Singlet fission in organic crystals : ultrafast spectroscopic study

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGLET FISSION IN ORGANIC CRYSTALS: ULTRAFAST
SPECTROSCOPIC STUDY

MA LIN

**SINGLET FISSION IN ORGANIC CRYSTALS:
ULTRAFAST SPECTROSCOPIC STUDY**

MA LIN

**SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES**

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SINGLET FISSION IN ORGANIC CRYSTALS: ULTRAFAST SPECTROSCOPIC STUDY

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Citations to published works

1. Chapter 3 is based on my publication:

L. Ma, K. Zhang, C. Kloc, H. Sun, M. E. Michel-Beyerle, and G. G. Gurzadyan, "Singlet fission in rubrene single crystal: direct observation by femtosecond pump-probe spectroscopy" *Phys. Chem. Chem. Phys.* 14, 8307 (2012).

2. Chapter 4 is based on my publication:

L. Ma, C. Kloc, C. Soci, M. E. Michel-Beyerle, and G. G. Gurzadyan, "Singlet fission in organic crystals" in *Ultrafast dynamics in molecules, nanostructures and interfaces*, Series in Optics and Photonics vol. 8, pp. 110. (2014) (book chapter).

3. Chapter 5 is based on my publications:

L. Ma, G. Galstyan, K. Zhang, C. Kloc, H. Sun, C. Soci, M. E. Michel-Beyerle, and G. G. Gurzadyan, "Two-photon-induced singlet fission in rubrene single crystal" *J. Chem. Phys.* 138, 184508 (2013).

L. Ma, Ke Jie Tan, Hui Jiang, Christian Kloc, and G. G. Gurzadyan, "Excited-State Dynamics in an α -Perylene Single Crystal: Two-Photon- and Consecutive Two-Quantum-Induced Singlet Fission" *J. Phys. Chem. A* 118, 838 (2014).

4. Chapter 6 is based on my publication:

L. Ma, K. Zhang, C. Kloc, H. Sun, C. Soci, M. E. Michel-Beyerle, and G. G. Gurzadyan, "Fluorescence from rubrene single crystals: Interplay of singlet fission and energy trapping" *Phys. Rev. B* 87, 201203 (2013).

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Summary

This thesis presents results on the ultrafast spectroscopic study of singlet fission in organic semiconductor crystals. It can be divided into three main parts as follows.

Chapters 1 and 2 are introductions to singlet fission, ultrafast spectroscopy and experimental techniques.

Part A: Singlet fission under one-photon excitation in organic crystals

In Chapter 3, for the first time, we directly observed the one-photon-induced singlet fission in a monomeric crystal rubrene. Time-resolved fluorescence study reveals a significant shortening of fluorescence lifetime for rubrene molecules in crystalline phase compared to those in solution. Transient absorption spectra were further measured under various conditions, e.g. excitation wavelengths ranging from 250 to 550 nm, in order to study the relaxation dynamics of upper excited states. Singlet fission was found to be the main depopulation channel in all cases studied. Both direct singlet fission from the highly excited singlet states S_N , the upper vibrational levels of S_1 , and thermally activated singlet fission from the lowest vibrational level of S_1 were investigated comprehensively.

In the following Chapter 4, one-photon-induced singlet fission was studied in another type of organic crystal with a dimeric crystalline structure, i.e., α -perylene. We found that, unlike the recently reported scenario that in solution the excimer acts as an intermediate state for singlet fission, excimer state does not play role as an

intermediate for singlet fission in the dimeric α -perylene crystal. On the contrary, the excimer formation is found to compete with singlet fission on an ultrafast time scale (<50 fs) which decreases the singlet fission efficiency.

Part B: Singlet fission under two-photon and two-quantum excitation in organic crystals

Chapter 5 extends our study to two-photon and two-quantum-induced singlet fission in both rubrene and α -perylene crystals, which has never been done before. The motivation is to figure out the mechanism of singlet fission in the subject materials, i.e., whether it occurs via direct coupling or it is mediated by a dark multiexciton state. We applied two-photon excitation to directly excite the dark state which is a forbidden transition under one-photon excitation, but no evidence was found for the presence of a dark intermediate state. The two-photon-induced singlet fission rate was demonstrated to follow the same law as that of one-photon excitation. Therefore, we confirmed that singlet fission in both studied samples occurs via direct coupling without participation of dark intermediate states.

Part C: Interplay between singlet fission and energy trapping

In Chapter 6, we revealed interplay between singlet fission and energy trapping in rubrene by studying the temperature-dependent singlet fission dynamics. At temperatures higher than 140 K the thermally activated singlet fission rate was found to follow the Arrhenius law. At low temperatures (< 140 K), singlet fission is suppressed while another energy trapping process becomes dominant. Together with

the fluorescence anisotropy and the polarization-dependent singlet fission measurements, we clarified the origin of three steady-state fluorescence bands which were the subject of a long-term controversy.

Publications

1. **L. Ma**, K. Zhang, C. Kloc, H. Sun, M. E. Michel-Beyerle, and G. G. Gurzadyan, "Singlet fission in rubrene single crystal: direct observation by femtosecond pump-probe spectroscopy" *Phys. Chem. Chem. Phys.* 14, 8307 (2012).
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3. **L. Ma**, K. Zhang, C. Kloc, H. Sun, C. Soci, M. E. Michel-Beyerle, and G. G. Gurzadyan, "Fluorescence from rubrene single crystals: Interplay of singlet fission and energy trapping" *Phys. Rev. B* 87, 201203 (2013).
4. **L. Ma**, Ke Jie Tan, Hui Jiang, Christian Kloc, and G. G. Gurzadyan, "Excited-State Dynamics in an α -Perylene Single Crystal: Two-Photon- and Consecutive Two-Quantum-Induced Singlet Fission" *J. Phys. Chem. A* 118, 838 (2014).
5. **L. Ma**, C. Kloc, C. Soci, M. E. Michel-Beyerle, and G. G. Gurzadyan, "Singlet fission in organic crystals" in *Ultrafast dynamics in molecules, nanostructures and interfaces*, Series in Optics and Photonics vol. 8, pp. 110. (2014) (book chapter).

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6. J. Luo, **L. Ma**, T. He, C. F. Ng, S. Wang, H. Sun, and H. J. Fan, "TiO₂/(CdS, CdSe, CdSeS) Nanorod Heterostructures and Photoelectrochemical Properties" *J. Phys. Chem. C* 116, 11956 (2012).
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 9. T. He, W. Wei, **L. Ma**, R. Chen, S. Wu, H. Zhang, Y. Yang, J. Ma, L. Huang, G. G. Gurzadyan, and H. Sun, "Mechanism Studies on the Superior Optical Limiting Observed in Graphene Oxide Covalently Functionalized with Upconversion NaYF₄:Yb³⁺/Er³⁺ Nanoparticles" *Small* 8, 2163 (2012).
 10. V. Duong Ta, R. Chen, **L. Ma**, Y. Jun Ying, and H. Sun, "Whispering gallery mode microlasers and refractive index sensing based on single polymer fiber" *Laser Photonics Rev.* 7, 133 (2013).
 11. J. Geng, K. Li, W. Qin, **L. Ma**, G. G. Gurzadyan, B. Z. Tang, and B. Liu, "Eccentric Loading of Fluorogen with Aggregation-Induced Emission in PLGA Matrix Increases Nanoparticle Fluorescence Quantum Yield for Targeted Cellular Imaging" *Small* 9, 2012 (2013).
 12. J. Geng, Z. Zhu, W. Qin, **L. Ma**, Y. Hu, G. G. Gurzadyan, B. Z. Tang, and B. Liu, "Near-infrared Fluorescence Amplified Organic Nanoparticles with

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- Aggregation-Induced Emission Characteristics for In Vivo Imaging" *Nanoscale*, 6, 939 (2014).
13. W. Wei, T. He, X. Teng, S. Wu, **L. Ma**, H. Zhang, J. Ma, Y. Yang, H. Chen, Y. Han, H. Sun, and L. Huang, "Nanocomposites of Graphene Oxide and Upconversion Rare-Earth Nanocrystals with Superior Optical Limiting Performance" *Small* 8, 2271 (2012).
14. J. Liu, G. Feng, R. Liu, N. Tomczak, **L. Ma**, G. G. Gurzadyan, and B. Liu, "Bright Quantum-Dot-Sized Single-Chain Conjugated Polyelectrolyte Nanoparticles: Synthesis, Characterization and Application for Specific Extracellular Labeling and Imaging" *Small*, (2014), published online. DOI: 10.1002/sml.201303505.

Chapter 1. Introduction

1.1 Introduction to organic semiconductor crystals

In recent decades, organic semiconductors have been intensively investigated due to their unique merits of low cost, structural flexibility, ease of tuning on the optical and electronic properties [1,2]. Another advantage over the traditional silicon-based inorganic materials is that they can be easily processed from solution through simple techniques, e.g., drop casting, spin coating or inkjet printing [3]. The assembly of all-organic electronic devices such as electrochemical circuits and memory cells have also been achieved in recent years, which makes an important stride towards the realization of all-organic electronics in the future industrial production [4-6].

The intermolecular dynamics of charge carriers, i.e., the ability for the charges to transfer from one molecule to another, is a crucial factor to improve the charge transport in organic semiconductors. Therefore the degree of molecular order is critical for the electrical conductivity. Hence, the single crystalline organic semiconductor is the best candidate to realize an ideal charge transport in organic-based electronic devices [7]. The high degree of order also makes them well suited to study the differences between the physics of organic and inorganic semiconductors [8]. The organic semiconductor crystals can be used to fabricate high-performance p- or n- type organic field-effect transistors (OFETs) [9], organic photovoltaic cells (OPVCs) [10], and organic light emitting diodes (OLEDs) [11].

Figure 1.1 Molecular projections of (a) rubrene and (b) α -perylene in their *ab* facets.

Among the various organic semiconductor materials, two small aromatic hydrocarbon molecules, rubrene and perylene, were taken as the representative models whose photophysical properties in crystalline phases were studied in detail in this thesis. Rubrene is a molecule with tetracene backbone and four phenyl substituents attached to each internal ring, which has attracted an increasing attention recently because of the following characteristics.

(1) High hole mobility. Rubrene is a common used material to fabricate OFETs [12]. The highest reported hole mobility of rubrene based OFET achieves $40 \text{ cm}^2/(\text{V s})$ [13].

(2) Long exciton diffusion length. The diffusion distance of triplet excitons in rubrene crystal can reach the macroscopic scale ($2\text{--}8 \mu\text{m}$) [14,15], while for other organic semiconductors it is usually on the scale of tens of nanometers.

(3) Candidate for flexible electronic devices [16]. The main applications of rubrene are in OLEDs and OFETs, which are the essential elements for flexible displays.

Rubrene single crystal grown by the physical vapor transport (PVT) technique possesses an orthorhombic structure with the $Cmca$ space group. Each unit cell contains 4 isolated molecules, with crystallographic dimensions $a=26.86 \text{ \AA}$, $b=7.193 \text{ \AA}$, $c=14.433 \text{ \AA}$ [17].

The other subject material is a dimeric organic crystal, α -perylene. Perylene and its derivatives are also widely used in OFETs [18], OLEDs [19], and organic photovoltaics [20]. The perylene crystalline structure belongs to the monoclinic crystal group, existing in two phases: α and β [21]. Similar to the rubrene single crystal, β -perylene is also monomeric with a single molecule located at each lattice point. However, α -perylene has a different structure from rubrene or β -perylene, i.e., a pair of perylene molecules resides at each lattice point, which is also called as a dimeric crystal. The crystalline structures of rubrene and α -perylene in their ab facets are shown in Figure 1.1.

In this thesis, both monomeric rubrene and dimeric α -perylene crystals are chosen as the subject materials in order to get a more comprehensive view of singlet fission process in organic semiconductor crystals.

1.2 Introduction to singlet fission

1.2.1 Background

Singlet fission (SF) usually occurs in a densely packed organic solid, where a molecule in its excited singlet state shares its energy with an adjacent molecule in the ground state, both molecules forming a pair of triplet states in a spin allowed process (Figure 1.2) [22]. This process was first proposed by Singh et al. in 1965 in order to explain the long-lived delayed fluorescence detected in anthracene crystal [23]. Interestingly, the inducement for the discovery of SF is actually due to its reverse process, i.e., triplet-triplet annihilation, reported by Kepler et al. in 1963 [24]. They used a 1.79 eV laser to excite the triplets (1.80 eV) in anthracene crystal, while a delayed fluorescence at higher energy (3.42 eV) was detected which indicates that singlet states were generated from the interaction between triplet states, i.e., via triplet-triplet annihilation [24]. After Singh's proposal, singlet fission was experimentally proven by the magnetic field effect on tetracene crystal by Geacintov [25] and Merrifield [26] in 1969. Despite the initial study on SF was started nearly half a century ago, there are not many experimental or theoretical studies up to now. A real explosion of studies on singlet fission has emerged only recently due to its potential for increasing the efficiency of organic-based photovoltaics.

The Shockley-Queisser limit predicts the maximal theoretical efficiency for one single p-n junction solar cell to be about 31% based on the assumption that the sub-bandgap photons remain unabsorbed and the excess energy of supra-bandgap

Figure 1.2 The schematics of singlet fission process.

photons is wasted as heat [27]. A number of different approaches have been used to significantly exceed this limit, e.g., tandem (multijunction) cells [28,29], hot carrier capture [30], and multiple exciton generation (MEG) [31]. Among them, the MEG is a process which creates multiple electron-hole pairs per absorbed photon with energy at least twice larger than the semiconductor's bandgap. It was firstly proposed by Nozik in 2001 [32] and then experimentally demonstrated in PbSe nanocrystals by Klimov in 2004 [33]. In the bulk semiconductors, there is also an analogue of MEG called impact ionization [34]. However, MEG is greatly enhanced in low dimensional materials, e.g., quantum dots (QDs), due to the large electron-electron interaction resulting from quantum confinement effect. The MEG-based QDs solar cells are capable to exceed 100 % external photocurrent quantum efficiency [35,36].

Singlet fission is an analogue of MEG in the case of organic materials. The SF efficiency can reach 100%, while the MEG efficiency is much lower due to the strong competition from other ultrafast decay channels such as Auger recombination. Moreover, triplet excitons are generated from SF with lifetimes usually on the μs or ms time scale which enables a more efficient charge carrier collection. Hanna and Nozik calculated that the theoretical efficiency for a SF sensitizer-based tandem solar cell which can reach 46% [37]. The study on a pentacene based photovoltaic stated that the peak external quantum efficiency achieves 109% due to singlet fission [38]. The recent developments and advances of SF up to 2013 were reviewed comprehensively by Smith and Michl [39,40].

In contrast to the conventional triplet generating process, i.e., intersystem crossing, SF is spin-allowed, which enables it to proceed on an ultrafast time scale (ps or sub-ps) as shown in Figure 1.2. For efficient SF the energy of one excited singlet state $E(S_1)$ must be at least twice that of the triplet energy $E(T_1)$, i.e., $\Delta E = E(S_1) - 2E(T_1) \geq 0$ [41]. Recently, efficient SF was also reported in noncrystalline systems, such as polycrystalline pentacene [42], amorphous films of DPT (5,12-diphenyl tetracene) [43] and rubrene [44,45], which takes an important step towards the large-scale application of singlet fission in organic-based solar cells.

Figure 1.3 The schematics of direct (red arrow) and mediated (blue arrow) singlet fission, redrawn from Ref. [39].

1.2.2 Basic theory

The number of theoretical and experimental studies on singlet fission in various organic materials keeps growing, however, an in-depth theory about the SF mechanism is still absent.

Similar to the model proposed by Merrifield to explain its reverse process triplet-triplet annihilation [46,47], a well-accepted simplified SF mechanism can be described by eq. (1.1) [39,40]:

$$S_0 + S_1 \xrightleftharpoons[k_2]{k_{-2}} {}^1(TT) \xrightleftharpoons[k_1]{k_{-1}} T_1 + T_1 \quad (1.1)$$

where S_0 is ground state, S_1 is excited singlet state, ${}^1(TT)$ is a triplet pair state which is coherently coupled into an overall pure singlet, $T_1 + T_1$ is the two free triplet states after dissociation. The interconversion between ${}^1(TT)$ and the initial state $S_0 + S_1$ is

described by the rate constants k_{-2} and k_2 , and the interconversion with the final state T_1+T_1 (two free triplets) is described by the rate constants k_{-1} and k_1 [39,40].

Although singlet fission is more inclined to refer to the conversion from S_0+S_1 to the triplet pair $^1(TT)$, the dissociation from $^1(TT)$ to two free triplets T_1+T_1 cannot be completely isolated from it. Suna [48] found that in a crystal only the ratio between k_{-1} and k_2 has physical significance but not individually. Therefore, singlet fission usually refers to the whole process described in eq. (1.1). According to the formation paths of the triplet pair, the singlet fission mechanism can be classified into two types [40]: a one-step via direct coupling and a two-step via intermediate state, as shown in Figure 1.3. Taking a pair of molecules as a whole, the initial state S_1S_0 denotes that one molecule is in the excited singlet state S_1 , and the other one in its ground state S_0 . The charge-transfer intermediate state is represented as either CA or AC.

Singlet fission by direct coupling. The S_1S_0 directly proceeds to the $^1(TT)$ state without assistance from intermediates, as demonstrated by the red arrow in Figure 1.3. The direct coupling mechanism was clearly demonstrated in organic single crystals. Chan et al. [49] observed the multiexciton (ME) state, i.e., $^1(TT)$, in pentacene. The ME state is found to be in coherent superposition with the excited singlet state S_1 . Burdett and Bardeen [50] concluded the triplet pair is formed via direct SF in tetracene crystal, based on the observation of quantum beats in delayed fluorescence.

