649 (2010).
196. Benk, H. & Sixl, H.
Theory of two coupled triplet states application to bicarbene structures.
Molecular Physics **42**, 779–801 (1981).
197. Ha, D. G., Wan, R., Kim, C. A., *et al.*
Exchange controlled triplet fusion in metal–organic frameworks.
Nature Materials **21**, 1275–1281 (2022).
198. Collins, M. I., McCamey, D. R. & Tayebjee, M. J. Fluctuating exchange interactions enable quintet multiexciton formation in singlet fission.
Journal of Chemical Physics **151** (2019).
199. Shao, M., Yan, L., Li, M., *et al.* Triplet–charge annihilation versus triplet–triplet annihilation in organic semiconductors. *J. Mater. Chem. C* **1**, 1330–1336 (7 2013).
200. Marin-Beloqui, J. M., Toolan, D. T. W., Panjwani, N. A., *et al.*
Triplet-Charge Annihilation in a Small Molecule Donor: Acceptor Blend as a Major Loss Mechanism in Organic Photovoltaics. *Advanced Energy Materials* **11** (24 June 2021).
201. Engi, G. Über neue Derivate des Indigos und anderer indigoider Farbstoffe.
Zeitschrift für Angewandte Chemie **27**, 144–148 (1914).
202. Buchanan, E. A., Kaleta, J., Wen, J., *et al.* Molecular Packing and Singlet Fission: The Parent and Three Fluorinated 1,3-Diphenylisobenzofurans.
The Journal of Physical Chemistry Letters **10**, 1947–1953 (2019).
203. Felter, K. M. & Grozema, F. C. Singlet Fission in Crystalline Organic Materials: Recent Insights and Future Directions.
The Journal of Physical Chemistry Letters **10**, 7208–7214 (2019).
204. Papadopoulos, I., Zirzlmeier, J., Hetzer, C., *et al.*
Varying the Interpentacene Electronic Coupling to Tune Singlet Fission.
Journal of the American Chemical Society **141**, 6191–6203 (2019).
205. Yost, S. R., Lee, J., Wilson, M. W., *et al.*
A transferable model for singlet-fission kinetics. *Nature Chemistry* **6**, 492–497 (2014).
206. Hestand, N. J. & Spano, F. C. Expanded Theory of H- and J-Molecular Aggregates: The Effects of Vibronic Coupling and Intermolecular Charge Transfer.
Chemical Reviews **118**, 7069–7163 (2018).
207. Schols, S. Control of the Triplet Concentration in Organic Light-Emitting Devices, 81–95 (Springer Netherlands, Dordrecht, 2011).

208. Jones, R. N. The ultraviolet absorption spectra of anthracene derivatives. *Chemical Reviews* **41**, 353–371 (1947).
209. Nielsen, B. R., Jørgensen, K. & Skibsted, L. H. Triplet-triplet extinction coefficients, rate constants of triplet decay and rate constants of anthracene triplet sensitization by laser flash photolysis of astaxanthin, β -carotene, canthaxanthin and zeaxanthin in deaerated toluene at 298 K. *Journal of Photochemistry and Photobiology A: Chemistry* **112**, 127–133 (1998).
210. Mizokuro, T., Kamada, K. & Sonoda, Y. Triplet–triplet annihilation photon upconversion from diphenylhexatriene and ring-substituted derivatives in solution. *Physical Chemistry Chemical Physics* **24**, 11520–11526 (2022).
211. Monguzzi, A., Tubino, R. & Meinardi, F. Multicomponent Polymeric Film for Red to Green Low Power Sensitized Up-Conversion. *The Journal of Physical Chemistry A* **113**, 1171–1174 (2009).
212. Cui, X., Zhao, J., Yang, P., *et al.* Zinc(ii) tetraphenyltetrabenzoporphyrin complex as triplet photosensitizer for triplet–triplet annihilation upconversion. *Chemical Communications* **49**, 10221 (2013).
213. Fallon, K. J., Churchill, E. M., Sanders, S. N., *et al.* Molecular Engineering of Chromophores to Enable Triplet-Triplet Annihilation Upconversion. *Journal of the American Chemical Society* **142**, 19917–19925 (2020).
214. Wang, L., Bai, S., Wu, Y., *et al.* Revealing the Nature of Singlet Fission under the Veil of Internal Conversion. *Angewandte Chemie - International Edition* **59**, 2003–2007 (2020).
215. Hu, J., Xu, K., Shen, L., *et al.* New insights into the design of conjugated polymers for intramolecular singlet fission. *Nature Communications* **9** (2018).
216. Bernardino, N. D., Brown-Xu, S., Gustafson, T. L., *et al.* Time-Resolved Spectroscopy of Indigo and of a Maya Blue Simulant. *Journal of Physical Chemistry C* **120**, 21905–21914 (2016).
217. Tavan, P. & Schulten, K. The low-lying electronic excitations in long polyenes: A PPP-MRD-CI study. *The Journal of Chemical Physics* **85**, 6602–6609 (1986).
218. Hashimoto, H., Uragami, C., Yukihiro, N., *et al.* Understanding/unravelling carotenoid excited singlet states. *Journal of the Royal Society Interface* **15** (2018).
219. Mencaroni, L., Alebardi, M., Elisei, F., *et al.* Unveiling the Double Triplet Nature of the 2Ag State in Conjugated Stilbenoid Compounds to Achieve Efficient Singlet Fission. *Physical Chemistry Chemical Physics* (2023).

