

Designing New Singlet Fission Materials for High Performance Organic Solar Cells

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Declaration

This thesis consists of the candidate's published articles, which are {Adv. Energy Mater. 2018, 8, 1801720}; {Adv. Energy Mater. 2019, 9, 1901069} and one article that is in progress which entitled "Competitive triplet formation and recombination in crystalline films of perylenediimide derivatives: implications for singlet fission" and submitted to the Journal of Physical Chemistry C. Co-authors included in the publications have signed agreement forms that certify the following:

- the candidate has contributed more than 50% to the content of the manuscripts including planning, preparation, and execution of the work described in each manuscript
- the candidate is the "primary" or "first" author of the manuscripts
- the manuscripts can be included in the candidate's thesis in its published form without redactions or omissions

These agreement forms are found in the Appendices section of this thesis.

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List of Publications and Conferences

Several publications were produced during my PhD candidature. The results described in this thesis have also been presented at both local and international conferences. These are listed herein for reference:

- ✓ **S. Masoomi-Godarzi**, M. Liu, Y. Tachibana, V.D. Mitchell, L. Goerigk, K.P. Ghiggino, T.A. Smith, D.J. Jones “Liquid Crystallinity as a self-Assembly Motif for High-Efficiency, Solution-Processed, Solid-State Singlet Fission Materials”, *Adv. Energy Mat.*, 8 (2019) 1901069.
- ✓ **S. Masoomi Godarzi**, M. Liu, Y. Tachibana, L. Goerigk, K.P. Ghiggino, T.A. Smith, D.J. Jones “Solution-Processable, Solid State Donor–Acceptor Materials for Singlet Fission”, *Adv. Energy Mat.*, 8 (2018) 1801720.
- ✓ **S. Masoomi Godarzi**, C.R. Hall, B. Zhang, J.M. White, W.W. Wong, K.P. Ghiggino, T.A. Smith, D.J. Jones “Competitive Triplet Formation and Recombination in Crystalline Films of Perylenediimide Derivatives: Implications for Singlet Fission”, *J. Phys. Chem. C.*, 2020, In press.
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- ✓ **S. Masoomi Godarzi**, T. Smith, D. Jones “Liquid crystallinity as a self-assembly motif for solid state singlet fission materials”, Australasian community for advanced organic semiconductors (AUCAOS) symposium, Dec 2018.
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Abstract

Singlet fission (SF) is the photophysical process of splitting one singlet state into two triplet states. The first requirement for SF is that the first excited singlet state of the chromophore should be at least twice the energy of the first triplet state. In the last decade, SF has received a lot of attention as a way of converting high energy photon above the semiconductor bandgap to two lower energy excitons closer to the bandgap and so overcoming the Shockley-Queisser limit (maximum theoretical efficiency of photovoltaic cells) of single-junction solar cells. However, the number of SF materials that can be included in photovoltaic devices is limited because of strict materials requirements. This is the main reason why only a small increase in the efficiency of photovoltaic devices by including SF materials has been reported so there is a need to design, synthesis and study new class of material for SF.

A new strategy to design a class of intramolecular SF (iSF) material is reported to be coupling two strong acceptors with low triplet energy level with a strong donor (A-D-A). This model not only takes the advantage of providing an excited electronic state with significant charge-transfer character that facilitate SF but also allows us to choose units based on the energy level requirement. Using this strategy, I have designed and synthesized the small molecule (BDT(DPP)₂) and polymer (p-BDT-DPP) systems by coupling benzodithiophene (BDT) as electron donor and bithiophene-pyrrolopyrrole-dione (TDPP) as electron acceptor with low lying triplet energy level. Various steady state and time-resolved spectroscopic techniques such as ultrafast and nanosecond transient absorption (TA) spectroscopy were used to study the excited state mechanism in the candidate compounds.

In most of highly efficient SF systems, a large degree of crystallinity is required, and the SF yield is highly sensitive to the crystal packing and intermolecular nearest-neighbour coupling. The first set of A-D-A material revealed that a stronger self-association is needed to drive SF in this class of material. To address this issue, a self-organizing core such as hexa-peri-hexabenzocoronene (HBC) is used as electron donor and is attached to TDPP as an electron acceptor and the results show a significant increase in the efficiency of triplet yield.

It has been demonstrated that the chromophore packing has a significant impact on the SF parameters such as yield and rate and understanding this relationship will help us to understand SF mechanism better. To investigate this relationship, four perylenediimide (PDI) derivatives were studied for SF comprising the same PDI core but with different substituents at their imide positions, 4-butylphenyl, butyl-terphenyl, diisopropylphenyl and mesityl which display distinct molecular geometries with varied intermolecular π - π interactions. The results demonstrate that SF occurs with different rates and yields in the PDI derivatives. Also, the results show that both decay rate and SF rate are sensitive to intermolecular packing.

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Chapter 1

Introduction

1.1. Broad context

The amount of solar energy that reaches the Earth's surface each year is about 6000 times more than the total annual global energy usage¹ so the efficient conversion of this energy to electricity is an attractive solution to the current energy crisis.²⁻³ In order to make this economically viable, the power conversion efficiency (PCE) of photovoltaic (PV) devices needs to be improved significantly. The PCE of PV devices has increased steadily in the past decade and the record is approaching the Shockley-Queisser limit, which is the maximum theoretical efficiency obtainable from a single junction PV cell.

The dominant loss mechanism in PV devices is thermalization which accounts for about 40% power loss for a silicon cell. Singlet fission (SF) is a potential way to mitigate the thermalization loss and increase the conversion efficiency. SF is a multiexcitonic process in which the absorption of one high energy photon results in the formation of two low energy triplet excitons. In 1979, the physicist David Dexter recognized the potential use of a SF material on top of a solar cell.⁴ He envisaged that two triplet excitons formed in the singlet fission material could be transferred efficiently across a carefully designed interface into a solar cell, where they are converted into an electric current. Doubling the electric current produced by the device is therefore possible. This strategy involves no extra electrical contacts or modification to the operation of the solar cell.

Although many studies have been performed on SF materials, the SF mechanism is yet not understood particularly well so far and most of the reports about the SF process concentrate on the experimental and computational work on the acene family of molecules. There is a need to study alternative SF systems, other than the acene family, to improve our understanding of this potentially important process. The field is now set on a route towards developing new SF materials for PV application.

The current knowledge of the SF mechanism is far from complete, and this hinders the rational design of new materials for PV applications, which is required to improve efficiencies further.

1.2. Motivation of the study

There are many challenges towards developing SF-enhanced PV devices. Choosing the right chromophore that undergoes SF is the first requirement. An efficient SF chromophore should have, i) a high triplet yield approaching 200%, ii) a long lived triplet, iii) a high molar extinction coefficient throughout the Uv-Vis region, iv) a good interface adhesion, v) a low cost and vi) be non-toxic. One other characteristic of SF chromophore for enhancing PV performance is having a singlet excited state energy near 2.2 eV and a triplet excited state of around 1.1 eV. Then, this material could be paired with a chromophore having a singlet excited state energy of 1.1 eV.⁵ We also need SF to compete with other photophysical process like charge extraction from S_1 state.

Most of the known efficient SF chromophores are not suitable for PV devices. The polyacenes, in particular tetracene, pentacene, and their derivatives, have been reported to

undergo singlet fission with high yield; however, many derivatives are oxidatively unstable in atmospheric condition.⁶ Diphenylisobenzofuran is another known SF chromophore with 200% triplet yield; however, its films convert to a polymorph with low triplet yield in several days.⁷ Other more robust chromophores like perylenediimides derivatives, carotenoids, some polymers and molecular dimers have been reported to undergo SF with varying yield. As a result, there is an urgent need to design and study new SF materials that are suitable for PV applications.

So far, using singlet fission materials to improve PV efficiency is at the early stage of fundamental research. Other practical issues to be overcome in this research field are basic molecular engineering problems of the SF layer in PV device, cost and long-term stability in sunlight, that have not yet been addressed. Remaining challenges include matching energy levels appropriately for fast yet low potential-loss charge separation and transfer, and preventing premature charge injection from the short-lived, originally excited singlet state while assuring efficient charge injection from the long-lived triplet excited state.⁸

Although solid-state SF has been reported in a limited number of partially disordered systems, highly efficient SF requires systems with a large degree of crystallinity and the SF yield is highly sensitive to the crystallinity of the film and intermolecular coupling in these systems; the so called “local-order constraint”.⁹ It has been found that SF is suppressed in polymorphs with geometries that differ from their usual crystal packing arrangements.¹⁰ For example, no SF in pentacene is reported for films grown on a polymer substrate,¹¹⁻¹² whereas the vapor deposited pentacene films show efficient SF¹³. To date, many attempts have been made to incorporate SF chromophores to photovoltaic devices with pentacene and tetracene being

particularly successful due to the high triplet yield and fast SF.¹⁴ External quantum efficiencies of over 100% have been reported for an organic photovoltaic consists of pentacene as the donor and C₆₀ as the acceptor¹⁵, and a hybrid inorganic-organic solar cell¹⁶⁻¹⁷. While these systems have yielded promising results, they are still some limitation such as thin optimal thicknesses of the SF chromophore.⁵ These results suggest the potential to enhance photovoltaic efficiency upon inclusion of SF materials. However, the sensitivity of device performance to the chromophore packing and the morphology of the active layer indicate new materials are required where the “local-order constraint” can be overcome.¹⁸

Mapping the relation between intermolecular coupling of chromophore pairs and SF efficiency can be very useful in understanding the SF mechanism. Several studies have shown that the rate of SF is highly sensitive to the intermolecular coupling and even minor variations in the relative disposition of chromophores in a solid can make a significant change in the efficiency of the SF process.¹⁹⁻²¹ As a result, it is necessary to develop rules relating to the favourable orientation of the coupled chromophores.

In light of recent advances in the understanding of the SF mechanism, approaches to the design of new SF systems that can overcome the “local-order constraint” should be considered. Reports with more focus on developing morphology independent SF systems are lacking in the literature. New SF systems must satisfy all normal material criteria for inclusion in any successful PV device, while remaining efficient SF chromophores. Also, approaches to better our understanding of the relationship between intermolecular coupling and SF efficiency will be examined.

1.3. Aims

This thesis aims to better understand the SF mechanism by controlling the morphology through molecular design, to eliminate the possibility of polymorphs, for materials to be used in PV applications. Also, approaches to understand the relationship between intermolecular coupling and SF efficiency will be examined. In particular, a focus on investigating SF properties is required to assess their ability to provide improved device efficiencies.

The rate of SF and the efficiency of generating triplets through SF have been investigated spectroscopically. In order to investigate SF properties, time-resolved techniques such as ultrafast transient absorption spectroscopy, time correlated single photon counting and flash photolysis will be utilized (described in Chapter 3). Other complementary photophysical techniques will also be used including steady-state absorption and steady-state fluorescence spectroscopy.

This thesis aims to advance the SF materials design rules to improve SF yields and rate, and morphology independent SF systems. These results will lead this research field to new directions and provide useful guidelines for the further development of efficient, solution processable SF materials for photovoltaic applications.

1.4. Overview of the thesis

This thesis consists of seven chapters with three main research chapters. Following this introduction, Chapter 2 reviews the current literature in this field including the recent advances in the mechanistic understanding of SF. A special focus is given to the inclusion of SF chromophores in PV devices.

In Chapter 3, the steady-state and time-resolved spectroscopic methodologies used in this work are discussed. The time-resolved methods include time correlated single photon counting, ultrafast transient absorption and flash photolysis. These methods are discussed in detail, including their advantages and limitations in investigating SF in organic chromophores.

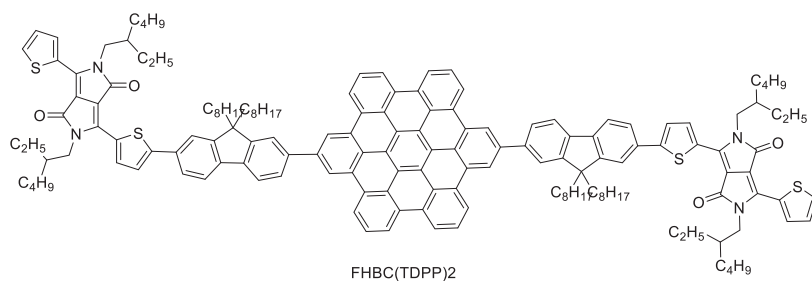
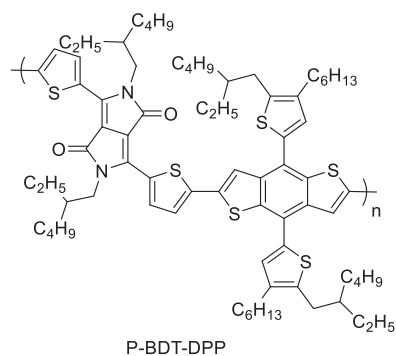
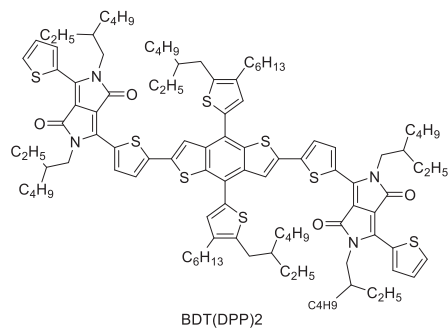
Chapter 4 investigates a new strategy for designing SF materials that is based on an acceptor-donor-acceptor motif first proposed by Busby et. al.⁹. Diketopyrrolopyrrole (DPP) is well reported as an efficient SF chromophore and was therefore chosen as the acceptor and triplet host for the new system. SF yields and triplet lifetimes are compared in both molecular and polymeric systems comprising DPP and benzodithiophene (BDT), namely BDT(DPP)₂ and P-BDT-DPP, and the results are explored spectroscopically.

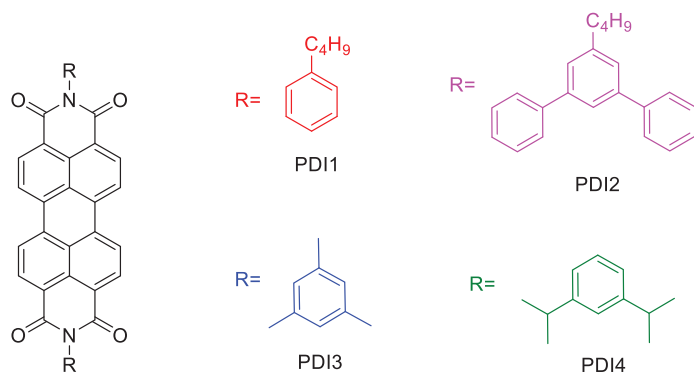
Chapter 5 explores the approach of increasing the self-assembly of an acceptor-donor-acceptor motif through a core while keeping the singlet energy level high enough to meet the energy level requirement for SF, that is $E(S_1) \geq 2 * E(T_1)$. This approach is investigated in FHBC(TDPP)₂ by replacing BDT with a hexa-peri-hexabenzocoronene (HBC) core. Results indicate an increase in the rate and yield of SF by increasing the self-assembly.

Chapter 6 examines the rules to map the relation between intermolecular coupling of chromophore pairs and SF efficiency. For this purpose, different derivatives of perylenediimide (PDIs) are studied and SF properties are investigated by functionalizing their imide position with different groups. The functional groups allow control over the relative orientation of neighboring molecules, providing a mechanism for control over the intermolecular interactions.

Finally, Chapter 7 contains the conclusions and a reflective evaluation of further research approaches and directions.

The name and structure of materials that will be discussed in the later chapters are summarised here:





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Chapter 2

Background

2.1. What is singlet fission

Singlet fission (SF) is a photophysical process that can occur in coupled organic molecules. SF is a spin allowed conversion of a singlet excited state into two triplet states within an assembly of two or more chromophores (Figure 2.1).¹ In such an organic molecule, the first singlet state must have at least twice the energy of the corresponding triplet state i.e. $E(S_1) \geq 2 \times E(T_1)$. In this energetic configuration SF can generate two triplet excitons upon absorption of a single high energy photon.

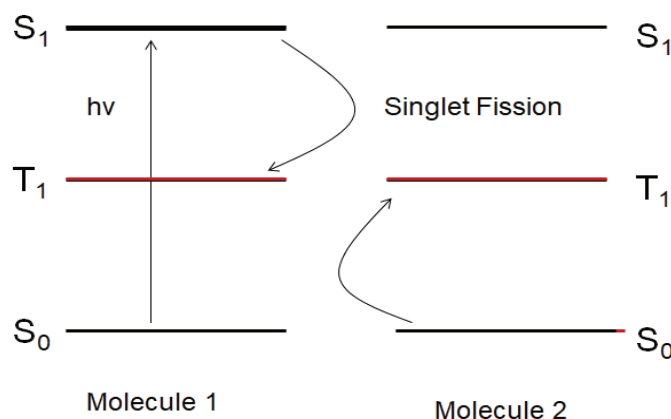


Figure 2.1. Schematic of singlet fission occurring in two organic chromophores

SF is a spin allowed process as the two resulting triplets are strongly coupled and have an overall singlet character so SF can be considered as a special case of internal conversion where a radiationless transition occurs between two electronic states with the same multiplicity. Although the mechanism of SF is not yet fully understood and is still the subject of

intense research, it is generally accepted that the singlet excitation converts to a triplet pair state $^1(TT)$, either coherently or incoherently, which later separates into two independent triplets ($2 \times T_1$) (see Figure 2.2).²⁻³

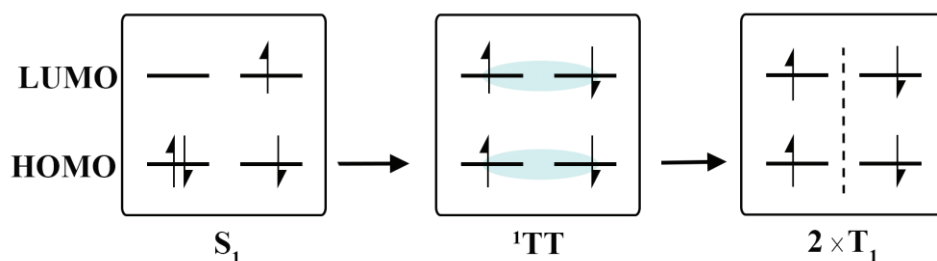


Figure 2.2. Molecular orbital diagram of two chromophores involved in a singlet fission process

Like other spin allowed processes, SF can be very fast on the time scale of picoseconds (ps, 10^{-12} s) or even sub-ps when it is isoergic or slightly exoergic ($E(S_1) \geq 2E(T_1)$) and the coupling is favourable.¹ As a result, it can compete with vibrational relaxation and fluorescence. The formation of excited state complexes and charge separated species can be even faster.¹

Since there are a number of different decay channels by which an organic chromophore can lose the energy it gained by photoexcitation, SF must be faster than competing processes such as intersystem crossing, internal conversion or fluorescence. Energetically, the $S_1S_0 \rightarrow TT$ process should be exoergic or at least isoergic, therefore the energy level requirement that should be met for SF is the energy of the lowest singlet state should be greater than or equal to twice the energy of the lowest triplet state ($E(S_1) \geq 2E(T_1)$).⁴ On the other hand, in most organic chromophores, $2E(T_1) - E(S_1)$ is strongly positive. There are other energy level requirements because even if the triplets are formed, they can annihilate each other to produce higher

energy singlet, triplet or quintet states. Thus, another energy level requirement for efficient singlet fission is $2E(T_1) - E(T_2) < 0$. One aim of this work is to identify candidate structures that meet these energy level requirements in large conjugated π -electron systems, as their absorption coefficients in the visible region will have to be high for solar photovoltaic applications.

2.2. History of singlet fission

Singlet fission has been known for about 60 years. It was first postulated to occur in anthracene crystals in 1956 to explain the unusual photophysics of this compound.⁵ It was then experimentally discovered in 1968⁶ in tetracene crystals to account for the low quantum yield of fluorescence in this compound and the proposal was proven correct in 1969⁷⁻⁸ by studying magnetic field effects. In 1980, new types of substrates were found to have SF properties. It was first observed for a carotenoid contained in a bacterial antenna complex.⁹ It has since been reported with high yields in polyacenes,^{7, 10} such as tetracene, pentacene and their derivatives, oligophenyls,¹¹ diphenylisobenzofuran,¹² carotenoids,¹³⁻¹⁴ rylene-based chromophores,¹⁵ perylenediimides,¹⁶ diketopyrrolopyrrole derivatives and conjugated polymers.¹⁷⁻¹⁸ However, most of our understanding of the SF process relies on the experimental and computational work on the acene family. Efficient SF has been reported mainly in condensed matter systems, e.g. crystals,¹⁹⁻²² polycrystalline films,²³⁻²⁵ amorphous films,²⁶⁻²⁷ nanoparticles and aggregates.^{14, 28} Although solid state SF has been reported in a limited number of partially disordered systems, highly efficient SF requires systems with a large degree of crystallinity and the SF yield is highly sensitive to the crystallinity of the film, crystal packing and intermolecular nearest-neighbour coupling in these systems. An increase in the interest and a burst of publications

were promoted when people found that SF can be useful in photovoltaic devices, see Figure 2.3.

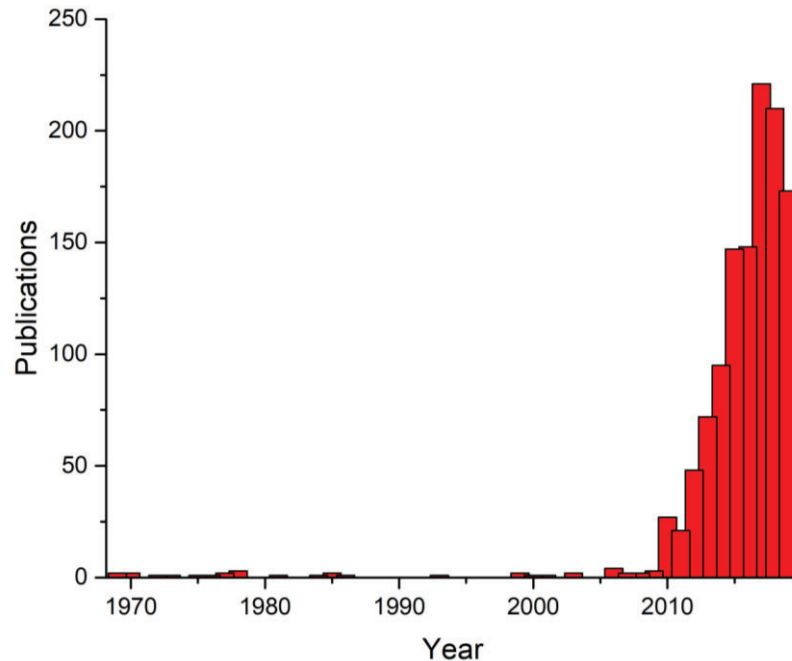


Figure 2.3. Number of published works related to SF in the past 50 years derived from Scifinder

2.3. The increasing interest in singlet fission

The power conversion efficiency (PCE) of PV devices has increased significantly in the past decade with the record approaching the Shockley-Queisser limit of 32%, which is the maximum theoretical efficiency for an ideal single junction PV device. Figure 2.4 shows the theoretical efficiency for an ideal single junction PV as a function of bandgap. The bandgap defines the energy of a photon that can still be absorbed by the cell. Thus, photons with less energy than the bandgap cannot be absorbed and will pass through the material, and photons with more energy will be absorbed but the excess energy will be lost as heat. The dominant loss mechanism in PV devices is thermalization which accounts for about 40% power loss for a

silicon cell.²⁹ Singlet fission (SF), which is an exciton multiplication process, is a promising technique to reduce thermalization losses and so increase the efficiency of solar cell (see Figure 2.4).

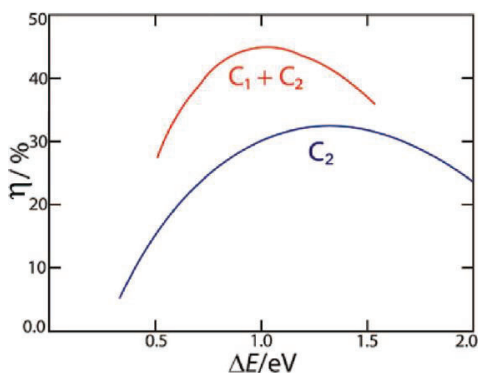


Figure 2.4. Schematic sketch of theoretical efficiency as a function of the S_0 - T_1 band gap for a singlet fission solar cell (red curve) and a conventional single junction PV device (blue curve) derived from reference¹ with permission

David Dexter suggested the use of a SF material on top of a silicon solar cell in 1979 in that the two triplet excitons formed in a SF chromophore can be transferred to the solar cell efficiently, so doubling the electric current produced by the device is possible (see Figure 2.5).³⁰ The quantitative analysis showed that the Shockley-Queisser limit of about 33% for the PCE of an ideal single junction PV cell would increase to about 45% in a cell with a layer of singlet fission material on the top assuming that the two triplets resulting from the absorption of a high energy single photon are independent of each other to produce charge carriers.

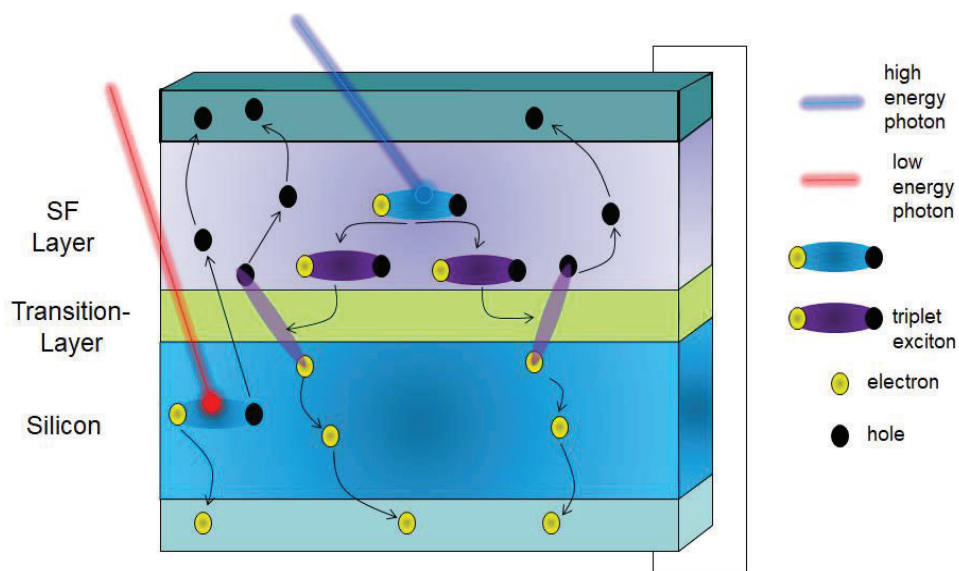


Figure 2.5. Schematic of an incarnation of a SF-enhanced solar cell device.

2.4. SF sensitized solar cell

The inclusion of SF materials in photovoltaic devices is an active research area. Different SF sensitized solar cells have been reported in the literature including: SF organic photovoltaics, SF-based dye-sensitized solar cells, SF inorganic photovoltaics, and a SF photon multiplier.²⁹ These are summarized in detail below, along with discussions about difficulties with each of them.

2.4.1. SF organic photovoltaics

Organic photovoltaics and photodetectors were the first devices that were used in conjugation with SF materials. The first organic devices incorporating SF materials were based on pentacene/ C_{60} , where pentacene is the electron donor capable of SF and C_{60} acts as the electron acceptor. Other acceptors have been used in conjugation with pentacene, including perylenediimide (PDI) derivatives and PbSe or PbS colloidal nanocrystals, see Figure 2.6.³¹⁻³² The

energy levels of quantum dots can be controlled by varying the quantum dot size.³³ These devices demonstrated maximum external quantum efficiencies (EQE) of 130%.³⁴

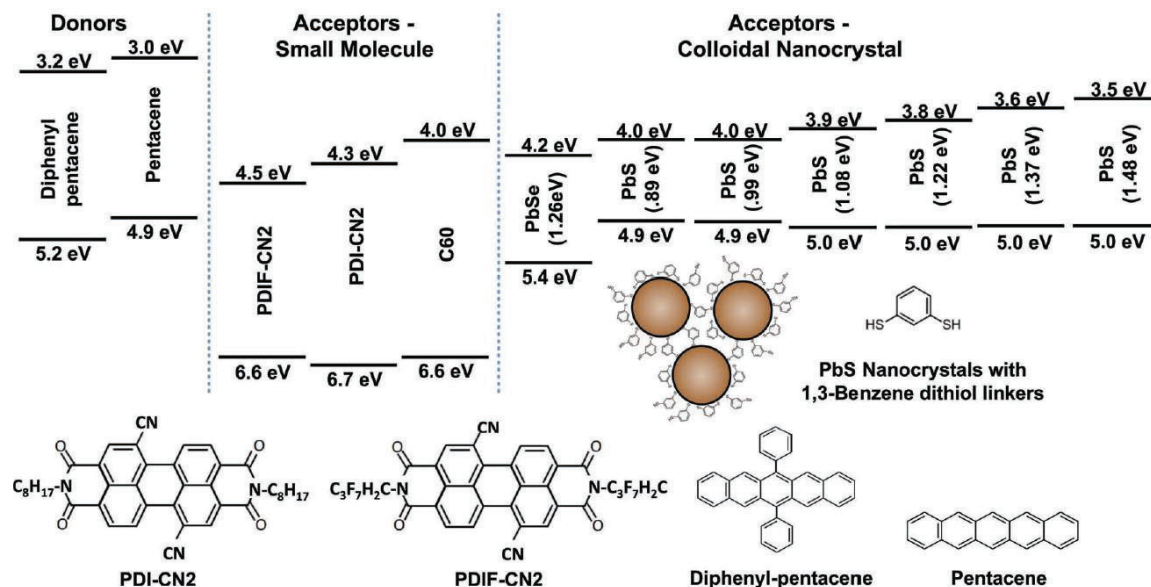


Figure 2.6. Energy levels and molecular structures of the materials used in reference³² with permission

There are two main challenges when including SF materials in organic PVs. First, no high performance OPV materials exist with a bandgap close to 1 eV to act as a low bandgap semiconductor to be used with SF materials, which is a requirement since using a high bandgap semiconductor, will reduce the PCE of the device. Second, the triplets need to be extracted at the heterojunction with the low bandgap semiconductors and most efficient OPV acceptors are fullerenes. Thus, new materials need to be developed to overcome these two challenges allowing either acceptors with bandgaps of 1 eV to combine with SF chromophore or efficient SF donor with bandgap of near 2 eV to be paired with efficient acceptor.²⁹

2.4.2. SF-based dye-sensitized solar cells

Dye-sensitized solar cells are made of a monolayer of a molecular dye attached to a mesoporous oxide scaffold (typically TiO_2) that absorbs light and injects an electron from the photoexcited state to the oxide. The remaining holes are transferred to the redox partner in the electrolyte. For SF-based dye-sensitized solar cells, two dyes are required and the SF dye should have a bandgap twice that of the other dye as shown in Figure 2.7.¹ The SF dye generates two electrons per each absorbed photon and the other dye injects one electron per low energy photon, but there are many outstanding challenges and issues relating to devices. First, the SF dye should form a monolayer on the oxide surface with the right packing to enables SF, and such a system has not been developed yet, other than a dimer-based system.²⁹ Another issue is that the triplets formed via SF might not be free to diffuse away from each other before charge separation. Also, triplet-charge annihilation is another problem in this system because after electron injection the remaining triplet can recombine with the generated hole. The results of work in this field suggest fundamental barriers in such a system as no improvements have yet been observed by employing SF in dye-sensitized solar cells.