“Intermediate states” such as “multiexciton state” [51], “dark state” [52] or “doubly excited state” [53] have also been reported. However, all terms refer to the

Figure 1.4 The schematics of overlapping HOMO (h_A and h_B) and LUMO (l_A and l_B) densities for perfect stacked (a), slip-stacked (b) geometries for a two molecule system, redrawn from Ref. [39].

coupled triplet pair state, i.e., $^1(TT)$. According to the way of justification in this thesis, they are still classified into the direct SF mechanism.

For a direct coupling mechanism the overlapping geometry between adjacent molecules is crucial for the SF efficiency. The SF efficiency is determined by the coupling between singlet and triplet pair states via the matrix element $\langle S_1 S_0 | H_{el} | ^1 TT \rangle$. According to the Fermi golden rule, the intrinsic singlet fission rate is proportional to the square of the matrix element $\langle S_1 S_0 | H_{el} | ^1 TT \rangle$ [39], i.e.,

$$k_{fiss} \propto |\langle S_1 S_0 | H_{el} | ^1 TT \rangle|^2 \quad (1.2)$$

$$\langle S_1 S_0 | H_{el} | ^1 TT \rangle = (3/2)^{1/2} [\langle l_A l_B | e^2 / r_{12} | l_A h_B \rangle - \langle h_A h_B | e^2 / r_{12} | h_A l_B \rangle] \quad (1.3)$$

where H_{el} is the electrostatic Hamiltonian, h_A and h_B represent the HOMO, l_A and l_B stand for the LUMO of molecule A and B. Therefore, we can see that the singlet fission rate k_{fiss} depends on the integrals of $\langle l_A l_B | e^2 / r_{12} | l_A h_B \rangle$ and $\langle h_A h_B | e^2 / r_{12} | h_A l_B \rangle$. Figure 1.4 presents the schematics of the charge density overlap for the perfect and slip stacking geometries of two molecules A and B. In the case of perfect-stacking geometry, the integrals of both elements $\langle l_A l_B | e^2 / r_{12} | l_A h_B \rangle$ and $\langle h_A h_B | e^2 / r_{12} | h_A l_B \rangle$ equal to 0. However, if two molecules are mutually shifted in the direction of the transition dipole moment, we will have nonzero integrals of $\langle l_A l_B | e^2 / r_{12} | l_A h_B \rangle$ and $\langle h_A h_B | e^2 / r_{12} | h_A l_B \rangle$. This kind of slip-stacked geometry is very common in organic molecular crystals. Therefore, singlet fission is more favorable in the crystalline structure.

Singlet fission via intermediate state. Apart from the direct coupling between $S_1 S_0$ and $^1(TT)$, the correlated triplet pair $^1(TT)$ can also be formed through an intermediate state such as charge-transfer (CT) state [39], dark multiexciton (ME) state [54] or excimer state [55]. Taking the CT mediated SF as an example, it can be considered as a two-step electron transfer process shown by the blue arrows in Figure 1.3. The singlet excited molecule (S_1) firstly transfers one electron to its adjacent molecule in the ground state (S_0) to generate a CT state (i.e., CA or AC). Then a second electron transfer event produces the correlated triplet pair $^1(TT)$ [56]. Similarly, if the above two electron transfer events occur simultaneously, it will come to the previously mentioned direct SF mechanism [56,57].

Unlike the direct coupling mechanism where the correlated triplet pair state is clearly observed, according to my best knowledge, the intermediate CT state has never been experimentally identified. All studies on the CT mediated SF stay on the theoretical level. Greyson et al. [58] investigated the indirect singlet fission with a CT intermediate state in several covalent organic dimers by theoretical calculations. They concluded that the CT state should lie relatively close to the S_1 and TT for a highly efficient SF. Teichen et al. [53] described the SF dynamics in the presence of solvent-induced energy level fluctuations. They used a microscopic model which considered only the CT intermediate by neglecting the direct coupling mechanism. Berkelbach et al. [56] also used a microscopic model to study the SF in pentacene dimers. They concluded that SF does occur via an intermediate CT state, even though the CT state may locate at higher energy than the first excited singlet state.

1.2.3 Identification of singlet fission

According to the definition of SF, three evidences can be used to identify singlet fission:

1. Triplet yield is higher than 100%. Assuming the SF efficiency above 50% provides the triplet yield above 100%. It is understandable that other triplet generating methods such as intersystem crossing (ISC) or triplet sensitization will not give a triplet yield beyond 100%. However, in order to accurately determine the triplet yield, basic knowledge about the triplet states such as the extinction coefficient should be known or measured in advance. This method is not valid any more when the SF

efficiency is much lower than 50%, since the possibility of other triplet generating mechanisms cannot be ruled out.

2. Ultrafast formation of triplet states. If the formation of triplet states is found to be on the ps or fs time scale, it is already a strong indication for SF since the traditional ISC is much slower (ns~ms). The ultrafast formation of triplet states can be easily monitored by the ultrafast transient measurements, e.g., transient absorption, time-resolved resonance Raman or time-resolved two-photon photoemission. Furthermore, if the subject material is a small molecule in solid state like thin film or crystalline phase where SF occurs on two neighboring molecules, then a control measurement in dilute solution can be performed. The molecules are well separated from each other in solution, which is not favorable for efficient SF. Therefore no triplet states via SF are expected. However, for the dimer or polymer samples this method is not applicable since the SF occurs in the same molecule.

3. Observation of delayed fluorescence when exciting the singlet states. During singlet fission, the excited singlet states are coupled with the triplet pair states. Thus the reverse process of SF, i.e., triplet-triplet annihilation is always accompanied with SF, which will reproduce the excited singlet state and give rise to the delayed fluorescence. Therefore, observation of delayed fluorescence in the μs to ms time window is another strong proof for SF.

1.2.4 Detection methods

Experimental techniques to characterize singlet fission are summarized below.

Magnetic field effect. In early 1970s, the magnetic field effect was the most common method to detect singlet fission [25,26,59,60]. An external magnetic field influences the spin wave functions, resulting in a change in the singlet triplet interconversion rates, i.e., affecting the SF and TTA processes. Therefore the yield of prompt and delayed fluorescence, as well as the photocurrent will be influenced [39]. The magnetic field effect study is indirect but practical, therefore, is used to characterize singlet fission until now [44,61]. However, the absence of magnetic field effect does not fully rule out singlet fission [39]. Based on the theoretical models such as Johnson-Merrifield [47] or the more accurate Suna model [48], it is possible to obtain the rates of both processes from fitting on the magnetic field effect data. However, these theoretical models only consider SF through dissociation of one singlet exciton into two triplet excitons. However, the possible intermediate states such as dark ME, CT, and excimer states have never been taken into account. Therefore, it is difficult to extract the accurate information about SF from magnetic field study, e.g., the SF rate, the formation of intermediate state, and the singlet/triplet exciton or polarons transport.

Time-resolved fluorescence. Based on the discussion above, TTA competes with SF, in particular when $E(S_1) \leq 2E(T_1)$. The SF will quench the fluorescence on a ps time scale resulting in prompt fluorescence. The TTA leads to the delayed fluorescence on μ s or ms time scale depending on the triplet state lifetime. Time-resolved fluorescence techniques on the time-scale of fs to ms are able to resolve both the prompt and

delayed fluorescence [50,62,63]. The SF rate can be obtained from the fitting of prompt and delayed fluorescence kinetics based on the model considering both SF and TTA [63].

Transient absorption spectroscopy. The state-of-the-art ultrafast optical spectroscopic techniques, such as the transient absorption (TA) [52,55], offer another option to characterize the dynamics of SF on a femtosecond time scale. Usually the fast formation time (ps or sub-ps) of triplet absorption bands in the TA spectra can be safely assigned to the singlet fission time because ISC of isolated molecules is much slower. However, the accurate assignment of the TA bands can be quite difficult. Recently, Wong et al. [64] by use of transient absorption microscopy studied the SF in TIPS-pentacene film; depending on the polarization of the probe beam the film subdomains show different TA signals. The TA microscopy offers more accurate information on SF in the nonuniform samples with different subdomains such as the amorphous or polycrystalline films.

Time-resolved resonance Raman (TRRR) or time-resolved two-photon photoemission (TR-2PPE) spectroscopy. Different from the transient absorption technique, time-resolved resonance Raman (TRRR) measures the vibrational spectra of different transient species. The time-resolved two-photon photoemission (TR-2PPE) measures the kinetic energy of the photoemitted electrons which are ionized by the high photon energy (UV) probe. Wang et al. [65,66] studied the SF in carotenoids by

use of TRRR. Chan et al. [49,51] investigated the SF in pentacene film by TR-2PPE. They observed the dark ME state for the first time [49].

In my PhD project, ultrafast spectroscopic techniques such as time-resolved fluorescence and transient absorption spectroscopy are used as the main characterization methods to study singlet fission in different materials. In order to draw conclusions on the single crystals, TA spectra were measured in dilute solution as a reference. Because of the low ISC efficiency in solution, only excited singlet states can be detected. However, in single crystals, strong triplet-triplet absorption was observed due to efficient singlet fission.

1.2.5 Previous studies on singlet fission

1. SF in crystalline films

Singlet fission is constrained to multichromophoric structures, e.g., dimer, oligomer, polymer, aggregates, and molecular crystals. The reason is that there have to be at least two neighbor sites in order to generate two triplet excitons [39]. Polyacene crystalline structures offer an excellent model for the investigation of singlet fission. Below, the SF studies on three polyacene crystalline structures including pentacene, tetracene and rubrene are summarized.

Pentacene. Singlet fission is most extensively studied in the pentacene polycrystalline films, SF is energetically allowed and therefore proceeds on an ultrafast time scale ~ 80 fs [42,67]. Because of the ultrafast reaction time, SF was initially considered to

occur through a direct coupling mechanism [67]. Some recent TA experiments and quantum chemical calculations suggest that SF in pentacene is mediated by intermediate states such as the excimer state [68,69], doubly excited excitonic state [70,71], or the dark ME state [54,72]. However, Friend et al. [73] later studied the temperature-dependent steady-state and transient absorption in the pentacene films which were deposited on substrates with different thermal conductivities. They claimed that all the TA features previously assigned to excimers and doubly excited excitonic states are due to a thermal artifact induced by the pump beam. Moreover, Chan et al. [49] by use of TR-TPPE technique have observed the multiexciton state, i.e., $^1(TT)$, which is in coherent superposition with the excited singlet state S_1 . Therefore, the SF mechanism in pentacene crystalline films most likely includes the existence of a multiexciton state, which further dissociates into two free triplet excitons. This mechanism can still be considered as direct SF.

Tetracene. The reports on SF in tetracene crystals can be tracked back to the early 1970s, mainly studied via magnetic field effect [25,74-76]. Compared with the well-studied pentacene, the SF mechanism in tetracene is less understood although there are plenty of publications. Since the energy difference in tetracene between one excited singlet and two triplet states is negative, $\Delta E = E(S_1) - 2E(T_1) = -0.18$ eV [77], SF in tetracene was considered to be thermally activated [39,63,77-79]. It means that SF proceeds with the assistance of phonons, and TTA always coexists with SF [80,81]. The reported SF times range from 9.2 to 200 ps [63,82,83], i.e., much slower than that of pentacene. The main experimental evidence for the thermally activated SF is from

the temperature dependent fluorescence yield studies [25,84]. The fluorescence intensity was found to be 100 times higher at 4 K than at room temperature [84]. Thorsmølle et al. [78] also observed that the transient signal $\Delta T/T$ at 200 ps was temperature dependent and followed the thermal activation law.

However, the recent time-resolved fluorescence and transient absorption studies have shown no temperature dependence which raised doubts on the long-held thermally activated fission model. Burdett et al. [85] studied the temperature dependent fluorescence kinetics in polycrystalline tetracene. They found the fluorescence spectra are indeed temperature dependent and explained that this dependence is due to different emitting species. The fluorescence decays with two time components: the 80 ps decay corresponding to SF is independent of temperature. However, the ns fluorescence decay shows clear temperature dependence. Later on, the same group [50,83] further observed the quantum beats in the delayed fluorescence of tetracene crystal and concluded that the triplet pairs are formed via direct SF. Tayebjee et al. [82] also studied the time-resolved fluorescence in tetracene thin film and obtained similar results. Wilson et al. [86] used TA spectroscopy to prove that the dynamics of SF in tetracene is temperature independent. Chan et al. [51] by use of TR-TPPE technique claimed that the higher energy ME state in tetracene can be accessed by coherent coupling and entropic gain without temperature dependence. Therefore, the previously observed temperature dependent fluorescence or transient absorption are most probably due to the delayed fluorescence or other

long lived species rather than singlet fission. The picture of SF in tetracene crystal is quite complicated, therefore, further investigations are needed.

Rubrene. The most attractive features of rubrene crystal are its high hole mobility and long diffusion length. Through photoconductivity study Najafov et al. [14] obtained a long exciton diffusion length up to 8 μm due to the long exciton lifetime, indicative of the existence of singlet fission. Then Ryasnyanskiy et al. [87] studied the time-resolved fluorescence decay and detected the delayed fluorescence. Afterwards our study by use of pump-probe technique directly observed the SF in rubrene crystal [88]. We identified both the decay of excited singlet states and formation of triplet states. Moreover, the direct SF from upper excited states was found to compete with the ultrafast polarons formation. We further studied the two-photon-induced SF and concluded the SF rate does not depend on the symmetries of excited states [89]. Our temperature-dependent time-resolved fluorescence study also revealed the interplay between SF and energy trapping [90]. Later on, similar measurements were done by various groups: Jankus et al. [45] also investigated the competition between SF and polaron pair formation in amorphous rubrene. Wen et al. [91] measured the temperature-dependent time-resolved fluorescence on the time scale from fs to μs . Their obtained activation energy of 30 meV corresponds well to our study (50 meV) [90]. Moreover, Zhang et al. [92] also studied the thermally activated SF in rubrene doped film by magnetic field effect. Biaggio et al. [93] investigated the power dependent fluorescence yield in rubrene crystal. They also emphasized the importance of interplay between SF and triplet-triplet fusion to the fluorescence yield.

Crystalline structure dependent SF. The molecular packing or crystalline structure decides the intermolecular coupling strength which is a crucial factor for the SF efficiency. Renaud et al. [94] made a theoretical calculation on SF via direct coupling mechanism for 22 different stacking geometries of perylenediimide (PDI) derivatives. The triplet yields range from 0 to 34%, which suggests that the SF efficiency is very sensitive to the geometry. Robert et al. [62] characterized SF rates in different crystalline structures of diphenylhexatriene; SF was preferable in the monoclinic (SF rate is 1.5 times faster) rather than in the orthorhombic structure.

2. SF in dimers

A local order in the material is considered to be essential for an efficient SF. Therefore, high efficient SF is mostly reported in the solid state such as single crystalline or polycrystalline phases. However, the crystalline material is usually too delicate to fabricate practical devices. Various attempts have been made in finding efficient SF in the solutions, since it is easier to do further processing from the liquid phase. Covalently linked dimer is an ideal system for studying SF in solution. It allows to study the SF in isolated molecules and investigate the effect of intermolecular coupling. However, the reported SF yields are quite low. For the covalently linked tetracene dimers, the SF yield is only between 1% [95] and 3% [96]. The first molecule specifically designed for efficient SF was 1,3-diphenylisobenzofuran [97]. However, the yields of triplets in its two covalent dimers can only reach ~9% which is much less than that of the neat film [98]. The low SF yield obtained in covalent

dimers may be due to weak coupling between the two chromophores, i.e., through the linkage bond as suggested by the theoretical calculations [96].

3. SF in polymers and aggregates

Lanzani and Dellepiane et al. [99-101] reported the ultrafast SF (< 200 fs) in polycarbazolyldiacetylene from the lowest excited $2A_g$ state. The theoretical calculations showed that the $2A_g$ state is the doubly excited singlet state which is responsible for SF in polyenes [102] and polydiacetylene oligomers [103]. However, the recent study on poly(thienylenevinylene) film suggested that SF directly proceeds from the $1B_u$ state [104]. Wohlgenannt et al. [105,106] studied the SF in both luminescent polymers, i.e., poly(para-phenylene-vinylene) [PPV] and poly(para-phenylene) [mLPPP], as well as the nonluminescent polymers, i.e., poly(di-acetylene) [PDA]. They used the photomodulation (similar to the steady-state pump-probe) technique to obtain the triplet action spectra. Theoretical calculations in oligothiophenes and polyacenes suggested that their dark double exciton intermediate states have biradical (diradical) characters [107,108]. Guo et al. [109] investigated the ultrafast excited state dynamics in poly(3-hexylthiophene) (P3HT) with different regioregularities, i.e., regiorandom (RRa-P3HT) and regioregular (RR-P3HT). SF was observed only in the RRa-P3HT film. The reason is probably that in the better ordered RR-P3HT film the interchain interaction is larger, which results in a more efficient polaron formation than SF. Carotenoids are the only systems where SF in aggregates is studied so far. It was originally observed by the

magnetic field effect [110], and considered to proceed from the dark $2A_g$ intermediate state [111]. By use of TRRR, high triplet yield (90-200 %) via SF was reported in all-trans 3R,3'R-zeaxanthin [65,66].