220. Albert-Seifried, S. & Friend, R. H. Measurement of thermal modulation of optical absorption in pump-probe spectroscopy of semiconducting polymers. *Applied Physics Letters* **98**, 223304 (2011).

Appendix A

Additional Figures to Chapter 4

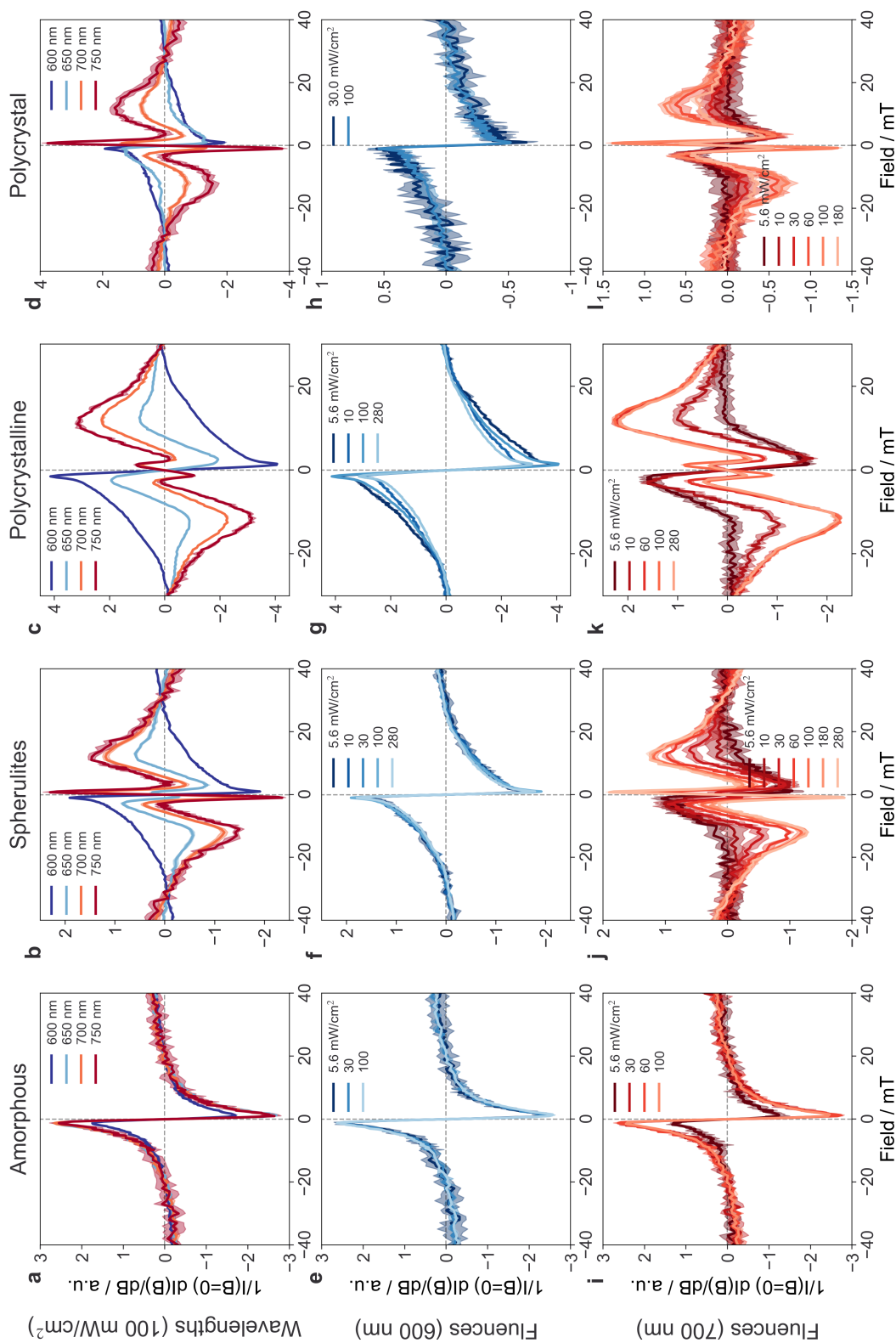


Figure A.1: A side-by-side comparison of modMPL data: amorphous, spherulites, polycrystalline (drop cast) and a polycrystal are shown left-to-right. Series at different wavelengths, and then fluences at 600 nm and 700 nm are shown top-to-bottom.