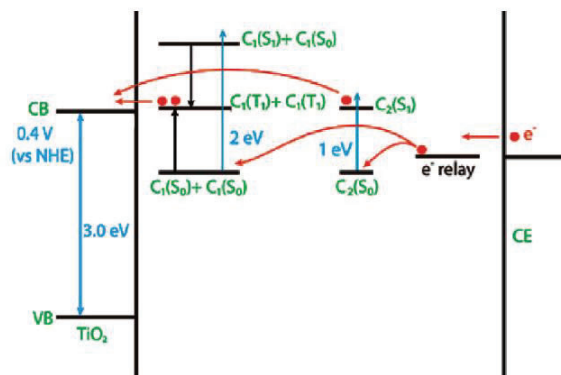


Figure 2.7. Schematic energy level diagram of SF-based dye-sensitized solar cells, C_1 is the SF sensitizer and C_2 is a conventional sensitizer, derived from reference¹ with permission

2.4.3. SF enhanced inorganic photovoltaics

Interest in inorganic PV devices has increased steadily in the past few decades and silicon based solar cells are the dominant PV technology. Other inorganic PV devices, such as those based on copper indium gallium selenide (CIGS) and CdTe, are also increasingly being developed.³⁵ The maximum reported PCEs for these devices are 26.6%, 22.6% and 21.1% for silicon, CIGS and CdTe, respectively.³⁵ Improving the efficiency of highly optimized solar cells without introducing substantial complexity or cost by using SF materials is a very interesting area of research. SF-enhanced PV can be achieved in two ways: charge transfer and energy transfer. In the charge transfer method, the SF generated triplets dissociate at a heterojunction between the SF material and the inorganic semiconductor and electron and holes are collected at the electrodes.³⁶ The challenge through the charge transfer method is to form a high quality organic-inorganic heterojunction to minimize the energy loss from the band offset and recombination across the interface. Only a few studies on the heterojunctions between organic/bulk inorganic semiconductors have been reported,³⁶ and it is found that control of the

interface is required through defect passivation. This increases the difficulty of this approach, but theory suggests this may lead to the best efficiency gain.³⁶ In the energy transfer approach, SF generated triplets undergo triplet energy transfer to an inorganic semiconductor where charge generation and collection occur, see Figure 2.8. In this method, both the electron and holes are collected in the inorganic semiconductors. This method was suggested by Dexter in 1979.³⁰ One of the issues is that triplets cannot undergo energy transfer through Förster resonance energy transfer (FRET) and instead it occurs through the shorter range exchange interaction called Dexter energy transfer. Castellano et. al. demonstrated that the triplets can be transferred from organic molecules to inorganic QDs and this transfer was 100% efficient for pentacene/PbSe and tetracene/PbS systems.³⁷ Although these studies involve inorganic quantum dots, many efforts are underway to check if the same effect can be achieved with bulk inorganic materials and M.A. Baldo et. al.³⁸ recently reported the triplet energy transfer from tetracene to silicon with the total yield of 133% which will open a new route in this field.

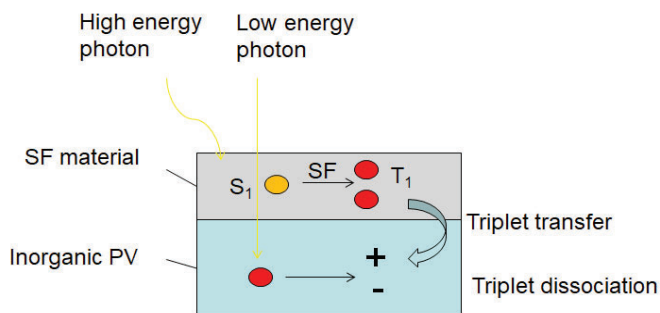


Figure 2.8. Schematic illustration of SF-enhanced PV through energy transfer

2.4.4. SF photon multiplier

In a new approach developed by A. Rao and R. Friend²⁹, termed the SF photon multiplication method, the SF generated triplet energy is transferred to an intermediate such as quantum dots, where two low energy photons are generated from a single high energy photon. Although triplets are dark states in SF, once their energy is transferred to quantum dots, a bright state is formed which can emit photons. The schematic of such a device is illustrated in Figure 2.9. It consists of a thin film of the SF material doped with a small amount of quantum dots. The low energy photons pass through the film and are not absorbed because of a low doping ratio of quantum dots but high energy photons are absorbed by SF materials and create two triplet excitons. Then, the triplets undergo energy transfer to the quantum dots which have a bandgap resonant with the triplet energy. The emitted photons are absorbed by a high performance conventional solar cell. This method has several advantages over other approaches. It can act as a passive optical film with no requirement for electrical contact. Also, such a device can be produced by high volume roll to roll processing techniques. The film can be used with existing high-performance PV modules such as silicon, CIGS, CdTe and perovskite-based cells, with no need to form interfaces with bulk inorganic semiconductors. This approach also has some issues though. For example, quantum dots with high photoluminescence quantum yield and appropriate band gap of about 1.2 eV are needed to be embedded in the SF material. The correct morphology of the device is essential in this approach because triplets need to be formed within their diffusion length from the quantum dots on one side and on the other side the concentration of quantum dots should be low to reduce the parasitic absorption effects. Also, when the SF material and quantum dots are processed together from the solution,

they are more likely to phase segregate and aggregation of the quantum dots can lower the photoluminescence quantum efficiency and reduce the triplet energy transfer efficiency. As a result, more work on the control over processing is required to obtain the correct morphology to produce a sample where quantum dots are evenly spread throughout the film. The efficiency limit of the SF photon multiplier approach matches the efficiency limit for a two-junction tandem solar cell. However, this method is more stable against changing irradiation, spectral change and temperature than tandem solar cells. Ehrler et. al. demonstrated that for silicon solar cells with PCE of 26.6%, the photon multiplier approach has the potential to increase the efficiency by up to 4.2% absolute in a realistic case, however, directly coupling the SF material to the silicon PV was still projected to increase the efficiency up to 38%.³⁹

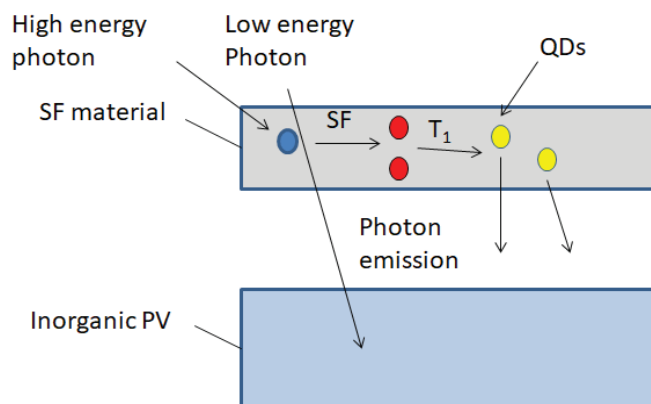


Figure 2.9. Schematic illustration of SF-enhanced PV through energy transfer

2.5. SF Mechanism

The SF mechanism is shown schematically using 2 chromophores, 4 orbitals and 4 electrons in Figure 2.10. After photon absorption to an allowed singlet state (S_1), a nonadiabatic transition leads to a correlated triplet pair $^1(TT)$ with an overall singlet state character that

makes SF a spin allowed process. Theoretical calculations demonstrate two distinct pathways for the formation of triplets through singlet fission. The first is a two-step, one electron mechanism where a charge transfer (CT) state acts as an intermediate species for the triplet formation.⁴⁰ These CT states can be real or virtual intermediates. It has been reported that this CT-mediated mechanism can efficiently support SF where the energy of the CT state is low and the intermolecular coupling is sufficiently large.⁴¹⁻⁴² The other mechanism is a one-step, two electron mechanism that does not involve any intermediate states and the coupling between the first excited state (S_1) and the correlated triplet pair state $^1(T_1T_1)$ is direct. Both experimental results and calculations have suggested that coupling mediated by CT states is stronger than direct coupling.^{40, 43-45}

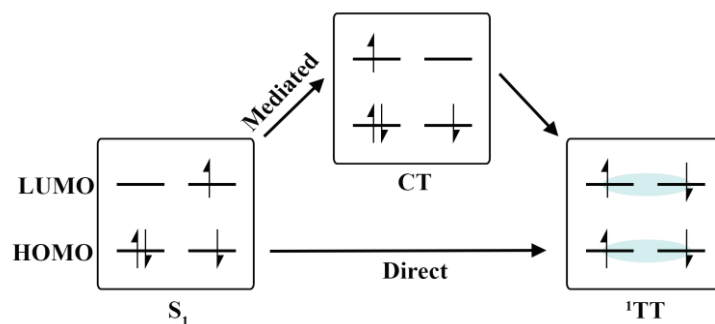


Figure 2.10. Molecular orbital diagram of two chromophores showing the singlet fission mechanism

To date, most efforts in this field have been dedicated to *intermolecular* singlet fission (xSF), where the absorption of one photon leads to the formation of two triplet excitons on adjacent molecules as shown in Figure 2.11. Due to the intermolecular nature of this process, strong electronic coupling between near neighbours is required and its efficiency is highly sensitive to the crystallinity of the film. Another mechanism that is more applicable to functional devices is based on intramolecular processes, in which the fission efficiency is an

intrinsic property of the designed material.⁴⁶ The central idea is to attain SF-favoured interchromophore configurations through the more covalent bonding and intramolecular steric effect.⁴⁷ In *intramolecular singlet fission* (iSF), two resultant triplet excitons are located on different moieties within the same molecule as shown in Figure 2.11. iSF is found mostly in conjugated polymers, in which the interactions between conjugated segments along the chain can be dominant over interchain effects, and in many cases the individual chromophores should be large enough to accommodate two triplet excitons. Thus, singlet fission should be an inherent property of these chromophores rather than a result of intermolecular coupling so it is not dependent on molecular orientation and intermolecular coupling.⁴⁸ Efficient intramolecular singlet fission systems have some advantages over the intermolecular singlet fission counterparts: (i) the molecule can be potentially bound to the electron acceptor and, the triplet exciton needs to travel a minimal distance to reach the acceptor, thus ensuring more efficient electron injection since it out-competes detrimental triplet–triplet annihilation processes, and (ii) the system efficiency is expected to be less susceptible to the defects such as those associated with the imperfections in microcrystalline structures.⁴⁹ Also, it has been demonstrated in solution that without a driving force triplets will remain in their initial triplet host, whereas if an energy cascade were built, the triplets can be separated and the triplet lifetimes will be increased significantly (20-50 μ s).⁵⁰ However, the mechanism of iSF is not understood clearly and more work in such systems would be very useful in this field.

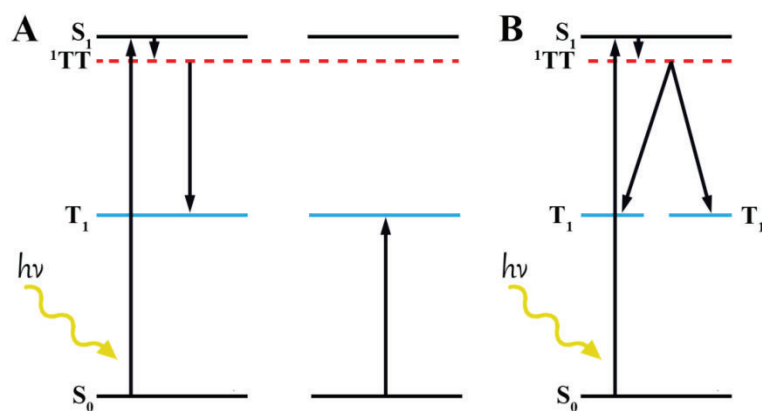


Figure 2.11. State diagram of two chromophores showing A) intermolecular singlet fission and B) intramolecular singlet fission

2.6. Reported SF compounds

Only a limited number of compounds are known to undergo SF. To lead to a better understanding of the SF mechanism and the design of new classes of SF materials, the existing materials that show SF properties are reviewed below.

2.6.1. Conjugated polymers

SF in conjugated polymers has been reported by several groups. However, SF in these systems is an activated process and occurs from a high singlet excited state formed by singlet-singlet annihilation. That is because in most cases the energy requirement ($E(S_1) \geq 2E(T_1)$) is not satisfied. Kraabel et al. ⁵¹ and Austin ⁵² reported SF in an isolated poly(diacetylene) chain. Also, Wohlgenannt ⁵³ showed SF in a ladder-type poly(para-phenylene). They showed that SF occurs at excitation energies higher than $2E_T$ and the singlet undergoes intersystem crossing at energies below $2E_T$. Guo et al. ⁵⁴ investigated SF in polythiophene films with different regioregularities. They found no triplet formation in highly ordered RR-P3HT films (Figure 2.12b)

while triplets are formed by SF in RRa-P3HT film (Figure 2.12a) where the π conjugation plane of the main chain is not ordered. Poly (3-dodecylthienylenevinylene) showed SF in both film and solution states. However, the triplet lifetime in the film is longer than in solution meaning that there is less chance of triplet recombination in the solid state compared to the solution where they can move freely.

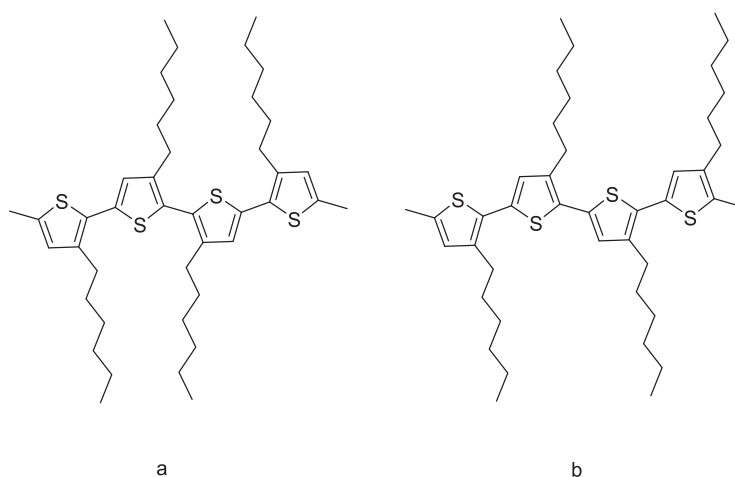


Figure 2.12. The chemical structure of a) RRa-P3HT and b) RR-P3HT film

2.6.2. Diketopyrrolopyrrole (DPP) derivatives

DPP derivatives have been demonstrated to meet the energy level requirement for SF. Wasielewski et. al⁵⁵ studied three DPP derivatives with phenyl (3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione, PhDPP), thienyl (3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione, TDPP), and phenylthienyl (3,6-di(5-phenylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione, PhTDPP) aromatic substituents in 100–200 nm thin films by time-resolved spectroscopic techniques; the structures are shown in Figure 2.13. Their results showed efficient SF only in TDPP and PhTDPP (with the triplet formation occurring in $k_{SF} = 220 \pm 20$ ps). This result is consistent with the greater degree of π -overlap and closer π -stacking in

TDPP and PhTDPP relative to PhDPP and demonstrates that SF in DPP is highly sensitive to the electronic coupling between adjacent chromophores. The results revealed that SF is nearly quantitative in PhTDPP films and that DPP derivatives are a promising class of SF chromophores for enhancing photovoltaic performance.⁵⁵

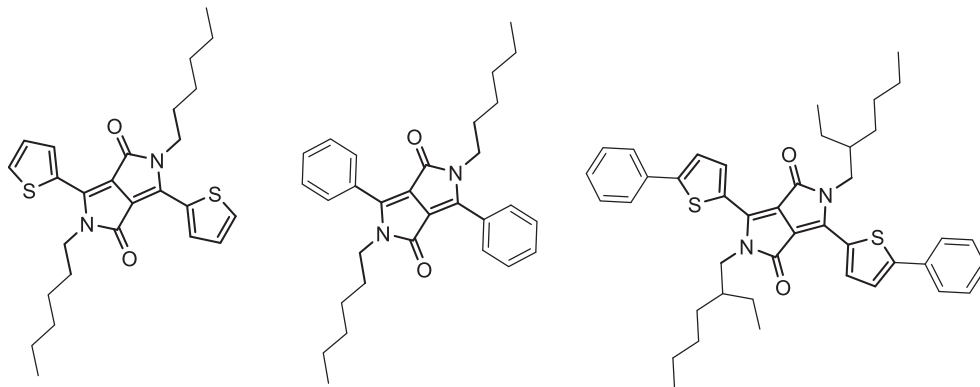


Figure 2.13. The chemical structure of DPP derivatives from left to right (1) 3,6-bis(thien-2-yl) DPP (TDPP), (2) 3,6-diphenyl-DPP (PhDPP) and (3) 3,6-bis(5-phenylthien-2-yl)-DPP (PhTDPP)

2.6.3. Perylenediimides (PDIs) derivatives

Perylenediimides (PDIs), in contrast to the acenes, have many properties that make them suitable for light harvesting applications.⁵⁶ They are photostable, resistant to photooxidation, have low production cost and display large molar extinction coefficients in the range of $5\text{-}10 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.⁵⁷⁻⁶¹ They also meet the energy level requirement for SF with reported triplet energy levels around 1.1 eV, suggesting PDIs as ideal chromophores for SF-based light harvesting applications. Calculations have predicted that SF in PDI dimers arranged into appropriate slip-stacked geometries can display high triplet yields⁴⁴ and rates of subpicosecond,^{42, 62} and experiments have demonstrated SF occurring in PDI thin films on a 180 ps time scale.⁵⁷

2.7. Designing new singlet fission chromophores

There are two considerations in the challenge of finding an efficient singlet fission system. The first is finding the right chromophore structure to maximize the singlet fission rate while minimizing the rate of reverse processes. The chromophore also needs to meet the energy level requirement, that is $E(S_1) \geq 2 \times E(T_1)$. The second is finding the right chromophore packing. The question in relation to this is how the neighbouring chromophores should be coupled. This is a challenging question as dissociation of the triplets is required for use in device applications; strong coupling is needed to make SF fast whilst a weakly coupled system is required to produce two free triplets.

2.7.1. Choice of chromophore structure

For most of the organic chromophores, the S_1 and T_1 states splitting is about twice the exchange integral that is called k_{hl} .¹ The physical significance of this parameter is the repulsion of two identical overlap charge densities, defined by the product of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Thus, most of these repulsions will be between charges located on the same atom. Organic chromophores capable of SF have large splitting between the S_1 and T_1 states, and so they should have more orbital overlap between the HOMO and LUMO in contrast to organic chromophores capable of thermally activated delayed fluorescence (TADF), where there is small orbital overlap between the HOMO and LUMO with a small splitting between the S_1 and T_1 states. It is suggested that in alternant hydrocarbons (hydrocarbons devoid of odd-membered rings), molecular orbitals occur in a pair of equal and opposite energy, and two paired orbitals have the same amplitudes with opposite sign on each atom. Thus, the overlap in this class of compound is maximum. The

HOMO and LUMO are inevitably paired in electroneutral alternant hydrocarbons so alternant hydrocarbons with an even number of carbons in the conjugated system have large k_{H} and that is why all compounds capable of SF were even-carbon alternant hydrocarbons in the first discovery of SF.⁶³ In order to find an efficient singlet fission chromophore, it is necessary to evaluate the S_0 , T_1 , S_1 and T_2 energies of candidate structures by a computational method. Time-dependent density functional theory (TD-DFT) is a method to calculate the energy levels accurately. The S_0 and T_1 state energy and geometry can be optimized using the DFT method. Optimized excited-state energies for S_1 and T_2 states were calculated using the TD-DFT method.⁶⁴

2.7.2. Donor-acceptor motif for intramolecular SF

Busby et al.⁴⁶ reported a new strategy for designing compounds that undergo intramolecular singlet fission, that is coupling two strong acceptor units with a low-lying triplet state with an appropriate donor, see Figure 2.14. This strategic design meets two main requirements for efficient iSF: i) a reduced singlet-triplet pair gap such that it matches the energy level requirement, and ii) the lowest-lying excitation has CT character that can mediate the singlet fission process. It is relatively straightforward to design and control intramolecular CT states in small molecules or polymers based on alternating donor and acceptor building blocks.⁴⁶ It has been shown that a material composed of alternating electron-rich (strong donor) moieties and electron-deficient (strong acceptor) units will contain a significant charge-transfer character in the lowest energy optical excitation.⁶⁵ The donor-acceptor model not only takes the advantage of providing an excited electronic state with significant charge-transfer character but also allows us to choose units based on the energy level requirement.



Figure 2.14. Acceptor-Donor-Acceptor motif strategy proposed by Busby et. al.⁷

Busby et al. reported highly efficient intrachain SF in a push-pull low band gap polymer comprising benzodithiophene (B) as the electron-rich unit and mono-thiophene-1,1-dioxide (TDO1) as strong electron acceptor, see the structure below (Figure 2.15).

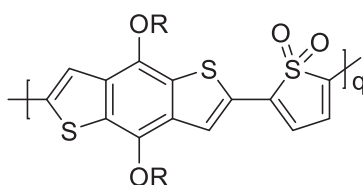


Figure 2.15. The chemical structure of P-B(TDO1)

Again based on this strategy, Kasai et al.⁶⁶ found SF in a push-pull low band gap polymer film, poly [(dodecyl-thieno-thiophene-2-carboxylate)-alt-2,6-(4,8-dioctylbenzodithiophene)] (PTB), see the structure below. It consists of benzodithiophene (B) as the electron-rich unit and as dodecyl-thieno-thiophene strong electron acceptor.

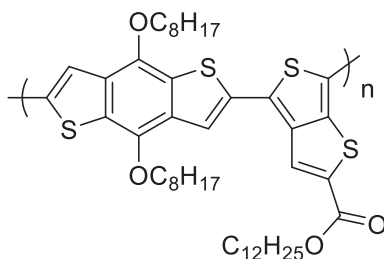


Figure 2.16. The chemical structure of PTB

Exploiting a molecular design based on the intramolecular donor-acceptor approach allows variation of the electron withdrawing building block to be used to tune the singlet

energy level relative to the triplet energy level to meet SF energy level requirements. This molecular design leads to a new series of compounds capable of singlet fission for third generation optoelectronic devices. For inclusion in organic solar cell devices, it is also desirable that the SF material can be solution processed, and in addition promote singlet fission in the solid state. This is important as many of the recent studies on SF materials have been carried out in solution and either studies in the solid state have not been undertaken or the materials do not show SF in the solid state.^[22, 34]

2.7.3. Choice of chromophore packing

SF through direct coupling

For SF through direct coupling in a dimeric composite system, the SF rate $[S_1S_0 \rightarrow T_1T_1]$ is proportional to the square of the matrix element $\langle S_1S_0 | H_{el} | T_1T_1 \rangle$ described below:

$$\langle S_1S_0 | H_{el} | T_1T_1 \rangle = \left(\frac{3}{2}\right)^{1/2} [\langle l_A l_B | e^2/r_{12} | h_B l_A \rangle - \langle h_A h_B | e^2/r_{12} | l_B h_A \rangle] \quad (1)$$

where H_{el} is the electrostatic Hamiltonian and l_A , l_B , h_A and h_B are the LUMO and HOMO orbitals of two chromophores A and B. To design a dimer structure with fast singlet fission by direct coupling, one should consider the physical interpretation of these repulsion integrals. Each electron repulsion integral ($\langle l_A l_B | e^2/r_{12} | h_B l_A \rangle$ and $\langle h_A h_B | e^2/r_{12} | l_B h_A \rangle$ (l_1 and l_2) represents the electrostatic interaction between two overlap charge densities. Such overlap densities can only be significant in regions of space where the orbitals of the chromophores A and B overlap. As shown in the first column of Figure 2.17, if the stacking is perfect, there is as much attraction as there is repulsion, and two integrals (l_1 and l_2) cancel each other. However, if the stacked molecules are mutually shifted in the direction of the HOMO to LUMO transition

moment like the one shown in the second column of Figure 2.17, the cancellation is no longer perfect and the two integrals differ in sign, which results in a nonzero integral. When the chromophores are connected by a linker in a planar or twisted mode, all four overlap densities are only confined to the region of the connecting bond. Thus, if the amplitudes of the four MOs at the regions where A and B are linked are large, the matrix element could be large. As a result, to have large overlap densities and fast singlet fission by direct coupling in linearly linked chromophores, two π -electron chromophores should be linked by a planar direct connection with a short distance between strongly overlapping orbitals of directly connected atoms.¹

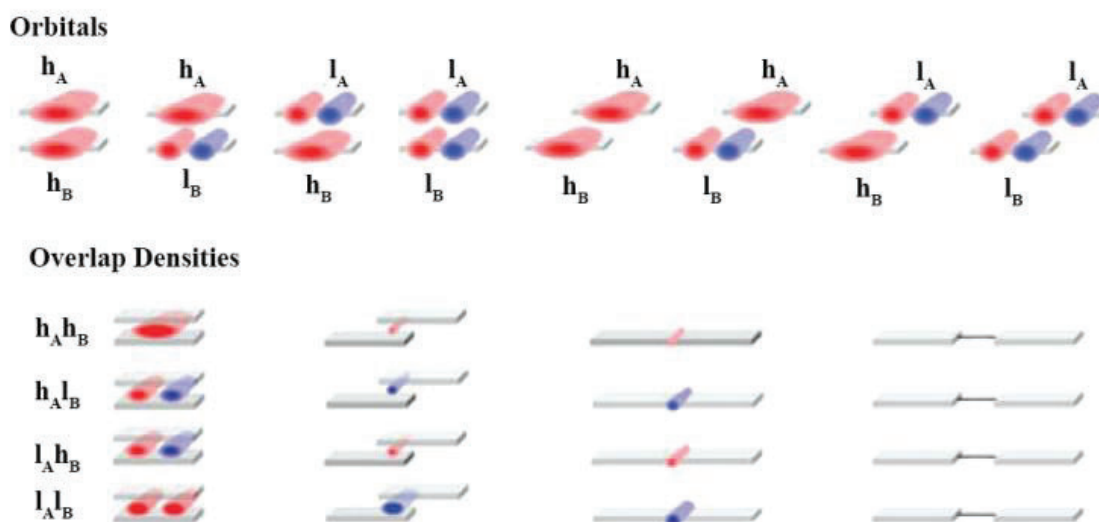


Figure 2.17. Schematic diagram of orbitals for stacked and slip-stacked dimer, and their overlap densities for stacked, slip-stacked, directly and indirectly linearly linked geometries derived from reference¹ with permission

SF mediated through charge transfer (CT) state

If the charge transfer state that can mediate SF is low in energy, the rate of SF consists of two parts: i) the coupling of S_1S_0 with the charge transfer states of $^1(C^A A^B)$ or $^1(A^A C^B)$ through

the $\langle {}^1\text{CA} | H_{\text{el}} | S_1 S_0 \rangle$ or $\langle {}^1\text{AC} | H_{\text{el}} | S_1 S_0 \rangle$ element and ii) the coupling of (${}^1\text{CA}$) or (${}^1\text{AC}$) with the correlated triplet pair ${}^1(\text{T}_1\text{T}_1)$ state through the $\langle {}^1\text{CA} | H_{\text{el}} | \text{T}_1\text{T}_1 \rangle$ or $\langle {}^1\text{AC} | H_{\text{el}} | \text{T}_1\text{T}_1 \rangle$ element, which is shown below. In the charge transfer state C stands for the ground state of the radical cation and A for the ground state of the radical anion of one of the chromophores and F is the Fock operator of the ground state.

$$\langle \text{CA} | H_{\text{el}} | S_1 S_0 \rangle = \langle l_A | F | l_B \rangle + 2 \langle h_A l_A | e^2 / r_{12} | l_B h_A \rangle - \langle h_A l_A | e^2 / r_{12} | h_A l_B \rangle \quad (2)$$

$$\langle \text{CA} | H_{\text{el}} | \text{T}_1 \text{T}_1 \rangle = \left(\frac{3}{2}\right)^{1/2} [\langle l_A | F | h_B \rangle + \langle l_A l_B | e^2 / r_{12} | h_B l_B \rangle - \langle l_A h_A | e^2 / r_{12} | h_B h_A \rangle] \quad (3)$$

$$\langle \text{CA} | H_{\text{el}} | S_0 S_1 \rangle = -[\langle h_A | F | h_B \rangle - 2 \langle h_B l_B | e^2 / r_{12} | l_B h_A \rangle + \langle h_B l_B | e^2 / r_{12} | h_A l_B \rangle] \quad (4)$$

In contrast to what is found for the case of singlet fission by direct coupling, the matrix elements might be favoured by direct linking of the chromophores A and B, as opposed to their stacking. Thus, symmetric and planar dimerization of an alternant hydrocarbon in its most reactive position seems to be a good candidate to design a dimeric system capable of fast singlet fission mediated by CT state. Unfortunately, there are some difficulties with this choice, as mentioned above. Converting the chromophores A and B into a single chromophore through direct conjugation disturbs the energy level matching of the singlet and triplet in the dimer by reducing the excitation energy of the S_1 state and decreases the ability of the dimer to support two triplet excitations.¹ The information on intrinsic singlet fission rates of different chromophores is summarized in table 1.