4. SF in solutions

Singlet fission was also studied in monomeric solutions. For example, SF in aqueous colloidal nanoparticles of 5,12-diphenyltetracene (DPT) was recently reported [112]. The triplet yield of DPT solution achieved 75% which offers a new platform for studying singlet fission. Walker et al. [55] reported 200% triplet yield in the highly concentrated TIPS-pentacene solution. The fluorescence spectrum was red shifted with increasing concentration, while the fluorescence lifetime is shortened down to 400 ps. This lifetime is in line with the triplet formation time due to SF obtained from the TA measurements. Therefore, the SF in highly concentrated solution is claimed to proceed via an excimer like intermediate state.

5. Harvest multiple carriers from SF

Zhu's group recently published several interesting works regarding harvesting the SF via either electron [49,113] or energy [114] transfer from the ME states. The common concern about extracting multiple electron-hole pairs through SF is the competition from excited singlet states S_1 . They concluded that the two-electron transfer from ME states is the dominant dissociation channel for materials with ultrafast SF such as pentacene [49]. The SF in pentacene (~100 fs) proceeds much faster than the charge transfer from S_1 . Therefore, in the pentacene/ C_{60} bilayer, carriers transferred to

fullerene are mainly due to a two-electron transfer process from ME states. However, for the materials with slower SF on ps time scale, e.g., tetracene, the one-electron transfer from S_1 strongly competes with the two-electron transfer from ME states [113], resulting in the latter process only having 40% contribution to the total extracted carriers. In this case, utilization of energy transfer from triplet pairs can be considered as an alternative solution to extract multiple carriers [114].

6. SF based solar cell devices with over 100% external quantum efficiency

Baldo et al. [38] fabricated a singlet fission based solar cell with 109% external quantum efficiency (EQE). The core of the solar cell is a donor-acceptor junction of pentacene/ C_{60} . Its anode consists of indium tin oxide (ITO) and poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS). Bathocuproine (BCP) with silver coating is used as cathode [38]. As a follow-up study, they fabricated the same solar cell device on top of a Distributed Bragg Reflectors (DBR) which prolongs the photon dwell time inside the device. This modified structure enhanced the EQE to 126% [115]. In Ref. [116], tetracene based solar cell singlet fission efficiency reaches $(71 \pm 18)\%$. SF-based photodetectors composed of 30 pentacene/ C_{60} bilayers also exhibited a quantum efficiency exceeding 100% [117]. Friend et al. reported the pentacene/PbS [118] and pentacene/PbSe [119] based solar cells with EQE up to 80% [120].

1.3 Introduction to ultrafast laser spectroscopy

The word “spectrum” was first used by Newton to describe the rainbow like dispersion of the light from the sun or lamp after passing through a prism [121]. Spectroscopy was then established as a scientific discipline to study the interaction between light and matter, which provides essential information about the electronic structures of atoms or molecules.

The spectroscopic techniques can be generally categorized into two kinds: steady-state and time-resolved [122]. The steady-state spectroscopy is carried out with continuous excitation and detection, i.e., the samples are illuminated by a continuous light source. The time-resolved spectroscopy is used to measure the intensity or anisotropy decays, wherein the samples are excited by an ultrashort pulsed light source with pulse width shorter or comparable to the sample’s decay time [122]. The time-resolved spectroscopy at $t < 1$ ps is also known as ultrafast spectroscopy.

The steady-state spectroscopy provides an integrated result of different time-resolved light-matter interactions over the sample’s intensity decay, which offers the information about the initial and final electronic states. As the saying goes, *it is better to travel hopefully than to arrive*, the process itself can be more fascinating than the final result. Let's take the example of a cat jumping from a high tree branch to the ground. Our naked eyes can only distinguish the two states of the cat, i.e., on the branch and on the ground. However, it is more appealing to see how the cat can survive falling from such a great height. Fortunately, the high speed camera is able to

Figure 1.5 Schematics of the ultrafast relaxations of excited electronic states [123].

record the snapshots of all movements during its jump, which enables us to “see” its real motion in the air and further try to simulate it (Figure 1.5). Similarly, it will be also interesting to see how the transitions between different electronic states are realized in real time in the case of atoms, molecules and solids, e.g., how do the excited states return to ground state, by emitting fluorescence, depopulating to other intermediate states, or just simply generating heat (Figure 1.5).

With the advent of commercial femtosecond lasers, ultrafast optical spectroscopy provides an unprecedented insight into the dynamics of the electronic and geometric structure of materials [124]. The ultrashort femtosecond duration of the laser pulse makes it possible to probe the elementary photophysical and photochemical processes in real time [124-126]. Ultrafast optical spectroscopy studies have been carried out in the gas phase [127-129], solutions [130-132], crystals [88,133,134], conjugated

Figure 1.6 Time-resolved single photon counting (TCSPC) measurement principle, redrawn from Ref. [135].

polymers [109,136,137], semiconductors [138-141], and biological systems [142-144].

In this dissertation, the ultrafast spectroscopic techniques including time-resolved fluorescence and transient absorption spectroscopy were implemented to characterize the singlet fission dynamics. Therefore, a brief introduction to these two techniques is presented below.

1.3.1 Time-resolved fluorescence techniques

For the fluorescent samples, time-resolved fluorescence can be applied to study their fluorescence intensity or anisotropy kinetics. The fluorescence emitted after excitation by an ultrashort laser is recorded either directly by fast electronic equipment or via nonlinear optical methods.

Time-correlated single photon counting (TCSPC) is a straightforward and powerful technique for sensitive time-resolved fluorescence measurements down to the single molecule level [145]. Bollinger and Thomas first introduced the basic idea in 1961 [146]. A detailed description of the TCSPC setup can be found in the book written by O'Connor and Phillips [147]. The TCSPC technique is based on the conception that the probability distribution of a single photon emission after each excitation reproduces the temporal distribution of all emitted photons [147]. A highly sensitive detector, e.g., single photon avalanche photodiodes (SPADs), photomultiplier tube (PMT), or micro-channel plate (MCP) makes it possible to record single photons [148]. The time difference between the emission and excitation (i.e., the time needed for each single photon to arrive at the detector) is recorded for each cycle. The probability distribution will be constructed by sampling $\sim 10^{10}$ cycles, which reveals the fluorescence decay profile as illustrated in Figure 1.6. The time resolution of TCSPC, i.e., instrument response function (IRF), is limited by the transit time spread in the detector. With fast detectors, IRF can reach 25 ps [135]. Shorter lifetimes ~ 10 ps can be achieved by deconvolution of the recorded decay data [147]. As discussed above, the TCSPC technique obtains the fluorescence kinetics at discrete

Figure 1.7 Schematics of the core part of fluorescence upconversion technique.

wavelengths. However, by recording kinetics at various wavelengths, it is possible to construct the time-resolved fluorescence spectra.

A streak camera can be used to obtain the time-resolved fluorescence spectra directly in a single shot with time resolution down to 1 ps [149]. However, if the fluorescence lifetime is on the ultrafast time scale of femtoseconds, neither TCSPC nor streak camera is able to offer useful information anymore. In that case the fluorescence upconversion technique should be used. The ultrahigh time resolution is provided by the method which bypasses the limitation of the time-resolution of electronic detectors, and is mainly limited by the pulse width of the ultrafast laser [150].

Basically, the fluorescence excited by a pulsed laser excitation source together with an ultrashort laser beam (“gate” beam) pass through a nonlinear crystal, e. g. BBO, and generates a new beam by sum frequency generation (Figure 1.7). The newly generated shorter wavelength, i.e., the upconverted wavelength, is detected instead of the original fluorescence. The time resolution is achieved by changing the time delay between the gate beam and the fluorescence via a mechanical optical delay stage. Only when the gate beam and the fluorescence transient overlap both spatially and temporally in the nonlinear crystal, the upconverted beam can be generated. The time-resolved fluorescence decay is then obtained by recording the intensity of the upconverted beam at different optical delay times. Therefore, the resolution of fluorescence upconversion setup is only dictated by the pulse width of the ultrashort laser.

1.3.2 Pump-probe technique

Unlike the time-resolved fluorescence method where the sample should be luminescent, the transient absorption spectroscopy can be carried out on nonluminous samples. The technique used to measure transient absorption is known as pump-probe technique since this method relies on two ultrashort pulses separated by a temporal delay Δt . One relatively stronger intensity beam termed as “pump beam” is used to initiate transient processes such as charge transfer, excited state relaxation, and stimulated emission in the sample. Another much weaker beam known as “probe beam” is used to detect these transient processes induced by the pump beam.

Figure 1.8 Schematics of the pump-probe technique.

The schematic diagram of a typical pump-probe setup is shown in Figure 1.8a. The probe beam is passed through an optical delay line, and its absorbance (sometimes transmittance or the reflectance) change (ΔA) in the presence and in the absence of the pump beam at different delay times is measured. As shown in Figure 1.8b, after excitation, the electrons are promoted from the ground state to the excited states. Therefore, when the probe beam arrives later, its absorption corresponding to steady-state absorption range will decrease (i.e., $\Delta A < 0$) compared with that without pump beam, which is called ground state bleaching (GSB). Furthermore, additional absorption (i.e., $\Delta A > 0$) will be observed which corresponds to the excited state absorption (ESA), also termed as photo-induced absorption (PIA). Therefore, the pump probe setup functions like an ultrafast camera taking snapshots of the temporal evolution of transient absorption spectra.

1.4 Objectives and significance of the study

This thesis contains three parts:

Part 1: Singlet fission under one-photon excitation of organic crystals.

Part 2: Singlet fission under two-photon and two-quantum excitation.

Part 3: Interplay between singlet fission and energy trapping.

The objective and significance of the first part

The first part aims to study the singlet fission mechanism in different crystalline structures under one-photon excitation. Through our study, we identify that in the monomeric rubrene crystal, singlet fission can directly proceed from the upper excited singlet electronic states S_N , upper vibrational levels of S_1 , and thermally activated from the lowest vibrational state of S_1 . The wavelength dependent singlet fission rate was proven to follow the Arrhenius law. In the dimeric α -perylene crystal, singlet fission takes place on an ultrafast time scale (< 50 fs) due to stronger intermolecular coupling, and efficiently competes with the excimer formation process. Unlike in the solution [55], the excimer is found to be a competitor rather than an intermediate for the SF in dimeric crystal.

The objective and significance of the second part

The second part endeavors to study the singlet fission under two-photon or two-quantum excitation to figure out the SF mechanism in the subject materials. The

previous study in pentacene suggests that there is an intermediate dark state on the pathway of singlet fission [54]. The dark intermediate state has a multiexciton character and is optically forbidden under one-photon excitation. Therefore, we used two-photon excitation in order to populate directly the dark excited states which are not attainable under one-photon excitation. We found that the SF rate depends on the energy rather than symmetry of the excited state. According to my best knowledge, the multi-photon-induced singlet fission has never been observed previously.

The objective and significance of the third part

The third part elaborates the dominant role of singlet fission in the steady-state fluorescence spectra of rubrene crystal. It should be mentioned that the origin of the rubrene fluorescence is under debate for a long time. Our results clearly show that both SF and energy trapping play a crucial role in the fluorescence spectra. The majority (99.9%) of the pristine rubrene emission is quenched by singlet fission, therefore, the intrinsic fluorescence is easily concealed by other side effects. However, in the previous publications singlet fission has never been taken into consideration.

Chapter 2. Experimental techniques

2.1 Materials and methods

2.1.1 Physical vapor transport technique

Rubrene and perylene single crystals were grown by use of physical vapor transport (PVT) technique [151], offered by Dr. Zhang Keke, Dr. Tan Ke Jie and Dr. Jiang Hui in the crystal growth group led by Professor Christian Kloc from School of Materials Science and Engineering (MSE), Nanyang Technological University. The rubrene and perylene source powders (Sigma-Aldrich, >99% purity) were purified by sublimation for several times before using them for the crystal growth. The carrier gases used in the PVT technique are Argon (Ar), Nitrogen (N_2), Hydrogen (H_2) and the forming gas, i.e., a mixture of H_2 and N_2 with varied mole fraction. Semi-transparent two-zone furnace is used for the crystals growth. The source powder is placed at the zone with higher temperature (e.g., 300 °C for rubrene), and the other zone is set to a slightly lower temperature (e.g., 260 °C for rubrene). The carrier gas flows from the higher temperature zone to the lower one, thus the sublimated source molecules are condensed at the wall of the inner quartz tube with lower temperature [152]. A schematic diagram for a two-zone furnace and an as-grown rubrene crystal are shown in Figure 2.1. The obtained as-grown single crystals are mostly of flake and needle shapes; their sizes can reach 1 cm. They are selected under the polarized microscope: only those with smooth surface and large size are chosen for optical characterization, i.e., steady-state spectroscopy, time-resolved fluorescence and transient absorption

Figure 2.1 Schematic diagram of a two-zone furnace (a) and one large size as-grown rubrene crystal (b), adopted from Ref. [153].

measurements. The thickness of the rubrene single crystal used in our experiments is about 10 μm , characterized by SEM and steady-state absorption spectra. The thickness of the α -perylene single crystal is only about 1 μm . The as-grown perylene crystals were characterized by powder XRD using Bruker AXS D8 Advance XRD. The experimental powder XRD spectrum's peak positions matches with those reported by Trotter et al. [154], indicative of an alpha phase perylene crystal. The as-grown samples were placed in the plastic petri dishes, sealed with paraffin film and stored in the desiccators.

2.1.2 Sample preparation

Crystalline samples: In order to implement different spectroscopic characterizations, the solid samples need to be fixed by suitable holders. In the case of organic crystals, we chose a simple method, i.e., to stick them at the edge of glass slides with double-sided adhesive, shown in Figure 2.2. Since the laser beam diameter after focusing (50 μm) is much smaller compared with the

Figure 2.2 The rubrene and α -perylene crystals fixed on the glass slides.

Figure 2.3 The prepared solution samples of rubrene and perylene in 1 mm cuvettes.

sample dimensions, we can ensure to measure only at the suspended part in order to avoid any influence from substrates.

Liquid samples: For preparing the samples in solution, rubrene and perylene powders were first dissolved in different solvents (e.g. toluene and hexane) to

make the stock solution. All solvents used are of analytical grade. After dilution to the desired concentrations, the solutions were then transferred into 1 mm quartz cuvettes (Hellma Analytics, QS 1.0 mm) by pipettes (Figure 2.3).

2.2 Optical characterization

2.2.1 Steady-state spectroscopy

Steady-state absorption spectra. The steady-state absorption spectra were measured by a double beam UV-Vis spectrophotometer (Cary 100 Bio, Varian), shown in Figure 2.4. The measurable wavelength range is 190-900 nm, offered by an UV (deuterium) lamp and a visible (tungsten) lamp. The UV lamp wavelength is within the range of 190-400 nm, and the range of the visible lamp is 350-900 nm. All steady-state absorption spectra are obtained by the Cary 100 Bio under the following settings: average time 0.1 s, data interval 1 nm and scan rate 600 nm/min. By changing different holders, both liquid and solid samples can be measured with an accuracy of 10^{-3} OD.

Figure 2.4 Cary 100 Bio UV-visible spectrophotometer.

Figure 2.5 HORIBA Jobin Yvon Fluorolog-3 spectrofluorometer.

Steady-state fluorescence spectra. The steady-state fluorescence emission and excitation spectra were measured by a spectrofluorometer (Fluorolog-3, HORIBA Jobin Yvon, Figure 2.5). A Xenon lamp is used as the excitation source, providing excitation from 200 to 600 nm. The fluorescence emission between 200 and 900 nm can be detected. The excitation and emission slit widths are adjusted according to the fluorescence intensity of the specific sample, usually for liquid sample 0.2~0.5 mm, for solid sample 0.5~1 mm, where 1 mm slit width corresponds to 4.2 nm spectral bandwidth. The integration time for each data point is 0.5 s.

Temperature-dependent steady-state fluorescence spectra can be recorded by the same spectrofluorometer (Fluorolog-3), with the sample placed in a nitrogen bath cryostat (OptistatDN, Oxford Instruments) which can be cooled down to 77 K.

Fluorescence anisotropy. Upon excitation with polarized light the emission from many samples is also polarized. The extent of polarization of the emission is described in terms of the anisotropy (r) [122]. The fluorescence anisotropy is defined by the eq. (2.1),

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \quad (2.1)$$

where $I_{\parallel}$ and $I_{\perp}$ are the fluorescence intensities measured in the directions parallel and perpendicular to the polarization direction of the excitation light. Two polarizing films were placed in the excitation and emission paths. For example, the polarization of excitation light is fixed along the horizontal direction, the fluorescence spectra were then collected in both horizontal ($I_{\parallel}$) and vertical ($I_{\perp}$) directions in order to calculate the fluorescence anisotropy r according to eq. (2.1).

2.2.2 Time-resolved fluorescence spectroscopy

Time-correlated single photon counting (TCSPC) technique. Our TCSPC setup was purchased from PicoQuant (Model: FluoTime 200), shown in Figure 2.6. The principle of TCSPC technique was introduced in Chapter 1. A tunable ultrashort excitation source (ranging from 230 to 1080 nm) is provided by a titanium-sapphire laser (Chameleon, Coherent Inc. 100 fs pulse width, 80 MHz repetition rate) combined with a harmonic generator (Coherent Inc.) which generates the second or third harmonics of the fundamental beam. The detector

Figure 2.6 *The time-correlated single photon counting (TCSPC) setup.*

used is a Microchannel Plate Photomultiplier Tube (MCP-PMT, model R3809U-50, Hamamatsu Corporation), which offers 10 ps temporal resolution and covers a spectral range from 200 to 850 nm. Temperature dependent fluorescence measurement is also implementable by combining TCSPC with an exchange gas continuous flow cryostat (OptistatCF, Oxford Instruments).