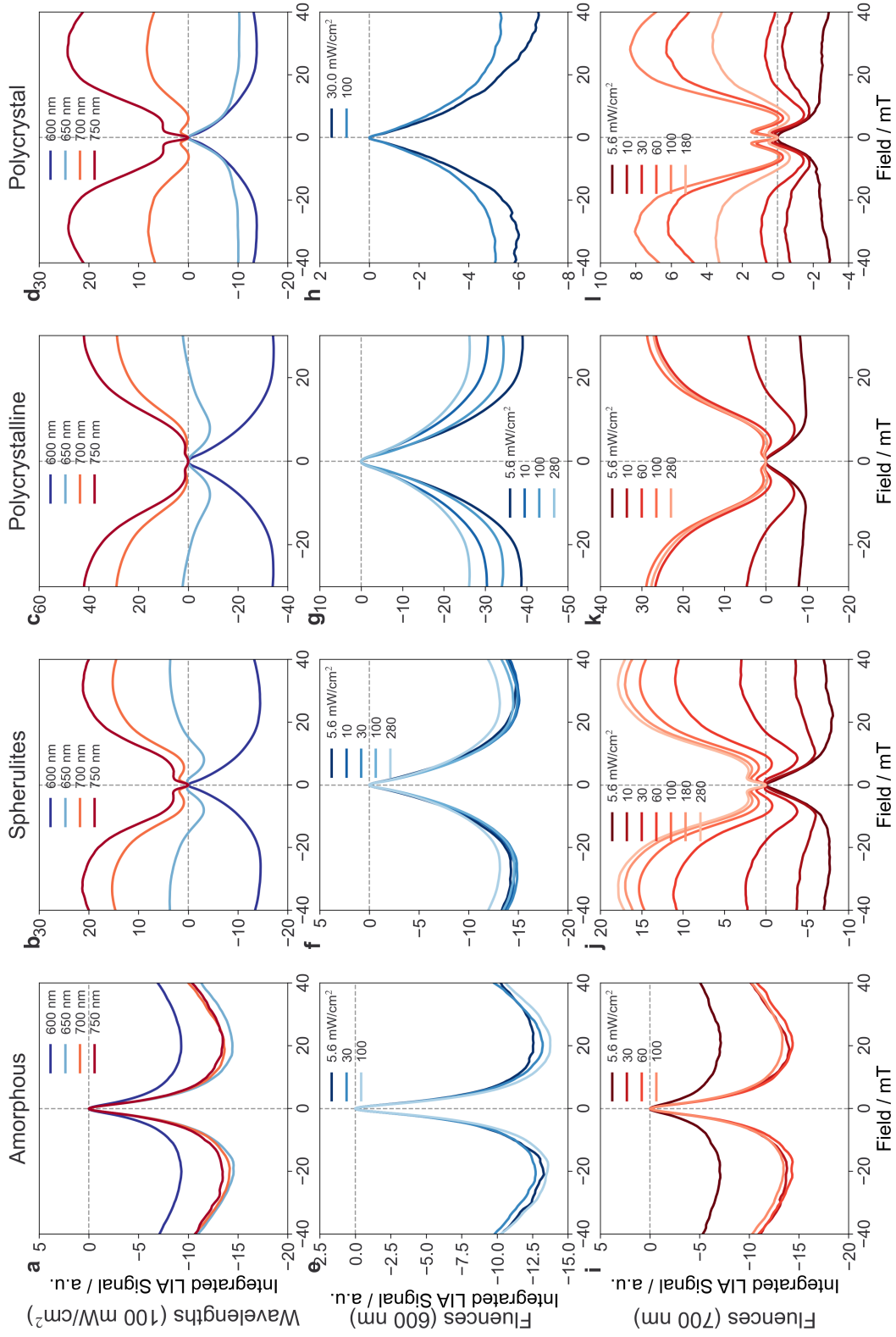


Figure A.2: A side-by-side comparison of integrated line shapes: amorphous, spherulites, polycrystalline (drop cast) and a polycrystal are shown left-to-right. Series at different wavelengths, and then fluences at 600 nm and 700 nm are shown top-to-bottom.