Table 1. The best candidate and potential difficulties of chromophores for fast SF

Type of chromophore	Direct coupling	Mediated by CT state
---------------------	-----------------	----------------------

Best candidate	✓ Stacked pairs shifted in the direction of dipole moment ✓ Linearly linked chromophores by a planar direct connection	✓ Symmetric and planar dimerization of an alternant hydrocarbon ✓ strong electronic coupling of CT- and Frenkel exciton-like electronic states
Potential difficulty	✓ Disturbing the energy level matching by direct linking of chromophores ✓ Low ability of linearly linked dimer to support two triplets ✓ Unfavorable charge transfer state energy of linearly linked dimer	✓ The same problem as direct coupling difficulties

2.8. Conclusion and outlook

A limited number of organic chromophores have the required properties to undergo SF. SF has the potential to increase the PCE of PV devices so these chromophores have received a great deal of attention recently. However, the known SF materials are not suitable for PV applications, for several reasons, and there is a need to design and study new chromophores for SF. The question is; what should be the rules to design new materials. The first requirement for SF is the energy level e.g. ($E(S_1) \geq E(T_1)$). There are many other requirements which have been discussed in this chapter in detail. This thesis reports my investigations of the new strategy towards this goal, that is, to use a Acceptor-Donor-Acceptor motif. Based on this strategy, I

designed, synthesized and investigated the SF properties of small molecular (BDT(DPP)₂) and polymeric (P-BDT-DPP) systems and the results are discussed in detail in chapter 4. The approach of increasing the self-assembly of an acceptor-donor-acceptor motif through exploiting the properties a core molecule were explored by studying FHBC(DPP)₂ and the results are discussed in detail in Chapter 5. Finally, in the last chapter, the rules to build an efficient intermolecular SF material are investigated.

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Chapter 3

Experimental Methods

3.1. Introduction

In order to design and optimize new materials capable of SF, it is necessary to know when SF is occurring and with what efficiency. SF is a spin-allowed process and occurs very quickly on the femtoseconds to nanoseconds timescale. It is suggested that SF quenches the singlet excitons through the formation of a triplet pair state. In principle, various steady-state and time-resolved spectroscopy techniques should be able to provide information about the yields and lifetimes of these states.¹ It is required to study the dynamics of excited states with an optical technique that is shorter in time than the dynamic process of interest. However, several challenges exist for the investigation of SF in organic materials. Firstly, triplet excitons are mostly dark states at room temperature since the triplet radiative transition to the ground state cannot compete with other non-radiative depletion processes, so they can rarely be detected by photoluminescence measurements. Ultrafast transient absorption (TA) spectroscopy has been demonstrated as a useful technique for investigating and characterizing photophysical properties of many classes of materials. This technique is capable of probing non-emitting states, and over the timescales associated with triplet formation and decay in SF materials. There are several challenges involved in the investigation of SF materials with TA spectroscopy, will be addressed here. Organic molecules often have photoinduced absorption spectra with overlapping signatures from singlets states, charged intermediates, excited state

aggregates, thermal artefacts and electro-absorption features. charged intermediates and excited state aggregates can form rapidly (sub-100 fs) and thus act as relaxation channels that compete with SF, along with radiative and non-radiative decay to the ground state. These artefacts can cause long-lived spectral features, making the identification of triplets challenging and leading to the potential misinterpretation of spectra. Some methods have been used to make assignment of triplets easier such as triplet sensitization and oxygen quenching of triplets. In this chapter, the sample preparation, steady-state and time-resolved spectroscopic techniques that have been employed during this thesis are described in detail. Also, in order to find more information about the triplet dynamics, nanosecond transient absorption (ns-TA) measurements can be a useful optical technique and is also discussed in detail later.

3.2. Sample preparation

3.2.1. BDT(DPP)₂ and P-BDT-DPP

Both BDT(DPP)₂ and p-BDT-DPP were synthesized using palladium-catalysed Suzuki coupling reactions of di-borylated-BDT with DPP-Br and Br-DPP-Br, respectively.² The detailed experimental procedure and full characterization of all new materials are presented in the Supplementary Information of Chapter 4.

Glass substrates with dimensions of 2.5 cm × 2.5 cm × 0.1 cm were cleaned by sonicating sequentially in acetone, isopropanol and chloroform. Before thin film casting, the substrates were dried with a strong flow of nitrogen and then subjected to UV/ozone treatment for 30 min. Solutions of BDT(DPP)₂ or p-BDT-DPP were prepared by dissolving the samples into chloroform with a concentration of 1 mg/100 μL, respectively. To prepare blend films for

sensitized experiments, solutions of BDT(DPP)₂ or p-BDT-DPP in chloroform mixed with palladium octaethyl porphyrin (PdOEP), were prepared by dissolving the compounds with mass ratio of 60:40 (sensitizer:organic dye). Solutions were then set to stir overnight in the dark under ambient conditions. Finally, thin films were cast onto clean glass substrates via spin coating at 1000 rpm/s and spun for 1 min.

3.2.2. FHBC(TDPP)₂

FHBC(TDPP)₂ was obtained from Dr. Wallace Wong for initial studies and a second batch was prepared according to the published procedures.³ The detailed experimental procedure and full characterization of all new materials are presented in the Supplementary Information of Chapter 5.

Glass substrates with dimensions of 2.5 cm × 2.5 cm × 0.1 cm were cleaned by sonicating sequentially in acetone, isopropanol and chloroform. Before thin film casting, the substrates were dried with a strong flow of nitrogen and then subjected to UV/ozone treatment for 30 min. Solutions of FHBC(TDPP)₂ were prepared by dissolving the samples into chloroform with a concentration of 5 mg/mL. To prepare blend films for sensitized experiments, solutions of FHBC(TDPP)₂ in chloroform mixed with palladium octaethyl porphyrin (PdOEP), were prepared by dissolving the compounds with mass ratio of 50:50. Finally, thin films were cast onto clean glass substrates via spin coating at 1000 rpm/s and spun for 1 min. The thermally annealed film was prepared by putting the as-cast film on the top of a hot plate with the temperature of 120° C for 10 min., then the film was allowed to cool down to room temperature slowly.

3.2.3. PDI derivatives

The synthesis procedures of PDI derivatives (1-4) have been reported in the literature.⁴⁻⁶ Preparation of PDI1-2 is credited to Dr. Bolong Zhang and PDI3-4 is performed by Dr. Mark A. Gregory. Palladium octabutoxyphthalocyanine ($\text{PdPc}(\text{OBu})_8$) was synthesized following the literature procedure.⁷ The detailed experimental procedure and full characterization of all new materials is presented in the Supplementary Information of Chapter 6.

Glass substrates with dimensions of 2.5 cm $\times$ 2.5 cm were cleaned by sonicating sequentially in acetone, isopropanol and chloroform. Before thin film casting, the substrates were dried with a strong flow of nitrogen. Solutions of PDIs were prepared by dissolving the samples into chloroform at a concentration of 5 mg/mL. To prepare blend films for sensitized experiments, solutions of PDI mixed with $\text{PdPc}(\text{OBu})_8$ were prepared by dissolving PDI and $\text{PdPc}(\text{OBu})_8$ with mass ratio of 50:50 in chloroform with the concentration of 5 mg/mL. Finally, thin films were cast onto clean glass substrates via spin coating at 1000 rpm/s and spun for 1 min.

Crystalline films were prepared by solvent vapor annealing (SVA) of the films, whereby chloroform was injected into a 30 mm glass Petri dish. The Petri dish was closed for 1 min to let the vapor saturate the treatment chamber. Then as-cast films were attached to the backside of a second Petri dish lid, which was quickly swapped with the lid covering the solvent-containing Petri dish. The film was about 1 cm above the solvent level during the SVA. The optimal duration of SVA treatment used in this study was 60 s.⁸

3.3. General material characterization

3.3.1. NMR and mass spectroscopy

^1H and ^{13}C NMR spectra in this thesis were recorded on the Agilent MR400 (400 MHz) spectrometer. All NMR spectra were measured at room temperature (25 °C) and internally calibrated against residual undeuterated solvent as reference. MALDI-time-of-flight mass spectrometry was performed on a Bruker microFLEX MALDI-TOF in reflector positive mode, using trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix.

3.3.2. Cyclic voltammetry

Cyclic voltammetry (CV) experiments were performed at a sweep rate of 100 mVs⁻¹ (Solartron). The supporting electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in DCM. The solutions were deoxygenated by sparging with argon prior to each scan and blanketed with argon during the scans. The glassy carbon working electrode was prepared by polishing with 5mm alumina, washed and dried. The ferrocene/ferrocenium redox couple was used as a standard. The HOMO and LUMO energy levels were calculated from the onset of the oxidation and reduction potential of the compounds as: $E(\text{HOMO}) = -(E_{1/2, \text{ox vs Fc}^+/ \text{Fc}} + 5.1) \text{ eV}$ and $E(\text{LUMO}) = -(E_{1/2, \text{red vs Fc}^+/ \text{Fc}} + 5.1) \text{ eV}$.

3.3.3. Crystal structure determination

Single-crystals of PDIs were grown by slow diffusion of methanol or isopropanol vapor into the solution of chloroform. The single-crystal X-ray data for PDI3 were collected at 100 K on

the MX1 beamline at the Australian Synchrotron.⁹ The structures of PDI1 and PDI4 were collected at 100K on a Rigaku Synergy diffractometer. The structures were solved by direct methods and difference Fourier synthesis. Thermal ellipsoid plots were generated using the program ORTEP-3 integrated within the WINGX suite of programs.¹⁰ The crystal data for PDI2 were published in our previous report.⁴ Structures for PDI1, PDI3 and PDI4 have been deposited at the CSD and assigned CCDC deposit codes are 1949528, 1958260 and 1958261, respectively.

3.3.4. Thin film characterization

Samples for grazing incidence wide angle X-ray scattering transmission measurements were prepared by loading the materials onto silicon wafers. The samples were analyzed at the SAXS/WAXS beamline at the Australian synchrotron with an X-ray energy of 10 keV.¹¹ A Pilatus 200K detector was used for wide-angle measurements. The substrates were silicon wafers that had been sonicated in acetone and isopropanol for 30 min each followed by 30 min of UV/ozone treatment. The beamline has a range of incident angles from $\Omega = 0.02$ – 0.35 in 0.005 increments to allow signal optimization near the critical angle of the film but below the critical angle of the substrate. Data from GIWAXS experiments were analyzed using a customized version of NIKA 2D based in IgorPro.¹²⁻¹³

3.4. Computational details

As the first requirement of a material capable of SF is the energy of the triplets should be no more than half of the first singlet energy level, e.g. $E(T_1) \leq 0.5 * E(S_1)$, estimating the first singlet and triplet energy levels for potential SF materials is a very important and challenging

aspect. TD-DFT calculations made this estimation possible. I performed TD-DFT calculation for all of the potential SF materials in this thesis before material synthesis to check whether they meet at least the energy level requirement.

All calculations were performed with the Gaussian09 program Rev. E.01.¹⁴ The geometry optimization of the ground state was carried out using dispersion-corrected density functional theory (DFT) at the TPSS-D3(BJ)^{15,16,17}/6-311G(d)¹⁸ level of theory and the environmental effects have been taken into account through the polarizable continuum model (IEFPCM)¹⁹. In order to reduce computational costs, the long side chains in the compound were replaced by methyl groups, as the length of the alkyl chains has no significant impact on the optical properties.²⁰ Vertical excitation energies and partial atomic charges of the electronically states were calculated via time dependent density functional theory within the Tamm-Dancoff Approximation (TDA-DFT)²¹ using the CAM-B3LYP²² range-separated hybrid functional approximation and the 6-311G**¹⁸ atomic-orbital basis set and IEFPCM based on the optimized geometry. A range-separated density functional approximation was chosen to ensure that potential charge-transfer (CT) states could also be appropriately treated. Moreover, it has been shown that this method is one of the most accurate hybrid functional approximations with an expected accuracy of 0.18 eV for medium-sized and large chromophores.²³ The pairs of hole and electron natural-transition-orbitals (NTOs)²⁴ for the S_1 and T_1 states were calculated to assess the CT and locally excited (LE) contribution of each excited state. DFT and TD-DFT calculation of partial atomic charge (PAC) were conducted using the Merz-Kollman (MK)²⁵ scheme. The method to define the CT distance (d_{CT}), the transferred charge (q_{CT}), the dipole

(μ_{CT}) and H index based on the partial atomic charges is discussed in detail in the supplementary information, and is similar to the procedure described by Jacquemin et al.²⁶

For FHBC(TDPP)₂, the geometry optimization of the ground state was carried out using Turbomole version 7.3^[27] with the efficient hybrid-DFT model PBEh-3c^[28] under inclusion of the continuum solvation model COSMO^[29] to simulate the effects of chloroform as a solvent. Vertical excitation energies were calculated via time dependent density functional theory within the Tamm-Dancoff Approximation (TDA-DFT)^[21] using the CAM-B3LYP^[30] range-separated hybrid functional approximation and the 6-311G**^[18] atomic-orbital basis set based on the optimized geometry with the Gaussian09 program Rev. E.01.^[31]

3.5. Steady state measurements

3.5.1. Absorption measurements

Steady state absorption spectra were recorded using a Varian Cary 50 UV-vis spectrophotometer. Solution measurements were recorded using quartz cuvettes of 10 mm path length. All spectra were baseline corrected using a solvent or blank film.

3.5.2. Photoluminescence measurements

Fluorescence spectra in the visible region were recorded on a Varian Eclipse spectrofluorimeter. Solution measurements were recorded in diluted samples to allow both sufficient excitation light penetration and to minimise re-absorption of emitted fluorescence using quartz cuvettes of 10 mm path length. For film measurements, films were positioned on a

home-built film holder with back face illumination to avoid excitation light reflection towards the detector.

Photoluminescence (PL) spectra in the near-IR region were recorded with a spectrometer (Horiba Jobin Yvon iHR320) and an amplified InGaAs photo-detector (Electro-Optical System). The excitation source was a supercontinuum laser (NKT Photonics, SuperK Extreme) for excitation wavelengths tunable across the 450-750 nm region. The excitation beam was mechanically chopped and the detector output was fed into a lock-in amplifier synchronized to the chopper frequency. A 750 nm high pass filter was used to remove the second order of the excitation and fluorescence. PL experiments at cryogenic temperatures were carried out in a liquid nitrogen cryostat (Oxford Instruments, Optistat DN).

3.6. Time-correlated single photon counting (TCSPC)

Time-correlated single photon counting (TCSPC) is a standard method of determining material emission as a function of time. It can measure the fluorescence decay in the range of tens of picoseconds to microseconds. Specifically, this method can be used for determining lifetimes of excited states which are radiatively coupled to the ground state. The excitation pulse produces a correlated electrical trigger pulse (usually using a photodiode). This trigger (after passing through a constant fraction discriminator) serves as the 'start' input for a time-to-amplitude converter (TAC) which initiates voltage ramp. When the excited sample emits a photon, this reaches the detector which produces an electrical pulse providing a suitable 'stop' signal for the TAC. The amplitude of the TAC signal is then proportional to the time delay between the start and stop signal, giving a numerical value which is stored through an

analogue-to-digital converter (ADC). This process is repeated until a desired number of photon counts is generated in the predefined time 'bins' stored in computational memory. The generated histogram is then representative of the fluorescence decay, which has been obtained statistically from a large number of emitted photons over many iterations.³²

In this technique, the excitation source is a mode-locked and cavity dumped Ti:Sapphire laser (Coherent Mira 900F/APE PulseSwitch) pumped by a Coherent Verdi-10 DPSS Nd:YVO₄ laser. The laser output (880 nm wavelength, 5.4 MHz repetition rate) was frequency doubled to provide an excitation wavelength of 440 nm. The individual fluorescence decay curves were collected using a time-correlated single photon counting (TCSPC) module (SPC-150, Becker & Hickl, Berlin, Germany). The instrument response function (IRF) was determined experimentally by measuring the response of excitation light from a non-fluorescent weakly scattering solution of colloidal silica (Ludox). The fluorescence decay parameters were extracted from the decay profiles using FAST software (Edinburgh Instruments Ltd) and a sum of exponentials analysis.

3.7. Transient absorption spectroscopy

3.7.1. Principle of transient absorption spectroscopy

TCSPC and fluorescence up-conversion techniques are useful for determining the lifetimes of excited states that are emissive but they are inapplicable for the detection of excited states that are not radiatively coupled to the ground state. The time-resolved absorption methods are used for detection of non-emissive (dark) excited states so this is an ideal method for probing charge-transfer or free charges states and triplet excited states.

The process of singlet fission occurs on fs (10^{-15}) to ps (10^{-12}) timescales so experimental techniques with relevant time resolution are required to analyse the dynamics of this process; enabled by the advent of ultrafast transient absorption spectroscopy. This is a pump-probe technique in which pulses of a pump laser excite the sample and the transmission of pulses from a second laser source is monitored to probe the absorption changes due to the production of short-lived photo-induced species in a solution or film sample. The pump and probe beams are generated by the same laser source, which is described later, to ensure the synchronicity between the pump and probe pulses. The probe can be of either a single wavelength or a broad spectrum so that an entire spectrum can be measured. In the system used here a femtosecond white light continuum is used and a high repetition rates spectrometer/detector is used to measure the transmitted signal intensity of the probe. The transient absorption is derived from the difference between the pump-on (A_{ex}) and pump-off (A_{unex}) absorption signals. The pump-off absorption is the ground state absorption while the pump-on is affected by the ground state absorption as well as those molecules that have been excited.

$$\begin{aligned}\Delta A &= A_{ex} - A_{unex} \\ &= \left(-\log\left(\frac{I_{ex}}{I_0}\right) \right) - \left(-\log\left(\frac{I_{unex}}{I_0}\right) \right) \\ &= -\log\left(\frac{I_{ex}}{I_{unex}}\right)\end{aligned}$$

where I_0 is the intensity of light incident on the material, I_{ex} is the intensity of transmitted light with the pump on and I_{unex} is the intensity of transmitted light with the pump off.

ΔA can be measured at different time delays to obtain $\Delta A(\lambda, t)$ at each delay point. A typical 3D transient absorption data set is illustrated in Figure 3.1 and by selecting a particular wavelength, or a certain delay time, the kinetic traces at a given wavelength and the full spectrum at the given time can be analysed.

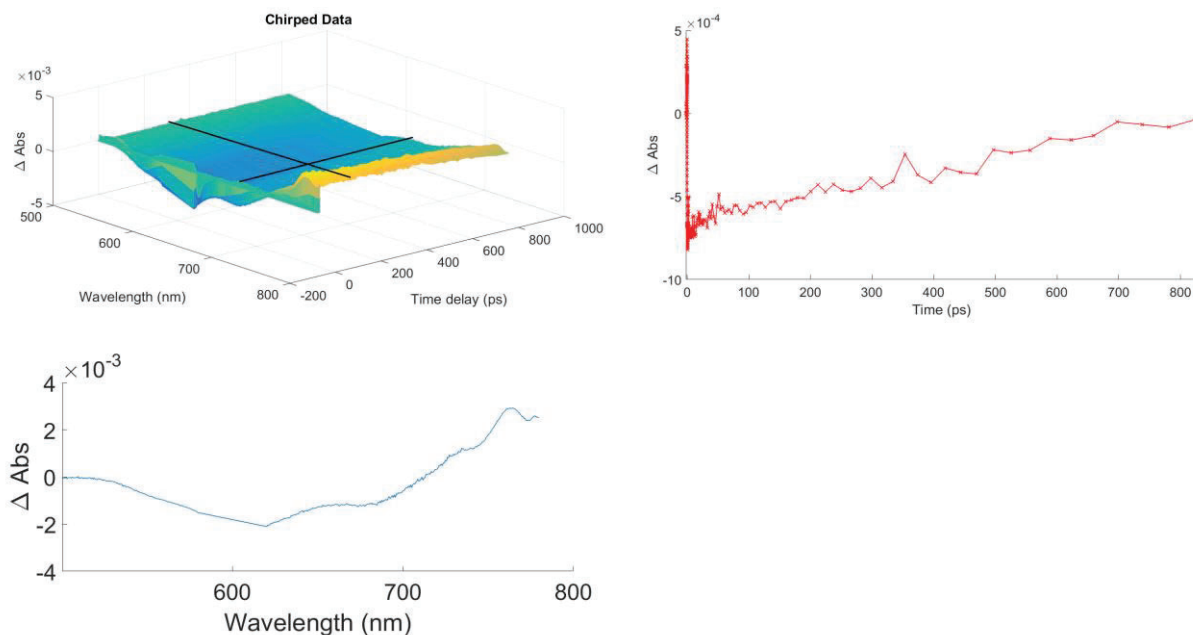


Figure 3.11. An example of a) 2D transient absorption data surface, with b) kinetic traces at a specific wavelength and c) spectral slices at specific time

A transient absorption spectrum may consist of three types of signal as shown in Figure 3.2. Two possible negative-going signals are assigned to the ground state bleach (GSB) and stimulated emission (SE) due to the increase in the number of photons detected following excitation, compared to the unexcited sample. The GSB signals are due to the ground state depletion after excitation and resemble the steady state absorption spectrum of the sample and contain useful information about the recovery time of the ground state.

The second potential negative area is SE that can occur when the probe pulse is resonant with a radiative electronic transition. This signal resembles the fluorescence spectrum of the sample. This signal is only observed when the first excited state is strongly optically coupled to the ground state. This signal contains useful information on the kinetics of the first excited singlet state (S_1).

The positive $\Delta A(\lambda, t)$ signal in Figure 3.2 is assigned to the photo induced absorption (PIA) that will arise from the electronic transition from the initially formed excited state to higher energy levels. These excited states can be populated directly from the pump-induced absorption e.g. S_1 , or they may result from other processes such as triplet formation or electron transfer. The PIA signal can be detected if the excited state absorbs light within the wavelength range of the probe beam.

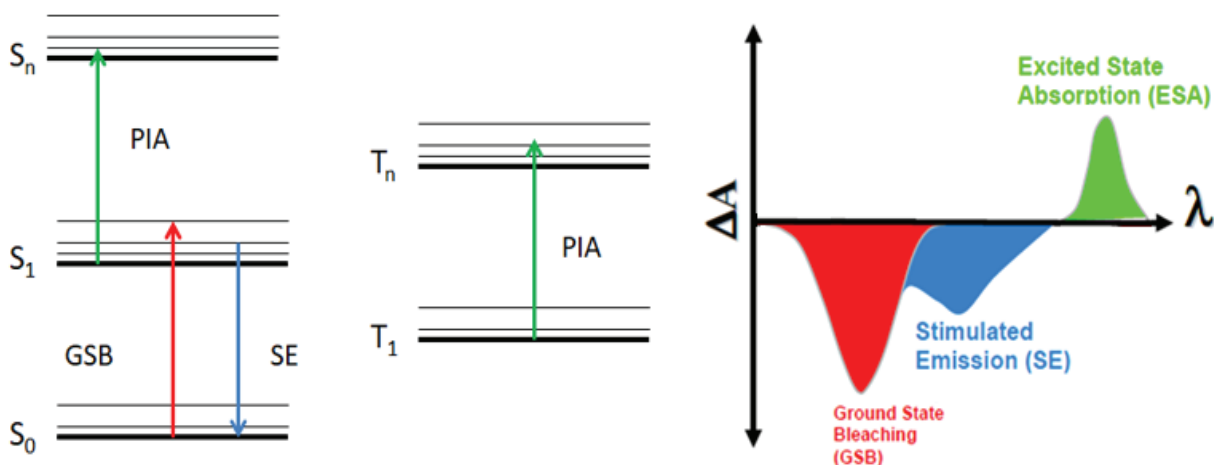


Figure 3.12. Possible transitions in a transient absorption experiment and corresponding observed signals

3.7.2. Experimental set-up of ultrafast transient absorption

The laser source for the transient absorption setup was a mode-locked Ti:sapphire oscillator (Coherent, Mira Seed) pumped by a green (532 nm) CW diode-pumped laser (Coherent, Verdi V18 or G20). A pulse shaper using a spatial light modulator (SLM) (MIIPS Box 640, Biophotonic Systems) was used on the seed to adjust the spectral phase and pulse shape of the seed beam. The oscillator output was then directed to a pulse expander (Coherent, EC9150) to stretch the pulses and reduce their peak power before they were used to seed a Ti:sapphire regenerative amplifier system (Coherent, RegA 9050). After typically 16 roundtrips, the pulses were ejected by the cavity dumper at a repetition rate of 92 kHz and a wavelength centered at 800 nm. The output was then finally recompressed (Coherent, EC9150) to produce pulses of <50 fs duration.

The output of the amplifier was split using a 50:50 beam splitter to direct half of the output to continuum generation for use as the probe pulse. The remainder was passed into an OPA (optical parametric amplifier) (Coherent, OPA9450) where the light was either frequency doubled with a BBO (barium borate) crystal or parametrically amplified to produce other pump wavelengths in the range from ~490-750 nm. The resultant pump beam was mechanically chopped (Thorlabs, MC1000/MC1F60) at 4.6 kHz, and the arrival time of the pump pulses relative to the probe was manipulated using a variable optical delay line (Newport, UTS150PP with ESP 300 controller). The broadband probe was derived from the residual 800 nm beam focused onto a 3 mm sapphire substrate (Crystal Systems) for measurements in the visible

region (450–800 nm) and a 5 mm undoped YAG substrate (Crystal Systems) for the infrared region (800–1400 nm).

The broadband probe so called white light is a possible source of noise in the transient absorption spectroscopy so optimizing and controlling the stability of white light generation is of importance to generate highly sensitive transient absorption measurements. Several parameters are important for generating stable white light. Bradler et al. have comprehensively reviewed many of these for white light generation in different bulk media.³³ Commonly used bulk materials for white light generation include single crystals of sapphire (Al_2O_3), calcium fluoride (CaF_2), yttrium aluminium garnet (YAG), yttrium vanadate (YVO_4), gadolinium vanadate (GdVO_4) potassium-gadolinium tungstate (KGW), and $\text{D}_2\text{O}:\text{H}_2\text{O}$ (7:1 mixture).

Despite the high repetition rate of our system, more than adequate pulse energies were available for supercontinuum generation. Between 100 and 300 nJ per pulse was required of the 800nm pulse for optimal supercontinuum generation with the sapphire and YAG crystals. For optimisation of the continua, the 800nm beam was carefully adjusted with a continuous neutral density (ND) filter.

Multifilamentation can also provide the source of unwanted artefacts within a transient absorption experiment. Non-optimal alignment of the pump and probe at the sample can result in some parts of the probe experiencing greater pump intensities (within its Gaussian distribution) than others. This is not ideal but not insurmountably detrimental to an experiment. However, if the probe is spectrally inhomogeneous, then this can result in significant artefacts in the transient spectra that cannot be removed easily.

After passing through the sample, the probe beam was analysed with fibre coupled spectrometers, using a 1024 pixel CMOS detector for the visible region (9200 spectra/s for divide-by 10 acquisition), and a 256 pixel InGaAs sensor for the IR region (both Ultrafast Systems), recorded at 7077 spectra/s for divide-by 13. To achieve synchronised detection of the 92 kHz pulse train, timing electronics were employed to record spectra at 9.2 kHz (integrating over every 10 probe pulses) and chop the pump beam at half the probe detector frequency (4.6 kHz). This results in each acquired spectrum comprising the integration of ten laser pulses for either the pump-on and pump-off signals. The excess 800 nm laser fundamental was blocked using low- and high-pass filters for the visible and IR regions, respectively. Further adjustments to the visible SC's spectral shape (to maximize uniformity across the wavelength region and optimise signal-to-noise) were made using an aqueous solution of CuSO_4 after the sample where optical density could be adjusted via solution concentration.

The stage was controlled to move in a logarithmic distribution of time points over the desired range, so that large signal changes at short times could be mapped with more data points than at long time delays to minimize data acquisition time. The relative orientation of the pump and probe polarization was 54.7° .

For samples in solution, stoppered glass cuvettes with a 2mm path length were used and were stirred with a magnetic stirrer bar coupled to an externally motor-mounted magnet (magnetic stirring system, Ultrafast Systems). For film measurements, the sample was translated in a raster pattern in x and y by two stepper motors (Oriel StepperMike, and Phidgets stepper controller 1602) with every movement of the delay stage to avoid photodegradation of

the film that would occur after an entire experiment. Nitrogen gas flow over the sample was used to further minimize sample degradation and effects of oxygen. For the majority of the measurements reported here, the pump beam was attenuated to a pulse power of $10 \mu\text{J}/\text{cm}^2$, to reduce artefacts associated with exciton-exciton and exciton-charge annihilation.

Following an experiment, data were processed using MATLAB codes, also developed in-house. A discrepancy beyond a certain threshold value would result in the exclusion of that data point. A transformation was applied to correct for the 'chirp' of the probe pulse, the wavelength dependent pump-probe delay that corresponds to the temporal overlap of pulses in the sample due to the spectral width of the probe. This wavelength dependence is mainly due to the group velocity dispersion (GVD) of the broadband pump and is more pronounced in the visible region than the IR. Chirp correction was implemented by examining the first few picoseconds of the experimental data. A cross correlation routine was applied and a 3rd order polynomial was fit to the chirped surface. The data were subsequently shifted by the appropriate temporal offset at each wavelength to produce the corrected dataset.