The instrument response function (IRF) is recorded by measuring the scattered excitation light (i.e., the fluorescence decay profile measured at the excitation wavelength). The obtained fluorescence decay data are analyzed by a nonlinear least-squares deconvolution method by a commercial software FluoFit (PicoQuant), which uses eq. (2.2) as fitting model [155]. The deconvolution fitting enables TCSPC to resolve the fluorescence lifetime down to 10 ps ($\pm 10\%$).

$$I(t) = \int_{-\infty}^t IRF(t') \sum_{i=1}^n A_i e^{-\frac{t-t'}{\tau_i}} dt' \quad (2.2)$$

Figure 2.7 The fluorescence upconversion setup and its schematics.

Where I is the fluorescence intensity, IRF is the instrument response function, A_i is the amplitude of the time constant τ_i .

Fluorescence upconversion technique. The fluorescence upconversion measurements were carried out by a femtosecond fluorescence upconversion spectrometer FOG 100 (CDP Systems Corp., Russia). The setup and its schematics are shown in Figure 2.7. The excitation light is tunable from 230 nm to 1 μm offered by the same excitation source as TCSPC. In our measurements, we have used mainly 400 nm as excitation. The fluorescence from the sample

after excitation was collected by two parabolic mirrors and focused onto a BBO crystal (cut angle 38 °, ooe interaction, 0.5 mm thickness), together with the fundamental beam at 800 nm (gate beam) to generate the sum-frequency radiation. The resulting radiation in the 300-373 nm range was passed through a double monochromator (model: CDP2022D) and then detected by a photomultiplier based photon counting electronics. The gate beam was sent through a variable translation stage which allows to vary the time delay between gate beam and fluorescence transient. Since the upconverted beam via sum-frequency generation is proportional to the intensity of both gate and fluorescence, its temporal profile reflects the fluorescence decay. The full-width-half-maximum (FWHM) of the instrument response function (100 ± 10 fs) can be determined from the Gaussian fit of the Raman scattering from the solvent. Therefore, the fluorescence upconversion setup can resolve the fluorescence kinetics with a 50 fs resolution after a deconvolution by use of IRF.

2.2.3 Transient absorption laser spectroscopy

The transient absorption (TA) spectra were measured by the femtosecond laser pump-probe setup (Figure 2.8). An ultrafast laser oscillator (Micra, Coherent) is used to seed a titanium-sapphire (Legend Elite, Coherent) regenerative amplifier. The output fundamental wavelength was at 800 nm with 65 fs pulse width, 1 kHz repetition rate, and 3.5 W average power. The majority (90%) of the fundamental beam was converted into visible and UV range through an

Figure 2.8 The sketch of the laser femtosecond pump-probe setup. Top: perspective view. Middle: top view. Below: schematic diagram.

optical parametric amplifier (OPA, Topas, Light Conversion) and further nonlinear processes such as second-harmonic and sum-frequency generation. The excitation source tunable from 250 to 2500 nm is used as pump beam. The remaining 10% of the 800 nm fundamental beam was translated through an 1.4 m long optical delay stage (OWIS, Germany) and then focused onto a CaF₂ or sapphire plate to generate a white light continuum probe beam (350-850 nm). The time delay between pump and probe is adjusted between 500 ps and 6.5 ns by moving the optical delay stage. In order to eliminate the contribution of rotational diffusion, the angle between the polarizations of pump and probe is fixed at the magic angle (54.7 °).

The detector used is composed of a photodiode arrays (PDA) based line scan camera system (CCD 2000, Stresing, Germany) together with a spectrograph (Jobin Yvon CP140). The slit width of the spectrograph is 25 µm. The probe is split into two beams: one is used as the reference to eliminate the fluctuation from the laser itself (I_0). The other beam is focused on the sample, and its transmission is recorded to calculate the absorbance change (ΔA). The pump beam is modulated by an electronic shutter. The transmitted probe intensity in the presence ($I_{\text{pump_on}}$) and in the absence ($I_{\text{pump_off}}$) of the pump are integrated for 50 or 150 ms sequentially and processed by the computer to calculate the absorbance change, $\Delta A = -\log\left(\frac{I_{\text{pump_on}}/I_0}{I_{\text{pump_off}}/I_0}\right)$, where I_0 is the reference signal.

The control program (ODM_MAIN.vi) was written by use of Labview software (version 8.6). The interface of this software is shown in Figure 2.9. The top left window displays the white light continuum signal detected from

Figure 2.9 The software interface of pump-probe setup.

Figure 2.10 The scan parameters setting page.

Figure 2.11 Transient spectra viewing software interface.

Figure 2.12 The data used for chirp correction.

both detectors. The top right window directly shows the TA spectra for each individual cycle, and the bottom right window presents the averaged TA spectra after accumulating all cycles. The overlap of pump and probe beam is optimized to get maximal TA signal. The delay stage position is also adjusted to

find the zero time. Then the TA spectra are recorded at different delay times to construct the transient decay profile. All scan parameters including integration time, averaging cycles, and the delay time range are set before starting the measurement (Figure 2.10).

After the measurements are finished, another program “TA-MAIN.vi” is used to view the recorded data and do further processing such as smoothing, baseline and chirp corrections (Figure 2.11). The baseline correction is done by subtracting the TA data at different delay times by the data recorded at negative delay times. The white light is chirped due to the group velocity dispersion (GVD) in the optical elements including the CaF₂ plate. In order to obtain the accurate TA spectra at early time delays ($t < 1$ ps), we need to do the chirp correction by use of the ultrafast nonlinear processes, e.g., Raman scattering, two-photon absorption, and cross-phase modulation [156,157] in the pure solvent (for liquid sample) or substrate (for solid sample). All those processes are of third order nonlinearity. Their duration is comparable with the temporal width of the pump–probe cross-correlation function [156]. Therefore, the full-width-half-maximum (FWHM) of the instrument response function (100 ± 10 fs) can be determined from the Gaussian fit of these “coherent artifact”. The TA maxima of these “coherent artifact” versus delay time is extracted and fitted by the formula $T = A * (1 - \exp(-L/B)) - C$, as shown in Figure 2.12. Here, T is the delay time, L is the probe wavelength, A , B , C are the parameters derived from the fit results. After obtaining all parameters, we can use the software to correct the measured TA data.

The experimental data were fitted by a multiexponential decay function, convoluted with the instrument response function $IRF(t-t_0)$ centered at t_0 :

$$\Delta A(t) = \int_{-\infty}^t IRF(t' - t_0) \sum_{i=1}^n A_i \exp\left(-\frac{t-t'}{\tau_i}\right) dt' \quad (2.3)$$

where $\Delta A(t)$ is the absorbance change at delay time t , and A_i is the amplitude of the time constant τ_i . This fitting method is able to obtain the lifetime down to 50 fs with deviation $< 10\%$, similar to the previously mentioned time-resolved fluorescence fitting model.

Chapter 3. One-photon-induced singlet fission in monomeric organic crystal

3.1 Introduction

Recently, singlet fission has been considered as a possible triplet generating process in rubrene single crystal [14,87,158], however, the specific photophysical picture is still under controversy. Najafov et al. [14] observed a long exciton diffusion length, from which they concluded that triplet excitons generated by singlet fission result in the high photoconductivity. Tao et al. [159] investigated the carrier dynamics and assigned a 100 ps process probed around 800 nm to the dissociation of singlet excitons into polarons. However, probing in a similar range, Furube et al. [160] reported that multiple exciton generation occurs within 10 ps. Consequently, there is still no direct experiment clarifying the features of singlet or triplet excitons in rubrene, especially the triplet formation and the role of singlet fission. Therefore, in this chapter, we use time-resolved fluorescence and femtosecond pump–probe spectroscopy to study the excited state dynamics of rubrene single crystal.

3.2 Rubrene molecular and crystalline structures

It is notable that the geometry of rubrene depends on the phase and state of the molecules. In solution or amorphous phase the rubrene molecule has D_2 (222) symmetry [161-163] with a twisted tetracene backbone (Figure 3.1a). In single

Figure 3.1 Rubrene molecular conformations in (a) solution (D_2), (b) single crystal (C_{2h}) and (c) optimized structure by quantum chemical calculation.

crystalline phase, it holds C_{2h} ($2/m$) symmetry [17,164] with a nearly planar tetracene backbone (Figure 3.1b). The C_{2h} rubrene is not stable in vacuum since its optimized ground state structure is a first-order saddle point [164]. However, C_{2h} rubrene is stabilized in crystal owing to the crystal-packing forces. We also did the quantum chemical calculation by use of Gaussian [165] on the electronic states of rubrene. The detailed calculation was done by our collaborator Dr. Gegham Galstyan from Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany. The ground state geometry of rubrene was optimized in vacuum by using B3LYP DFT functional with 6-31G(d,p) [166-168] basis set. The computational results revealed that the backbone of C_{2h} -rubrene is not exactly planar. Eight of its carbons are located 8° or 2° out of plane made by the other ten carbons of the backbone (Figure 3.1c).

Rubrene crystal is orthorhombic, space group $Cmca$, with 4 molecules per

Figure 3.2 (a) Rubrene single crystal unit cell; (b) Rubrene molecular axes; (c) Molecular packing on the ab facet; (d) Molecular packing on the bc facet.

unit cell [17] (Figure 3.2a). The molecular and crystallographic axes, as well as the packing on different facets are shown in Figure 3.2b-d. The short molecular axis, i.e., M-axis is parallel to the crystal c axis (Figure 3.2b-c). There is a 31.2° angle between the long molecular axis (L) and the crystallographic b axis [169].

3.3 Spectroscopy of rubrene solution

3.3.1 Steady-state spectra

The steady-state absorption and fluorescence spectra of rubrene in toluene are presented in Figure 3.3. The absorption of the lowest transition $S_0 \rightarrow S_1$ has four maxima located at 526, 492, 462 and 434 nm, respectively. The corresponding vibronic progression is $\Delta\omega = 1300 \text{ cm}^{-1}$, in good agreement with the previous

Figure 3.3 Steady-state absorption and fluorescence spectra of rubrene in toluene, $\lambda_{exc}=450$ nm.

report [170]. The reported fluorescence quantum yield of rubrene is close to 100% [171]. The fluorescence spectrum of rubrene in solution shows two maxima at 557 and 591 nm, i.e., $\Delta\omega = 1030$ cm^{-1} . The difference between emission and absorption progressions are due to the different Franck-Condon factors.

3.3.2 Time-resolved fluorescence spectra

Fluorescence kinetics of rubrene in toluene was measured by TCSPC technique under excitation at $\lambda_{exc}=450$ nm (Figure 3.4). At all wavelengths (550-700 nm) the decay is monoexponential with a lifetime $\tau = 10$ ns. Compared to the reported 16 ns lifetime for the deaerated solution [172], the relatively shorter lifetime 10 ns obtained from our measurement is due to quenching by oxygen.

Figure 3.4 Time-resolved fluorescence kinetics of rubrene in toluene, $\lambda_{exc} = 450$ nm.

3.3.3 Transient absorption spectra

Figure 3.5 shows the transient absorption spectra of rubrene in toluene under 510 nm excitation. The TA spectra have only one positive band at $\lambda = 434$ nm which decays monoexponentially with $\tau = 11$ ns, in good agreement with the TCSPC data. Therefore, this TA band is due to the singlet-singlet absorption $S_1 \rightarrow S_N$. The absence of a negative transient signal due to ground state bleaching indicates that the molar extinction coefficient of the $S_1 \rightarrow S_N$ transition is much larger than that of the $S_0 \rightarrow S_1$: $\epsilon = 12000 \text{ M}^{-1}\text{cm}^{-1}$ (at 526 nm, from Ref. [170]). Since the intersystem crossing efficiency of isolated rubrene molecules is very low ($\phi_{isc} < 0.05$ [173]), the triplet state TA signal was not visible in rubrene solution. Significant amount of triplet can be produced only by use of special sensitizers, e.g. biacetyl [173], anthracene or benzophenone [174].

Figure 3.5 (a) Transient absorption spectra for rubrene dissolved in toluene solution, $\lambda_{exc} = 510$ nm. The scattered excitation light in the region of 490–530 nm is removed. (b) Transient kinetics at 434 nm (scattered) and the monoexponential fit curve (solid line).

In order to study the upper excited states relaxation, we also measured the TA spectra of rubrene solution under excitation at 250 nm (Figure 3.6). To avoid the influence from the absorption of toluene, we change the solvent to hexane which has no linear absorption at 250 nm. Comparing the TA spectra under 500 and 250 nm excitation, the peak positions of the main TA bands are

Figure 3.6 (a) Transient absorption spectra for rubrene in hexane, $\lambda_{exc} = 250$ nm. (b) Transient kinetics at 432 and 560 nm (scattered dots) and the fit curves (solid line).

the same. However, under 250 nm excitation, the TA band width becomes broader and there is an additional flat absorption in the region of 550-800 nm. This spectral position is in good agreement with the reported absorption spectra of cation and anion generated in rubrene solution [175]. The kinetics at 560 nm indicates that the cation and anion are generated immediately (within 50 fs)

Figure 3.7 Steady-state absorption and fluorescence spectra of rubrene single crystal, $\lambda_{exc} = 450$ nm.

after excitation, followed by a picosecond recombination: $\tau_1 = 1$ ps (49%), $\tau_2 = 17$ ps (34%). The remaining 17% lasts longer than 1 ns.

3.4 Singlet fission in rubrene crystal

3.4.1 Steady-state spectra

Steady-state absorption of rubrene single crystal also shows four maxima at 528, 496, 464 and 436 nm, indicative of vibronic progression $\Delta\omega = 1300$ cm^{-1} . Fluorescence of rubrene crystal shows two maxima at 646 and 693 nm with $\Delta\omega = 1050$ cm^{-1} . The bandgap of rubrene single crystal can be determined from the absorption edge as 2.23 eV, consistent with previous reports [159,176]. The fluorescence intensity maximum at 646 nm is different from the commonly

Figure 3.8 Three types of steady-state fluorescence spectra for rubrene crystals.

reported 615 nm which is usually considered to be the pristine rubrene emission [176].

It is noteworthy that there are three different types of steady-state fluorescence spectra reported according to the spectral peak positions (Figure 3.8), which are summarized as follows.

(1) 565 nm type. When the polarization of the excitation light is parallel to the crystalline *c* axis (Figure 3.2b), the steady-state fluorescence intensity maximum locates at 565 nm. The 565 nm emission is usually attributed to the M-polarized transition [169] or *c*-polarized emission [177].

(2) 610 nm type. When the excitation polarization is changed to parallel to *ab* facet, the 565 nm fluorescence emission will vanish, and rubrene crystals exhibit another two types of fluorescence spectra. The first type is with

fluorescence peak located at 610 nm, which is generally regarded as the emission from pristine rubrene molecules [176].

(3) 650 nm type. The other type of fluorescence spectrum under ab-polarized excitation is with intensity maximum at around 650 nm. The disputed origin of this emission band is from either the oxidation related defect [169,178]/bandgap state [179] or the amorphous rubrene phase [176]. In the later Chapter 6, we studied the origin of different fluorescence spectra in detail. We proved that the 650 nm fluorescence emission is from the hole trap state which is induced by the oxidized rubrene form embedded in the single crystalline structure.

3.4.2 Time-resolved fluorescence spectra

Figure 3.9 presents the fluorescence kinetics in rubrene crystal. Compared with the above solution study, the fluorescence lifetime in crystal shows an obvious shortening. The fitting results for different emission wavelengths are shown in Table 3.1. All kinetics can be well fitted by two time components. For the shorter emission range, i.e., 585 and 605 nm, the fluorescence decays mainly (90%) with a fast time constant $\tau_1 \leq 50$ ps (limited by the time resolution of TCSPC setup), and another longer time constant $\tau_2 \sim 300$ ps (10%). The amplitude of the fast time component τ_1 decreases with increasing emission wavelength. At 700 nm, there is no more contribution from $\tau_1 < 50$ ps, instead, a new time constant $\tau_3 \sim 3$ ns appears and dominates the decay process (65%). Based on the difference of fluorescence decay between rubrene solution and crystal, we can conclude that there are additional quenching channels which shorten the fluorescence lifetime in the crystal.

Figure 3.9 Time-resolved fluorescence kinetics of rubrene crystal, $\lambda_{exc} = 450$ nm.

Table 3.1 TCSPC fit results of rubrene crystal.

Emission (nm)	τ_1 (ns)	A_1	τ_2 (ns)	A_2	χ^2
585	0.047	0.88	0.26	0.12	1.0238
605	0.053	0.90	0.28	0.10	1.0061
645	0.078	0.84	2.9	0.16	1.0152
700	0.13	0.35	3.5	0.65	0.9674

In order to resolve the ultrafast time constant $\tau_1 < 50$ ps, we performed fluorescence upconversion measurements with 50 fs time resolution. The fluorescence kinetics from 540 to 700 nm and their corresponding fit curves are plotted in Figure 3.10a. The fluorescence intensity at 600 nm shows a linear power dependence (inset of Figure 3.10a), indicative of one-photon absorption

Figure 3.10 (a) Fluorescence upconversion measurement results (scattered dots) and the biexponential fit curves (solid lines), $\lambda_{exc} = 400$ nm. Inset: Fluorescence intensity at 600 nm as a function of input power, indicative of one-photon excitation process. (b) Amplitudes of two time constants versus emission photon energy.

process. All fluorescence kinetics were processed by global fitting, i.e., fit all decay traces with identical time constants but variant pre-exponential factors [180-182]. The two time constants obtained are 2.2 and 28 ps. Figure 3.10b presents the relation between the amplitudes of each time constant and emission

photon energy. The amplitude of $\tau_1=2.2$ ps increases while the amplitude of $\tau_2=28$ ps decreases with increasing photon energy. It suggests there are two emitting states with a large spectral overlap, and the shorter-lived excited state (2.2 ps) locates at higher energy level relative to the longer-lived emission state (28 ps).