Appendix B

Additional Figures to Chapter 5

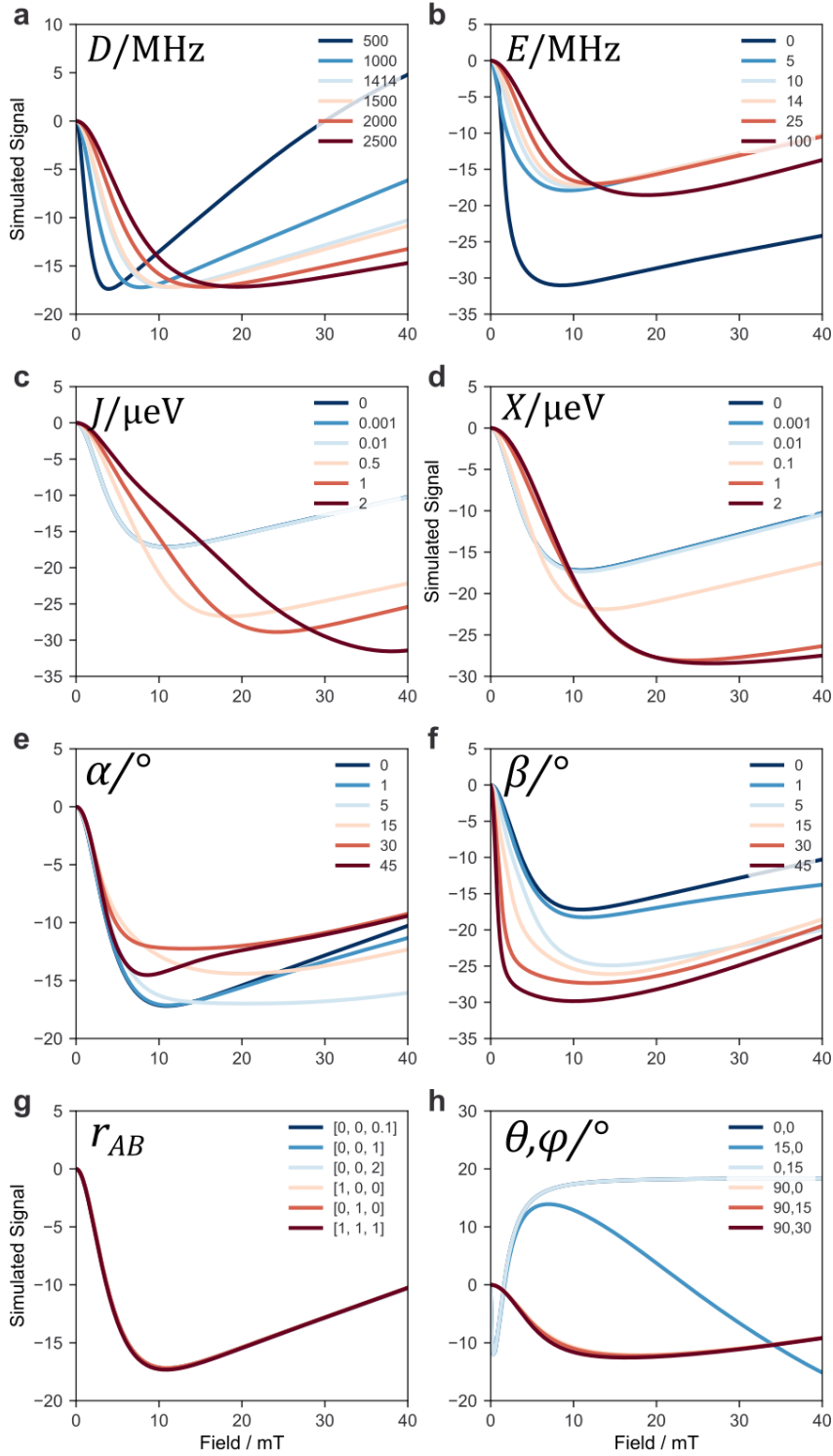


Figure B.1: Effects of the Hamiltonian on a simple model: each parameter of the Hamiltonian is varied independently, with the remaining parameters as listed in **Table 5.1**. Each curve is unnormalised and not differentiated, such that it is comparable to the magPL lineshape.