Further details about the setup can be found in reference.³²

3.7.3. Experimental noise and error in transient absorption

The first sources of noise in the transient absorption experiments are fluctuation in the probe pulse, fluctuation in the pump pulse energy and readout noise in the detection systems. The first requirement for having an experiment with good signal-to-noise is having an extremely stable laser. Bradler et al. reviewed the correlation of energy fluctuations in broadband white light generation (in a YAG crystal) with that of the seed laser, and found a slight amplification

occurred during the generation process.³³ The non-linear processes that take place in the SHG/OPA generation for the pump, and supercontinuum generation for the probe, are extremely sensitive to mode quality, beam alignment and environmental conditions so non-optimal conditions can also introduce significant noise into the experiment. Noise arising from the detection system is also very important. In low excitation density measurements such as carried out here, the low population of the excited state can only attenuate the probe transmission intensity by a small amount compared to the noise of the signal so for such a measurement, high probe light intensity is required to fill photodiode bins. Other sources of noise may originate from the chopper, stirrer bar or inhomogeneity of the film and other environmental noise which should be minimized for a sensitive measurement. To improve the sensitivity of transient absorption measurements, other than minimizing the noise, averaging and maximizing the number of samples should be considered. This increased sensitivity through averaging is the main advantage of a high repetition rate instrument used in this work.

3.7.4. Signal assignment

Transient absorption spectroscopy detects different spectroscopic features which can have overlapping signals. In organic candidates for singlet fission, singlet excitons, correlated triplet pairs, free triplets, excited state aggregates, or charge transfer states can be detected. Some of these signals may be sensitive to their surroundings. Understanding the singlet fission mechanism requires accurate interpretation of the spectroscopic data although this is very challenging. Some elements of the signal assignment are clarified and critically reviewed here to help in the interpretation of the reported transient spectra.

The photo-induced absorption (PIA)

PIA is a positive signal caused by the absorption of the excited states in the spectral area. Generation of the first singlet excited state (S_1) is the first process that occurs in singlet fission materials. Matching decay rates of the photo-induced absorption signal with the ground state bleach signal dynamics suggests that the first singlet exciton generation is the only excited state depopulation process occurring i.e. no additional excited states are involved. The lifetime of the exciton can be obtained from the temporal decay of these signals. A stimulated emission feature can also provide information on the lifetime of the first singlet exciton although in most cases this negative signal has an overlap with other transient signals. In order for charge generation to proceed efficiently, its rate must compete with that of the exciton decay. Reduced exciton lifetimes can indicate quenching via triplet formation which may be accompanied by the appearance of another positive absorption band.

Ground state bleach (GSB)

The GSB is a negative signal that resembles the steady state absorption spectrum of the material mirrored. The GSB contains information on what is happening in an organic chromophore. The dynamics of the ground state depletion recovery provides valuable information on all the excited state processes occurring in a material. A partial decay of the GSB on the same timescale as the decay of another process can indicate its direct relaxation or recombination back to the ground state. When two or more ground state species are present, an increase in the GSB spectral feature of one component (if not accounted for by any overlapping signals), can indicate that energy or charge is being transferred to that material. It

can also give us the information on the number of molecules that are excited in the chromophore.

Triplet species

The most direct method to detect triplet states is to investigate their sensitivity to a magnetic field. Another way is to make use of triplet sensitization techniques in which the molecule of interest is surrounded by a number of photo-excited triplet sensitizer molecules. In this case, the triplet sensitizer is excited directly to generate its S_1 state and it undergoes efficient intersystem crossing to form a high triplet state population. The sensitizer then transfers its energy to the triplet of the molecule of interest. Finally, the triplet spectrum of a given material will be identified. In this method, the sensitizer should have two main characteristics: i) the sensitizer's triplet energy level should be above that of the SF molecule to allow triplet energy transfer to form populations of the triplet exciton and ii) the SF molecule should not absorb light in the absorption region of the sensitizer in order to directly excite only the sensitizer. If the second requirement is not met and both of the molecules are excited, the absorption spectrum of the neat SF film should be subtracted from the blend film of the SF-sensitizer to find the corresponding $T_1 \rightarrow T_n$ spectrum. Widely used sensitizers include platinum(octaethyl)porphyrin (PtOEP), palladium(octaethyl)porphyrin (PdOEP), meso-tetraphenylporphyrin (TPP), anthracene, tetracene, and pentacene. Using a selection of sensitizers and detecting the efficiency of the energy transfer process can provide an upper and lower limit for the energy of the triplet state. A difference between the lifetime of correlated triplets generated via the sensitization method and free triplets formed from the SF process can

be used to confirm the presence of SF in a given material. A further practical difference is the high sensitivity of the triplet state to quenching by oxygen (triplet in its ground state) compared to other non-triplet species. This quenching will proceed if the triplet energy level is greater than oxygen's triplet energy level of 0.98 eV (which is not the case for the molecules of interest in this thesis).

3.7.5. Global target analysis

To study the mechanism from a large transient absorption data set requires advanced modeling and data analysis techniques such as global and target analysis to derive models and decompose TA spectra into their overlapping component spectra. Specifically, Global Target Analysis (GTA) is an approach based on differential equations that is employed to analyze multidimensional data sets for kinetic modeling and spectral interpretation. In this study, the program Glotaran³⁴, which is an easy-to-use modeling and data analysis tool, was used for such analysis. This approach starts with a simple model with a defined number of components and a set of starting values for the rate constants describing the kinetic connectivity between the components. The whole transient absorption data set is fit by generating the time dependent population evolution of spectral intensities from a set of first order differential equations. Then, the parameters are optimized by re-adjusting the starting values based on the resulting model. The quality of the fit can be judged from the fitted spectra and time traces as well as residual matrices. Any residual structure in the singular vectors displays a potential misfit and the need for another component in the proposed model. After checking and accepting the fitted model, the program generates kinetic traces, the evolution of populations and spectra of each

component. GTA was used to separate the overlapping features and generate the population profiles for each component versus time.

3.7.6. Experimental set-up for nanosecond transient absorption spectroscopy

To measure the triplet lifetime and find more information on the dynamics of correlated and free triplets, nanosecond transient absorption spectroscopy (ns-TA) was employed in both visible and near-IR spectral area. The nanosecond visible transient absorption spectroscopy (ns-TA) measurements were conducted by a home-built transient absorption set-up with a N₂ laser (LTB Lasertechnik Berlin GmbH, MNL 202-C) pumped dye laser (LTB Lasertechnik Berlin GmbH, ATM200, 700 ps pulse duration) as an excitation source. Transient absorption signal was probed by a Xe lamp (Photon Technology International) light through two monochromators (Acton, Princeton Instruments), and detected by a Si based nanosecond detection system (Unisoku Co., Ltd., TSP-2000SN, time resolution: 1.2 ns (FWHM), monitoring wavelengths: 400~1,100 nm) with a fast oscilloscope (Tektronix, TDS 3052C, Digital Phosphor Oscilloscope 500 MHz 5 GS/s).^[65] Transient data were collected with 400 nm excitation with a repetition rate of 2 Hz at 22 °C. The pulse excitation intensity was adjusted to 30 μJ/cm².

Nanosecond near infrared transient absorption spectroscopy (ns-TA) was employed to monitor the triplet excited state lifetime of p-BDT-DPP. The measurements were conducted by a home-built transient absorption spectrometer with a Nd:YAG laser (EKSPLA, NT340 series, 5 ns pulse duration) as an excitation source. Transient absorption signal was probed by a Xe lamp light, and detected by a InGaAs based nanosecond detection system (Thorlabs, DET20C/M, time rise: 25 ns, monitoring wavelengths: 800~1700 nm) with a fast oscilloscope (Tektronix, TDS 520,

Two channel digitizing Oscilloscope 500 MHz 500 MS/s).³⁵ Transient data were collected with 550 nm excitation with a repetition rate of 10 Hz. The pulse excitation intensity was adjusted to 30 $\mu\text{J}/\text{cm}^2$. Decay curve fitting was performed using FLASH software (Edinburgh Instruments Ltd) and an exponential components analysis.

For PDI work, flash photolysis was employed to monitor the triplet excited state lifetime. The measurements were conducted on a home built transient-absorption apparatus. The 5 ns duration pump pulses are generated by a Nd:YAG laser/OPO (Ekspla, NT340, 10 Hz repetition rate), centered at 550 nm. For the probe we use a pulsed white light LED (Thorlabs, MCWHLP1) synchronized to the laser pump source. The trigger pulse timing and duration are controlled with a BNC (Model 7010) delay generator and BK Precision 4064 waveform generator. The electronic trigger pulse train is connected to the modulation input of the Thorlabs LED controller (DC2200). The pump and probe beams are focused to 0.5 cm FWHM spot at the sample position. After the sample, the probe beam is collimated and re-focused onto the entrance slit of a spectrometer (SpectraPro-300i, Acton Research Corporation, 0.3 meter spectrograph, 150 l/mm grating blazed at 500 nm). A photomultiplier tube (1P28, Haamatsu) detected the spectrometer output at a given probe wavelength. The PMT analogue voltage is acquired with a digitizing oscilloscope (Teledyne LeCroy WaveSurfer 10). The signal kinetics were analyzed using FLASH software (Edinburgh Instruments Ltd).

3.8. Triplet yield calculation

There are several common methods to calculate the triplet yield of singlet fission materials. One is calculating the number of molecules in the singlet state that are converted to

the triplets by measuring the changes in the ground state bleach during the interconversion process.³⁶ Another method is triplet sensitization in which a well-known triplet sensitizer such as PdOEP is used to transfer triplet energy to the triplet states of the molecule of interest and so the extinction coefficient for triplet-triplet absorption can be calculated.³⁷ The triplet concentration can then be determined from the magnitude of the TA signal and the triplet yield can be calculated. The triplet yields for FHBC(TDPP)₂ in thin films were determined using the singlet depletion method, one of the well accepted methods of triplet yield determination which has been used to calculate the triplet yield in various DPP derivatives and has been shown to be comparable with triplet sensitization methods.³⁸ This method is based on two assumptions:

(1) That the triplet and singlet state do not absorb in the same region, i.e. their peak absorption maxima may lie close to one another but are not identical, and

(2) that all photoexcited molecules relax only by returning to the ground state directly or by formation of the triplet state.

To obtain the triplet-triplet absorption, it is assumed that:

$$A(T_1) = \Delta A_{800\text{ps}} + [\phi_T \times A(S_0)] \quad (1)$$

where $A(T_1)$ is triplet-triplet absorption, $A(S_0)$ is the expected GSB for one singlet depleted per triplet, and $\Delta A_{800\text{ps}}$ is the ultrafast TA spectrum of the film at 800 ps, after which the singlet state should be fully converted into the triplet state. As the singlet should be completely converted to triplet states by the end of the ultrafast TA experiment, we restrict our yield

analysis to the end of the ultrafast TA spectra. Therefore, the singlet GSB spectrum is added to the ΔA spectrum of the ultrafast TA signal until a singlet ground state peak (initially appearing as negative ΔA signal) is removed, and the region of the peak becomes linear in the $A(T_1)$ spectrum. By adding multiples of this spectrum (i.e., $\Phi_T = 10\%$ – 200%) to the ΔA spectrum of ultrafast TA at 800 ps, the triplet yields could be estimated for the annealed and as cast films. The details of this calculation are described in chapter 5.

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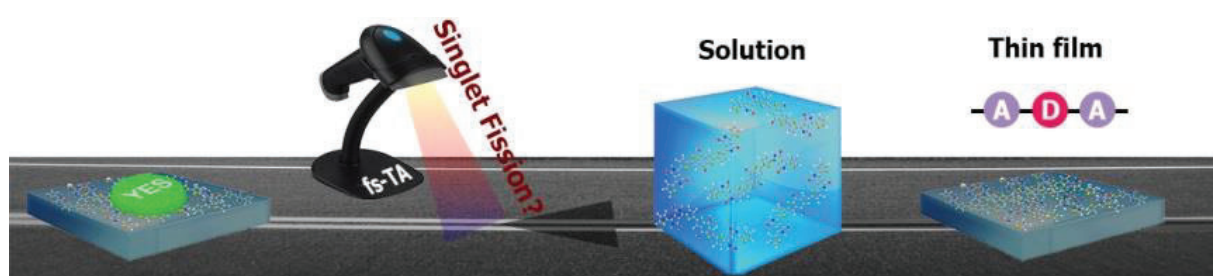
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Chapter 4

Solution-Processable, Solid State Donor–Acceptor Materials for Singlet Fission



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4.1. Preface

In most reported highly efficient SF systems, a large degree of crystallinity is required, and the SF yield is highly sensitive to the crystal packing and intermolecular nearest-neighbor coupling in these systems, the so called “local-order constraint”. This is one of the main reasons why only a small increase in PCE has been achieved to date by using SF materials in OPV devices. To overcome this issue, a new class of materials should be designed and synthesized. One method is using an electron acceptor-donor-acceptor (A-D-A) motif for designing highly efficient SF materials. As mentioned in Chapter II, in singlet fission materials, the energy of the singlet state should be greater than or equal to twice the energy of the triplet state. Also, previous experimental and calculation studies have demonstrated that direct coupling between the singlet state (S_1) and multiexcitonic state (T_1T_1) is weak but the coupling mediated by an

intermediate charge transfer (CT) state is stronger.¹⁻² As a result, an efficient singlet fission material should satisfy these two key requirements: i) a reduced singlet-triplet gap and ii) a lowest-lying singlet excitation with CT character.³ The suggested compound that is composed of alternating electron-rich units and electron deficient moieties can benefit the significant CT character in the first singlet excitation which then can be coupled to multiexciton triplet states more strongly. The A-D-A model not only takes advantage of providing an excited electronic state with significant charge-transfer character but also allows the choice of units based on the energy level requirement.

To achieve a highly efficient SF system based on the A-D-A motif, at least two strong-acceptor (SA) units with a low-energy triplet state are required. Among organic chromophores, dihydropyrrolo pyrrole dione (DPP) shows efficient SF and has a low triplet energy level. Therefore, BDT(DPP)₂ was designed for SF in which DPP was used as the acceptor unit with a low lying triplet and benzodithiophene (BDT) was used as the donor unit.⁴ DFT calculations were performed on the proposed compound to check if it meets the energy level requirements for SF.

In this chapter, a new SF material based on an A-D-A framework is introduced and characterized for SF, and SF parameters were investigated using ultrafast transient absorption (TA) and ns-transient absorption (ns-TA) spectroscopies.⁴ The experimental results reveal information on how to design a morphology independent SF system and compared the SF properties of the molecular system with the polymeric system.

There are previous reports on using A-D-A materials for SF in the literature. Busby et al. reported highly efficient intrachain SF in a push-pull low band gap polymer comprising benzodithiophene (B) as the electron-rich unit and mono-thiophene-1,1-dioxide (TDO1) as a strong electron acceptor.³ Again based on this strategy, Kasai et al.⁵ found SF in a push-pull low band gap polymer film, poly [(dodecyl-thieno-thiophene-2-carboxylate)-alt-2,6-(4,8-dioctoxybenzodithiophene)] (PTB). This material consists of benzodithiophene (B) as the electron-rich unit and dodecyl-thieno-thiophene as a strong electron acceptor.

In this chapter, the development of a solution processable, solid state SF material based on an A-D-A motif was studied to investigate the question ‘Can we use the donor in an intramolecular singlet fission A-D-A material to drive self-assembly and overcome the “local order constraint”?’ BDT has been coupled as the strong electron donor with DPP as the electron acceptor with low triplet energy level, to synthesize the molecule (BDT(DPP)₂) and a corresponding polymer (p-BDT-DPP). Time-dependent density functional theory with the Tamm–Dancoff approximation (TDA-DFT) and natural transition orbital (NTO) calculations were performed and confirmed the possibility of singlet fission in terms of the energetic landscape. The photophysical properties of both the molecule and polymer were fully characterized to study singlet fission in the solid state and in solution. The research results have been published in the following article:⁴

Saghar Masoomi-Godarzi, Maning Liu, Yasuhiro Tachibana, Lars Goerigk, Kenneth P. Ghiggino, Trevor A. Smith, and David J. Jones. Solution-Processable, Solid State Donor–Acceptor Materials for Singlet Fission. *Adv. Energy Mater.* 2018, 8, 1801720. DOI: **10.1002/aenm.201801720**.

The experimental details are included in the Supplementary Information section following the main manuscript. Reprinted with the permission from Ref [4], copyright © 2019 Wiley.

Contribution of the candidate:

- All of the material synthesis
- All of the steady state spectroscopy
- Cyclic Voltammetry measurements
- Ultrafast transient absorption measurements
- Global target analysis
- Computational calculations

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Solution-Processable, Solid State Donor–Acceptor Materials for Singlet Fission

Saghar Masoomi-Godarzi, Maning Liu, Yasuhiro Tachibana, Lars Goerigk, Kenneth P. Ghiggino, Trevor A. Smith, and David J. Jones*

The exploitation of singlet fission (SF) materials in optoelectronic devices is restricted by the limited number of SF materials available and developing new organic materials that undergo singlet fission is a significant challenge. Using a new strategy based on conjugating strong donor and acceptor building blocks, the small molecule (BDT(DPP)₂) and polymer (p-BDT-DPP) systems are designed and synthesized knowing that bithiophene-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP) has a low lying triplet energy level, which is further confirmed by time-dependent density functional theory (TD-DFT) calculations. TD-DFT and natural transition orbital (NTO) analysis are conducted to gain insight into the photophysical properties and features of excited states in BDT(DPP)₂, respectively. Femtosecond and nanosecond transient absorption spectroscopies are used to investigate the excited state kinetics in the synthesized compounds. Fast formation of triplet pairs in thin film of p-BDT-DPP and BDT(DPP)₂ and the equilibrium formation of correlated triplet pairs and S₁ from triplet–triplet annihilation in solution of BDT(DPP)₂ are further evidence of SF in these compounds. The short triplet lifetime, as a result of fast biexcitonic recombination, provides additional support for triplet pair formation through singlet fission.

1. Introduction

Singlet fission (SF) is a spin-allowed process in which absorption of one photon in an assembly of two nearby chromophores forms two triplet excitons from an excited singlet.^[1] It can be

observed under favorable energetics when the energy of the first singlet state ($E(S_1)$) is at least twice that of the corresponding first triplet ($2 \times E(T_1)$).^[2,3] The first report of singlet exciton fission dates back to 1965 where it was proposed to explain the photophysics of anthracene crystals.^[4] SF has attracted great attention in recent years as it has the potential to increase the maximum efficiency of solar cells from the Shockley–Queisser limit of 32% to nearly 45%.^[5,6] To exceed the single junction limit, two charge carriers must be extracted from the triplets generated through SF.^[7]

High triplet population efficiencies and long triplet-state lifetimes make singlet fission particularly attractive for practical applications. SF has been reported in a limited number of systems such as polyacenes,^[8,9] oligophenyls,^[10] diphenylisobenzofuran,^[11] carotenoids,^[12,13] conjugated polymers,^[14,15] and dimers.^[16,17] Although the range of compounds capable of undergoing singlet fission continues to grow, a highly efficient system incorporated into real photovoltaic applications remains to be discovered^[18]

with only limited literature reports of SF materials that have been successfully incorporated into a solar cell.^[19] Furthermore, a detailed understanding of the SF mechanism remains obscure.

In most of the existing systems, the singlet fission mechanism is intermolecular in which the initial singlet state shares its energy with a neighboring chromophore and this leads to the formation of two triplets on adjacent molecules.^[20] The formation of a bimolecular excimer in these systems is a limiting step because of its intermolecular nature, and it requires strong electronic coupling between the nearest neighbors.^[21] A potentially more attractive alternative is to promote multiexciton generation based on intramolecular processes, in which two triplet excitons are generated in the same molecule. The fission in these systems is less dependent on molecular orientation and does not require intermolecular coupling.^[22,23] Intramolecular singlet fission (iSF) has been observed in some conventional conjugated polymers and dimers but the yields to date have not exceeded 30%.^[24,25] Recently, highly efficient iSF has been reported in polytetracene, polypentacene, and electron donor

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(D)–acceptor (A) polymers.^[20,22,26–28] The key requirements for iSF in these systems are: the triplet state energy should be close to half of the photoexcited singlet energy level;^[2] and a significant charge transfer character should exist to facilitate the SF process.^[29]

Singlet fission can be achieved through two mechanisms:^[30] i) coupling the first singlet state (S_1) directly to the correlated triplet state (TT), which is a two electron process, or ii) coupling these two states via a charge transfer state, which is achieved through two consecutive one-electron processes. It has been demonstrated that the second coupling is stronger than the first resulting in the charge transfer state playing a significant role in the singlet fission process.^[31,32]

The following kinetic model was proposed from previous experimental and numerical simulations studies^[1]



This accepted model describes the conversion of an excited and ground singlet state to an intermediate state known as the correlated triplet pair, which plays an important role in the SF process. The intermediate state subsequently converts into two independent triplet excitons. Recent advances in ultrafast spectroscopy make it possible to observe the intermediate steps in more detail. To date, there is very little information about the dynamics of the correlated triplet pair.^[33] However, this intermediate state is crucial in mediating SF as it is an overall singlet state,^[7] so investigating its dynamics can help understanding more about the mechanism of SF.

Exploiting molecular design based on the intramolecular donor–acceptor approach allows variation of the electron withdrawing building block to be used to tune the singlet energy level relative to the triplet energy level to meet SF energy level requirements. This molecular design leads to a new series of compounds capable of singlet fission for third generation optoelectronic devices. For inclusion in organic solar cell devices, it is also desirable that the SF material can be solution processed, and in addition promote singlet fission in the solid state. This is important as many of the recent studies on SF materials have been carried out in solution and either studies in the solid state have not been undertaken or the materials do not show SF in the solid state.^[22,34]

Bisthiophene-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP)-based systems have recently demonstrated singlet fission with high yield.^[35–37] Due to its polyene character, DPP exhibits a low-lying triplet excited state and so is a promising structure upon which to base new molecules for singlet fission applications.^[38] In this work, we describe the development of a solution processable, solid state SF material where we have combined 4,8-bis(5-(2-ethylhexyl)-4-hexylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) as the strong electron donor and DPP as the electron acceptor with low triplet energy level, to synthesize the molecule (BDT(DPP)₂) and a corresponding polymer (p-BDT-DPP). Time-dependent density functional theory with the Tamm–Dancoff approximation (TDA-DFT)^[39] and natural transition orbital (NTO) calculations were performed and confirmed the possibility of singlet fission in terms of the energetic landscape. We investigated singlet fission in both the molecule and polymer in the solid state and in solution. We report

singlet fission in BDT(DPP)₂ in solution and in a thin film, and p-BDT-DPP in a thin film, with triplet yields of 20% and 80%, respectively.

2. Results

2.1. Structural and Electronic Properties

TDA-DFT (with the Coulomb-attenuating method Becke three-parameter Lee–Yang–Parr (CAM-B3LYP)^[40] functional approximation to take into account possible charge transfer (CT) excitations) and NTO analyses were conducted to gain insight into the photophysical properties and features of the excited states in BDT(DPP)₂, respectively. The optimized structure of BDT(DPP)₂ is shown in Figure S1 (Supporting Information) and its coordinates are reported in the Table S1 (Supporting Information). The thiophene ring, which is attached to the BDT core, is twisted at an angle of 44° relative to the BDT core, whereas the backbone structure is coplanar. The lowest-lying singlet excited state (S_1) is strongly dipole-allowed ($f = 1.73$) with the vertical excitation energy of 2.24 eV. Moreover, the first triplet excited state (T_1), which is a dark state, has the vertical energy of 1.15 eV. It is found that for this compound and chosen level of theory highest occupied molecular orbital (HOMO) → lowest unoccupied molecular orbital (LUMO) excitation acts as the main configuration. The electron and hole NTO patterns for the S_1 and T_1 states, and the distribution patterns of the HOMO and the LUMO, are illustrated in Figure 1. It was demonstrated that the splitting between the singlet and triplet is proportional to the exchange integral $K_{\text{HOMO,LUMO}} = K_{\text{hl}}$, which is the repulsion of two identical overlap charge densities, defined by the product of HOMO (h) and LUMO (l).^[1] The important factor for the K_{hl} is the degree to which the HOMO and the LUMO avoid residing on the same atoms. As a result, the large degree of spatial overlap between HOMO and LUMO supports the large singlet and triplet energy gaps and the electrons are delocalized over the whole molecule in which the LUMO is mostly located on the electron rich nitrogen and sulfur atoms. The exciton wave function in the electron and hole NTOs for the S_1 state has large overlap similar to HOMO/LUMO patterns. As a result, the S_1 state in BDT(DPP)₂ has a mixture of locally excited (LE)/CT character. On the other hand, the NTO electron and hole pairs of the T_1 state are localized within the DPP unit, so the T_1 state of BDT(DPP)₂ is characterized dominantly by LE character. Therefore, the energies of such LE states are not influenced by $\Delta E_{\text{H-L}}$, whereas the excitation energy of the S_1 state is directly influenced by $\Delta E_{\text{H-L}}$. Knowing this fact can assist the design of new structures with optimized energy levels.

It has been reported in several organic chromophores, including pentacene, push–pull polymers, diketopyrrolopyrrole, and diphenylisobenzofuran, that CT states play an important role in mediating the singlet fission process.^[22,36,41,42] It was demonstrated that fast singlet fission needs the contribution of a CT state, either through a singlet state with strong CT character or a virtual state.^[33,36,43] Also, the amount of CT character of the excited state affects the singlet–triplet energy level splitting. Therefore, we investigated the CT character of the first excited state for BDT(DPP)₂ and the results are summarized in Table S2 (Supporting Information). The results show

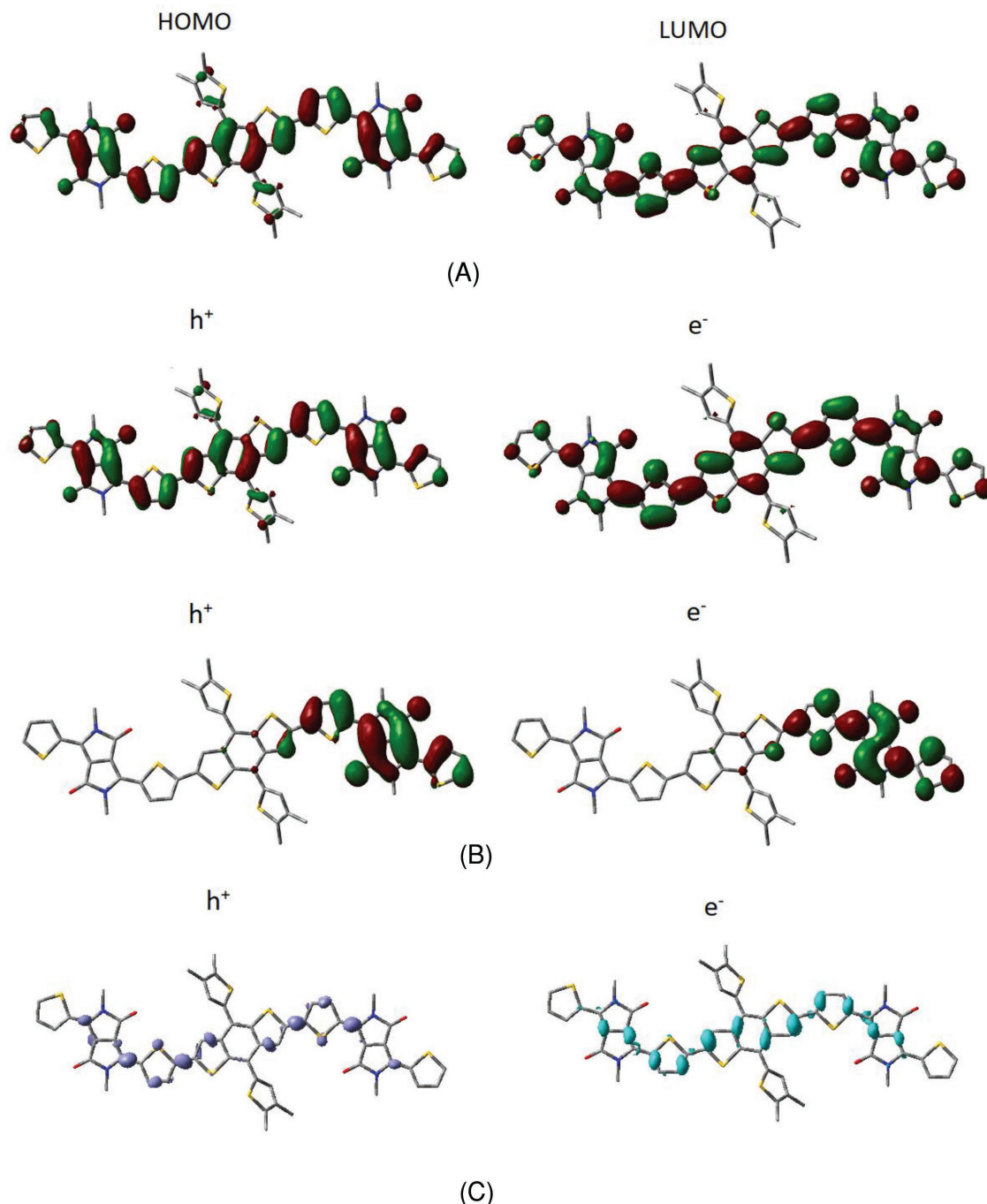


Figure 1. A) Representation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), B) NTO electron and hole pairs for the S₁ state (top) and T₁ state (bottom), and C) negative (right) and positive (left) difference densities of BDT(DPP)₂.

a smaller charge transfer distance for BDT(DPP)₂ compared to DPP,^[44] and also confirms that the S₁ state has a mixture of LE/CT character. Another of the main requirements for a compound to undergo SF is that the energy of the first triplet state of the molecule is less than or at least equal to half of the first singlet state energy level. In addition, we can deduce the mixed LE/CT character from inspection of the difference densities between the S₀ and S₁ states, as shown in Figure 1C. While this figure clearly indicates that there must be partial LE

character, we can qualitatively see the partial CT character for this state from additional TDA-DFT calculations with a functional approximation that is known to severely underestimate CT transitions, namely B3LYP.^[45–47] TDA-B3LYP, when applied with the same basis set as before, predicts the S₁ state to be redshifted by nearly 0.5 eV (excitation energy of 1.76 eV). If the transition was a conventional local valence excitation, we would expect a redshift of about 0.15 eV between both the methods.^[48]

To conclude, based on our calculations, the triplet excitation energy level for BDT(DPP)₂ ($E(T_1) = 1.15$ eV) is nearly half of the first singlet excited state energy ($E(S_1) = 2.24$ eV). These theoretical results suggest that BDT(DPP)₂ is a potential candidate for SF.