3.4.3 Singlet fission from the lowest excited singlet state S_1

Transient absorption spectra of rubrene crystal. In order to excite the lowest excited singlet state S_1 , the transient absorption spectra of rubrene crystal was measured under excitation at the absorption edge, i.e., 500 nm. There are two positive TA bands with maxima located at 444 and 510 nm, respectively (Figure 3.11a). Similar to the TA spectra of rubrene solution, the 444 nm TA band is attributed to the singlet-singlet absorption ($S_1 \rightarrow S_N$). The 10 nm red shift is due to solvation [183,184]. This TA band decays with three time components: $\tau_1 = 5.2$ ps (24%), $\tau_2 = 51$ ps (31%), and $\tau_3 > 10$ ns (45%) (Figure 3.11b).

The TA band centered at 510 nm develops with two rise components $\tau_1 = 2.3$ ps (33%), $\tau_2 = 23$ ps (45%), and does not decay within 1 ns. The band position is in agreement (with 10 nm red shift) with the triplet-triplet absorption signal reported in rubrene solution [173]. Therefore, we assign the 510 nm TA band to the triplet-triplet absorption $T_1 \rightarrow T_N$. The two time constants for triplet formation correspond well with the fluorescence decay time (2.2 and 28 ps). As shown in Figure 3.11b, the decay of S_1 is accompanied by the formation of triplet states T_1 . The isosbestic point at 455 nm is an indication of a single transformation process, i.e., the singlet states are converted into triplet states ($S_1 \rightarrow T_1$).

Figure 3.11 (a) Transient absorption spectra of rubrene single crystal, $\lambda_{exc} = 500$ nm. (b) Transient kinetics at 444 and 510 nm (scattered dots) and the fit curves (solid line).

Singlet fission. Based on the low triplet yield of individual rubrene molecules, we should not expect the observation of triplet states formed via intersystem crossing. However, we did see a pronounced triplet state absorption signal in rubrene crystal, as well as the conversion of excited singlet states into triplet states. Therefore, we conclude that the fast formation of triplets in rubrene

Figure 3.12 Normalized triplet TA kinetics under various excitation wavelengths ($\lambda_{exc}=400\text{-}550\text{ nm}$).

crystal is due to singlet fission, where two triplets are formed from one excited singlet state [22,185], which is constrained to multichromophoric systems, such as molecular crystals [39]. The triplet state formation time 2.3 and 23 ps corresponds to the SF rate. Efficient SF requires the energy of the excited singlet state $E(S_1)$ to be no less than twice that of the triplet state $E(T_1)$, i.e., $E(S_1) \geq 2 E(T_1)$ [60]. For rubrene crystal, $E(S_1) = 2.23\text{ eV}$, and $E(T_1) = 1.14\text{ eV}$ [159,176,186], resulting in $\Delta E = E(S_1) - 2E(T_1) = -0.05\text{ eV}$. Therefore SF from the lowest vibrational level of S_1 is via thermal activation with the assistance from phonons. The thermally activated SF usually proceeds on a tens of ps time scale [39,78]. Thus we conclude that the long time constant $\tau_2=23\text{ ps}$ is due to the thermally activated SF from the lowest vibrational level of S_1 . It is consistent with the studies on tetracene ($\Delta E = -0.21\text{ eV}$, $\tau_{SF} = 9.2\text{ ps}$ [63], 50 ps

Figure 3.13 (a) Transient absorption spectra for rubrene single crystal, $\lambda_{exc} = 250$ nm. (b) Transient kinetics at 512 and 566 nm (scattered dots) and the fit curves (solid line).

[78]) and 1,3-diphenylisobenzofuran ($\Delta E = -0.1$ eV, 2 and 25 ps [187]).

In order to identify the origin of the short rise time of triplet state formation (2.3 ps), we applied the TA measurements under excitation at other wavelengths, $\lambda_{exc} = 400$ and 550 nm. The obtained TA spectra are similar to

those under 500 nm excitation, while the triplet formation time changes slightly. The triplet kinetics (probe at 510 nm) after normalization are shown in Figure 3.12. We can see that the triplet formation time $\tau_{400\text{ nm}} < \tau_{500\text{ nm}} < \tau_{550\text{ nm}}$, that is, SF proceeds faster from upper vibrational states of S_1 . With a global analysis, the fast rise component is found to follow the Arrhenius law (see below). Therefore, we conclude that the fast time constant $\tau_1 = 2.3\text{ ps}$ is due to the direct SF from upper vibrational states of S_1 .

3.4.4 Singlet fission from upper excited singlet electronic states S_N

To study the SF from upper excited states S_N , we also measured the TA spectra of rubrene crystal under 250 nm excitation (Figure 3.13).

Polaron formation under 250 nm excitation. The TA spectra under 250 nm excitation are similar to the ones under 500 nm excitation. However, the TA band width becomes broader and there is an additional flat TA absorption between 550 and 800 nm. This spectral position is in good agreement with the previously reported absorption spectra of polarons in rubrene crystal [159]. The kinetics of this TA band is shown in Figure 3.13b (blue line), which indicates that the corresponding species were formed immediately after photoexcitation ($< 50\text{ fs}$). Therefore, we assign the TA signal between 550 and 800 nm to the polarons generated directly from upper excited singlet states S_N . The instantaneous formation suggests that the excess thermal energy of the excitation photons overcomes the Coulombic binding energy in order to form polarons [109]. According to the fitting of the TA decay, 25% of the polarons

Figure 3.14 (a) Schematics of the TA signal at negative delay times measured by a 1 kHz pump-probe setup. TA spectra of rubrene crystal at -5 ps and 5 ns under (b) $\lambda_{exc} = 500$ nm and (c) $\lambda_{exc} = 250$ nm. The blue dotted line is indicative of polaron absorption.

recombine via geminate recombination within 1 ps. 55% of the polarons recombine on a time scale of 10-200 ps through the secondary recombination process via diffusion [188]. The remaining 20% of the polarons do not decay within the measurement time window of 5 ns.

Discussion on the negative delay time TA signal. In our pump-probe setup, the repetition rate of the femtosecond laser system is 1 kHz, i.e., the time interval between two adjacent pump pulses is 1 ms. A positive delay time ($\tau > 0$) means

the pump beam arrives earlier than the probe beam, and a negative delay time ($\tau < 0$) indicates the probe pulse comes earlier than the pump (Figure 3.14a). If the transient effect induced by the previous pump pulse decays very slowly, the current probe is able to detect the signal induced by the previous pump pulse, i.e., the negative delay time can be also considered as the time delay of “1 ms” between the previous pump and the current probe.

As shown in Figure 3.14b-c, under excitation at 250 nm, there is still a remarkable ESA signal in the 400-600 nm region at negative delays. Moreover, the features due to ground state bleaching become more pronounced. The strong ESA signal remains longer than 1 ms, which suggests that the polarons are generated efficiently in rubrene under 250 nm excitation. By fitting the TA signals at “1 ms” and 5 ns, the lifetime of polarons is estimated $\tau = 700 \mu\text{s}$.

Direct singlet fission from upper excited state S_N . In contrast to the TA spectra under 500 nm excitation, the isosbestic point (at 455 nm) disappears under 250 nm excitation. It suggests that there is more than one process contributing to the TA between 350 and 550 nm. The kinetics of triplet states (at 512 nm) also forms with two time constants: 200 fs and 2 ps (Figure 3.13b). Compared with the 500 nm excitation case ($\tau = 2$ and 20 ps), the SF becomes 10 times faster under $\lambda_{\text{exc}} = 250$ nm. The ultrafast 200 fs rise is due to direct SF from the upper excited states S_N , i.e., $S_N \rightarrow 2T_1$. It also indicates that the internal conversion from S_N to S_1 is slower than or comparable to 200 fs [78]. The direct SF from upper excited states was also observed in other systems such as pentacene, with SF time ranging from 80 fs to 1 ps [67,78].

Figure 3.15 Normalized triplet TA kinetics under various excitation wavelengths ($\lambda_{exc}=250$ -550 nm, $\lambda_{probe}=510$ nm).

Based on the above discussion, we conclude that under various excitation wavelengths from 250 to 550 nm, both direct and thermally activated SF take place in rubrene. The direct SF from upper excited states S_N or upper vibrational states of S_1 is ultrafast, ($\tau_1=200$ fs-2 ps). The thermally activated SF proceeds 10 times slower ($\tau_2\sim 20$ ps). Since the thermally activated SF is from the lowest vibrational level of S_1 , we can expect τ_2 is invariant, while τ_1 varies with the excitation wavelength. Therefore, for all TA kinetics in Figure 3.15, we performed a global fit by use of free τ_1 and fixed τ_2 . The obtained τ_2 is 34 ps, τ_1 ranges from 2.4 to 3.5 ps. The singlet fission rate k_{fiss} versus the excitation photon energy is shown in the inset of Figure 3.15; the $\ln(k_{fiss})$ increases linearly with increasing energy, i.e., singlet fission rate follows the Arrhenius

Figure 3.16 Scheme for the mechanism of singlet fission under one-photon excitation in rubrene single crystal.

law:

$$k_{fiss} = A \exp\left(-\frac{E_a}{RT}\right) \quad (3.1)$$

where A is pre-exponential factor, R is molar gas constant, T is temperature, and E_a is the activation energy, i.e. $E_a = 2E(T) - E_{exc}$ (E_{exc} is the excitation photon energy).

3.5 Conclusion

In this chapter, for the first time we have directly observed singlet fission in rubrene single crystal. The energy structure of rubrene crystal is plotted in Figure 3.16. SF from the lowest excited singlet state S_1 , i.e., $S_1 \rightarrow 2T_1$ directly proceeds within 2 ps from upper vibrational states or on 20 ps time scale from

the lowest vibrational state via thermally activated SF. The ultrafast SF from upper excited states S_N (200 fs) was detected under 250 nm excitation. The upper excited states S_N have three competing relaxation channels: (1) direct singlet fission, (2) polaron generation, and (3) internal conversion to S_1 . Polarons are generated promptly after excitation (< 50 fs). 80% of the polarons recombine within 1 ns and the remaining 20% stay up to 1 ms.

Chapter 4. One-photon-induced singlet fission in dimeric organic crystal

4.1 Introduction

In the previous Chapter 3, singlet fission (SF), including direct fission from upper excited singlet states S_N , upper vibrational states of S_1 , as well as thermally activated fission from the lowest vibrational level of S_1 , plays an important role in the excited state dynamics of rubrene crystal. In this chapter, SF is studied under one-photon excitation in another organic crystal: α -perylene. The α -perylene crystal has a dimeric structure with four molecules per unit cell, and each lattice point is occupied by a pair of molecules. The schematic structures of isolated perylene molecule, perylene dimer, monomeric β -perylene and dimeric α -perylene are shown in Figure 4.1.

Excimers, which can be considered as dimers with associated excited states and dissociated ground states, are found to be formed in dimeric crystals like pyrene and perylene [189]. Walker et al. [190] by use of temperature-dependent fluorescence spectroscopy studied the excimer formation in α -perylene. A two-step excimer formation mechanism was proposed: the excited monomeric states first relax to the “hot” excimers (Y state), followed by a further formation of the relaxed excimers (E state). Dimer cations were also detected by Tamai et al. [134] via TA spectroscopy. In contrast to the solutions, the molecules in dimeric crystals do not need diffusion to collide in order to form excimers.

Figure 4.1 Schematic structures of perylene isolated molecule, dimer, β -perylene and α -perylene crystals.

Therefore, the excimer formation process reflects exclusively the crystals' photophysical properties [191]. In addition to excimer formation, singlet fission was also reported by magnetic field effect study in α -perylene [60,191].

This chapter aims to study the one-photon-induced singlet fission in the dimeric organic crystal via ultrafast spectroscopic study. We want to clarify whether a dimeric crystalline structure will make any difference compared with monomeric crystal. Unlike in the solution [55], the excimer is found to be a competitor rather than an intermediate for singlet fission in dimeric crystal.

Figure 4.2 Steady-state absorption and fluorescence spectra of perylene in hexane, $\lambda_{exc}=400$ nm.

4.2 Spectroscopy of perylene solution

4.2.1 Steady-state spectra

The steady-state absorption and fluorescence spectra of perylene in hexane are presented in Figure 4.2. The fluorescence spectrum is a typical mirror image of the absorption spectrum of the transition $S_0 \rightarrow S_1$, which indicates that the energy spacing of the vibrational levels of the excited states is similar to that of the ground state.

Figure 4.3 Time-resolved fluorescence kinetics of perylene in hexane, $\lambda_{exc} = 400$ nm.

4.2.2 Time-resolved fluorescence spectra

Fluorescence kinetics of perylene in hexane were measured by TCSPC under excitation at 400 nm, shown in Figure 4.3. The decay at all wavelengths (550–700 nm) is monoexponential with a lifetime $\tau = 3.9$ ns, which is in excellent agreement with the reported value (3.8 ns) [192].

4.2.3 Transient absorption spectra

The TA spectra were also studied in perylene solution with different concentrations shown in Figure 4.4. In the dilute solution, the TA spectra are dominated by a positive ESA band centered at 700 nm. There is also a weak negative TA band located at 470 nm due to the stimulated emission. The ESA band decays monoexponentially with 4 ns, which agrees well with the TCSPC

Figure 4.4 Transient absorption spectra of perylene in (a) diluted solution ($2.2 \times 10^{-5} \text{ mol L}^{-1}$); (b) concentrated solution ($8.7 \times 10^{-4} \text{ mol L}^{-1}$).

data. Therefore, we assign this band to the singlet-singlet absorption (S_1 - S_N). Our measurement results are in good agreement with Refs. [192] and [193]. The absorption of triplet state in perylene solution was reported to locate at 485 nm, with lifetime 4.8 ms [194-196]. No triplet absorption was visible due to the low intersystem crossing efficiency $\phi_{isc} = 0.01$ [196].

Figure 4.5 Steady-state absorption, emission, and fluorescence excitation spectra of α -perylene crystal, $\lambda_{exc} = 400$ nm.

In the saturated solution with concentration of 8.7×10^{-4} mol L⁻¹, in addition to the excited singlet state absorption, there is another ESA band at 610 nm. The isosbestic point indicates that this band is formed from excited singlet states. The location of this TA band corresponds well with the reported excimer absorption (620 nm) [134,193,197]. Therefore, we assign this conversion process to excimer formation. Moreover, at 5 ns there is also a weak but visible TA band at 490 nm (Figure 4.4b), which is due to the triplet-triplet absorption.

4.3 Singlet fission in α -perylene crystal

4.3.1 Steady-state spectra

Steady-state absorption, fluorescence emission and excitation spectra of α -perylene crystal are displayed in Figure 4.5. The absorption is plotted in a linear scale in terms of absorbance ($1-T$, where T is the transmittance). The interference pattern in the absorption spectrum between 500 and 750 nm can be used to estimate the sample thickness: $L=1\ \mu\text{m}$ [198]. The fluorescence spectrum does not depend on the excitation wavelength. The broad and structureless fluorescence band at 615 nm corresponds to the emission from the well-known perylene excimers [199]. The absorption and fluorescence excitation spectra are in line with each other above 465 nm, as shown in Figure 4.5. However, a discrepancy appears when the wavelength goes below 465 nm, and becomes even stronger below 340 nm. This deviation indicates for additional nonradiative decay channels for the excited states of α -perylene (see below).

4.3.2 Time-resolved fluorescence study on excimer formation

The fluorescence kinetics was first studied by TCSPC in the entire α -perylene emission range from 460 to 750 nm (Figure 4.6). The fitting results are listed in Table 4.1. For the emission between 460 and 510 nm, the fluorescence decays biexponentially with two time constants $\tau_1 \leq 10\ \text{ps}$ (limited by the time resolution of TCSPC), and $\tau_2 = 7\ \text{ns}$. With increasing emission wavelength, the

Figure 4.6 Time-resolved fluorescence kinetics of α -perylene crystal via TCSPC measurements under excitation at 400 nm.

Table 4.1 TCSPC fit results in α -perylene crystal.

Emission (nm)	τ_1 (ns)	A_1	τ_2 (ns)	A_2	χ^2
460	0.010	0.89	5.7	0.11	1.0204
470	0.010	0.87	6.4	0.13	1.0099
480	0.010	0.86	7.3	0.14	1.0176
510	0.010	0.75	7.5	0.25	0.9775
540	-	-	10	1	1.0305
570	-	-	17	1	1.0319
600	-	-	18	1	1.1257
630	-	-	19	1	1.1800
660	-	-	20	1	1.0761
690	-	-	20	1	1.0711
720	-	-	21	1	1.1169
750	-	-	22	1	1.0185

amplitude of τ_1 decreases, while that of τ_2 increases correspondingly. Moreover, when the emission wavelength goes above 540 nm, the contribution from τ_1 disappears and τ_2 becomes longer (20 ns). This is in agreement with the reported excimer lifetime for perylene in solution (17.6 ns) [192] and α -peryene crystal (42-160 ns) [190,200,201].