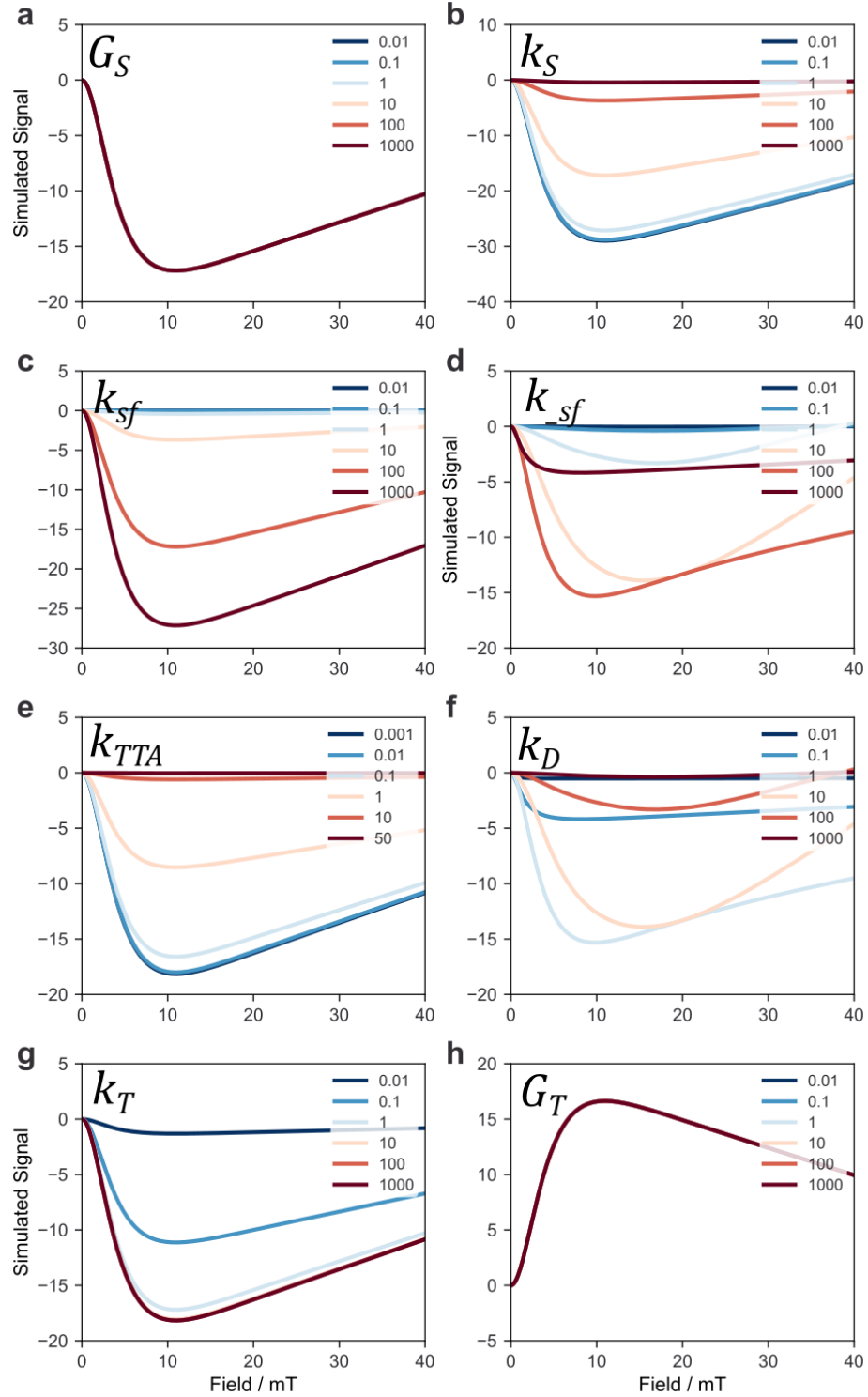


Figure B.2: Effects of kinetics on a simple model: Each parameter of the kinetic matrix is varied independently, with the remaining parameters as listed in **Table 5.1**. Each curve is unnormalised and not differentiated, such that it is comparable to the magPL lineshape.

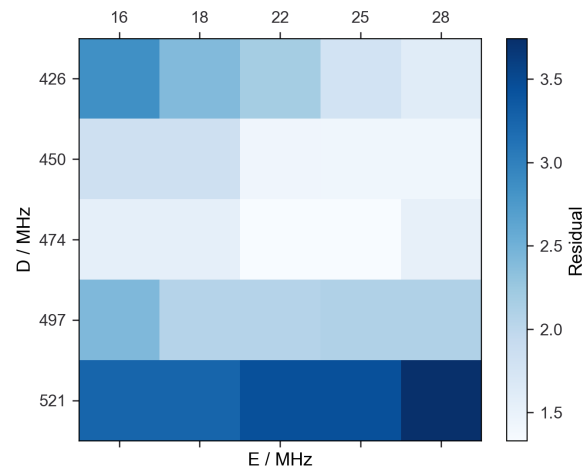


Figure B.3: A heat map of the sum squared differences of the peak positions of the 700 nm lineshape and lineshapes simulated with differing values of D and E , close to $D_Q = 474\text{ MHz}$ and $E_Q = 22.5\text{ MHz}$. D is varied $\pm 10\%$, and E varied $\pm 25\%$. The effective residual of the peak positions is more sensitive to D than E , and shows there is a local minimum at the values of D_Q and E_Q .

$$\begin{bmatrix}
 -kS - k_{sf} \sum_{i=1}^9 c_i^2 & k_{sf} c_1^2 & k_{sf} c_2^2 & \dots & k_{sf} c_9^2 & 0 & \dots & 0 \\
 k_{sf} c_1^2 & -k_d - k_{sf} c_1^2 & 0 & \dots & 0 & \frac{k_{TTA}}{9} & \dots & 0 \\
 k_{sf} c_2^2 & 0 & -k_d - k_{sf} c_2^2 & \dots & 0 & \frac{k_{TTA}}{9} & \dots & 0 \\
 \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \dots & \vdots \\
 k_{sf} c_9^2 & 0 & 0 & \dots & -k_d - k_{sf} c_9^2 & \frac{k_{TTA}}{9} & \dots & 0 \\
 0 & 2k_d & 2k_d & \dots & 2k_d & -k_T - 2k_{TTA} - 2k_{TTA_2} & 2k_{d2} & 2k_{d2} \\
 0 & 0 & 0 & \dots & 0 & \frac{k_{TTA_2}}{9} & -k_{d2} - k_{TT} c_1^2 & 0 \\
 \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \vdots & \vdots \\
 0 & 0 & 0 & \dots & 0 & \frac{k_{TTA_2}}{9} & \dots & -k_{d2} - k_{TT} c_9^2
 \end{bmatrix} \quad (\text{B.1})$$

Equation B.1: Rate equation matrix for model 4, as shown in **Figure 5.9**.