2.2. Optical and Electrochemical Properties

The steady state absorption and fluorescence spectra of BDT(DPP)₂, p-BDT-DPP, DPP, and BDT in chloroform solution and in thin films are shown in Figure 2A–D. BDT shows a sharp absorption peak at 405 nm and a broad absorption band in the region of 500–700 nm, Figure 2A. The compounds p-BDT-DPP, BDT(DPP)₂, and DPP each show two absorption bands in solution with maxima positioned, respectively, at about 750, 620, and 550 nm for the low energy band, and at 435, 385, and 340 nm for the high energy band, see Figure 2A. The high energy band is attributed to a $\pi-\pi^*$ transition and the low energy band is ascribed to the HOMO $\rightarrow$ LUMO $\pi \rightarrow \pi^*$ intramolecular charge transfer (ICT) transition between the donor and acceptor. There is a slight redshift in the absorption and fluorescence spectra of BDT(DPP)₂ by decreasing the polarity of the solvent, Figure S4 (Supporting Information),

which suggests some charge transfer character of the lowest energy optical excitation, which is also well characterized for DPP-based molecules in several reports.^[49–51] The absorption and fluorescence profiles of BDT(DPP)₂ show a bathochromic shift compared to BDT and DPP in both solution and thin film, which is the result of the intramolecular charge transfer process between BDT and the DPP units. In addition, the polymer of BDT-DPP displays a large (≈ 150 nm) redshifted, broad absorption spectrum in both solution and thin film and a red-shifted fluorescence in comparison to BDT(DPP)₂ as a result of the –A–D–A–D– type structure. A new redshifted feature appears in the absorption profiles of BDT(DPP)₂ and DPP in thin films, which is more distinct for BDT(DPP)₂. Also, there is a large bathochromic shift in the fluorescence of BDT(DPP)₂ and DPP in the thin films compared to the solution suggesting the formation of J aggregates in the solid state. The absorption spectrum of p-BDT-DPP in the solution of chloroform shows fine vibronic structures with resolved 0–0 and 0–1 peaks, similar to the absorption spectrum of the film and there is no spectral shift between solution and solid state absorption spectra. These results show that the p-BDT-DPP aggregates strongly in solution just as in the film. This behavior was already observed for other D–A copolymers^[52,53] as a result of the high planarity

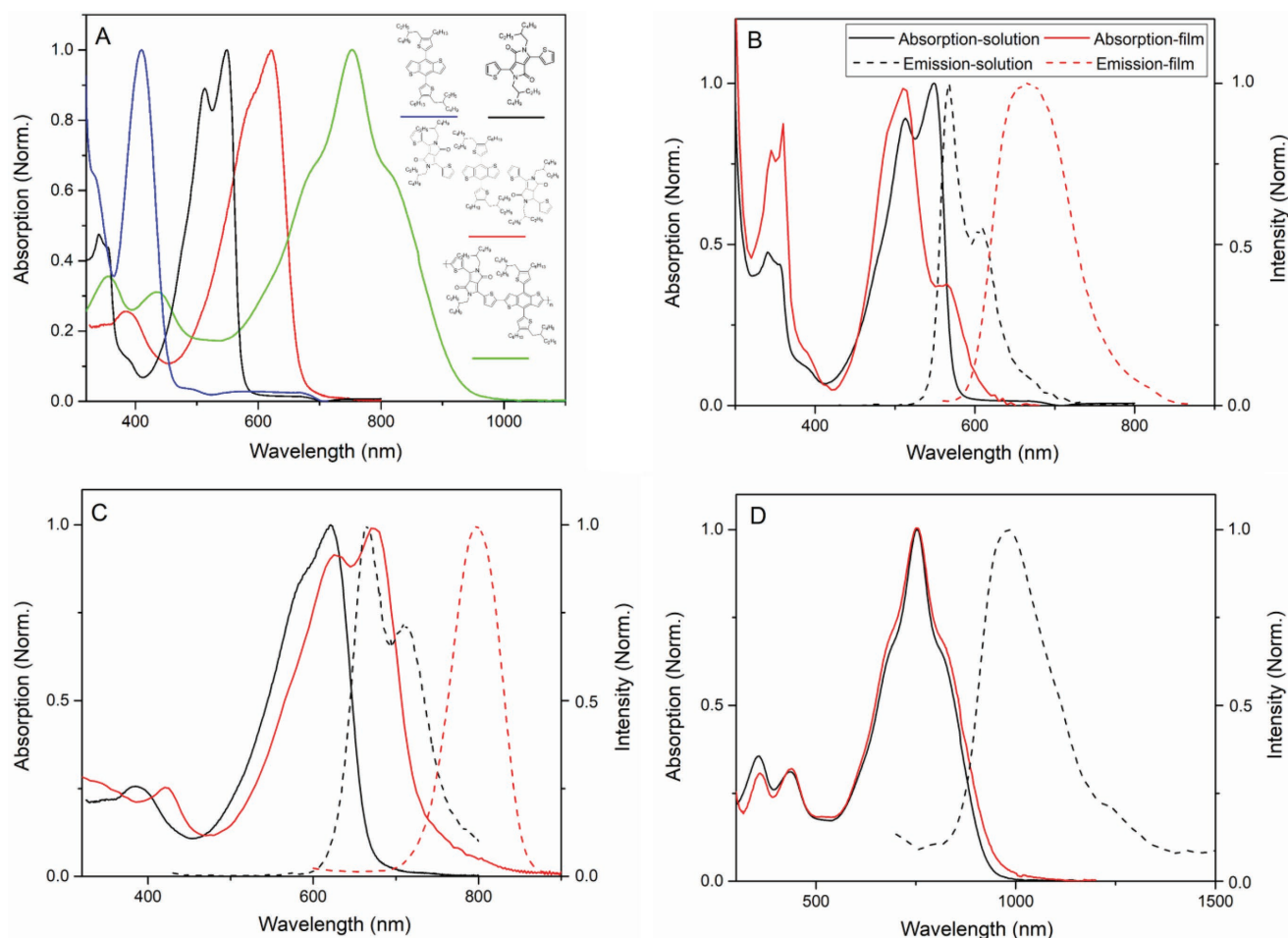


Figure 2. A) Absorption spectra of BDT(DPP)₂, p-BDT-DPP, DPP, and BDT in solution of chloroform and absorption and fluorescence spectra of B) DPP, C) BDT(DPP)₂, and D) p-BDT-DPP in chloroform solution and thin film.

and rigidity of the backbones and it means that even in solution the chains do not lose their conjugation length and their π - π stacking. To investigate this phenomenon in more detail, we performed a temperature-dependent UV-vis absorption measurement in chloroform solution, Figure S5 (Supporting Information). The results show that interchain interactions decrease and copolymer chains are allowed to separate at higher temperatures.

The fluorescence of p-BDT-DPP is significantly quenched in the thin film to such a degree that the fluorescence spectrum could not be determined. This may suggest that a new pathway exists for singlet state quenching in the polymer in the solid state. The optical bandgaps of BDT(DPP)₂, p-BDT-DPP, and DPP in solution and the solid state are calculated from the onset of absorption (Figure 2A–D) and are summarized in Table S3 (Supporting Information).

To observe the phosphorescence of a purely organic compound, the radiative rate of phosphorescence should outcompete the nonradiative rate. To meet this criterion, spectroscopy at cryogenic temperature (77 K) is required.^[54–56] The emission of BDT(DPP)₂ in 2-methyl-tetrahydrofuran (MTHF) at room temperature and 77 K in the spectral area of 1000–1500 nm (with >1200 nm high-pass filter) is shown in Figure S2 (Supporting Information). By decreasing the temperature to 77 K, the nonradiative loss pathways are frozen out,^[57] and a peak appears at about 1300 nm (0.95 eV) which is assigned to emission from the triplet state. This suggests that BDT(DPP)₂ in solution matches the energy level requirement for SF, that is, the triplet energy (0.95 eV) is close to half of the singlet energy level (1.88 eV).

An estimate of the absolute energy levels against vacuum can be determined from cyclic voltammetry and the cyclic voltammograms of BDT(DPP)₂, p-BDT-DPP, and DPP are shown in Figure S3 (Supporting Information). The HOMO and LUMO energy levels and the electrochemical bandgaps of BDT(DPP)₂, p-BDT-DPP, and DPP are estimated from the onsets of the oxidation and reduction peaks and are summarized in Table S3 (Supporting Information).

2.3. p-BDT-DPP Excited State Dynamics in Solution and Thin Films

The polymer p-BDT-DPP was designed based on the donor-acceptor interactions in a polymer chain and appears to be strongly aggregated in solution. Femtosecond transient absorption (fs-TA) measurements were used to probe the excited state dynamics in this compound. The TA spectra in the near-infrared (NIR) region and kinetic traces at selected wavelengths of p-BDT-DPP, following excitation at 630 nm in both solution and thin film, are shown in Figure 3A–D. In solution, a ground state bleach (GSB) in the region of 800–900 nm and a broad photoinduced absorption (PIA1) in the 900–1250 nm region are observed in the TA spectra, with similar but mirrored kinetics (see Figure 3C). After 100 ps, there is no detectable TA signal in either region, indicating that the exciton generated from photoexcitation of p-BDT-DPP decays quickly to the ground state with a $\approx$ 10 ps time constant without forming any long-lived intermediates. On the other hand, the TA spectra (Figure 3B)

of the thin film show a GSB in the 850–960 nm range and a broad positive absorption signal (PIA1) in the 960–1250 nm region. In contrast to the solution, the PIA1 and GSB features are still observed at delay times of 300 and 850 ps in the thin film (Figure 3D). Comparing the excited state kinetics of p-BDT-DPP in solution and film at 1100 nm, see Figure 3D, indicates the formation of a long-lived feature. As shown in Figure 3D, the decrease in ΔA of the $S_1 \rightarrow S_n$ absorption band follows the growth of another feature on a time scale of about 100 ps, suggesting that PIA1 in the film sample comprises the overlap of more than one feature which is confirmed by other evidence discussed below.

To find more detail about the kinetics of the long-lived species in p-BDT-DPP in thin film, we have conducted nanosecond transient absorption (ns-TA) measurements with excitation at 630 nm. The kinetic trace at 1200 nm is shown in Figure S10 (Supporting Information). It shows a single exponential decay with the time constant of 150 ns.

In light of the fast decay of the singlet excited state as indicated from time-correlated single photon counting (TCSPC) at low temperature (Figure S6, Supporting Information), the presence of a long-lived species in the ns-TA measurement and nonexponential kinetics at 1150 nm in the fs-TA measurements (Figure 3D), a two species sequential scheme $A \rightarrow B \rightarrow GS$ was assumed as the simplest model of p-BDT-DPP in the thin film. We tentatively assign species A to the S_1 state, which decays with a time constant $\tau_A = 10$ ps from the fast component in fs-TA and species B to the T_1 state that decays with a time constant of 150 ns from ns-TA.

The triplet sensitization technique has been used to find the triplet absorption spectrum and the molar extinction coefficient for triplet-triplet absorption. Palladium octaethylporphyrin (PdOEP) was chosen as the triplet sensitizer. Since PdOEP has two narrow and isolated absorption bands at 400 and 550 nm (Figure S7, Supporting Information) and they both overlap with the absorption band of p-BDT-DPP, the sensitizer cannot be excited selectively. As a result, the sensitized transient absorption spectrum is a linear combination of the PdOEP, p-BDT-DPP triplet spectra, and the nonsensitized p-BDT-DPP spectrum. Thin film TA spectra of PdOEP show a narrow, negative GSB at 550 nm and no positive photoinduced absorption following excitation at 400 nm, as shown in Figure S8 (Supporting Information). The kinetic traces of the sensitized and nonsensitized p-BDT-DPP films at selected wavelengths of 650 and 1100 nm are shown in Figure 4A,B, respectively. The population of the triplet state occurs at a time delay of about 100 ps, and is assigned to triplet energy transfer from the PdOEP to p-BDT-DPP. To find the triplet absorption spectrum, global target analysis was performed on the p-BDT-DPP: PdOEP blend film (Figure S9, Supporting Information). A global target analysis (GTA) was used to analyze the transient absorption data to help identify the individual features and their population variation with time.^[22] GTA yields the associated spectra and concentration profile for S_1 and T_1 , which are shown in Figure S9 (Supporting Information).

Fast triplet formation (<100 ps) in p-BDT-DPP films can be one piece of evidence for ruling out intersystem crossing (ISC) as the dominant mechanism of triplet formation, because ISC on such a short timescale is mostly observed in the systems with heavy atoms that facilitate spin orbit coupling, however,

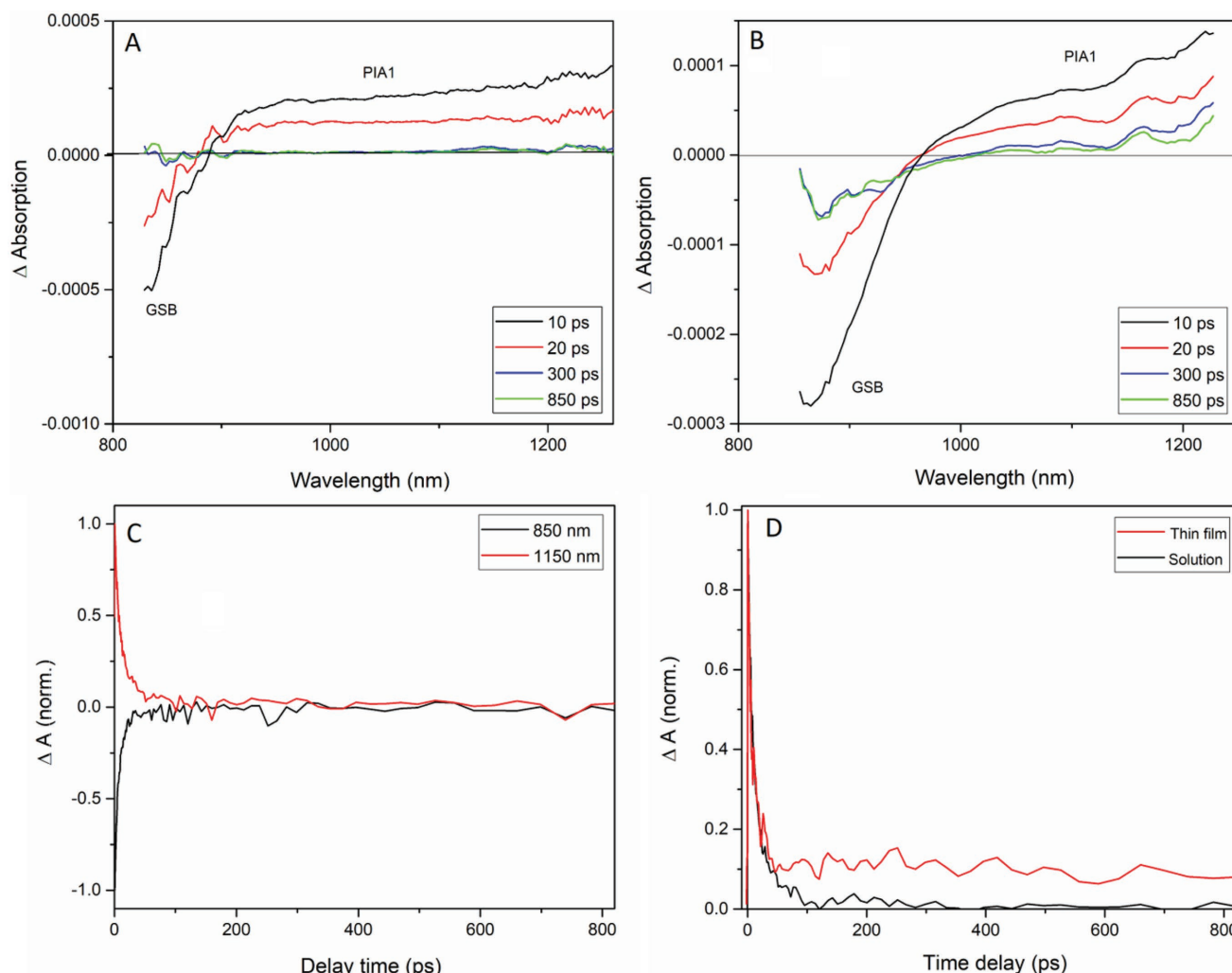


Figure 3. Transient absorption spectra of p-BDT-DPP in A) chloroform solution and B) thin film at a time delays of 10, 20, 300, and 850 ps. Kinetic traces of p-BDT-DPP at 850 and 1150 nm in C) chloroform solution, and D) 1150 nm in solution and thin film. The solution and thin film of p-BDT-DPP were excited at 630 nm with a fluence of $10 \mu\text{J cm}^{-2}$.

there are a few counterexamples in the literature.^[22] To find more detail about the dynamics of the sensitizer-generated triplet species in p-BDT-DPP films, we have conducted ns-TA measurements with excitation at 400 nm. The triplet state decay for the sensitized p-BDT-DPP film, monitored at 1200 nm, is shown in Figure S10 (Supporting Information). The best fit analysis indicates biexponential decay with time constants of about 130 ns and 2 μs , indicating two different triplet excited states in the p-BDT-DPP:PDOEP blend film. The longer-lived triplet exciton is assigned to the single triplet species formed from the sensitization experiment and the shorter-lived component corresponds to the triplet pair that is generated from direct excitation of p-BDT-DPP, which matches with the results of ns-TA of pure p-BDT-DPP. A faster recombination rate for SF-generated triplets would be expected for correlated triplet pairs, resulting in an enhanced contribution of spin-allowed geminate triplet-triplet annihilation compared to the sensitizer generated single triplets, with a slower recombination rate. The results are strongly suggestive that singlet fission

occurs in the thin film of p-BDT-DPP but not in aggregated solution although the ground state absorption spectra are similar in both solution and thin film. We believe that the singlet is very low in energy in solution, and the localized triplet states are not very strongly affected by the presence of many repeat units in the polymer, so the energy requirements of $2T_1 < S_1$ are difficult to satisfy thereby inhibiting singlet fission in solution.

2.4. BDT(DPP)₂ Excited State Dynamics in Thin Film

Ultimately, for inclusion into printed solar cells, new SF materials must be solution processable and promote SF in the solid state. Therefore, solid state dynamics of BDT(DPP)₂ were examined using TA measurements on thin films of BDT(DPP)₂. TA spectra and kinetics of BDT(DPP)₂ after exciting at 630 nm, are shown in Figure 5A,B, respectively. A negative GSB signal in the region of 520–740 nm, mirroring the steady state absorption and a broad positive PIA1 in the NIR region with maximum

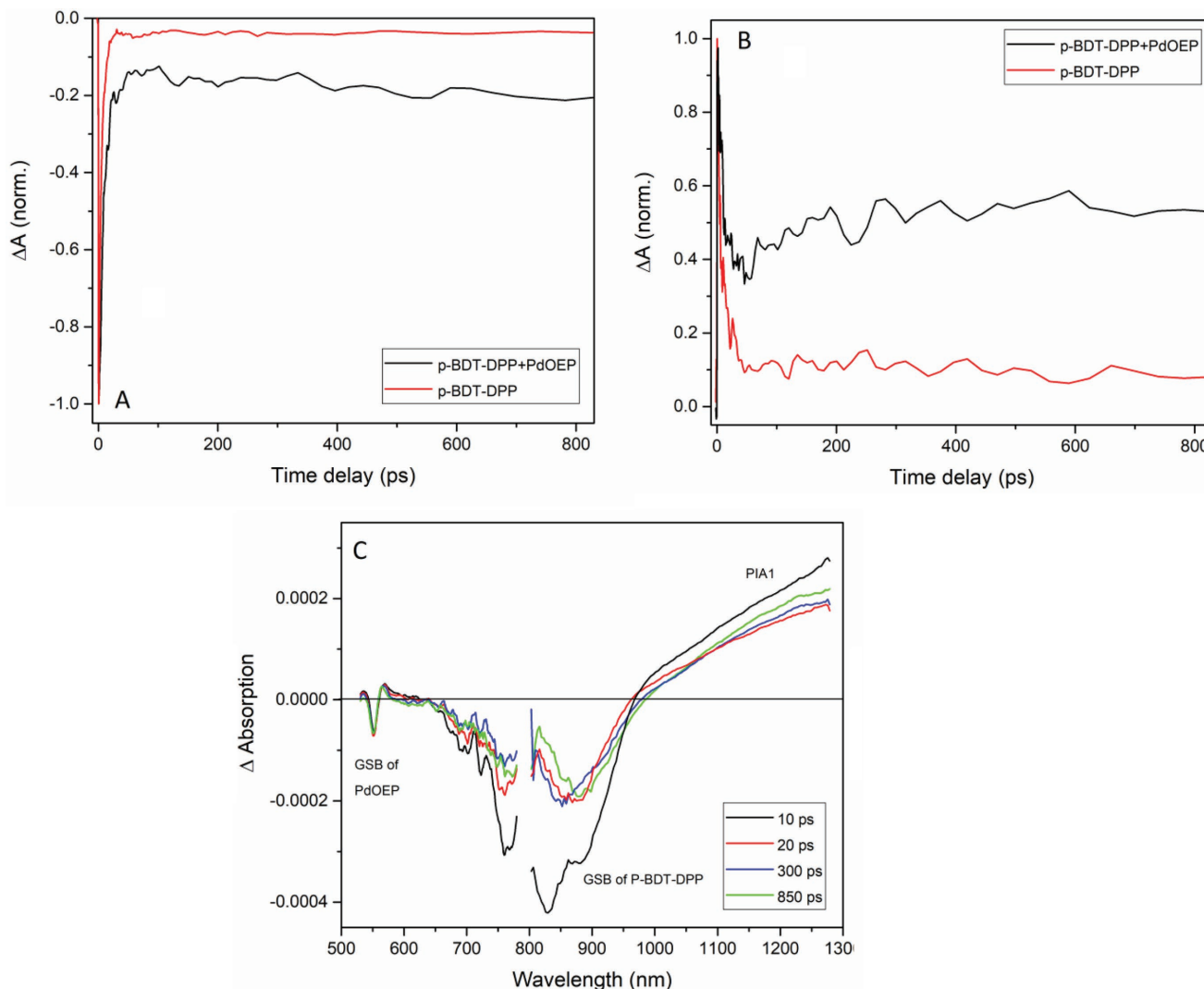


Figure 4. A,B) Kinetic traces of p-BDT-DPP thin films with and without palladium octaethylporphyrin (PdOEP) as a sensitizer at 650 and 1100 nm, respectively. C) Transient absorption spectra of a p-BDT-DPP:PdOEP blend film for time delays of 10, 20, 300, and 850 ps, following excitation at 400 nm, with a fluence of $10 \mu\text{J cm}^{-2}$.

intensity at 1100 nm, appear at the first delay period of the measurement, Figure 5B. The shape of the PIA1 in the TA spectrum at a time delay of 600 ps is different from the spectrum at the earlier times, as shown in the inset graph of Figure 5A, suggesting that this broad peak comprises more than one overlapping excited state feature. To confirm this, a GTA was performed on the transient absorption data set of BDT(DPP)₂ in thin film using a sequential $A \rightarrow B \rightarrow GS$ model. The associated spectra and concentration profile for A and B are shown in Figure 6. The spectrum of species B is very similar to that of the triplet absorption of BDT(DPP)₂, which is derived from the PdOEP-sensitized experiment and is discussed in more detail in the next section (Figure 7). As a result, we assigned A to the S_1 state, which decays in $\tau_A = 85$ ps, and B to the T_1 state that decays in $\tau_B = 380$ ps.

To confirm the assignment of species B from the GTA as a triplet, the triplet sensitization technique has again been used. Before performing time-resolved measurements, the steady

state emission of PdOEP in the presence of BDT(DPP)₂ was investigated to find out more about triplet energy transfer. A Stern–Volmer quenching plot of the sensitizer (PdOEP), see Figure S11 (Supporting Information), indicates a decrease of the phosphorescence of the sensitizer (PdOEP) by increasing the concentration of BDT(DPP)₂, suggesting triplet energy transfer from the sensitizer to BDT(DPP)₂. Finally, TA experiments were performed for PdOEP-sensitized BDT(DPP)₂ thin films (60:40 weight ratio) to find the triplet absorption spectrum and the lifetime of generated triplets. The kinetic traces of the sensitized and nonsensitized BDT(DPP)₂ films at 650 and 1100 nm are shown in Figure 7A,B, respectively. In the BDT(DPP)₂:PdOEP blend film, the kinetic trace of the GSB shows that the excited state of BDT(DPP)₂ is being repopulated on timescales exceeding 300 ps attributed to triplet exciton energy transfer from the PdOEP to BDT(DPP)₂. The same trend is observed in the dynamics of the positive peak centered at 1100 nm when BDT(DPP)₂ is sensitized, showing the

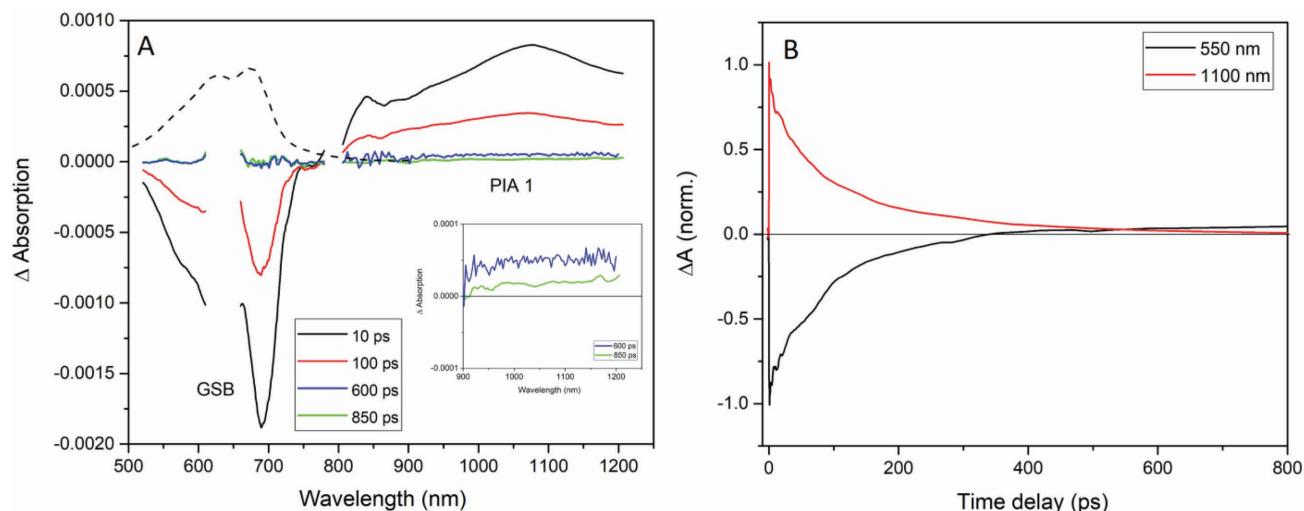


Figure 5. Thin film transient absorption measurement data for BDT(DPP)₂ with 630 nm excitation at $10 \mu\text{J cm}^{-2}$. A) Spectral slices at 10, 100, 500, and 850 ps, the steady state absorption (dashed line) is also shown for comparison. B) Kinetic traces of the GSB and PIA1.

repopulation of triplet state in that system. The thin film TA spectra for BDT(DPP)₂ in the presence of PdOEP following excitation at 400 nm are shown in Figure 7C for different time delays. The broad, positive photoinduced absorption peak in the NIR region in the neat BDT-DPP₂ decays to zero within 850 ps film, whereas in the photosensitized experiment, the signal at 1100 nm is still present at longer times, which is assigned to the triplet ($T_1 \rightarrow T_n$)-induced absorption arising from triplet generation on BDT(DPP)₂ due to sensitization from PdOEP. As previously mentioned, the sensitizer cannot be excited selectively, so the sensitized TA spectrum is a linear combination of the PdOEP, BDT(DPP)₂ triplet spectrum, and the PdOEP-sensitized BDT(DPP)₂ spectrum. As there is no TA signal at a time delay of 800 ps for either BDT(DPP)₂ thin films (Figure 5), or PdOEP, any positive photoinduced absorption band of the PdOEP sensitized BDT(DPP)₂ thin film at time delay of 800 ps can be associated with triplets on BDT(DPP)₂ generated via

sensitization (Figure 7D). The associated spectrum of species B from the GTA is similar to the triplet-induced absorption from the sensitization technique, as shown in Figure 7D. The spectral agreement of the T_1 -induced absorption spectra from the sensitization experiment and the second excited state from GTA suggests that triplets are being generated on an ultra-fast time scale following the excitation of the BDT(DPP)₂ in the solid state. As discussed above, the fast triplet formation (<100 ps) supports ruling out ISC as the main mechanism of triplet formation in BDT(DPP)₂.