Figure 4.7a shows the time-resolved fluorescence spectra constructed from all measured fluorescence decay traces by spline fitting. The fluorescence spectral evolution with time can be clearly seen: within 50 ps after excitation, the fluorescence peak is first located at 520 nm, and then shifted to 612 nm after 100 ps which resembles the recorded steady-state fluorescence spectrum. Previously reported temperature-dependent fluorescence studies [190,202,203] demonstrated that the fluorescence spectrum of α -peryene exhibits a strong temperature dependence: when the temperature is above 50 K, the fluorescence spectra are broad and structureless with intensity maximum at 620 nm, corresponding to the emission from the relaxed excimers (E state). At temperatures below 50 K, the fluorescence peak is blue shifted to 530 nm due to the emission from unrelaxed excimers (Y state). Furthermore, the appearance of fine structures in the fluorescence spectrum indicates that the Y state has many vibronic sublevels. Therefore, the fluorescence spectral evolution measured by TCSPC can be explained by this two-step excimer formation mechanism (Figure 4.7b) [190]. At early times after excitation ($t < 50$ ps), the fluorescence is mainly from the unrelaxed Y states emission. The Y states are

Figure 4.7 (a) Time-resolved fluorescence spectra of α -perylene crystal constructed from TCSPC measurements under excitation at 400 nm. (b) Schematics of the two-step excimer formation mechanism.

short-lived by quickly relaxing to the E state, whose emission dominates the fluorescence spectra at longer times ($t > 100$ ps).

The fluorescence upconversion is used to further resolve the lifetime of the short lived Y state, i.e., τ_1 in the TCSPC measurements. The analogous trend as in TCSPC study was observed: the fluorescence decays slower with increasing

Figure 4.8 The (a) individual and (b) normalized fluorescence decay of α -perylene crystal measured by fluorescence upconversion technique, $\lambda_{exc} = 400$ nm.

Table 4.2 The fitting results of fluorescence upconversion measurement in α -perylene.

Emission (nm)	τ_1 (ns)	A_1	τ_2 (ns)	A_2	χ^2
480 nm	0.53	0.92	7.2	0.08	0.859
500 nm	0.81	0.93	7.4	0.07	0.986
510 nm	0.81	0.97	7.4	0.03	0.992
540 nm	1.2	0.82	10	0.18	0.976
570 nm	1.6	0.74	15	0.26	0.965
580 nm	1.5	0.70	15	0.30	0.899
590 nm	2.7	0.45	20	0.55	0.872
600 nm	1.5	0.25	20	0.75	0.765
630 nm			20	1	

emission wavelength. As shown in Table 4.2, for the 460 nm emission, the fluorescence decays mainly with an ultrashort lifetime $\tau_1 = 500$ fs (92%). However, for emission at 630 nm, fluorescence decays with only one lifetime $\tau > 1$ ns. The dependence of fluorescence lifetime on the emission wavelength suggests that the Y state contains many sublevels with lifetimes covering a range from 500 fs to 3 ps.

It should be mentioned that no rise time was obtained from all fluorescence decays owing to the large spectral overlap between the emission of Y and E states. As shown in Figure 4.7a, the Y state emission lineshape spans from 450 to 700 nm within the first 50 ps; only the E state emission (450-750 nm) remains after 100 ps. The absence of rise time for Y state emission decays suggests that the formation of Y state from the excited monomeric state is ultrafast (< 50 fs) at room temperature.

4.3.3 Singlet fission

Transient absorption spectra in α -perylene crystal under 340 nm excitation is shown in Figure 4.9a. After baseline correction (subtracting the negative delay TA signal), there remains a prominent TA band at 505 nm, together with a broad and flat TA band between 600 and 800 nm. As shown in the inset of Figure 4.9a, the linear power dependence of TA signal at 510 nm indicates a one-photon excitation process. The 505 nm transient absorption band is assigned to dimer cations, whose absorption in solution phase is at 503 nm

Figure 4.9 Transient absorption spectra for α -perylene crystal at different delay times, under excitation at (a) $\lambda_{exc} = 340$ nm (b) $\lambda_{exc} = 250$ nm. Inset of (a): The power dependence of TA signal at 510 nm.

[204]. According to previous studies, the broad absorption band of excimer in α -perylene crystal is located at about 620 nm [134,193,197]. Thus the 600-800 nm TA band is attributed to the excimers, including both Y and E states.

Similar to the rubrene TA spectra discussed in Chapter 3, there are also visible TA signals at negative delay times, indicative of the generation of a long-lived species. A positive TA band at 480 nm, accompanied by a broad negative band covering from 560 to 750 nm is detected at -3 ps time delay (Figure 4.9a). As discussed in the previous Chapter 3 (Figure 3.14a), negative delay times actually stands for a time delay of 1 ns between pump and probe. The intensity of the negative TA band (560-750 nm) does not depend on the delay time, thus it is attributed to the perylene fluorescence emitted after excitation. Since our computer program for the TA measurements does not subtract the contribution from steady-state fluorescence, the emitted fluorescence is integrated and averaged over the measuring time (15 seconds). The blue shift of the negative TA peak position with respect to the steady-state fluorescence spectrum is due to the spectral overlap between the positive and negative TA bands. Under the assumption of the first-order decay, we can estimate the lifetime of the positive TA band (at 480 nm) to be 1.8 ns. However, there may also be influence from the exciton-exciton annihilation. Then the real lifetime can be faster than this estimation.

Now we will discuss the origin of the positive TA band at negative delay times. The transient absorption of triplet state of perylene in solution was reported to locate at 485 nm, with lifetime 4.8 ns [194-196]. The only measurement on triplet TA in perylene crystal claims the triplet absorption is at shorter wavelengths than 520 nm, reported by Katoh et al. [201]. The reported

triplet lifetime in crystal is 0.4 ms [205]. In the present study, the observed 480 nm TA band at negative delay times agree well with the reported triplet state TA in terms of both spectral location and lifetime. Therefore, it is assigned to the absorption from triplet states in α -perylene crystal. Furube [193] and Tamai [134] also studied the transient absorption spectra in α -perylene crystal. However, because of either thicker sample used or a limited probe wavelength range, they did not approach the 480 nm wavelength range, i.e., could not detect the triplet TA signal.

As discussed in Figure 4.4, for perylene in solution, no triplet absorption was visible due to the low intersystem crossing efficiency of isolated perylene molecules. Therefore, we can rule out the possibility that the triplets detected in α -perylene are generated through intersystem crossing. Moreover, no rise time was obtainable from the triplet transient kinetics: hence we conclude that the efficient ultrafast (< 50 fs) triplet formation in α -perylene is due to singlet fission.

In order to explore the upper excited electronic states dynamics, TA spectra were also studied under excitation at 250 nm, as shown in Figure 4.9b. The TA spectra is analogous to those of under 340 nm excitation (Figure 4.9a). However, the signal ratio between triplet state and dimer cations becomes much higher. It suggests that SF from upper excited states in α -perylene is more efficient, which agrees well with our conclusions in Chapter 3 (rubrene).

According to my best knowledge, the only report on SF in α -perylene was carried out through the magnetic field effect under excitation by xenon lamp [60,191], where the threshold for SF was obtained at 3.51 eV (353 nm). Excimer formation was also considered to be the competing process for SF. In our study, we observed the ultrafast formation of excimer, dimer cation and triplet states, which act as three strongly competing deactivation channels for the excited state of α -perylene crystal.

Now we can explain the discrepancy between the steady-state absorption and fluorescence excitation spectra. Comparison of the absorption and fluorescence excitation spectra (Figure 4.5) shows that they correspond well only above 465 nm. However, below 465 nm there is a drop of the excitation spectrum indicating an efficient quenching process. This is due to dimer cation formation from ion pair (IP): the threshold according to Ref. [193] is 2.65 eV. At wavelengths below 350 nm there is a drastic drop of the fluorescence although the absorption becomes much larger. It is indicative of an efficient singlet fission which proceeds directly from the upper vibrational levels of S_1 . The threshold of this process is 3.51 eV [60,191].

Recently, a study on the singlet fission in highly concentrated solution was reported by Friend et al. [55], where excimer was claimed to be an intermediate state for the singlet fission. Moreover, singlet fission proceeds on a relatively slow time scale of 500 ps since an excited molecule needs to diffuse in order to collide with another ground state molecule. In our study, we found that in the

Figure 4.10 Scheme for the mechanism of singlet fission under one-photon excitation in α -perylene single crystal.

case of a dimeric crystal, due to the strong intermolecular coupling, the singlet fission is ultrafast and does not need an excimer intermediate state.

The scheme of singlet fission under one-photon excitation in α -perylene crystal is shown in Figure 4.10. The Y and E stand for “hot” and relaxed excimer states, respectively; T_1 represents the lowest triplet state; α^{3*} , α^{4*} , α^{**} and α^{***} denote the symmetry-allowed excited states in α -perylene under one-photon excitation [193]; and IP is the ion-pair state. Under the strong competition with the ultrafast dimer cation generation and excimer formation, SF can proceed directly from different excited states, bypassing the relaxed excimer state.

4.4 Conclusion

In this chapter, for the first time by use of transient absorption spectroscopy, singlet fission was observed in the dimeric α -perylene crystal. It proceeds from the upper excited singlet electronic states within 50 fs bypassing the excimer intermediate. The excited state relaxation was studied by TCSPC and fluorescence upconversion techniques. Three ultrafast competing deactivation channels for the excited singlet state are observed, i.e. excimer formation, dimer cation generation and singlet fission.

We conclude that the dimeric structure is favorable for singlet fission due to the stronger intermolecular coupling, however, the overall efficiency of SF is decreased due to competition with other ultrafast processes such as excimer and dimer cation formation. Therefore, for the design of novel singlet fission materials, the geometry factor should be taken into consideration in order to achieve a moderate intermolecular coupling, while suppressing other competing processes.

Chapter 5. Two-photon and two-quantum-induced singlet fission

5.1 Introduction

In Chapters 3 and 4, singlet fission was studied in detail in both monomeric and dimeric organic single crystals (rubrene and α -perylene) under one-photon excitation condition. In this chapter, SF under two-photon and two-quantum excitation is studied in both crystals. Rubrene and perylene molecules are centrosymmetric, therefore, the selection rules for one- and two-photon absorption (TPA) are different [206,207]: For one-photon transition, a change of parity is required, i.e., the symmetries of initial and final states are different. For two-photon transition, the parity needs to change twice, i.e., the initial and final states should have the same symmetry. Therefore, the one- and two-photon excited states have different symmetries, which allows us to study whether singlet fission depends on the symmetry of excited state.

Zimmerman et al. [54] theoretically studied singlet fission in pentacene and claimed that SF proceeds through rapid internal conversion to a multi-exciton (ME) state. SF process is then described as starting from a transition from S_1 to ME state, followed by an immediate separation of ME state into two coupled triplets localized on individual molecules (1TT) [54]. This ME state has the same symmetry as the ground state (A_g symmetry), therefore it is optically dark, i.e., under one-photon excitation, the transition from ground state S_0 to the ME

Figure 5.1 Scheme for the mechanism of singlet fission with an ME intermediate state under one- and two-photon excitation.

state is forbidden. However, it will become an allowed transition under two-photon excitation. We can expect a faster singlet fission (triplet formation) rate under two-photon excitation if there is really a dark ME intermediate state (Figure 5.1). This inspired us to study the two-photon-induced singlet fission.

During the study of α -perylene crystal, we found an interesting phenomenon, that is, when we excite with much lower photon energy, i.e., below the thresholds of both dimer cation formation and singlet fission, we still detect both processes. Our theoretical simulations show that the experimentally observed nonlinear but not “purely” quadratic power dependence is due to the coexistence of two-quantum and two-photon absorption.

Figure 5.2 TA spectra under 650 nm excitation in rubrene crystal (after chirp correction). The region 625–675 nm of strong scattered excitation light is removed. The upper and lower figures show the TA spectra at early (<500 fs) and later (>1 ps) delay times.

5.2 Two-photon-induced singlet fission in rubrene crystal

5.2.1 Nondegenerate two-photon absorption spectra

We applied the pump-probe technique in order to study the two-photon-induced singlet fission. The pump wavelength was chosen at 650 nm where there is no linear absorption. Due to the group velocity dispersion (GVD) in the optical elements including the CaF₂ plate, the white light continuum probe is

temporally chirped. We used the ultrafast nondegenerate two-photon absorption signal (vide infra) to do the chirp correction [208]. The chirp corrected TA spectra under excitation at 650 nm are presented in Figure 5.2. In Chapter 3, we have studied the one-photon-induced SF in rubrene crystal by femtosecond pump-probe spectroscopy under 500 and 250 nm excitation. The two-photon-induced TA spectra after 3 ps show similar behaviour as one-photon TA spectra (Figure 3.11). Triplet-triplet absorption at 510 nm is still dominant in the two-photon-induced TA spectra, however, the decay of the excited singlet states S_1 is not as pronounced as that of one-photon-induced TA spectra. Moreover, under two-photon excitation, the isosbestic point at 455 nm in OPA TA spectra disappears. This is indicative that triplets states form not only from excited singlet state S_1 , but there is also another channel for triplet states population. In the whole TA spectra, there are always two troughs located at 465 and 495 nm, which correspond well with the peak positions of the steady-state absorption spectrum (Figure 3.3). It is due to the overlap of negative ground state bleaching and the positive TA signal. The transient signal at negative time delays is indicative for long-lived transient states (Figure 5.2). The pulse repetition rate of our laser system is 1 kHz, i.e., the negative time delay is equivalent to 1 ms decay time. The ground state bleaching at negative times in Figure 5.2 is due to the long-lived triplet states (about 0.2 ms) formed via singlet fission.

Figure 5.3 (a) TA decay traces at 444 and 510 nm. Inset shows the kinetics within 5 ps. (b) Log-log plot of TA signals at 0.2 and 50 ps versus pump power, $\lambda_{exc} = 650$ nm. The inset displays the temporal positions chosen for studying the fast process at 550 nm.

There is a significant difference for the transient spectra between the early ($t < 0.5$ ps) and longer times ($t > 3$ ps). Moreover, the kinetics at different probe wavelengths (Figure 5.3a) show a fast process within hundred femtoseconds, and followed by a slower process at longer times. In femtosecond transient

absorption spectroscopy, when the pump and probe beams spatially and temporally overlap, transient absorption spectra are sometimes distorted by the signal from “coherent artifact”. The “coherent artifact” including two-photon absorption, stimulated Raman amplification and cross-phase modulation [156,157,209], is caused by the third order nonlinear susceptibility $\chi^{(3)}$.

The fast (<500 fs) and slow (>500 fs) TA spectra are induced by the nondegenerate and degenerate two photon absorption, respectively, based on the power dependence study. The power dependence of TA signal at 510 nm (maximum of the slow process) at 50 ps and that of 550 nm (large absorption from the fast process but small influence of slow process) at 0.2 ps are presented in Figure 5.3b. The 550 nm TA signal at 0.8 ps (when the fast process has finished) is subtracted from the signal at 0.2 ps in order to get the pure contribution from the fast process (inset of Figure 5.3b). Both the transient signal and pump power are plotted on the log-log scale, where the slope of the power dependence curve is indicative of the order of corresponding nonlinear process. The slope is 0.9 for the fast process, indicative of a linear power dependence. Since there is no linear absorption at 650 nm, this linear pump power dependence is attributed to the nondegenerate two-photon absorption (ND-TPA) process, i.e., one pump and one probe photon are absorbed simultaneously to excite the sample molecules to a two-photon excited state [210,211]. However, for the slow process, the slope is 1.9, i.e., quadratic dependence on the pump power. Therefore, the slow process is assigned to the

Figure 5.4 (a) Schematics of one-photon absorption (OPA), nondegenerate two-photon absorption (ND-TPA), and degenerate two-photon absorption (D-TPA) processes. (b) ND-TPA spectra calculated from TA spectra ($\lambda_{\text{pump}} = 650, 750$ nm) and linear absorption (OPA) spectrum.

degenerate two-photon absorption (D-TPA), i.e., absorption of two photons with the same energy. The schematics of the ND- and D-TPA, together with OPA are depicted in Figure 5.4a. The ND-TPA spectra obtained from pump-probe technique show a good agreement with the D-TPA spectra

measured by other methods, e.g., Z-scan [212] or two-photon fluorescence spectroscopy [211].

In order to get the ND-TPA spectrum, the electronic energy of two-photon excited states was calculated according to equation (5.1):

$$h\nu_{TPA} = h\nu_{pump} + h\nu_{probe} \quad (5.1)$$

Therefore, we have

$$\frac{1}{\lambda_{TPA}} = \frac{1}{\lambda_{pump}} + \frac{1}{\lambda_{probe}} \quad (5.2)$$

where λ_{pump} and λ_{probe} are the wavelengths of pump and probe, respectively. The calculated ND-TPA spectra under excitation at 650 and 750 nm, together with the linear absorption spectrum are presented in Figure 5.4b. The two ND-TPA spectra under different excitations correspond very well, only the valley features are shifted in terms of λ_{TPA} . We should note that in the original TA spectra the valley structures are caused by ground state bleaching which are determined by the one-photon absorption spectrum. Therefore, in the original TA spectra under 650 and 750 nm excitation, they are at the same locations. However, after converting to λ_{TPA} according to eq. (5.1), they are shifted due to different λ_{pump} . Comparing the obtained OPA and ND-TPA spectra, we can see that the two-photon excited states are located well above the one-photon excited states. This is the result of different selection rules for centrosymmetric molecules.

5.2.2 Quantum chemical calculations

Quantum chemical calculations on the excited singlet states of rubrene were done by Dr. Gegham Galstyan from Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany. Computation of transition energies and transition dipole moments for the first 20 singlet vertical excited states of rubrene was carried out using TDDFT method employing BH&HLYP [213,214] DFT functional and TZVP [215] basis set. Two-photon allowed transitions were then selected among the computed singlet excited states according to the selection rules.