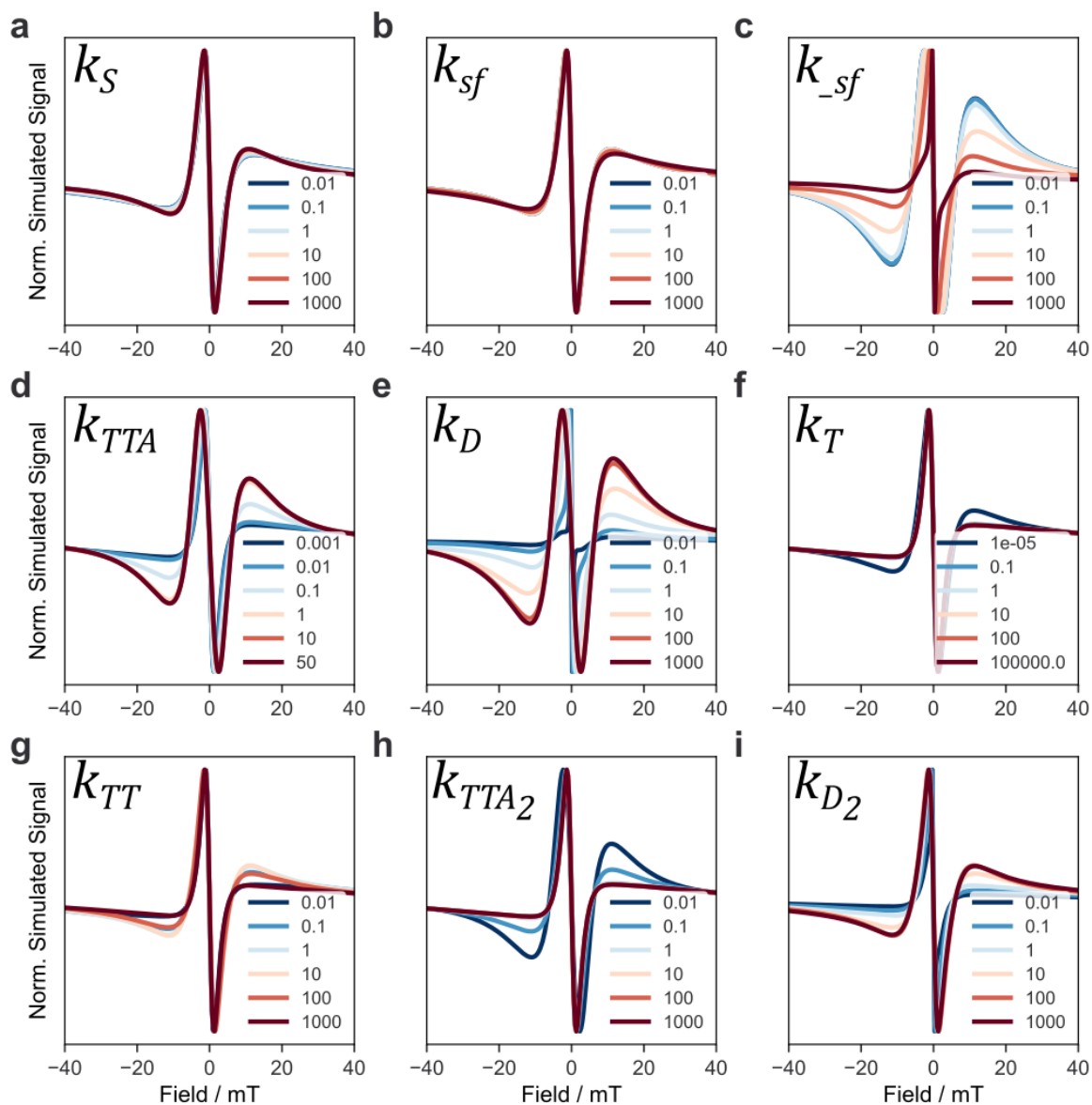


Figure B.4: Effects of the kinetic parameters on model 4 (Figure 5.9) on the S₁ emission: each parameter of the rate equation matrix is varied independently, with the remaining parameters as listed in Table 5.1. Each curve is normalised.