To further investigate the dynamics of the triplet feature in the sensitized BDT(DPP)₂ film, we have conducted ns-TA measurements for the BDT(DPP)₂:PdOEP blend film excited at 400 nm, and monitored the triplet state decay at 1050 nm, see Figure S12 (Supporting Information). In the sensitized experiment, the generated triplets on the sensitizer are transferred to the organic chromophore and form isolated triplets.^[34] The

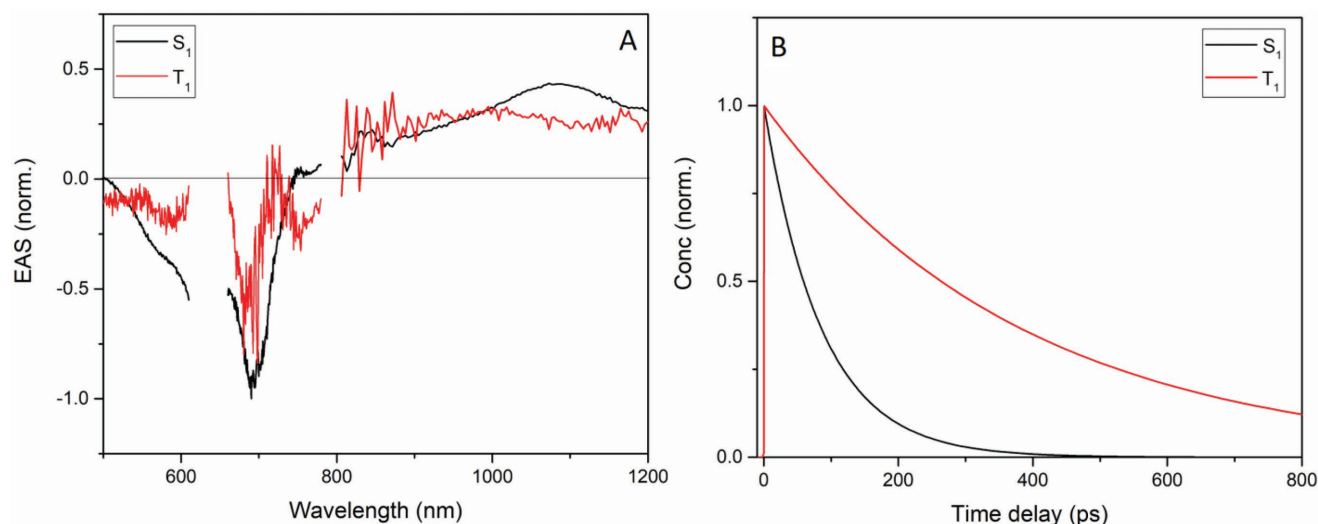


Figure 6. A) The associated spectra and B) concentration profile versus time for S_1 and T_1 from the global target analysis for BDT(DPP)₂ in thin film.

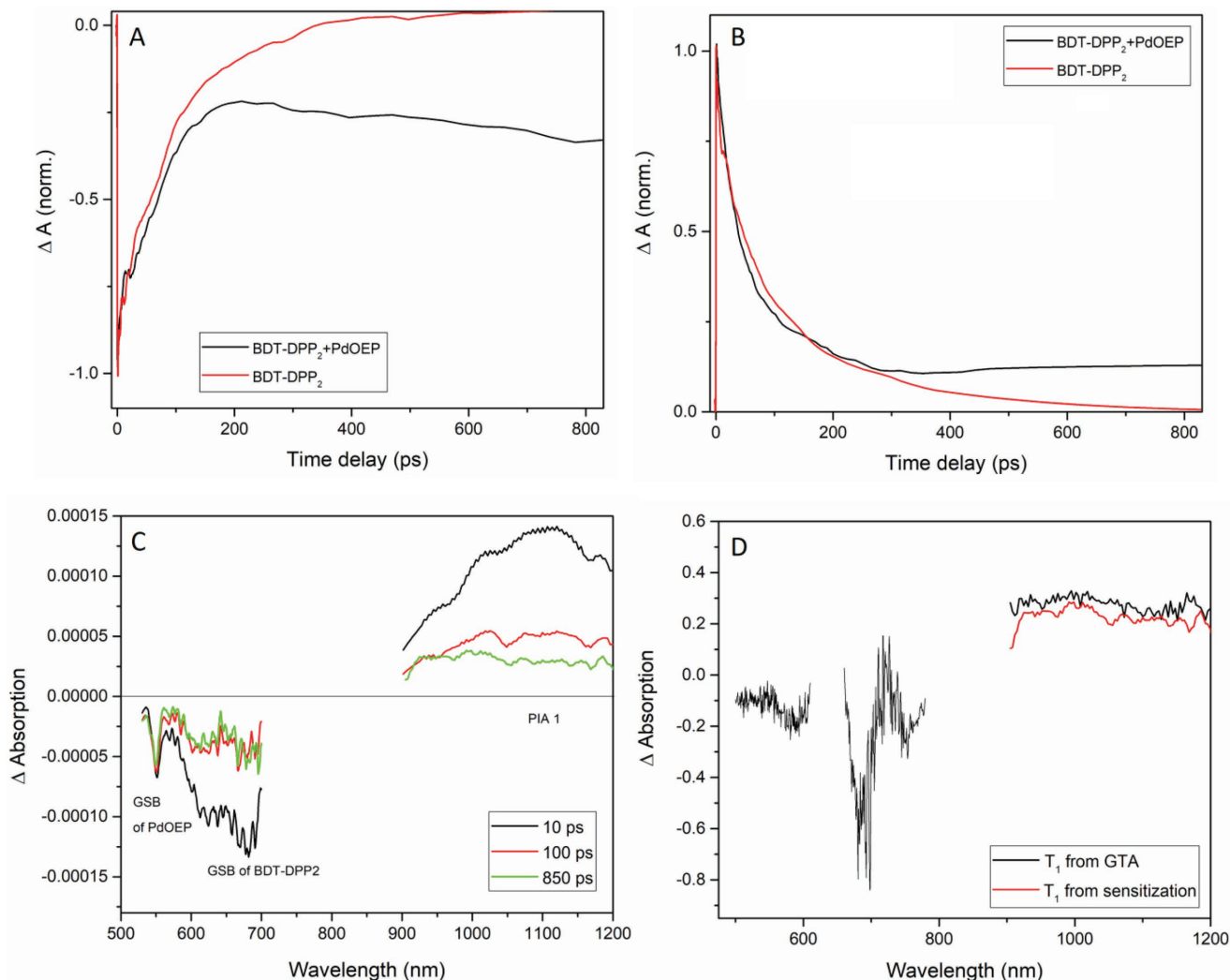


Figure 7. A,B) Kinetic traces of sensitized and nonsensitized thin films of BDT(DPP)₂ for selected wavelengths of (A) 650 nm and (B) 1100 nm. C) TA spectra of thin film sensitized BDT(DPP)₂ for time delays of 10, 100, and 850 ps after exciting at 400 nm at 10 $\mu\text{J cm}^{-2}$. D) T₁-induced absorption spectrum of the BDT(DPP)₂ derived from triplet sensitization technique and associated spectrum of second excited state species from GTA.

isolated triplets formed via photosensitization have a single, long lifetime of 2.2 μs compared to the lifetime of the triplets generated in the BDT(DPP)₂ unsensitized film (about 1 ns). This fact suggests the formation of the triplet pair in BDT(DPP)₂ thin films is via SF, and the faster recombination rate of triplet pairs compared to the isolated triplets may be due to the enhanced contribution of spin-allowed geminate triplet-triplet annihilation rather than the slower recombination of isolated triplet excitons. The results are strongly suggestive that the triplet pairs are formed via SF in thin film.

2.5. BDT(DPP)₂ Excited State Dynamics in Dilute Solution

One remaining question is whether the SF in BDT(DPP)₂ is inter- or intramolecular. We have examined the excited state dynamics of BDT(DPP)₂ in a dilute chloroform solution (10×10^{-6} M), to reduce possible bimolecular interactions. Selected fs-TA spectra and extracted kinetic traces of BDT(DPP)₂ after exciting

at 630 are shown in **Figure 8A,B**, respectively. A negative GSB signal in the region of 520–690 nm is seen in the TA spectra, mirroring the steady state absorption, along with a negative stimulated emission (SE) peak at 690–780 nm that corresponds to the BDT(DPP)₂ fluorescence. Also, a broad positive PIA1 in the NIR region with maximum intensity at 1100 nm appears at the first delay time. A second photoinduced absorption (PIA2) at 550 nm, strongly overlapping the GSB, is also observed and grows in with the decaying of PIA1, **Figure 8B**. The kinetic trace of this signal, a mix of the decreasing GSB and increasing PIA2, shows that it changes from negative to positive ΔA at about 400 ps. The steady state absorption and emission spectra of BDT(DPP)₂ are also plotted for comparison with the GSB and SE signals, **Figure 8A**. According to the kinetic traces at the selected wavelengths of 570 and 710 nm, the GSB and SE signals decay at different rates, indicating that the first excited state (S_1) populates another excited state, i.e., the TA data of BDT(DPP)₂ in dilute solution comprise the overlapping of more than one excited state features, confirmed by global target analysis discussed below.

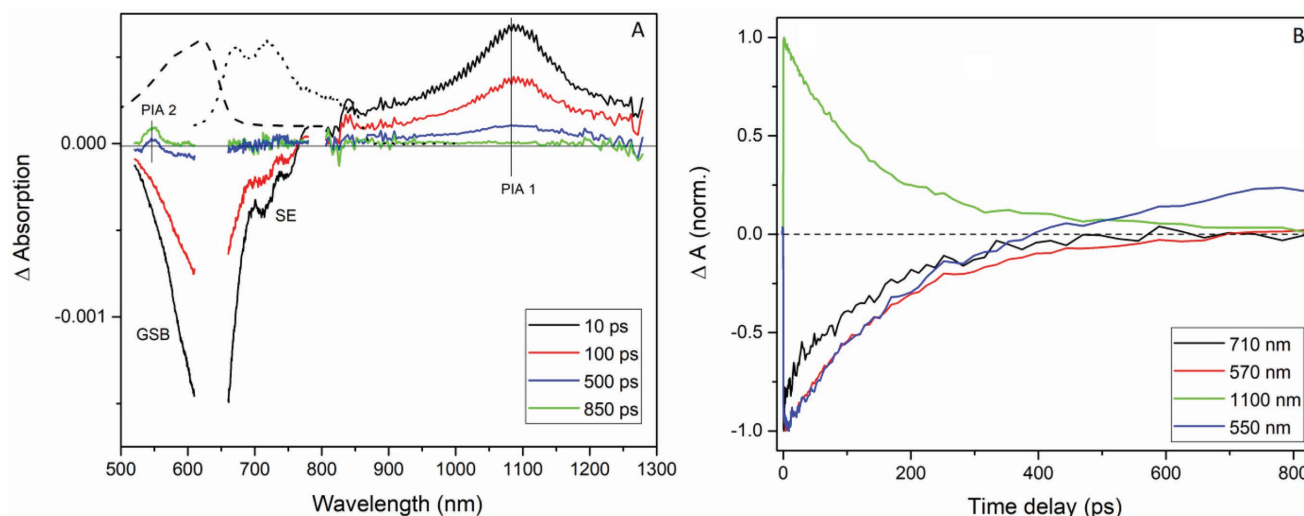


Figure 8. Transient absorption measurement data for BDT(DPP)₂ in dilute solution of chloroform with 630 nm excitation at 10 $\mu\text{J cm}^{-2}$. A) Spectral slices at 10, 100, 500, and 850 ps, the steady state absorption (dashed line) and fluorescence (dotted line) are also shown for comparison. B) Kinetic traces at selected wavelengths of 550, 570, 710, and 1100 nm.

To further characterize the excited states in a dilute solution of BDT(DPP)₂, TA measurements were performed in a series of solvents with different polarities. The kinetic traces of PIA1 for BDT(DPP)₂ in cyclohexane, dichloromethane, and chloroform are shown in Figure S13 (Supporting Information). There is no polarity dependence on the decay kinetics of the PIA1 at 1100 nm, suggesting the lack of charge transfer character in this state.

We performed a global analysis on the transient absorption data of BDT(DPP)₂ in dilute solution using a two-species model ($A \rightarrow B \rightarrow \text{GS}$). The associated spectra and concentration profiles versus time for the A and B features are shown in Figure 9A,B. The first component is ascribed to the photogenerated singlet exciton which has a lifetime of about 50 ps according to target analysis. The first singlet exciton forms species B with a rate (K_{SF}) of 0.019 ps^{-1} , which subsequently decays with a rate (K_{TT}) of 0.006 ps^{-1} . Species B has a different transient absorption spectrum to that of the PdOEP-sensitized triplet absorption of BDT(DPP)₂ (Figure 7D) at short wavelengths. By looking closer at the fitted model, we found that the residual spectrum at time delays greater than 600 ps is very similar to the absorption from the S_1 state. According to the literature,^[58–60] the vibronic progression of the isolated triplet transition might be different from the triplet-pair state resulting in a different absorption spectrum. As a result, we assign species B as a correlated triplet-pair (T_1T_1) state that results from SF equilibrium. We proposed the model shown in Figure 9C for BDT(DPP)₂ in dilute solution. In this model, the singlet exciton undergoes a spin-allowed internal conversion to an overall singlet, correlated triplet-pair state on the picosecond time scale. However, the evidence shows that this correlated triplet pair could not diffuse apart to form separated correlated triplets and they annihilate together to reform the S_1 excited state. It was reported that chemical systems in which triplet exciton interactions are very strong and the triplet pair cannot spatially separate might yield only the interacting triplet pair.^[7] This is clearly apparent in the short triplet-pair lifetimes reported in

some systems such as conjugated polymers and covalently tethered molecular pairs.^[59,61] We assume that SF in BDT(DPP)₂ is of an intramolecular character and confinement of two triplet excitons on one molecule results in faster biexcitonic recombination rates. The results are strongly suggestive that the triplet pairs are formed via SF in both solution and thin film of BDT(DPP)₂.

2.6. Determining the Triplet Yield

There are several common methods to calculate the triplet yield of singlet fission materials. One is calculating the number of molecules in the singlet state that are converted to the triplets by measuring the changes in the ground state bleach during the interconversion process, however this method is not very accurate for our system due to the large overlap between singlet and triplet state absorption.^[22] Another method is triplet sensitization in which a well-known triplet sensitizer such as PdOEP is used to transfer triplet energy to the triplet states of the molecule of interest and so the extinction coefficient for triplet–triplet absorption can be calculated.^[62] The triplet concentration can then be determined from the magnitude of the TA signal and the triplet yield can be calculated. Using the triplet sensitization technique, it is determined that the triplet yields are 70% and 18% for p-BDT-DPP and BDT(DPP)₂ in thin film, respectively (more details in the Supporting Information). Although BDT(DPP)₂ is believed to undergo SF in dilute solution, as indicated by the very short fluorescence time constant and formation of the correlated triplet-pair (T_1T_1) state, no signals for triplet (T_1) are detected in the GTA. Therefore, the triplet yield cannot be determined. Also, in thin films of BDT(DPP)₂, the triplet yield calculation contains significant errors, as the BDT(DPP)₂ SF-generated triplets have a short lifetime, undergo fast recombination, and the singlet and triplet absorption spectra of BDT(DPP)₂ have a large overlap. The triplet yields, single triplet, and triplet-pair lifetimes of P-BDT-DPP and

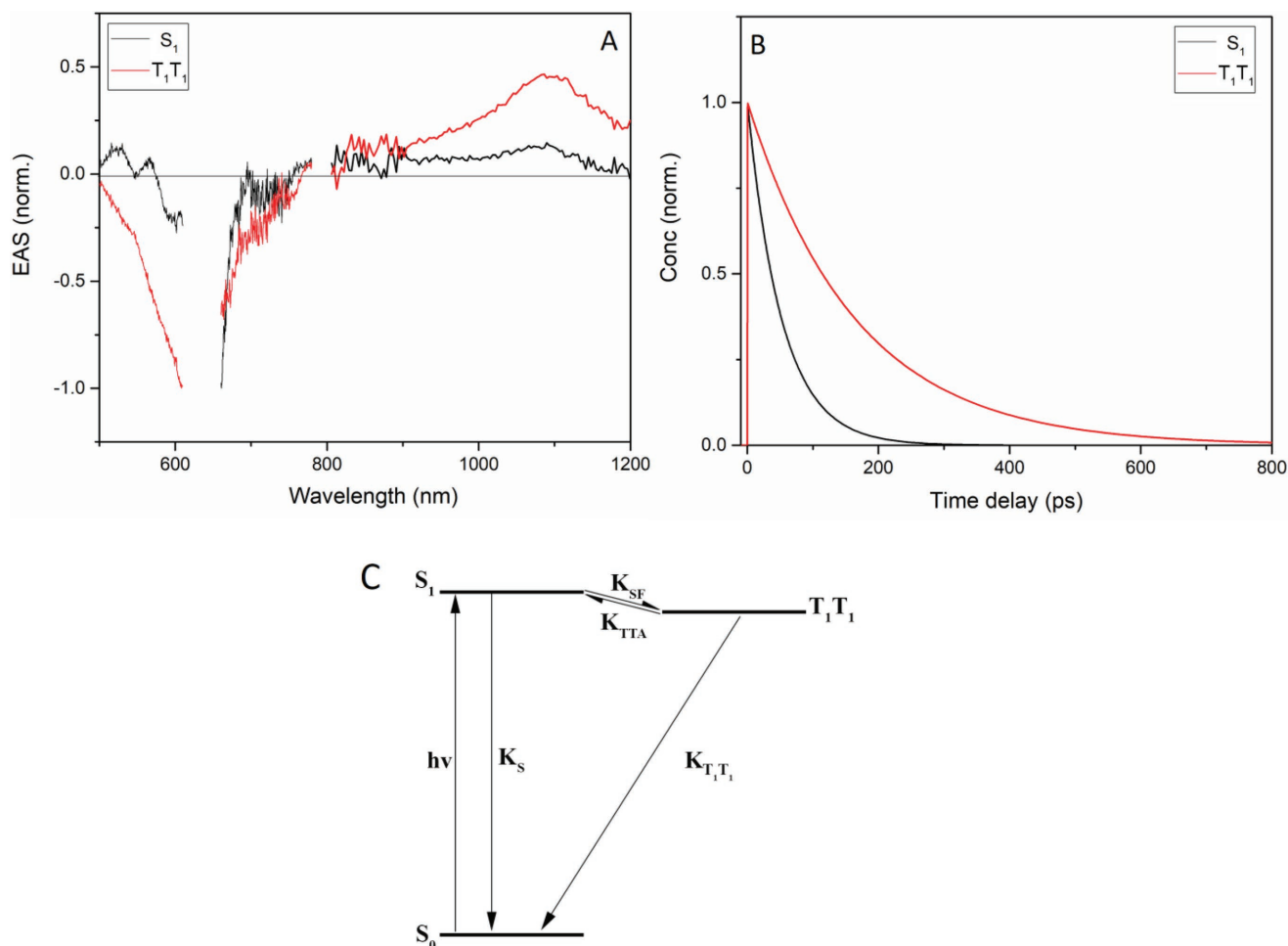


Figure 9. A) The associated spectra and B) concentration profile versus time for S_1 and T_1T_1 from the global target analysis for BDT(DPP)₂ in dilute solution. C) Energy level schematic and kinetic model for SF dynamics in solution.

BDT(DPP)₂ in solution and the solid state are summarized in Table 1. The results suggest that BDT(DPP)₂ undergoes singlet fission in both dilute solution and thin film and p-BDT-DPP shows singlet fission only in the thin film. However, p-BDT-DPP has a higher singlet fission yield and longer triplet pair lifetime in the thin film compared to BDT(DPP)₂.

3. Discussion

The results indicate that triplet pairs are formed in BDT(DPP)₂ in thin film through SF, as shown in Figure 10B. The evidence

Table 1. The triplet yields, isolated triplet, and triplet-pair lifetimes of p-BDT-DPP and BDT(DPP)₂ in dilute solution and thin film.

Sample	Triplet pair lifetime [ns]	Isolated triplet lifetime [μ s]	SF yield
p-BDT-DPP in film	150	2	70%
p-BDT-DPP in solution	–	–	No SF
BDT(DPP) ₂ in solution	–	–	Cannot be determined
BDT(DPP) ₂ in film	≈ 1	2.04	18%

also shows that correlated triplet pairs are formed via SF in a single chromophore of BDT(DPP)₂ in solution but they did not diffuse apart to form separated triplet pairs before recombination. The results show that the SF mechanism is independent of intermolecular orientation and coupling, which is an indirect indication of iSF. Also, the short lifetime of the triplet pairs and triplet–triplet annihilation provide additional support to the intramolecular nature of singlet fission in BDT(DPP)₂, as confinement of two triplet excitons on one molecule results in faster biexcitonic recombination rates. However, p-BDT-DPP shows SF only in thin film but not in solution although the ground state absorption spectra are similar in both solution and thin film, as shown in Figure 10A. We believe that the singlet is very low in energy in solution, and the localized triplet states are not very strongly affected by the presence of many repeat units in the polymer, so the energy requirements of $2T_1 < S_1$ are difficult to satisfy in the solution and that is why it does not undergo singlet fission in solution. There is a higher probability for efficient localization of the resulting triplets in well-separated polymer chains, which would result in slower biexcitonic recombination rates, suggesting why singlet fission is more efficient and the triplets live longer in the polymer

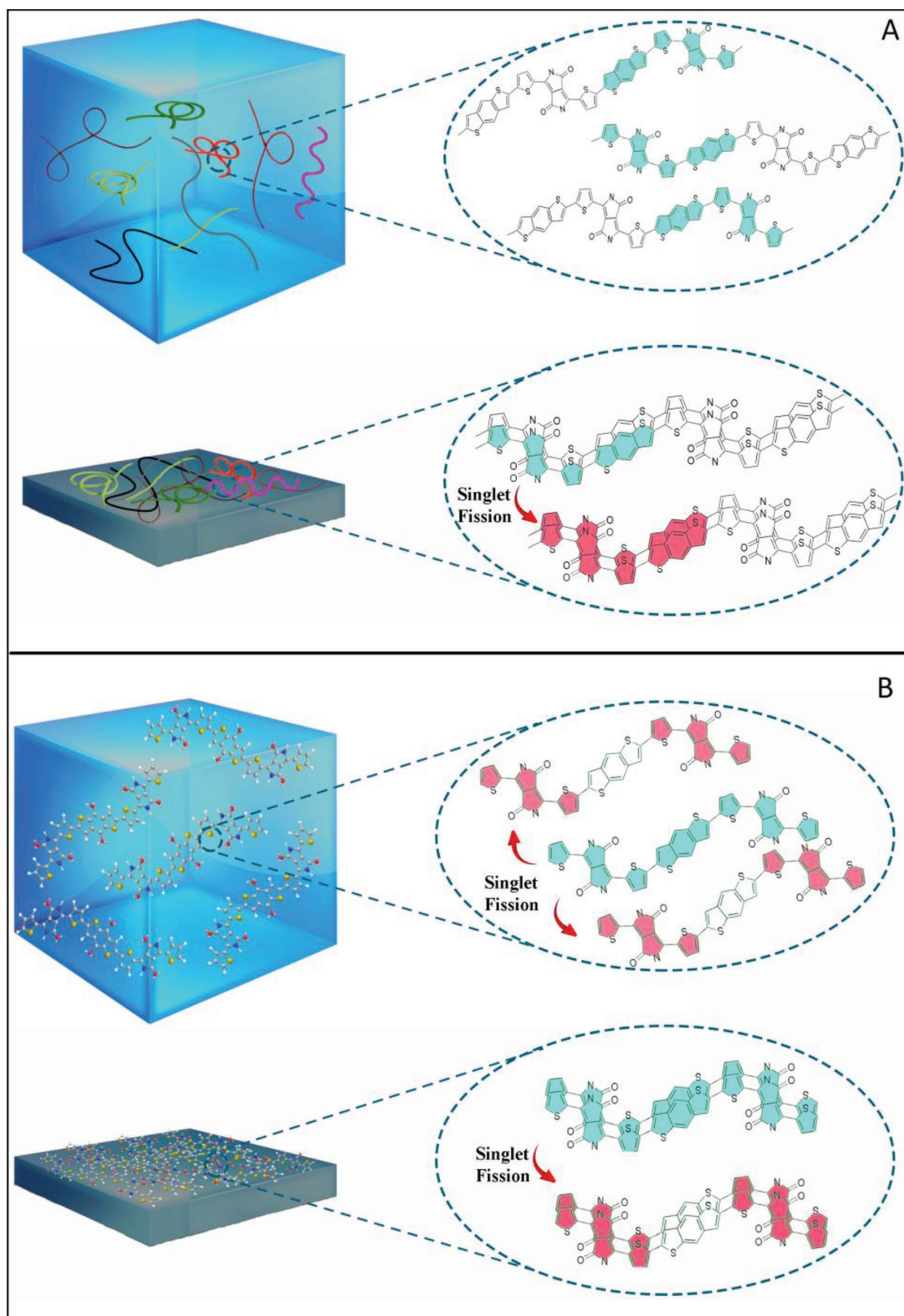


Figure 10. Cartoon of A) intermolecular singlet fission process where a singlet exciton (blue) splits into two triplet excitons (red) on neighboring molecules in aggregate form, B) intramolecular singlet fission process where a singlet exciton (blue) splits into two triplet excitons (red) on the same chromophore in both solution and aggregate form.

sample. In addition, the triplets are separated in p-BDT-DPP, resulting in slower biexcitonic recombination rates.

According to Smith and Michl,^[1] the best choice of chromophore for charge transfer mediated SF is through symmetric and direct linking of two chromophores when the link is planar. The charge transfer state can act as a real intermediate state in the incoherent transformation of the locally excited state (S_1) to the double triplet state (TT) and facilitate SF^[1] so the acceptor–donor–acceptor module with linear backbone is a good candidate structure for designing new chromophores for mediated SF. However, the problem for such a system is that direct linking of two chromophores converts the two chromophores into a single chromophore that reduces the first singlet energy level (S_1) and might even lie below twice the energy of first triplet and make the SF endothermic. Thus, it is important to choose the right donor such that there is sufficient charge transfer for SF while keeping the singlet energy level higher than twice the energy of first triplet for exothermic SF. These considerations can assist toward new molecular designs with higher SF yields in future work. It is also shown that the distance between two triplets that are generated in one chromophore through the intramolecular SF process plays an important role, so introducing a spacer between the donor and acceptor can result in separating the two triplet excitons resulting in longer lived triplets and more efficient SF.

4. Conclusion

Designing new compounds based on conjugating strong donor and acceptor building blocks provides a pathway for the generation of new materials capable of singlet fission suitable for optoelectronic devices. An organic molecule (BDT(DPP)₂) and polymer (p-BDT-DPP) based on a donor–acceptor framework comprising BDT as electron rich and DPP as electron deficient were designed, synthesized, and investigated for singlet fission. TDA-DFT calculations show that the electrons and holes in the first singlet excited state of BDT(DPP)₂ are delocalized over the whole molecule and the first singlet excited state in BDT(DPP)₂ has a mixture of LE/CT character. However, the electron and hole NTOs of the T_1 state are localized within the DPP unit. It also shows that the first triplet excited state has the excitation energy level of about half of the first singlet excited state. The steady state measurements also confirm that this compound meets the energy level requirement for singlet fission. The nanosecond and femtosecond transient absorption spectroscopy measurements were used to investigate the excited state kinetics in the synthesized compounds. Fast formation of the triplet state (<100 ps) in p-BDT-DPP in thin film suggests singlet fission is operating, but there is no sign of triplet formation in the solution. On the other hand, singlet fission occurs in BDT(DPP)₂ in both thin film and in dilute solution, suggesting that the SF mechanism is more probably intramolecular than intermolecular in this molecule. The results suggest the formation of correlated triplet pairs in a single chromophore of BDT(DPP)₂, but they did not diffuse apart to form well-separated triplet pairs. The triplet pair lifetimes and the triplet yields in p-BDT-DPP and BDT(DPP)₂ in thin film are about 150, 1 ns and 70%, 20%, respectively. The short lifetime of triplets in

BDT(DPP)₂ provides additional support to the intramolecular nature of the singlet fission as confinement of two triplet excitons on one molecule results in faster biexcitonic recombination rates. The results of this work can lead to the development of a new class of SF materials for potential application in third generation optoelectronic devices.

5. Experimental Section

Material Synthesis: The commercially available chemicals were purchased from Sigma-Aldrich, Boron Molecular, Matrix Scientific, Ajax Finechem, Univar, Luminescence Technology Corp., and Suna Tech Inc. and all chemicals were used as received. BDT and di-borylated-BDT were prepared according to published procedures.^[63] Both BDT(DPP)₂ and p-BDT-DPP were synthesized using palladium-catalyzed Suzuki coupling reactions. The detailed experimental procedure and full characterization of all new materials are presented in the Supporting Information.

Film Preparation: Glass substrates with dimensions of 2.5 cm × 2.5 cm × 0.1 cm were cleaned by sonicating sequentially in acetone, isopropanol, and chloroform. Before thin film casting, the substrates were dried with a strong flow of nitrogen and then subjected to UV/ozone treatment for 30 min. Solutions of BDT(DPP)₂ or p-BDT-DPP were prepared by dissolving the samples into chloroform with a concentration of 1 mg per 100 μ L, respectively. To prepare blend films for sensitized experiments, solutions of BDT(DPP)₂ or p-BDT-DPP in chloroform mixed with PdOEP were prepared by dissolving the compounds with mass ratio of 60:40 (sensitizer:organic dye). Solutions were then set to stir overnight in the dark under ambient conditions. Finally, thin films were cast onto clean glass substrates via spin coating at 1000 rpm s⁻¹ and spun for 1 min.

Steady State Spectroscopy: Absorption spectra were recorded for BDT(DPP)₂, p-BDT-DPP, and DPP samples using a Varian Cary 50 UV-vis spectrophotometer. Fluorescence spectra were recorded on a Varian Eclipse spectrofluorimeter using excitation wavelengths of 630, 730, and 550 nm for BDT(DPP)₂, p-BDT-DPP, and DPP, respectively.