The calculation results for the first 20 vertical excited singlet states of C_{2h} -rubrene are presented in Table 5.1. According to the selection rules for centrosymmetric molecules, transitions are allowed between electronic states with parity opposite to that of one-photon absorption, and between electronic states with the same parity as two-photon absorption. Therefore one- and two-photon allowed transitions for C_{2h} -rubrene are mutually exclusive and clearly distinguishable.

The dominant dipole-allowed one-photon transition in the visible region at 490 nm (Table 5.1) is due to an electron migration from the donor (HOMO) to the acceptor (LUMO) molecular orbital, accompanied by a parity change from even to odd, i.e., from initial A_g to the final A_u symmetry. It agrees well with the steady-state absorption maximum of rubrene crystal (Figure 3.3). The 6 nm deviation from the experiment is due to only moderate quality basis set which

was used in calculations. According to the selection rules, TPA transitions of C_{2h} -rubrene will have the same parity (even parity) as ground state A_g . Among all theoretical calculated excited states with even parity shown in Table 5.1, the

Table 5.1 Summary of TDDFT calculation results for the first 20 singlet excited electronic states of C_{2h} -rubrene at its ground state geometry.

Symmetry of the electronic ground state: A_g

Excited State	Wavelength (nm)	Oscillator Strength	Symmetry	Major Contributions*
1	489.7	0.2	A_u	HOMO->LUMO (99%)
2	347.2	0.0	B_u	H-4->LUMO (19%) H-1->LUMO (30%) HOMO->L+1 (44%)
3	313.3	0.0	B_g	H-3->LUMO (34%) H-2->LUMO (56%)
4	302.5	0.0	B_g	H-3->LUMO (56%) H-2->LUMO (40%)
5	296.3	0.1	B_u	H-4->LUMO (24%) H-1->LUMO (63%) HOMO->L+1 (10%)
6	290.6	0.0	B_g	HOMO->L+2 (86%)
7	277.7	0.0	A_g	HOMO->L+3 (97%)
8	274.7	0.0	A_u	HOMO->L+4 (96%)
9	267.9	1.6	B_u	H-4->LUMO (50%) HOMO->L+1 (43%)
10	261.8	0.0	A_u	H-5->LUMO (88%)
11	258.6	0.0	A_g	H-6->LUMO (97%)
12	254.3	0.0	A_u	HOMO->L+5 (89%)
13	252.2	0.1	B_g	HOMO->L+6 (92%)
14	249.3	0.0	B_u	H-9->LUMO (76%)
15	248.2	0.0	A_g	HOMO->L+8 (86%)
16	247.1	0.0	B_g	HOMO->L+7 (86%)
17	246.6	0.0	A_u	H-10->LUMO (57%) H-1->L+2 (10%)
18	240.7	0.0	B_u	H-7->LUMO (91%)
19	240.0	0.0	B_g	H-8->LUMO (96%)
20	239.5	0.0	A_g	H-10->LUMO (17%) HOMO->L+9 (57%)

Figure 5.5 Normalized transient absorption kinetics under one- and two-photon excitation, $\lambda_{exc}=250$ -650 nm. Inset: the singlet fission rate under one-photon (OPA) and two-photon absorption (TPA) versus pump photon energy.

one with the lowest energy is at 313 nm ($A_g \rightarrow B_g$), which is well separated from the allowed one-photon transition (HOMO $\rightarrow$ LUMO). Therefore, theoretical calculations confirm our previous conclusion that the two-photon excited states of rubrene crystal locate well above the one-photon excited states. Compared with our experimental ND-TPA spectra (Figure 5.4b), the computed $A_g \rightarrow A_g$ transition at 278 nm is assigned to plausible two-photon allowed transition under 650 nm excitation. Now we can revisit Figure 5.4a and label the symmetries of the electronic states of rubrene crystal, i.e., the ground state with $1A_g$, the lowest OPA excited state with $1A_u$, and TPA excited states with mB_g and nA_g .

Table 5.2 Global fit results for 510 nm TA kinetics under different excitation wavelength (λ_{pump}).

λ_{pump} (nm)	τ_1 , ps	A_1	τ_2 , ps	A_2	τ_3 , ps	A_3
250	1.2 (± 0.09)	-0.50	34 (± 1.6)	-0.27	1400 (± 72)	1.0
650 (TPA)	1.9 (± 0.13)	-0.36	34 (± 1.6)	-0.26	10000 (± 0)	1.0
400	2.4 (± 0.28)	-0.27	34 (± 1.6)	-0.36	10000 (± 0)	1.0
500	3.0 (± 0.25)	-0.42	34 (± 1.6)	-0.35	10000 (± 0)	1.0
550	3.5 (± 0.27)	-0.32	34 (± 1.6)	-0.43	10000 (± 0)	1.0

$\chi^2 = 0.9952$

5.2.3 Two-photon-induced singlet fission rate

After confirming the location of one- and two-photon excited states both experimentally and theoretically, the most interesting part comes to the singlet fission rate, i.e., whether it becomes faster under two-photon excitation. This might be the case since the dark intermediate state can be directly populated by TPA. Therefore, we need to check the transient kinetics for $S_1 \rightarrow S_N$ (444 nm) and $T_1 \rightarrow T_N$ transition (510 nm) shown in Figure 5.3a. Taking ND-TPA into consideration, one ultrafast time constant $\tau_0 \leq 150$ fs is needed for both transient decays. Apart from the fast τ_0 due to ND-TPA, excited singlet TA at 444 nm decays with another two components: $\tau_1 = 11$ ps (31%) and $\tau_2 > 2$ ns (69%). Triplet TA signal at 510 nm develops with two rise constants: $\tau_1 = 1.6$ ps ($A_1 = 56\%$), $\tau_2 = 23$ ps ($A_2 = 44\%$), which is similar to the one-photon-induced singlet fission. Here we use the rise time of triplet TA signal to denote the singlet

fission rate. Figure 5.5 presents a comparison of the triplet rise time under different excitation wavelengths, redrawn from the previous Figure 3.15. All transient decays at 510 nm are normalized at their maxima. In the OPA region (250~550 nm), the triplet states formation becomes faster with increasing pump photon energy. It suggests that singlet fission proceeds directly from various excited states, i.e., upper excited singlet states S_N ($\lambda_{exc} = 250$ nm) or upper vibrational states of S_1 ($\lambda_{exc} = 400$ -550 nm).

As discussed in Chapter 3, the energy difference $\Delta E = E(S_1) - 2E(T_1) = -0.05$ eV, SF is faster from upper excited states since it is exoergic, however, it proceeds slower from the lowest excited state S_1 as it is endoergic. Under different excitation wavelengths, all the triplet TA kinetics show two rise components: $\tau_1 \sim 2$ ps and $\tau_2 \sim 20$ ps. The faster τ_1 is due to the direct SF from upper excited singlet states S_N or vibrational levels of S_1 , while the longer $\tau_2 \sim 20$ ps is due to the thermally activated fission from the lowest excited state S_1 . The same global fitting was done for all TA traces, and the results were shown in Table 5.2. The obtained thermally activated fission time is $\tau_2 = 34$ ps, while the fast direct fission time τ_1 ranges from 1.2 to 3.5 ps. The singlet fission rate from TPA excited states is faster than from S_1 state but slower than that of from S_N , which indicates that the two-photon excited states are located between S_1 and S_N . The direct singlet fission rate $k_{fiss} = 1/\tau_1$ versus the pump photon energy is also shown in the inset of Figure 5.5. The linear dependence of $\ln(k_{fiss})$ confirms the singlet fission rate follows the Arrhenius law, described in eq.

Figure 5.6 (a) Transient absorption spectra for α -perylene crystal at different delay times under excitation at 470 nm. (b) Power dependence of TA signal at 510 nm at 5 ps time delay.

(3.1).

Here we should notice that the singlet fission from two-photon excited dark state does not show an obvious faster rate compared to the one-photon excitation. On the contrary, it follows the same pump power dependence (see

the orange spot in the inset of Figure 5.5), which means the direct singlet fission rate from upper excited states does not depend on the symmetry but on the energy level of the corresponding state. Therefore, our study suggests that the singlet fission in rubrene crystal occurs via direct coupling, rather than via intermediate ME state.

5.3 Two-quantum-induced singlet fission in α -perylene crystal

The ion pair state (precursor of dimer cations) is reported to be at 2.65 eV (468 nm) [193]. The energy threshold of singlet fission in α -perylene is at 3.51 eV (353 nm) [60,191]. The TA spectra under 475 nm excitation, i.e., below the thresholds of both singlet fission and dimer cation generation, were also measured in α -perylene. Therefore, neither dimer cation nor triplet state is expected under one-photon excitation at 475 nm. However, the obtained TA spectra (Figure 5.6a) show similar signatures to those of under 340 nm excitation (Figure 4.9a), that is, the transient absorption from dimer cation, excimer and triplet states still dominate the whole TA spectra.

The power dependence of the TA signal at 5 ps time delay, with probe at 510 nm (corresponding to dimer cation absorption) is shown in Figure 5.6b. The power dependence is nearly linear when the excitation intensity is below 100 GW/cm², while it becomes nonlinear instead of going to saturation when intensity is above 150 GW/cm². The triplet TA signal (480 nm) at negative delay time displays similar power dependence. We describe this nonlinear

Figure 5.7 Schematic diagram of TPA and TQA transitions.

power dependence in terms of two-photon absorption (TPA, i.e., simultaneous absorption of two photons) and consecutive two-quantum absorption (TQA, i.e., two-step absorption of two photons via an intermediate state [216,217]). The schematics for TPA and TQA are presented in Figure 5.7. The TPA and TQA in the nonlinear crystal KDP were studied in detail in Refs. [218] and [219]. Therate equations for TQA process are as following [218-220]:

$$\frac{dN_0}{dt} = -\sigma_1 I N_0 + \frac{N_1}{\tau} \quad (5.3)$$

$$\frac{dN_1}{dt} = \sigma_1 I N_0 - \phi_2 \sigma_2 I N_1 - \frac{N_1}{\tau} \quad (5.4)$$

$$\frac{dN(T_1)}{dt} = \phi_2 \sigma_2 I N_1 \quad (5.5)$$

Here N_0 , N_1 and $N(T_1)$ stand for the populations of ground state (S_0), intermediate excited state (S_1) and triplet state (T_1), respectively. σ_1 and σ_2 are the absorption cross sections for $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_N$ transitions. σ_1 is taken as $7.6 \times 10^{-17} \text{ cm}^2$ according to Ref. [221]. ϕ_2 is the quantum yield of triplet states generated from singlet fission ($\phi_2 = 2 * k_{fiss} / \sum k$). Assuming the excitation laser pulse shape is rectangular, we computed the numerical solution of the rate

Figure 5.8 (a) The fitting results of the power dependent population of TQA excited state. (b) The fitting results of the power dependent population of TQA and TPA excited states.

equations (5.3)-(5.5) by use of Matlab software, based on different intermediate state lifetime τ (100 fs - 20 ns) and various ratios between $\phi_2\sigma_2$ and σ_1 (0.05-50), shown in Figure 5.8a. Taking into consideration TPA process which has a quadratic intensity dependence, the population of two-quantum excited

states will become $N_2=N(TQA)+N(TPA)=N(TQA)+A*I^2$. The best fit of the experimental data is obtained under $\phi_2\sigma_2 = 50 \sigma_I$, as shown in Figure 5.8b. The lifetime of intermediate state S_1 is taken as $\tau = 2$ ps, i.e., the lifetime of Y state. In fact, according to our simulation (Figure 5.8a), the intermediate state lifetime does not make a real difference under a femtosecond pulse excitation. Based on the above discussions, we explain that under excitation at 475 nm, both SF and dimer cation generation are from the two-quantum excited states populated by the coexistence of TPA and TQA.

5.4 Conclusion

In this chapter, to my best knowledge, for the first time, we have observed the two-photon and two-quantum induced singlet fission. We conclude that in rubrene crystal singlet fission can proceed on picosecond time scale directly from the two-photon excited electronic states bypassing S_1 . In α -perylene, SF from two-quantum excited states occurs within 50 fs. Our study proves that the singlet fission rate does not depend on the excited state symmetry in both studied crystals. In other words, the singlet fission mechanism in both rubrene and α -perylene crystals are due to the direct intermolecular coupling without participation of dark intermediate states.

Chapter 6. Interplay between singlet fission and energy trapping

6.1 Introduction

As discussed in Chapter 3, three types of steady-state fluorescence spectra in rubrene single crystal are reported in the literature (Figure 3.8). The 610 nm type is generally taken as the pristine rubrene emission [176], while the nature of 650 nm type fluorescence is still under controversy. The origin of the 650 nm emission band is disputed to be from either the oxidation related defect [169,178], bandgap state [179] or from the amorphous phase [176].

In this chapter, we have clarified the origin of the steady-state fluorescence of rubrene crystal in terms of interplay between singlet fission and energy trapping. Singlet fission in rubrene efficiently quenches the fluorescence and thus shortens the fluorescence lifetime to 10 ps. Therefore, the intrinsic fluorescence emission is concealed in the steady-state fluorescence spectrum, since even a little amount of nonhomogeneity can distort the shape of the steady-state fluorescence spectrum. Through temperature-dependent time-resolved fluorescence study, we further proved that the 650 nm fluorescence is from the hole trap state induced by the oxidized rubrene embedded in the crystalline structure.

Figure 6.1 Position-dependent two-photon-induced fluorescence in rubrene crystal under excitation at 800 nm (after normalization). The inset shows the schematic of seven different positions in *ab* plane where the fluorescence spectra were recorded. For comparison, the one-photon-induced fluorescence spectrum under 400 nm excitation is also plotted (dashed line).

6.2 Efficient fluorescence quenching by singlet fission

In Chapter 3, the fluorescence upconversion measurements in rubrene crystal resolved two fast excited state lifetime components (Figure 3.10). The short one $\tau_1 = 2.2$ ps is caused by the direct fission from upper vibrational states, and the slow one $\tau_2 = 28$ ps is owing to the thermally activated fission from the relaxed S_1 . For rubrene in deaerated solution, the fluorescence lifetime is 16 ns with quantum yield close to 100% [171]. Thus we can consider that the rubrene radiative lifetime (τ_{rad}) equals to 16 ns. In rubrene crystals, if we assume singlet

fission is the only quenching process, the singlet fission yield Φ_{fiss} can be estimated from equation (6.1) :

$$\Phi_{fiss} = \frac{k_{fiss}}{k_{fl}} = \frac{k_{fiss}}{k_{fiss} + k_{rad}} \quad (6.1)$$

where k_{fiss} is singlet fission rate, and k_{rad} is radiative rate constant ($k_{rad} = 1/\tau_{rad}$). For $\tau_{fiss} = 2.2$ ps, $\Phi_{fiss} = 99.99\%$; and for $\tau_{fiss} = 28$ ps, $\Phi_{fiss} = 99.83\%$. For fluorescence between 540 and 600 nm, the amplitude is larger than 60% for $\tau_{fiss}=2.2$ ps, i.e., 99.93% of the rubrene emission is quenched by SF. In the long lived fluorescence emission range (620-740 nm), the SF quenching efficiency is still above 99.9%. Therefore, the steady-state fluorescence spectrum only reflects 0.1% information from the intrinsic fluorescence emission. As a consequence, the steady-state fluorescence spectrum will be drastically distorted by the existence of impurities with very low concentrations.

The steady-state fluorescence spectra were measured at different spots in the same rubrene crystal, shown in Figure 6.1. We used two photon excitation at 800 nm to obtain the fluorescence spectra from inside the bulk. As a comparison, the fluorescence spectrum under one-photon excitation is also plotted. The inset of Figure 6.1 shows the positions from 1 to 7 where the fluorescence spectra were recorded. The fluorescence spectra present either 610 nm or 650 nm type randomly, does not show a dependence on the position. It indicates the 650 nm fluorescence band is emitted by a nonuniform distribution of “impurity” with a low concentration. Therefore, observations from Refs.

Figure 6.2 Temperature dependent spectra of (a) steady-state fluorescence spectra, (b) 2D color fluorescence intensity map after normalization for every temperature.

[176] and [169] that the crystals grown at various positions of the furnace show different fluorescence spectra are not surprising.

6.3 Temperature-dependent steady-state and time-resolved fluorescence

6.3.1 Temperature-dependent steady-state fluorescence spectra

The steady-state fluorescence spectra measured at different temperatures (80-295 K) are shown in Figure 6.2a. By decreasing temperature, the fluorescence intensity increases drastically. The spectral signatures can be described by four bands located at around 560, 610, 650 and 700 nm, respectively. The fluorescence intensity map (after normalization) presented in Figure 6.2b indicates that for 650 and 700 nm bands there is no spectral shift. The emission bands centred at 560 and 610 nm become more pronounced when temperature goes below 140 K, accompanied by a blue shift with decreasing temperature. It shows that 560 and 610 nm fluorescence bands have a different origin compared with 650 and 700 nm emission bands.

Arrhenius plots, i.e. dependences of the integrated fluorescence intensity (in log scale) versus the inverse temperature ($1/T$) are shown in Figure 6.3. The steady-state fluorescence spectra at different temperatures are fitted by six Gaussian functions centered at 567, 585, 608, 647, 700 and 770 nm (Figure 6.4). According to the Arrhenius law [78,96]:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (6.2)$$

Therefore, the relation for the integrated fluorescence intensity I will become,

Figure 6.3 Arrhenius plot of the integrated fluorescence intensity I versus the inverse temperature ($1/T$).