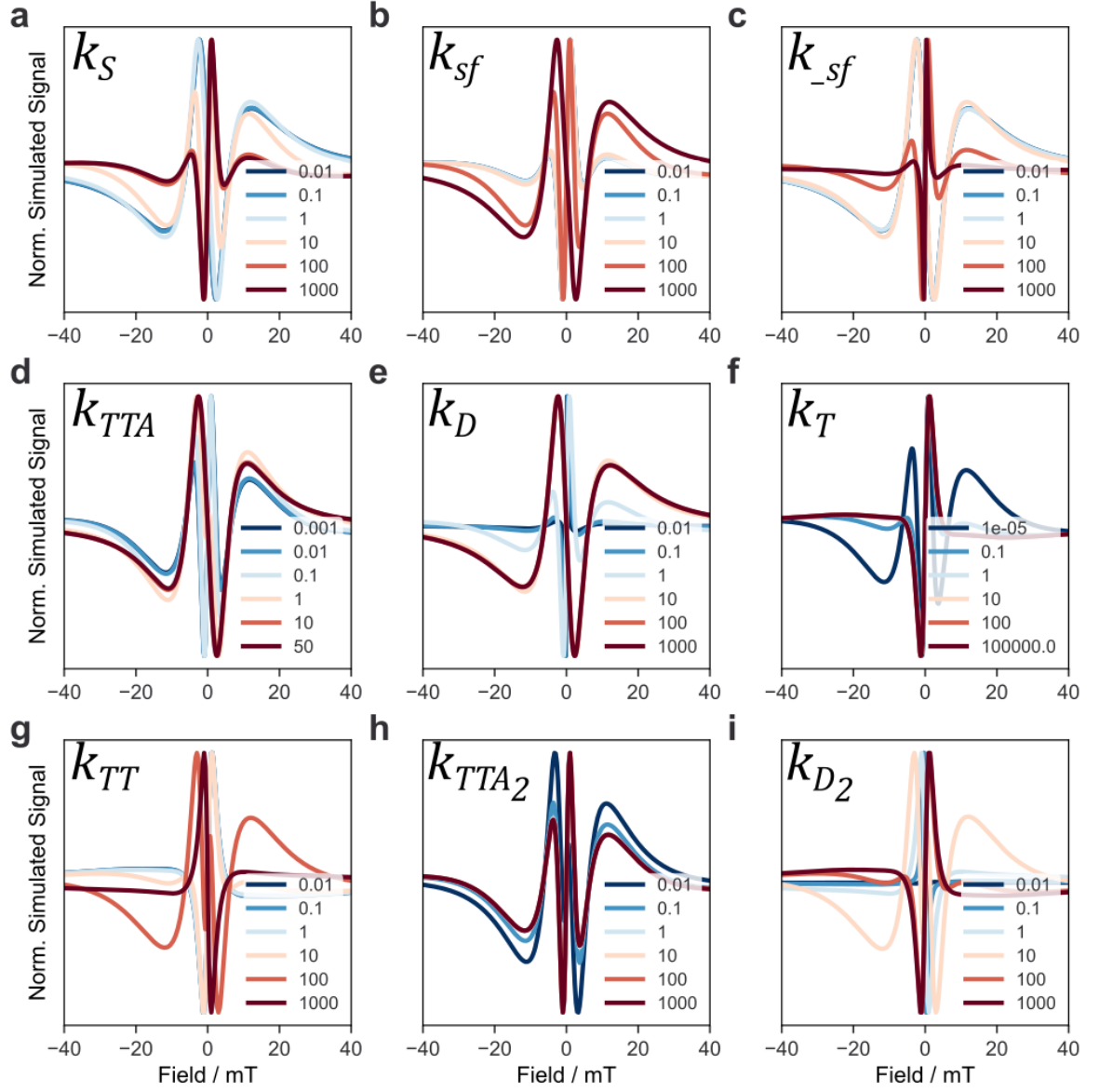


Figure B.5: Effects of the kinetics on model 4 (**Figure 5.9**) on the TT pair emission: each parameter of the rate equation matrix is varied independently, with the remaining parameters as listed in **Table 5.1**. Each curve is normalised.