Photoluminescence (PL) spectra in the near-IR region were recorded with a spectrometer (Horiba Jobin Yvon iHR320) and an amplified InGaAs photodetector (Electro-Optical System). The excitation source was a supercontinuum laser (NKT Photonics, SuperK Extreme) for excitation wavelengths tunable across the 450–750 nm region. The excitation beam was mechanically chopped and the detector output was fed into a lock-in amplifier synchronized to the chopper frequency. A 750 nm high-pass filter was used to remove the second order of the excitation and fluorescence. PL experiments at cryogenic temperatures were carried out in a liquid nitrogen cryostat (Oxford Instruments, Optistat DN).

TCSPC in the near-IR region (800 nm) was performed using the supercontinuum laser described above as the excitation source at a pulse repetition rate of 7.8 MHz and a single photon avalanche diode (EG&G Optoelectronics, SPCM) coupled to the NIR spectrometer described above.

Cyclic Voltammetry: Cyclic voltammetry (CV) experiments were performed at a sweep rate of 100 mV s⁻¹ (Solartron). The supporting electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in dichloromethane (DCM). The solutions were deoxygenated by sparging with argon prior to each scan and blanketed with argon during the scans. The glassy carbon working electrode was prepared by polishing with 5 mm alumina, washed, and dried. The ferrocene/ferrocenium redox couple was used as a standard. The HOMO and LUMO energy levels were calculated from the onset of the oxidation and reduction potential of the compounds as: $E(\text{HOMO}) = -(E_{1/2,ox} \text{ vs } \text{Fc}^+/ \text{Fc} + 5.1) \text{ eV}$ and $E(\text{LUMO}) = -(E_{1/2,red} \text{ vs } \text{Fc}^+/ \text{Fc} + 5.1) \text{ eV}$.

Sub-Nanosecond Transient Absorption Spectroscopy: A mode-locked Ti:sapphire oscillator (Coherent, Mira Seed) seeded a Ti:sapphire regenerative amplifier system (Coherent, RegA 9050) to produce pulses of about 50 fs duration at a repetition rate of 92 kHz and a wavelength

centered at 800 nm. A portion of the light was used to generate the 400 nm pump beam using a barium borate (BBO) crystal, and the 630 and 730 nm pump beams were generated with an optical parametric amplifier (OPA9450, Coherent). The pump beam was mechanically chopped at ≈ 3.5 kHz, and the arrival time of the pump pulses relative to the probe was manipulated using a variable optical delay line (Newport, UTS150PP with ESP 300 controller). The broadband probe was derived from the residual 800 nm beam focused onto a 3 mm sapphire substrate (Crystal Systems) for measurements in the visible region (450–800 nm) and a 5 mm undoped yttrium aluminium garnet (YAG) substrate (Crystal Systems) for the infrared region (800–1400 nm). After passing through the sample, the probe beam was analyzed with a CMOS detector (Ultrafast Systems) at 7077 spectra s^{-1} , and the excess 800 nm laser fundamental was blocked using low- and high-pass filters for the visible and IR regions, respectively. The relative orientation of the pump and probe polarization was 54.7° and all spectra were corrected for the chirp of the supercontinuum probe. Nitrogen was blown over films for all measurements.^[64]

Nanosecond Visible Transient Absorption Measurements: Visible ns-TA spectroscopy was employed to monitor the triplet excited state lifetime of BDT(DPP)₂. The measurements were conducted by a home-built transient absorption spectrometer with a N₂ laser (LTB Lasertechnik Berlin GmbH, MNL 202-C)-pumped dye laser (LTB Lasertechnik Berlin GmbH, ATM200, 700 ps pulse duration) as an excitation source. The transient absorption signal was probed by a Xe lamp (Photon Technology International) light through two monochromators (Acton, Princeton Instruments), and detected by a Si-based nanosecond detection system (Unisoku Co., Ltd., TSP-2000SN, time resolution: 1.2 ns full-width-at-half-maximum (FWHM), monitoring wavelengths: 400–1100 nm) with a fast oscilloscope (Tektronix, TDS 3052C, Digital Phosphor Oscilloscope 500 MHz 5 GS s^{-1}).^[65] Transient data were collected with 400 nm excitation with a repetition rate of 2 Hz at 22 °C. The pulse excitation intensity was adjusted to 30 $\mu J cm^{-2}$.

Near-infrared ns-TA spectroscopy was employed to monitor the triplet excited state lifetime of p-BDT-DPP. The measurements were conducted by a home-built transient absorption spectrometer with a Nd:YAG laser (EKSPILA, NT340 series, 5 ns pulse duration) as an excitation source. The transient absorption signal was probed by a Xe lamp light, and detected by an InGaAs-based nanosecond detection system (Thorlabs, DET20C/M, time rise: 25 ns, monitoring wavelengths: 800–1700 nm) with a fast oscilloscope (Tektronix, TDS 520, two channel digitizing Oscilloscope 500 MHz 500 MS s^{-1}). Transient data were collected with 550 nm excitation with a repetition rate of 10 Hz. The pulse excitation intensity was adjusted to 30 $\mu J cm^{-2}$.

Computational Details: All of the calculations were performed with the Gaussian09 program Rev. E.01.^[66] The geometry optimization of the ground state was carried out using dispersion-corrected DFT at the TPSS-D3(BJ)^[67–69]/6-311G(d)^[70] level of theory and the environmental effects have been taken into account through the polarizable continuum model through the polarizable continuum model using the integral equation formalism (IEFPCM)^[71] using ethanol as a solvent. In order to reduce computational costs, the long side chains in the compound were replaced by methyl groups, as the length of the alkyl chains had no significant impact on the optical properties.^[72] Vertical excitation energies and partial atomic charges of the electronically states were calculated via TDA-DFT^[39] using the CAM-B3LYP^[40] range-separated hybrid functional approximation and the 6-311G**^[70] atomic-orbital basis set and IEFPCM based on the optimized geometry. A range-separated density functional approximation was chosen to ensure that potential CT states could also be appropriately treated. Moreover, it was shown that this method is one of the most accurate hybrid functional approximations with an expected accuracy of 0.18 eV for medium-sized and large chromophores.^[48] The pairs of hole and electron NTOs^[73] for the S₁ and T₁ states were calculated to assess the CT and LE contribution of each excited state. DFT and TD-DFT calculations of partial atomic charge (PAC) were conducted using the Merz–Kollman (MK)^[74] scheme. The method to define the CT distance (d_{CT}), the transferred charge (q_{CT}), the dipole (μ_{CT}), and H index based on the partial atomic charges is discussed in detail in the Supporting Information, and was similar to the procedure described by Jacquemin et al.^[44]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

intramolecular singlet fission, organic photovoltaics, photophysics, singlet fission

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Supporting Information

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**Solution-Processable, Solid State Donor–Acceptor Materials
for Singlet Fission**

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Lars Goerigk, Kenneth P. Ghiggino, Trevor A. Smith, and
David J. Jones**

Supporting Information

Solution-processable, solid state donor-acceptor materials for singlet fission

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Material synthesis

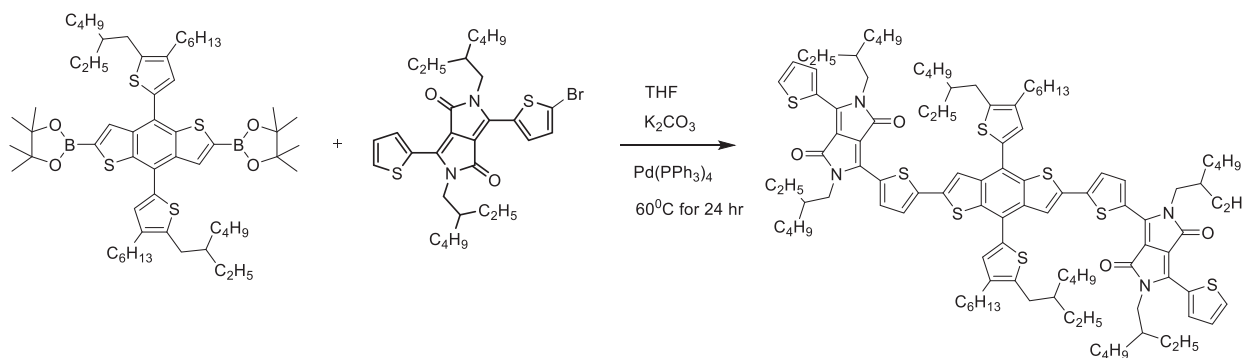
¹H and ¹³C NMR spectra were recorded on a Varian Inova-400 (400 MHz) spectrometer. MALDI-time-of-flight mass spectrometry was performed on a Bruker microFLEX MALDI-TOF in reflector positive mode, using trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix.

BDT(DPP)₂: To a dry 25 ml Schlenk tube, di-borylated substitution of BDT (50 mg, 0.05 mmol) and 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (63 mg, 0.105 mmol) were added. The flask was placed under high vacuum for an hour. The mixture was flushed with Nitrogen, and 5 ml of THF was added via syringe followed by 3 ml of K₂CO₃ aqueous solution (0.1 M). The solution was stirred at room temperature under N₂ for 30 minutes. Pd(PPh₃)₄ (17 mg, 0.015 mmol) was added to the mixture. The solution was then heated to 60 °C and stirred for overnight. The solution was cooled to room temperature, extracted with DCM and the resulting organic layer was washed with brine three times and dried over magnesium sulfate. The solvent removed to dryness. The mixture was washed several times with IPA to remove the impurities and starting materials. The

product was purified via column chromatography employing a mobile phase of petroleum ether and chloroform (10:5.5 v:v) to afford BDT-DPP₂ in 55% yield as a blue powder, MS (ESI) m/z $[M+H]^+ = 1791.927.6$.

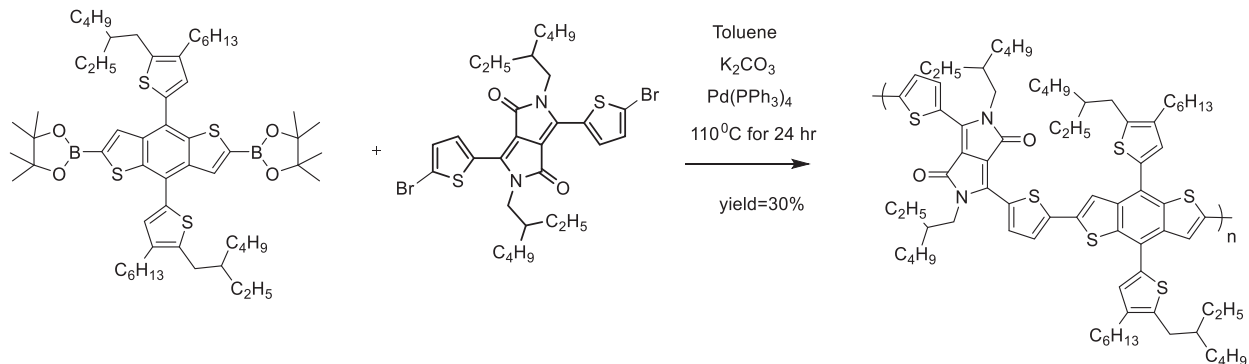
¹H NMR (400 MHz, CDCl₃) δ 8.92 (d, 1H), 8.90 (d, 1H), 7.85 (s, 1H), 7.64 (d, 1H), 7.42 (d, 1H), 7.28 (d, 1H), 4.00 (m, 5H), 3.17 (t, 1H), 2.81 (d, 2H), 2.65 (t, 2H), 1.50- 1.24 (m, 39H), 1.50-1.24 (m, 39H), 1.03-0.81 (m, 28H).

¹³C NMR (101 MHz; CDCl₃): δ 161.5, 140.1, 139.9, 139.5, 139.2, 135.3, 130.6, 129.9, 129.5, 128.4, 126.3, 124.08, 121.1, 108.5, 108.1, 58.7, 46.01, 39.2, 39.07, 32.7, 32.3, 31.7, 30.8, 30.3, 30.2, 29.3, 28.9, 28.5, 28.3, 25.9, 23.8, 23.7, 23.5, 23.0, 22.7, 19.6, 14.1, 14, 13.53, 10.99, 10.54, 10.49.



P-BDT-DPP: To a dry 25 ml Schlenk tube, Di-borylated substitution of BDT (100 mg, 0.14 mmol) and 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (97 mg, 0.14 mmol) were added. The flask was placed under high vacuum for an hour. The mixture was flushed with nitrogen, and 10 ml of toluene was added via syringe followed by 2 ml of K₂CO₃ aqueous solution (0.3 M). The solution was stirred at room temperature under N₂ for 30 minutes. Pd(pph₃)₄ (18 mg, 0.015 mmol) was added to the mixture. The solution was

then heated to 110 °C and stirred for overnight. The mixture was precipitated in methanol. The solid material was collected and purified by Soxhlet in methanol (0 mg), acetone (0 mg), petroleum spirits (0 mg), DCM (0 mg) and chloroform (160 mg) to yield BDT-DPP in 30% yield as a dark green powder. GPC: Mw = 263.1 kg/mol, Mn = 108.4 kg/mol, PDI = 2.42.



Theoretical method to define CT parameters

First, the difference of partial atomic charge (PAC) for the excited state and ground state was calculated for each atom with position of $r_i = (x_i, y_i, z_i)$:

$$\delta q_i = q_i^{ES} - q_i^{GS} \quad (1)$$

Then, the atoms were divided into two categories based on the increase or decrease of their PAC. In each group, q_i^+ and q_i^- are defined as:

$$q_i^+ = \begin{cases} \delta q_i & \text{if } \delta q_i > 0 \\ 0 & \text{if } \delta q_i < 0 \end{cases} \quad (2)$$

$$q_i^- = \begin{cases} 0 & \text{if } \delta q_i > 0 \\ \delta q_i & \text{if } \delta q_i < 0 \end{cases} \quad (3)$$

Therefore, the amount of charge transferred is defined as:

$$q^{CT} = \sum_i q_i^+ = -\sum_i q_i^- \quad (4)$$

The barycenters corresponding to q_i^+ and q_i^- can give us the starting and ending points of the charge transfer according to the following equation:

$$r^+ = \frac{\sum_i r_i q_i^+}{q^{CT}} \quad (5)$$

$$r^- = \frac{\sum_i r_i q_i^-}{q^{CT}} \quad (6)$$

The distance between these two points gives us the charge transfer distance:

$$d^{CT} = |r^+ - r^-| \quad (7)$$

And, the variation of dipole moment between ground and excited state is:

$$\|\mu^{CT}\| = d^{CT} q^{CT} \quad (8)$$

To describe the spread of the charge on the electron donating and electron accepting groups within the molecule, the root mean square deviations of the positive component along the x axis was computed as follows:

$$\sigma^{+x} = \sqrt{\frac{\sum_i (x_i - x^+)^2 q_i^+}{q^{CT}}} \quad (9)$$

Finally, H index along the x axis can be defined as:

$$H = \frac{\sigma^{+x} + \sigma^{-x}}{2} \quad (10)$$

The ground state optimized structure of BDT(DPP)₂



Figure S1. The TPSS-D3(BJ)/6-311G(d)/IEFPCM-optimized structure of the electronic ground state of BDT(DPP)₂

Table S1. Coordinates (Å) of the TPSS-D3(BJ)/6-311G(d)/IEFPCM-optimized structure of the electronic ground state of BDT(DPP)₂ and ground and excited state MK charges

Atom	X	Y	Z	Ground state charges	Excited state charges
C	-1.39906	0.104616	0.029238	-0.077805	-0.072029
C	-0.70688	-1.14715	-0.02419	-0.03609	-0.022887
C	0.689361	-1.25435	-0.04051	0.182968	0.182051
C	1.411284	-0.02606	-0.02943	-0.054115	-0.042058
C	0.718872	1.225679	0.026956	-0.032792	-0.020994
C	-0.6772	1.332861	0.040931	0.184306	0.185215
C	-2.80887	-0.07213	0.135738	-0.099663	-0.090917
C	-3.21231	-1.38981	0.137702	-0.06634	-0.070665

S	-1.8366	-2.50156	0.018489	-0.045314	-0.054804
C	2.821228	0.151503	-0.13168	-0.134086	-0.132322
C	3.225297	1.469228	-0.12511	-0.062933	-0.064525
S	1.848114	2.580323	-0.00874	-0.052655	-0.064695
C	-1.39251	2.609444	0.054739	-0.178778	-0.189927
C	1.402889	-2.53178	-0.05475	-0.17733	-0.189267
C	-4.55682	-1.89144	0.208792	0.104003	0.118273
C	4.569586	1.972308	-0.18289	0.128681	0.146566
S	5.91905	0.862011	-0.07098	-0.072449	-0.12949
C	7.086582	2.182728	-0.21733	0.028512	0.090471
C	6.412263	3.403938	-0.33335	-0.168291	-0.19511
C	5.013128	3.285593	-0.3124	-0.22786	-0.222243
S	-5.90265	-0.79356	-0.0067	-0.038361	-0.082657
C	-7.07278	-2.09702	0.234752	-0.023819	0.025749
C	-6.40188	-3.30547	0.455652	-0.16227	-0.184098
C	-5.0022	-3.19023	0.438553	-0.196586	-0.192467
C	8.485049	1.881292	-0.19151	0.119661	0.033825
C	-8.47062	-1.7965	0.17647	0.189844	0.116843
C	9.114202	0.631297	-0.05291	-0.170853	-0.110025
C	10.52463	0.809259	-0.07392	-0.491221	-0.4174
C	10.80839	2.214072	-0.23212	0.615026	0.615137

N	9.507255	2.826504	-0.29953	-0.056986	-0.065211
C	8.830127	-0.77409	0.109661	0.497403	0.481653
N	10.13501	-1.38603	0.178858	-0.098815	-0.106696
C	11.14975	-0.44274	0.070533	0.319384	0.263479
O	11.85314	2.873356	-0.30765	-0.573075	-0.567142
O	7.787105	-1.43158	0.186197	-0.504754	-0.495814
C	9.401025	4.270762	-0.46889	-0.253421	-0.255982
C	12.55804	-0.70979	0.10295	-0.120339	-0.092686
C	13.55446	0.261974	-0.00278	-0.037438	-0.055481
C	14.86262	-0.2686	0.058641	-0.243978	-0.241539
C	14.87761	-1.63888	0.210544	-0.181945	-0.180183
S	13.28663	-2.30624	0.280742	0.054881	0.044532
C	-9.09552	-0.54746	0.015401	-0.281462	-0.229186
C	-10.5066	-0.72155	0.029578	-0.367454	-0.319732
C	-10.7948	-2.12665	0.190177	0.598177	0.595385
N	-9.49361	-2.74047	0.279932	-0.075345	-0.078167
C	-8.8089	0.859657	-0.12565	0.571285	0.557202
N	-10.1106	1.477068	-0.17063	-0.128232	-0.129464
C	-11.1307	0.531628	-0.07523	0.253196	0.211885
O	-11.8408	-2.78105	0.236716	-0.571481	-0.568554
O	-7.7635	1.512353	-0.21747	-0.532175	-0.524289

C	-10.218	2.912298	-0.4075	-0.191471	-0.185129
C	-9.39079	-4.18937	0.404521	-0.262692	-0.265572
C	-12.5304	0.852128	-0.07731	-0.095627	-0.073598
C	-13.1748	2.083537	0.048705	-0.051135	-0.066854
C	-14.5854	1.990518	0.002142	-0.232362	-0.227008
C	-15.0255	0.69569	-0.16225	-0.198512	-0.198591
S	-13.7266	-0.43801	-0.2444	0.076453	0.069491
C	10.25128	-2.83026	0.344624	-0.158043	-0.145022
C	-2.4872	2.975889	-0.69904	-0.245502	-0.237143
C	-3.00489	4.276206	-0.40604	0.169887	0.167177
C	-2.29115	4.912055	0.591881	-0.028058	-0.022983
S	-0.98171	3.903552	1.170976	-0.015549	-0.01473
C	2.499613	-2.89993	0.695292	-0.256665	-0.245468
C	3.012126	-4.20242	0.40293	0.172499	0.168993
C	2.292259	-4.83835	-0.59056	-0.019108	-0.01388
S	0.983113	-3.82738	-1.16613	-0.018675	-0.017759
C	-4.19176	4.853818	-1.13583	-0.417791	-0.417823
C	-2.47335	6.28462	1.174293	-0.279541	-0.281104
C	4.200033	-4.78224	1.129307	-0.425346	-0.424686
C	2.468616	-6.21249	-1.17105	-0.293496	-0.29465
H	-3.50505	0.752795	0.24138	0.168115	0.167512

H	3.517999	-0.67355	-0.23245	0.188868	0.190919
H	6.908533	4.35886	-0.43283	0.185691	0.186023
H	4.340283	4.133474	-0.39749	0.207244	0.208345
H	-6.90134	-4.24588	0.641413	0.1893	0.189549
H	-4.33052	-4.0262	0.608085	0.194077	0.19513
H	10.42574	4.640844	-0.52817	0.120907	0.120812
H	8.873122	4.519507	-1.394	0.120387	0.122232
H	8.900998	4.731245	0.388143	0.120752	0.122636
H	13.3126	1.315185	-0.11996	0.156514	0.157141
H	15.76483	0.330666	-0.00578	0.191744	0.192054
H	15.73042	-2.30177	0.285377	0.224115	0.223178
H	-10.8889	3.114355	-1.24624	0.113658	0.112705
H	-10.5646	3.43852	0.487209	0.10427	0.103607
H	-9.21052	3.25489	-0.6493	0.104233	0.102341
H	-10.4147	-4.56533	0.369762	0.131683	0.131734
H	-8.81932	-4.61353	-0.42587	0.126933	0.128457
H	-8.93834	-4.47278	1.359463	0.114479	0.116324
H	-12.656	3.020865	0.19623	0.15026	0.151506
H	-15.2506	2.843081	0.090207	0.184421	0.184074
H	-16.0448	0.336505	-0.23033	0.225171	0.224882
H	10.77077	-3.07899	1.274467	0.097916	0.096156

H	9.229019	-3.21014	0.390925	0.099564	0.095864
H	10.76629	-3.28395	-0.50701	0.099431	0.097359
H	-2.90455	2.332245	-1.4686	0.202302	0.200518
H	2.921765	-2.25638	1.462283	0.204062	0.201196
H	-5.04143	4.160959	-1.10364	0.131325	0.131268
H	-4.51542	5.805246	-0.70575	0.142756	0.142741
H	-3.9537	5.029743	-2.19241	0.121924	0.122058
H	-3.47335	6.665786	0.949465	0.094279	0.094602
H	-2.35254	6.280701	2.26287	0.124293	0.12425
H	-1.74405	6.993878	0.762378	0.125788	0.126185
H	5.050843	-4.09093	1.094958	0.127395	0.127016
H	3.964568	-4.958	2.186509	0.126524	0.126474
H	4.52075	-5.73418	0.698151	0.145432	0.145376
H	3.468009	-6.59632	-0.94806	0.098043	0.098277
H	1.738182	-6.91878	-0.75606	0.129243	0.129578
H	2.345073	-6.21007	-2.25933	0.126819	0.126705

CT character of the first excited state for BDT(DPP)₂

Table S2. The CT parameters of the first excited state for BDT(DPP)₂. Q^{CT} is in e, μ^{CT} is in Debye, and d^{CT} and H are in Å.

State	q^{CT}	d^{CT}	μ^{CT}	H
S_1	0.59	0.06	0.18	8.64

Phosphorescence spectra of BDT(DPP)₂

Figure S2 compares the emission of 5 μ M BDT(DPP)₂ at room temperature and 77 K in m-THF, which is a known glassy solvent used for spectroscopy at cryogenic temperature. When the temperature is lowered to 77 K, a peak is observed at about 1300 nm (0.95 eV), which is assigned to emission from the triplet state.

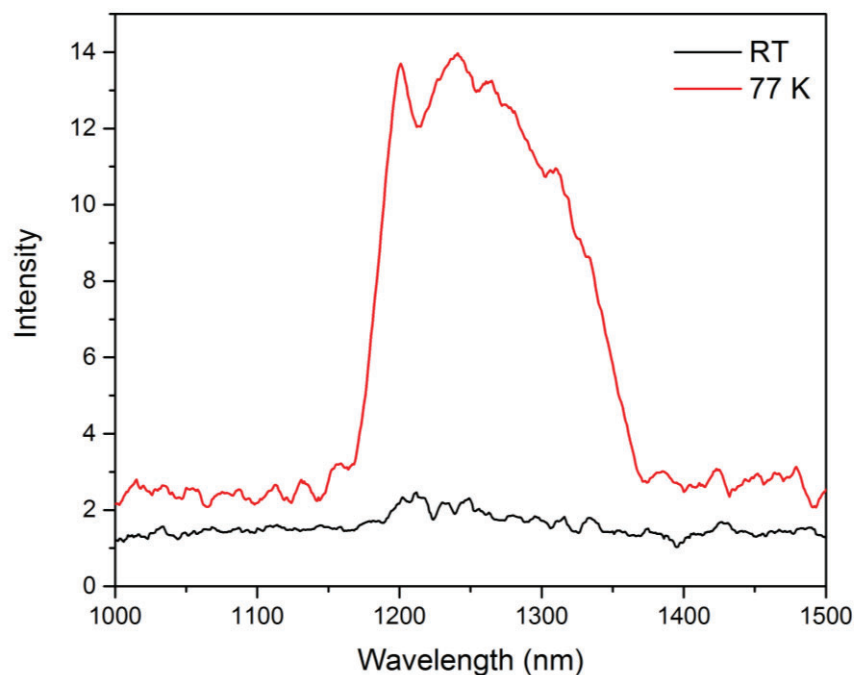


Figure S2. The emission of 5 μ M BDT(DPP)₂ in m-THF at room temperature and 77 K excited at 630 nm in the spectral region of 1200-1500 nm (>1200 nm highpass filter used).

Cyclic voltammetry

Figure S3 shows the cyclic voltammetry (CV) of BDT(DPP)₂, p-BDT-DPP and DPP using a linear-voltage CV experiment on 1 mg/mL of the compounds in dichloromethane. The redox potentials were calibrated with the redox potential of ferrocene/ferrocenium (Fc/Fc⁺) which is located at 0.31 V relative to the reference electrode. The redox potential of Fc/Fc⁺ is considered to have an absolute energy level of -4.8 eV relative to vacuum. The oxidation peak is clear in all of the experiments but the reduction peak is obscured by the background in the DPP molecule so we determined all of the HOMO energy levels directly from the oxidation onsets. However, the LUMO energy levels were determined from the HOMO energy level and optical bandgap.

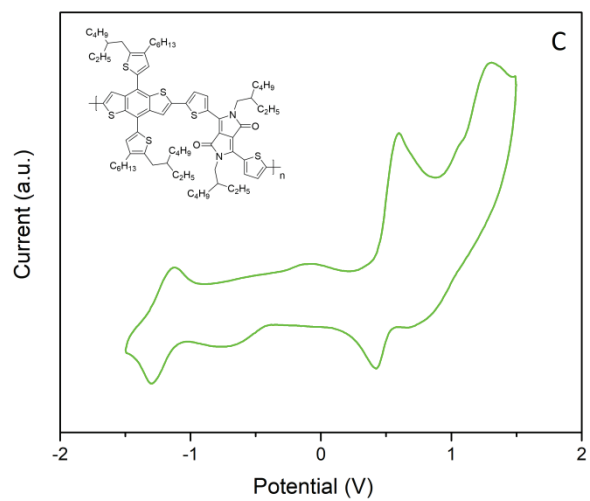
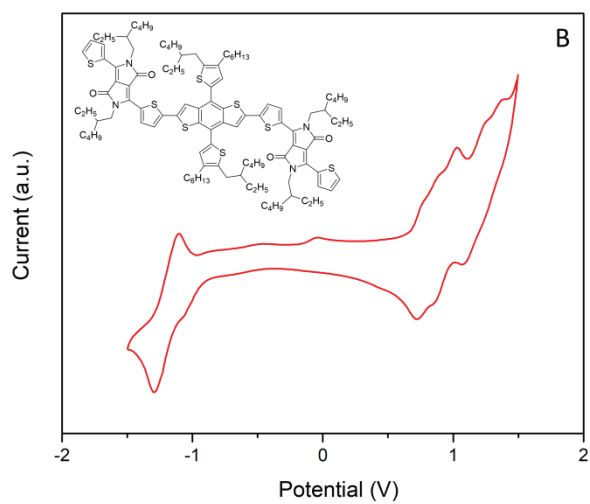
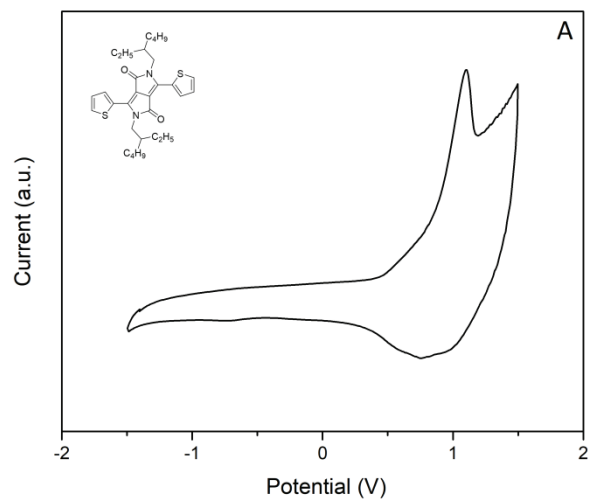


Figure S3. Cyclic voltammetry (CV) of BDT(DPP)₂, p-BDT-DPP and DPP using a linear-voltage CV experiment on 1 mg/mL of the compounds in dichloromethane.

Absorption and fluorescence spectra of BDT(DPP)₂ in different solvents

As shown in Figure S4, there is a slight red shift in the absorption and fluorescence spectra of BDT(DPP)₂ by decreasing the polarity of the solvent, which suggests the charge transfer character of the lowest energy optical excitation, which is also well characterized in several reports.