Figure 6.4 The steady-state fluorescence spectrum at 80 K and the fit result by use of 6 Gaussians.

$$I = B \exp\left(\frac{E_a}{RT}\right) \quad (6.3)$$

where A and B are the pre-exponential factors, R is the molar gas constant, and E_a is the activation energy. We can calculate the activation energy E_a from the slope of the linear dependence of $\ln(I)$ versus $1/T$. As indicated in Figure 6.3, there are two temperature regions with different linear dependence slopes. Region 1 is from 140 to 295 K; the obtained activation energy is $E_a = 0.05$ eV, which corresponds well to the energy difference of $\Delta E = E(S_1) - 2E(T_1) = -0.05$ eV [88], i.e. SF is dominant at higher temperatures. Region 2 is from 80 to 120 K, with activation energy $E_a = 0.01$ eV, which indicates that SF is suppressed and some other process becomes dominant at lower temperatures (see below).

6.3.2 Temperature-dependent time-resolved fluorescence kinetics

In order to clarify the origin of the process which has a dominant contribution to the low temperature fluorescence spectra, the time-resolved fluorescence of rubrene single crystal were measured at different temperatures (80-295 K) (Figure 6.5). All fluorescence kinetics are well fitted biexponentially. At room temperature (295 K, Figure 6.5a), the majority (90%) of fluorescence below 620 nm decays with $\tau_1 \leq 50$ ps, limited by the time resolution of TCSPC setup. The remaining 10% decays with $\tau_2 \approx 270$ ps. On the basis of fluorescence upconversion measurements mentioned in Chapter 3, $\tau_1 \leq 50$ ps is assigned to the thermally activated SF. With decreasing temperature, the short time constant τ_1 becomes longer (up to 1 ns at 80 K) due to the suppression of singlet

Figure 6.5 Temperature dependent fluorescence kinetics at 80-295 K, measured by TCSPC under excitation with $\lambda_{exc}=450$ nm.

fission at low temperatures.

Tao et al. [222] also studied the photoexcited exciton dynamics in rubrene crystal via temperature-dependent transient absorption spectroscopy. The decay time of the TA signal also increases with decreasing temperature, and reaches 1 ns at 5 K, in good agreement with our fluorescence data. However, this TA

Figure 6.6 Arrhenius plots of fluorescence lifetime (τ_{fiss}) versus inverse temperature ($1/T$). The slope of the linear fit (solid lines) corresponds to the activation energy E_a .

decay was attributed to the exciton dissociation into charge carriers instead of singlet fission. The reason why they did not observe singlet fission in their measurements is due to the limitation of either their probe beam or the thickness of the sample. Their reported TA spectra were measured above 560 nm, however, the triplet absorption band locates at 510 nm.

For longer emission range at 295 K (Figure 6.5a), e.g., at 650 nm, $\tau_1 = 70$ ps (80%), $\tau_2 = 3$ ns (20%); at 700 nm, $\tau_1 = 130$ ps (35%), $\tau_2 = 3.5$ ns (65%). It indicates there is a spectral overlap between the emission from pristine rubrene which undergoes fast singlet fission and the “impurity” emission signal at 650 and 750 nm. At $T < 140$ K, a rise time is clearly visible for the fluorescence

decays at 650 and 700 nm (Figure 6.5 d-f). Moreover, the rise time at longer wavelengths (650 and 700 nm) is equal to the fast decay of the shorter emission range (585 and 605 nm). It suggests that singlet fission is suppressed at low temperature, while there is another energy relaxation process becoming dominant where the shorter emission species act as donors and longer emission species act as acceptors. The rise time at 650 and 700 nm becomes slower when temperature is further decreased, which indicates the energy relaxation is also endoergic. Arrhenius plots of the fluorescence lifetime versus the inverse temperature are shown in Figure 6.6. According to Arrhenius law mentioned in eq. (6.2), the relation between lifetime τ versus $1/T$ can be described by

$$\tau = B \exp\left(\frac{E_a}{RT}\right) \quad (6.4)$$

Different linear dependence slopes for $\ln(\tau)$ were observed in the same temperature regions with those of $\ln(I)$ versus $1/T$. The activation energy E_a obtained from the temperature dependent τ_1 (singlet fission) in region 1 is $E_a = 0.05$ eV, while in region 2, $E_a = 0.01$ eV, in a good agreement with the temperature-dependent fluorescence intensity data (Figure 6.3). For the longer time component τ_2 at 645 and 700 nm, there is only one slope with $E_a = 0.01$ eV.

Now we will discuss the nature of the donor/acceptor states which leads to the energy relaxation at low temperatures. Based on the above discussion, we can safely assign the donor to the intrinsic rubrene molecule. However, the

Figure 6.7 Steady-state absorption (or fluorescence excitation) and fluorescence spectra for pristine rubrene in toluene solution (a); under sunlight for one day (b); film made from (b) deposited on glass slide (c); amorphous film made from (a) deposited on glass slide (d).

nature of the state with 645 and 700 nm fluorescence is still disputed: Mitrofanov et al. [169] proposed that the oxygen defects in rubrene produces an acceptor state which emits at 650 nm. Krellner et al. [223] experimentally located this oxygen-induced hole trap state at 0.27 eV above the valence band. However, Podzorov et al. [176] claimed the 650 nm fluorescence band is due to the amorphous phase rather than the oxidized rubrene.

We first consider the possible candidates among the oxidized rubrene (rubrene peroxide [224]) and the amorphous phase of rubrene [176]. In order to study the steady-state properties of rubrene oxides and amorphous rubrene, the rubrene powder was first dissolved in toluene solution, then a portion of the stock solution was exposed to sunlight for one day for oxidation. After that, the color of rubrene in solution changed from bright red (inset of Figure 6.7a) to transparent (inset of Figure 6.7b). We dipped two glass slides into the pristine (red) and oxidized (transparent) rubrene in solution, and dried them up in order to make the films (insets in Figure 6.7c and d). Figure 6.7 shows the steady-state absorption and fluorescence spectra for all prepared samples. For Figure 6.7b-c, the fluorescence excitation spectra are plotted instead of absorption spectra because their absorption overlap with the solvent or substrate (glass) absorption. We can see that the fluorescence maxima of oxidized rubrene in solution, oxidized rubrene film, and rubrene amorphous film locate at 485, 548, and 585 nm, correspondingly. There are no visible emission peaks located at 650 or 700 nm, therefore, we conclude that the 650 nm emission band does not originate from oxidized or amorphous samples.

The hole trapping states in rubrene induced by oxygen defects have previously been experimentally observed [179,223] and theoretically discussed [225]. If we consider that the 650 nm fluorescence originates from these trap states, then the trapping depth can be calculated as $\Delta E = 2.19 \text{ eV (567 nm)} - 1.92 \text{ eV (647 nm)} = 0.27 \text{ eV}$. It corresponds well with the data reported in Refs.

[179,223] (0.25-0.27 eV). Therefore, we explain the 650 nm band as being due to the energy trapping process from the excited rubrene to the hole trap states induced by oxygen.

6.4 Anisotropy of fluorescence and singlet fission

Fluorescence anisotropy. After resolving the origin of the most disputed 650 nm fluorescence emission band, we come to the origin of the other ambiguous 610 nm band. This emission is generally considered to originate from the ab-polarized [177] or L-polarized transition [169]. Just to remind, a, b are crystallographic axes, and L is the molecular long axis which is parallel to the ab facet.

In order to identify the specific transition which corresponds to the 610 nm band, we measured the fluorescence anisotropy at 450 nm excitation with polarization parallel to the ab plane. The molecular and crystallographic axes of rubrene crystal are shown in Figure 6.8. The fluorescence anisotropy r is shown in Figure 6.9a, calculated by equation (2.1) mentioned in Chapter 2:

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}$$

Here $I_{\parallel}$ and $I_{\perp}$ are fluorescence intensities recorded with polarizations parallel and perpendicular to the polarization of the excitation beam, respectively. The excitation polarization is parallel to the crystallographic b axis. If we assume the transition dipole moment is in the ab plane, the anisotropy can be derived as

Figure 6.8 (a) Rubrene molecular structure and molecular axes; (b) Molecular packing on the *ab* facet; (c) Molecular packing on the *bc* facet.

$$r = \frac{I \cos^2 \theta - I \sin^2 \theta}{I \cos^2 \theta + 2I \sin^2 \theta} \quad (6.5)$$

where θ is the angle between the transition dipole moment and the direction of excitation polarization (i.e., *b* axis). In Figure 6.9a, fluorescence anisotropy $r = 0.4$ at 610 nm, we can calculate $\theta = 30^\circ$. It is in good agreement with the angle 31.2° between long molecular axis (*L*) and the crystallographic *c* axis [169]. Therefore, the 610 nm band is due to the *L*-polarized transition. The anisotropy r reaches the maximum 0.73 at 565 nm. Because the crystal surface cannot be perfectly parallel to the excitation polarization, the measured anisotropy under *b*-polarized excitation will contain the contribution from *c*-polarized emission. For pure *c*-polarized emission, $r = 1$ under *b*-polarized excitation, since there is

Figure 6.9 Fluorescence anisotropy of rubrene crystal (a); polarization dependent normalized fluorescence kinetics, $\lambda_{em} = 560$ nm (b).

no fluorescence component on the direction parallel to the a axis, i.e., $I_{\parallel}=0$.

The obtained fluorescence intensity at 565 nm is due to both c -polarized emission ($r=1$) and the L -polarized emission ($r=0.4$), which results in the measured value of 0.73.

It is known that the energy transfer will cause a fluorescence depolarization, therefore, r for the acceptor can be decreased to zero in a randomly oriented system [226]. In the well-ordered solid films, r may go to some nonzero value if the acceptor is also highly oriented [227]. In Figure 6.9a, r decreases with increasing emission wavelength until 650 nm, due to the energy trapping process, i.e., energy relaxation from the intrinsic rubrene excited state to the oxygen-induced defect states.

Polarization-dependent singlet fission. The origin of the 565 nm fluorescence emission band in rubrene crystal is well known: it is from the c-polarized emission [179] or M-polarized transition [169], i.e., the transition dipole moment for 565 nm fluorescence is parallel to the short molecular axis (M). Furthermore, the intensity of 565 nm band under c-polarized excitation is more than twenty times higher than that of 610 nm band under a- or b- polarized excitation [177]. We explain this intensity difference in terms of polarization-dependent singlet fission. In the previous Chapters 3 and 5, we studied the singlet fission in rubrene crystal under both one- and two-photon excitation, there is no evidence for an intermediate state, therefore, singlet fission in rubrene is concluded to be via direct coupling between singlet and triplet states through the matrix element $\langle S_1 S_0 | H_{el} | TT \rangle$ [39]. As discussed in Chapter 1, in the case of perfect stacking for adjacent molecules, the matrix element $\langle S_1 S_0 | H_{el} | TT \rangle$ will be zero (Figure 1.4). However, the simultaneous

shift in the direction of their transition dipole moment will result in a nonzero $\langle S_1 S_0 | H_{el} | TT \rangle$.

In the case of rubrene single crystal, the neighboring molecules mutually shift along the L axis, which favors singlet fission under L-polarized excitation. When the excitation is polarized parallel to a or b axis, the L-polarized transition can be excited and therefore singlet fission is very efficient. However, when the polarization of the excitation is along c axis, only M-polarized transition is excited, which is perpendicular to L direction (Figure 6.8), leading to a zero matrix element $\langle S_1 S_0 | H_{el} | TT \rangle$. Thus, SF under the c-polarized excitation is less efficient than under a- or b-polarized excitation, i.e., less fluorescence will be quenched by singlet fission. This is the reason why the steady-state fluorescence is much stronger under c-polarized excitation.

We studied the polarization dependent singlet fission by use of the fluorescence upconversion technique under b-polarized excitation, since it is difficult to directly excite the c-polarized transition. As shown in the inset of Figure 6.9b, the crystal was placed with its ab-facet either parallel or 50° relative to the excitation polarization direction. In the latter case, the excitation light has projections on both b and c crystallographic axes, therefore, both b- and c-polarized singlet fission can be studied. The fluorescence kinetics becomes slower when the direction of excitation beam is at 50° ($\tau_1 = 5.9$ ps, $A_1 = 0.64$; $\tau_2 = 80$ ps, $A_2 = 0.36$) relative to ab-facet ($\tau_1 = 3.3$ ps, $A_1 = 0.50$; $\tau_2 = 29$

ps, $A_2 = 0.50$). In that case, SF is less efficient (under c-polarized excitation) and therefore the quenching of fluorescence is less pronounced.

6.5 Conclusion

In this chapter we investigated the origin of the long-term disputed fluorescence spectra of rubrene crystal. It is demonstrated that singlet fission plays an important role in fluorescence quenching which was not considered in the previous studies. SF can influence both the shape and intensity maxima of the steady-state fluorescence spectra. The 565 and 610 nm bands are due to the emission of pristine rubrene which undergoes fast and efficient SF. More specifically, according to the fluorescence anisotropy study, the 565 nm band is from the M-polarized transition while the 610 nm band is from the L-polarized transition. The most controversial 650 nm fluorescence band is confirmed to be from the oxygen induced hole trapping states. All three types of steady-state fluorescence spectra reported in rubrene crystal can be explained in concordance by taking into consideration the polarization-dependent singlet fission and energy trapping by the hole trap states.

One point needs to be emphasized: the steady-state fluorescence spectrum in the presence of strong quenching (i.e. SF) includes a very small amount of information about the intrinsic fluorescence. In this case the contribution from other side effects, e.g. impurities and/or trapping states, will strongly be reflected in fluorescence spectra. Moreover, the steady-state fluorescence

spectrum should not be used as a criteria to judge the quality of the sample, and the time-resolved fluorescence offers deeper understanding.

Chapter 7. Conclusions and future work

7.1 Conclusions

In this thesis, singlet fission in organic crystals was studied by use of ultrafast spectroscopic techniques. Various excitation conditions were applied in order to investigate both the direct and thermally activated singlet fission from different excited states. To sum up, this dissertation can be classified into three main parts. The first part is focused on the one-photon-induced singlet fission in two kinds of organic single crystals: monomeric rubrene and dimeric α -perylene. The second part is dedicated to the two-photon and two-quantum-induced singlet fission. The main aim was to explore the singlet fission mechanism, i.e., whether it originates via direct coupling or through intermediate state. Finally, the third part demonstrates the importance of singlet fission in explaining the origin of the steady-state fluorescence spectra.

7.1.1 One-photon-induced singlet fission

We first studied the singlet fission in one monomeric organic crystal, rubrene. Direct singlet fission is proven to proceed from the upper excited states S_N or the upper vibrational states of S_1 bypassing the lowest excited state S_1 . It occurs on an ultrafast time scale (200 fs - 2 ps), which needs to compete with other deactivation channels such as internal conversion or polaron generation. Secondly, we did further study on SF in a dimeric organic crystal, α -perylene,

in order to investigate the role of excimer states. We found that in the dimeric crystal, both singlet fission and excimer formation are ultrafast; they compete with each other in contrast to the case in solution where excimer state is considered as an intermediate state for singlet fission [55].

7.1.2 Two-photon and two-quantum-induced singlet fission

Singlet fission mechanism is actively discussed in literature. Two pathways are considered: either by the direct coupling between the excited singlet and triplet pair states, or via an intermediate state, such as multiexciton or charge-transfer state. The intermediate state is considered to be optically dark, i.e., forbidden under one-photon excitation. Therefore, in order to populate this dark state, we studied the singlet fission under two-photon excitation. Our experimental results show no evidence for the existence of a dark intermediate state for singlet fission in both rubrene and α -perylene crystals. Singlet fission rate depends only on the excited states energy and not on their symmetry.

7.1.3 Singlet fission and fluorescence

In the last part, we studied the temperature and polarization dependent singlet fission of rubrene. The singlet fission is highly efficient which quenches > 99.9% of the intrinsic rubrene fluorescence. By taking singlet fission into consideration, we explained the origin of all fluorescence emission bands which were under controversy for a long time. We suggest the researchers to not focus too much on the steady-state fluorescence spectra when the material possesses

an ultrafast fluorescence quenching channel. As in this case, the steady-state fluorescence spectrum can be influenced drastically by any side effect or impurity, and only provides a limited amount of information about the intrinsic fluorescence emission. Deeper knowledge can be obtained from time-resolved measurements.

7.2 Future work

In this thesis, we have studied singlet fission in the well-ordered neat crystals which contain only one kind of molecule with the focus on determining the singlet fission mechanism. We did prove that the SF occurs with high efficiency in the studied organic crystals. However, a key question up in the air is how to utilize singlet fission to improve the efficiency of organic solar cells. More specifically, how to extract multiple electron-hole pairs from the triplet pair generated by SF?

The singlet fission taking place on two identical molecules is called “homofission”, while on different kinds of molecules it is called “heterofission” [39]. The heterofission was reported through the magnetic field effect study in the charge-transfer crystals where the donor and acceptor molecules are alternatively packed [228]. The CT cocrystal can be considered as a highly ordered analogue of the bulk heterojunction polymers currently used in organic photovoltaics [229]. Therefore, it will be interesting to extend our study to singlet fission in the CT crystal, to see the fate of the triplet states after

generation from SF. For example, whether the generated triplet states can be dissociated into charge carriers via inherent charge transfer, and whether the charge carrier extraction efficiency can exceed 100%, or there are other quenching channels for the triplet states in the mixed crystalline structure. Our methodology can also be extended to other hybrid systems to harvest the multiple electron-hole pairs from the triplet states via either electron- or energy-transfer. An attempt has been made in some hybrid systems such as pentacene/C₆₀ to extract multiple charge carriers from the triplet pairs [49,89,114], however, there is not yet an unambiguous picture. The extensive study on singlet fission in the hybrid systems will also offer a guideline for designing the optimal material configuration for the design of efficient solar cell based on singlet fission.

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