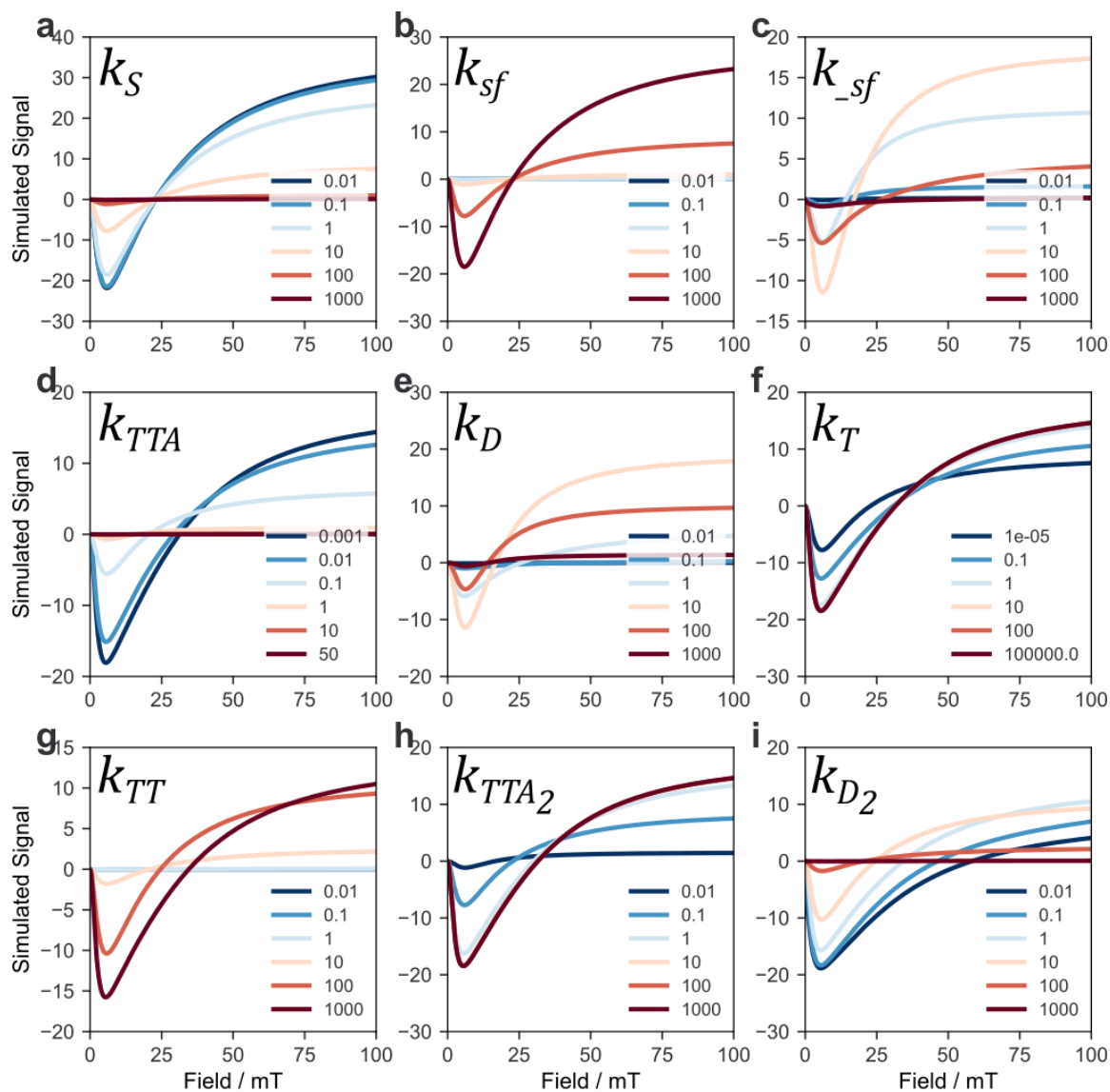


Figure B.6: Effects of the kinetic parameters on model 4 (**Figure 5.9**) on the S_1 emission: Each parameter of the rate equation matrix is varied independently, with the remaining parameters as listed in **Table 5.1**. Each curve is unnormalised and integrated.

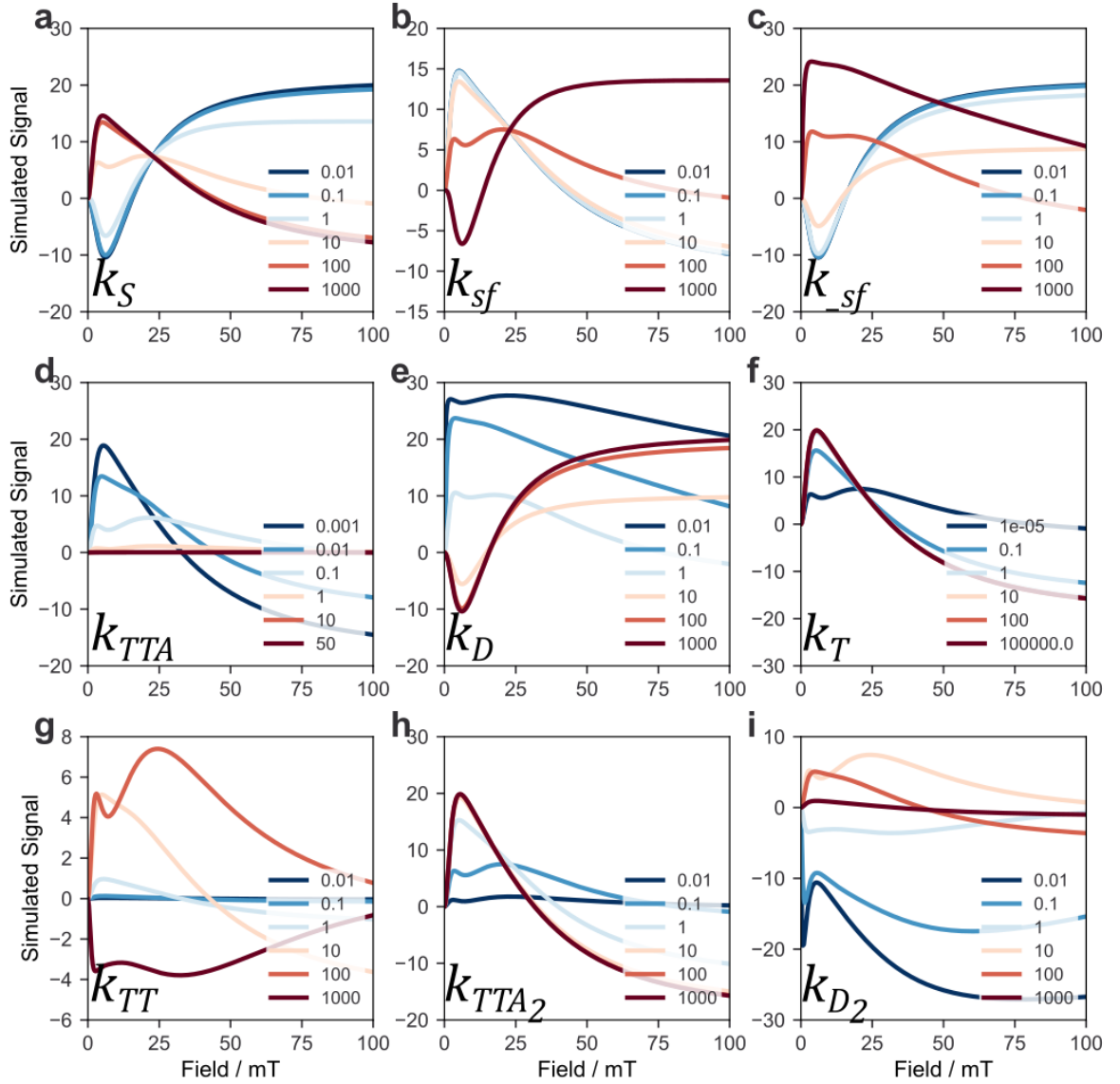


Figure B.7: Effects of the kinetics on model 4 (Figure 5.9) on the TT pair emission: Each parameter of the rate equation matrix is varied independently, with the remaining parameters as listed in Table 5.1. Each curve is unnormalised and integrated.