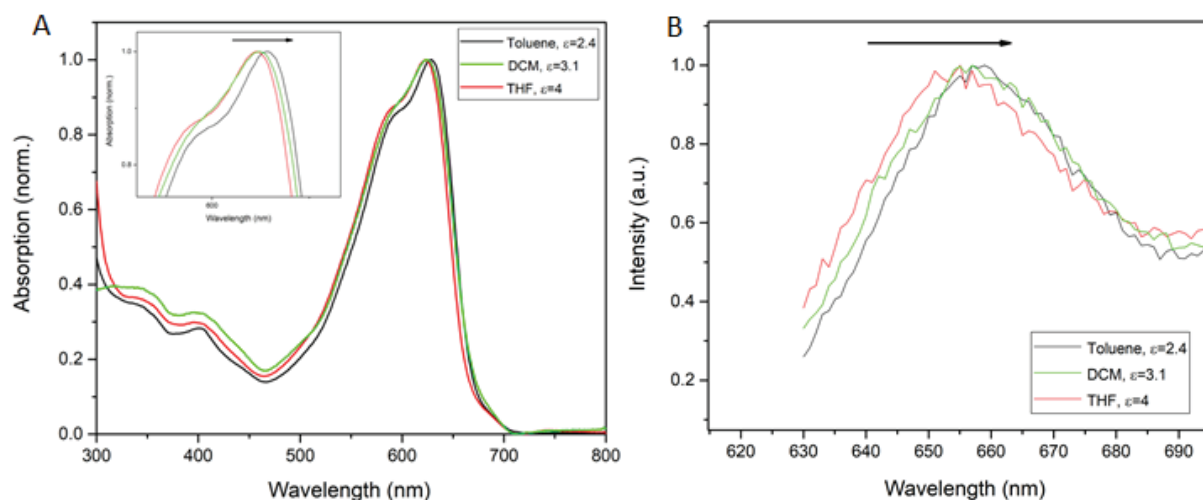


Figure S4. (A) The absorption spectra and (B) fluorescence spectra of BDT(DPP)₂ in different solvents

Temperature dependent UV-vis absorption measurement of P-BDT-DPP

We performed a temperature dependent UV-vis absorption measurement in the chloroform solution of p-BDT-DPP in the range of 30-100°C, Figure S5. The temperature promotes the separation of the copolymer chains and also decreases the size of the aggregates. Figure S5

shows that the 0–0 peak intensity has a different temperature dependence compared to the 0–1 peak. The intensity of the 0–0 peak decreases in intensity continuously with temperature, but the 0–1 peak remains constant. There is a slight blue shift with increasing temperature. The results show that interchain interactions decrease and copolymer chains are allowed to separate at higher temperatures.

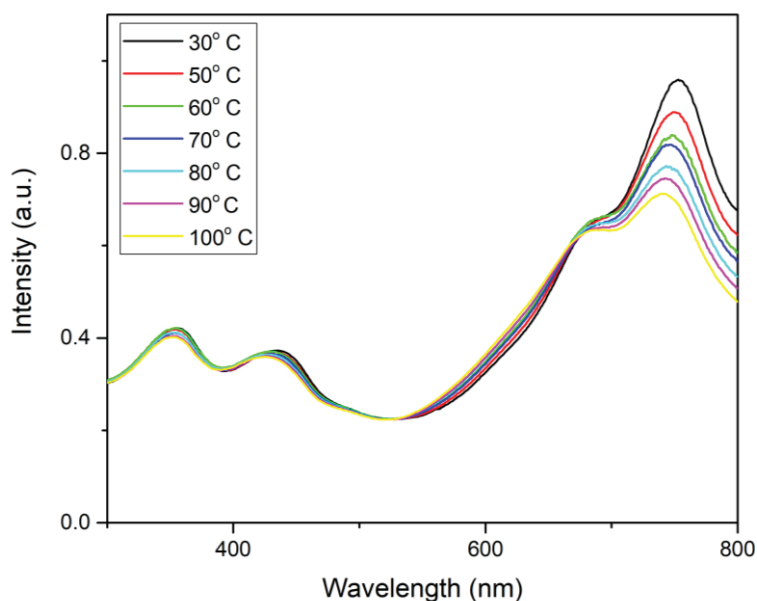


Figure S5. Temperature dependent UV-vis absorption measurement in chloroform solution of p-BDT-DPP

Table S3. Optical and electrochemical properties of BDT(DPP)₂, p-BDT-DPP and DPP

	$\lambda^{\max}$ (nm)	E_g^{Opt} (eV)	E_g^{Opt} (eV)	HOMO	LUMO
	(Solution)	(Film)	(Solution)	(eV)	(eV)
DPP	550	1.98	2.14	-5.26	-3.12
BDT(DPP) ₂	620	1.64	1.88	-5.19	-3.34

p-BDT-DPP	750	1.30	1.32	-4.92	-3.6
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Time correlated single photon counting (TCSPC) measurement of p-BDT-DPP at low temperature

To find out more information about the dynamic of singlet exciton in thin film of p-BDT-DPP, we performed a TCSPC measurement at cryogenic temperature. When the temperature is lowered to 77 K, a fluorescence spectrum was observed with maximum at about 1000 nm for p-BDT-DPP in thin film. We measured the fluorescence time decay by TCSPC technique at the wavelength of 800 nm. Figure S6 shows the decay of p-BDT-DPP in thin film and instrument response function which suggests that the singlet excited state of p-BDT-DPP is a fast component which is quenched by triplet state with the time constant of less than 3 ns within the instrument response function.

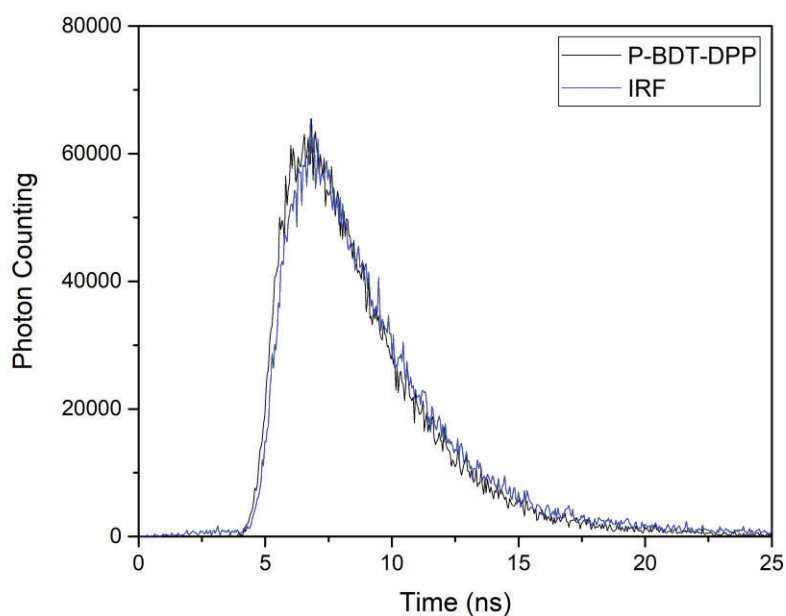


Figure S6. TCSPC decay curve of p-BDT-DPP film monitored at 800 nm following excitation at 630 nm at 77 K.

Steady state absorption of PdOEP

The steady state absorption of Palladium octaethyl-porphine (PdOEP) in thin film is shown in Figure S7. It shows two narrow and isolated absorption bands at 400 and 550 nm which are attributed to the Soret and Q bands, respectively.

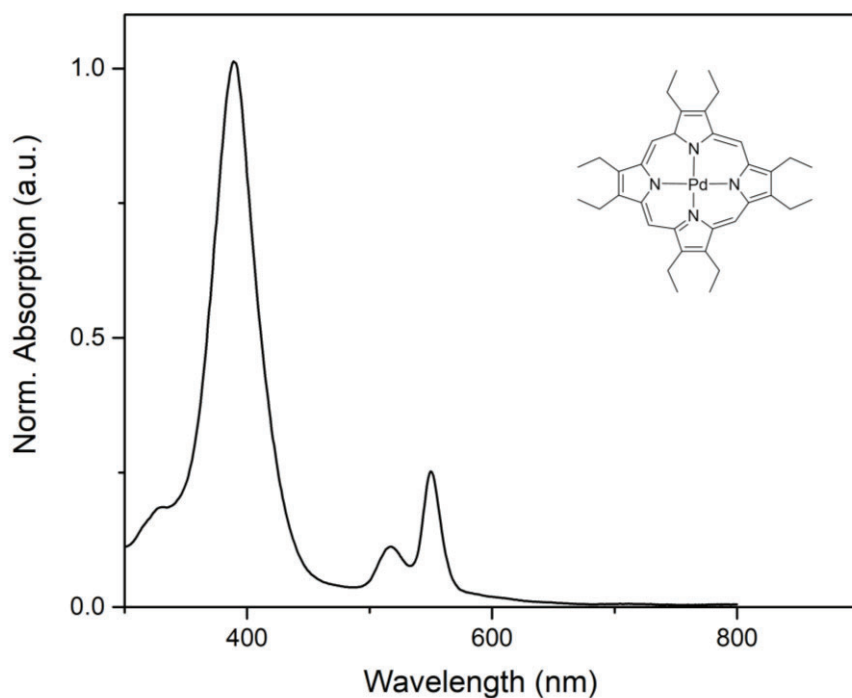


Figure S7. The absorption spectrum of PdOEP in thin film.

fs-transient absorption (TA) of PdOEP

The thin film TA spectra of PdOEP in the spectral region of 500-1300 nm following excitation at 400 nm are shown in Figure S8. It shows a narrow negative ground state bleach (GSB) at 550

nm, mirroring the Q band in the steady state absorption, at both time delay of 100 and 800 ps and no positive photoinduced absorption after excitation at 400 nm.

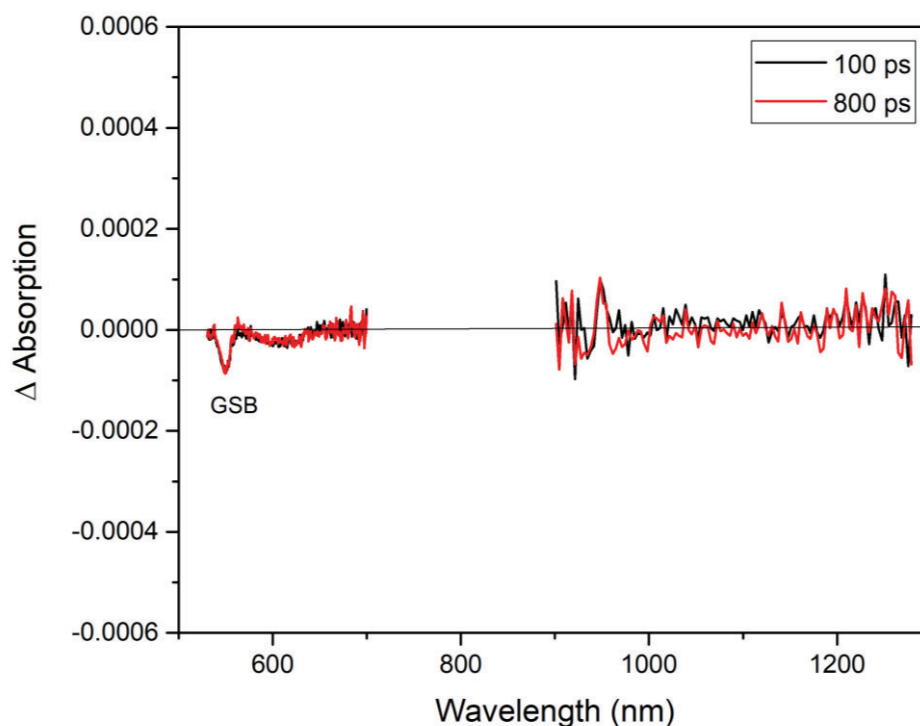


Figure S8. TA spectra of PdOEP in thin film at time delay of 100 and 800 ps excited at 400 nm with fluence of $10 \mu\text{J}/\text{cm}^2$.

Global target analysis of p-BDT-DPP: PdOEP blend film

To study the mechanism from a large transient absorption data set, advanced modeling and data analysis techniques such as global and target analysis are needed to derive models and decompose spectra into their overlapping component spectra. Specifically, Global Target Analysis (GTA) is an approach based on differential equations that is employed to analyze multidimensional data sets for kinetic modeling and spectral interpretation. In our study, the program Glotaran,^[1] which is an easy-to-use modeling and data analysis tool, was used for such

analysis. This approach starts with a simple model with a defined number of components and a set of starting values for the rate constants describing the kinetic connectivity between the components. The whole transient absorption data set is fitted by generating the time dependent population evolution of spectral intensities from a set of first order differential equations. Then, the parameters are optimized by re-adjusting the starting values based on the resulting model. The quality of the fit can be judged from the fitted spectra and time traces as well as residual matrixes. Any residual structure in the singular vectors displays a potential misfit and the need for another component in the proposed model.^[1] After checking and accepting the fitted model, the program generates kinetic traces, the evolution of populations and spectra of each component. GTA was used to separate the overlapping features and generate the population profiles for each component versus time.

To find the triplet absorption spectrum, global target analysis was performed on the p-BDT-DPP:PdOEP blend film. For the p-BDT-DPP:PdOEP blend film, a simple sequential $A \rightarrow B \rightarrow GS$ model was considered and the resulting associated spectra for each species are shown in Figure S9.

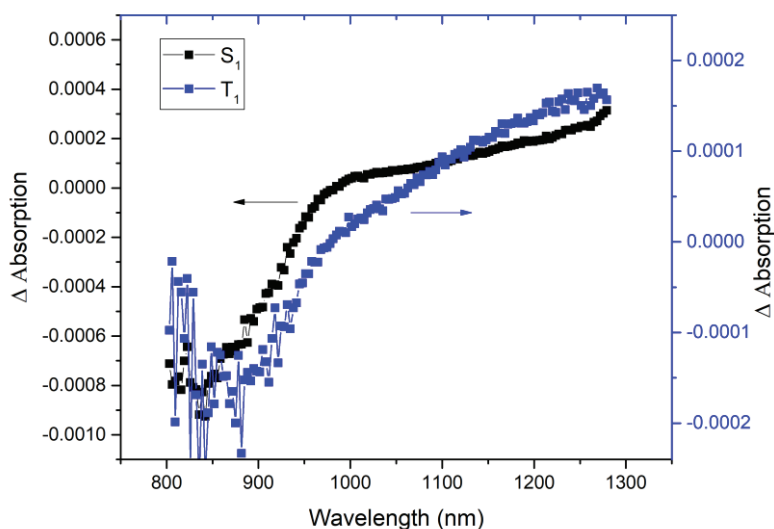


Figure S9. Extracted associated spectra for A and B which are assigned to S_1 and T_1 for p-BDT-DPP:PdOEP blend system.

ns-TA of p-BDT-DPP and p-BDT-DPP: PdOEP blend film

The dynamics of the long-lived species in p-BDT-DPP films and the sensitizer-generated triplet species were investigated using nanosecond transient absorption (ns-TA) measurements with excitation at 630 and 400 nm, respectively. The decay monitored at 1200 nm, is shown in Figure S10. The results show a faster recombination rate for SF generated triplets comparing to the sensitizer generated single triplets resulting in an enhanced contribution of spin-allowed geminate triplet-triplet annihilation.

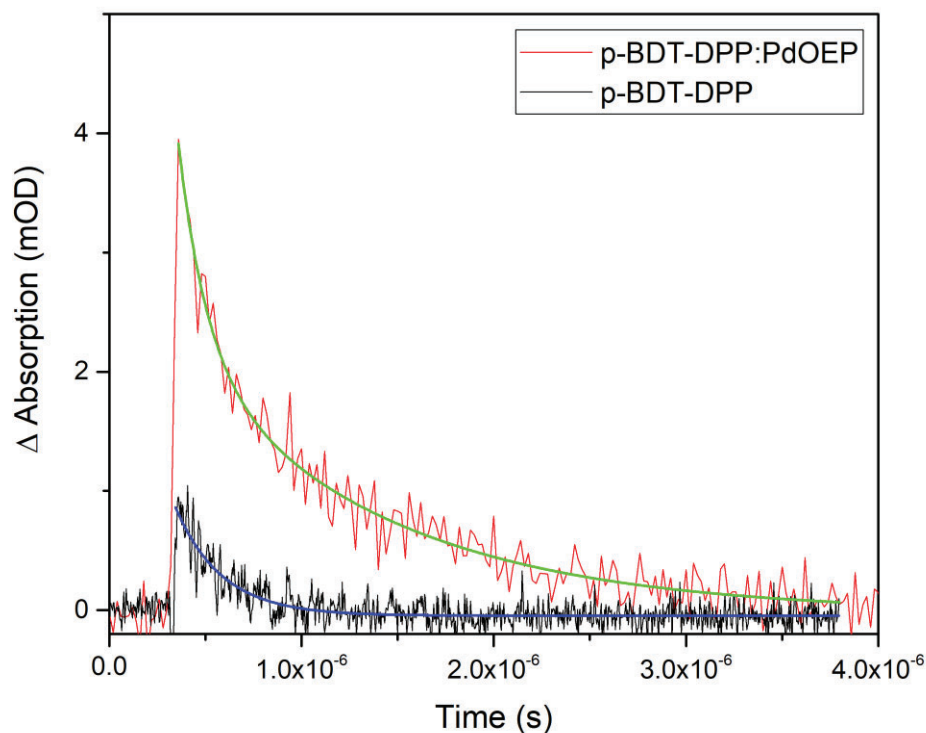


Figure S10. TA decay curve of the p-BDT-DPP and p-BDT-DPP: PdOEP blend film monitored at 1200 nm following excitation at 630 and 400 nm with excitation density of $30 \mu\text{J}/\text{cm}^2$. The solid green and blue lines show fitted results using a biexponential and monoexponential functions.

Stern-Volmer quenching plot of PdOEP

To find more details about triplet energy transfer to BDT-DPP₂, the phosphorescence spectra of 8.7 μM PdOEP was measured by adding BDT-DPP₂ in the concentration range of 2-90 μM . There is no self-annihilation for PdOEP at this low concentration. The phosphorescence intensity of PdOEP is quenched by the introduction of BDT-DPP₂ suggesting triplet energy transfer from PdOEP to BDT-DPP₂. Figure S11 is the corresponding Stern-Volmer phosphorescence quenching plot of PdOEP. The rate constant for triplet energy transfer (K_{TET}) and the triplet energy transfer efficiency (Φ_{TET}) can be calculated from the Stern-Volmer equation (Equation S11 and 12).

$$\frac{I_0}{I} = 1 + K_{TET}\tau_0[A] \quad (11)$$

$$\phi_{TET} = 1 - \frac{I}{I_0} = 1 - \frac{1}{1 + K_{TET}\tau_0[A]} \quad (12)$$

where τ_0 is the lifetime of the unquenched sensitizer, I and I_0 are the quenched and unquenched emission intensities of the sensitizer, respectively; and $[A]$ is the concentration of BDT-DPP₂ added. The lifetime of the unquenched PdOEP triplet was reported to be 90 μ s in degassed solution.^[2] According to the results, the rate constant for triplet energy transfer (K_{TET}) and triplet energy transfer efficiency (Φ_{TET}) for 90 μ M BDT-DPP₂ are $4.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and 0.97, respectively

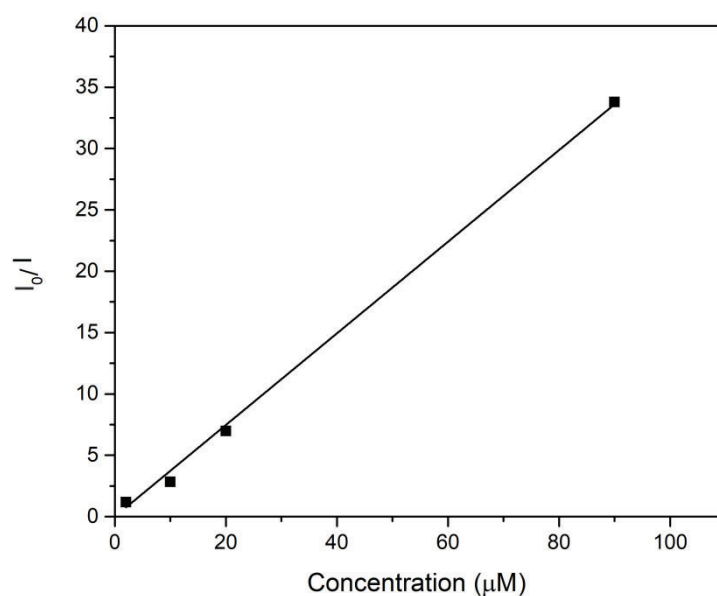


Figure S11. Stern-Volmer phosphorescence quenching plot of 8.7 μ M PdOEP.

The ns-TA of BDT(DPP)₂: PdOEP blend film

The dynamics of the sensitizer-generated triplet species in BDT(DPP)₂ films was investigated using nanosecond transient absorption (ns-TA) measurements with excitation at 400 nm. The triplet state decay for sensitized p-BDT-DPP film, monitored at 1050 nm, is shown in Figure S12.

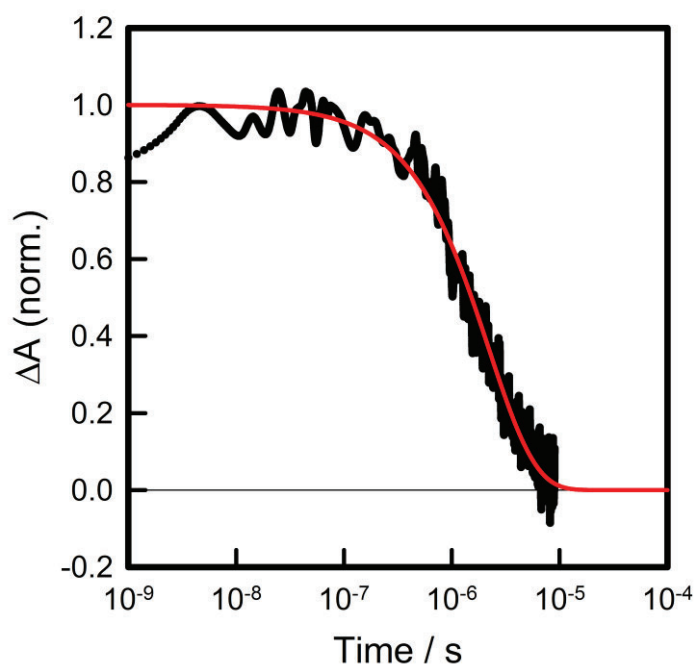


Figure S12. TA decay curve of the BDT(DPP)₂: PdOEP blend film monitored at 1050 nm with excitation density of 30 $\mu\text{J}/\text{cm}^2$.

Solvent independent dynamics

To ensure that the dynamics of excited states does not have charge transfer character, the kinetic traces of PIA1 were investigated in three solvents with different polarities. Figure S13 shows kinetic traces of 10 μM of BDT(DPP)₂ in cyclohexane, dichloromethane and chloroform at 1100 nm with an excitation wavelength of 630 nm at 10 $\mu\text{J}/\text{cm}^2$. The results indicate very minor

effects of solvent polarity on the dynamics of PIA1 suggesting the lack of charge transfer character in this feature.

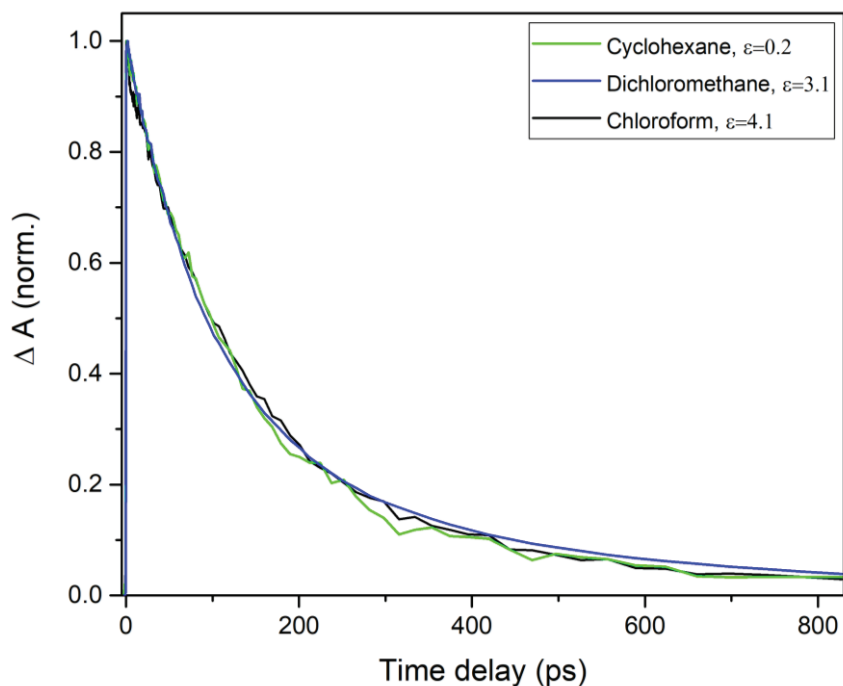


Figure S13. Kinetic traces of 10 μM of BDT-DPP₂ in cyclohexane, dichloromethane and chloroform at 1100 nm with an excitation wavelength of 630 nm at 10 $\mu\text{J}/\text{cm}^2$.

Global target analysis of dilute solution of BDT(DPP)₂

The fitted model and real transient absorption spectrum of BDT(DPP)₂ in a dilute solution of chloroform at time delay of 700 ps are compared in Figure S14. It was found that there is a difference between the fitted model and real transient absorption at time delay > 700 ps by the appearance of a new photoinduced absorption (PIA2). The residual spectrum is similar to the associated spectrum of the S₁ excited state which was extracted from GTA.

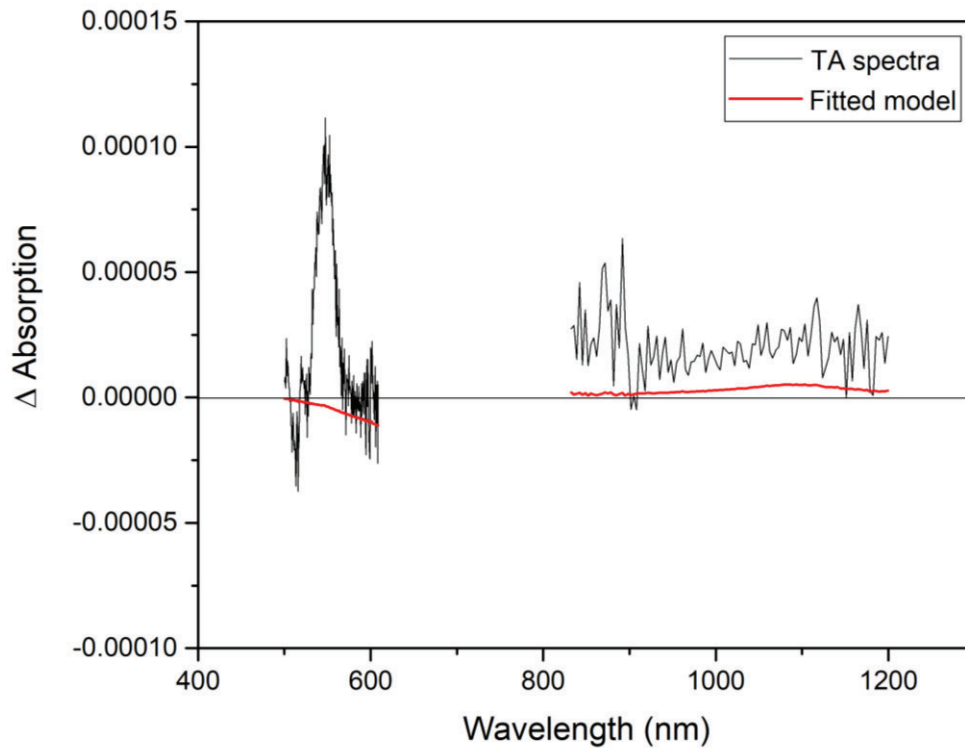


Figure S14. TA spectra and fitted model from global target analysis of BDT(DPP)₂ in dilute solution at time delay of 700 ps.

Singlet fission yield determination using triplet sensitization method

To determine the number of triplet excitons formed in PdOEP upon excitation, we assume that the intersystem crossing rate in PdOEP is high enough that all of the initial excited states are converted to triplets. The number of excitons is calculated based on the thickness of the film (L) that is measured from AFM images and the energy of excitation (E) using the following equation for the ground state bleach of PdOEP in the p-BDT-DPP: PdOEP blend film at $\lambda=550$ nm:

$$Triplet(PdOEP) = \frac{E\lambda K(1-10^{-A})}{lL} = 5.95 \times 10^{16} \text{ exciton/cm}^3 \quad (13)$$

Assuming that all of the triplets that formed in PdOEP are transferred to p-BDT-DPP, the number of triplets that are transferred to p-BDT-DPP is also 5.95×10^{16} per area. By comparing the magnitude of the p-BDT-DPP triplet absorption peak at the blend film with the number of triplet excitons that are transferred to p-BDT-DPP, the triplet extinction coefficient of p-BDT-DPP [$\epsilon(p_triplet)$] is calculated. Then, the triplet extinction coefficient is used to calculate the number of triplets formed in p-BDT-DPP from the magnitude of the p-BDT-DPP triplet absorption peak of the p-BDT-DPP film.

$$\epsilon(p - triplet) = \frac{\Delta ABS(p-triplet \text{ in blend})}{Triplet (transferred to p) L} = 7.6 \times 10^{-17} \left(\frac{molecule}{cm^3} \right)^{-1} cm^{-1} \quad (14)$$

$$Triplet(p) = \frac{\Delta ABS(p-triplet \text{ in p-BDT-DPP film})}{\epsilon(p-triplet) L} = 1.45 \times 10^{16} \quad (15)$$

The number of singlet excitons formed in p-BDT-DPP film upon excitation is calculated from Equation S16 at the ground state bleach of the p-BDT-DPP in the film at $\lambda=863$ nm:

$$singlet(p) = \frac{E\lambda K(1-10^{-A})}{IL} = 2.1 \times 10^{16} \text{ exciton/cm}^3 \quad (16)$$

The ratio of the number of triplet:singlet gives the SF yield:

$$SF \text{ yield} = \frac{Number \text{ of triplet exciton}}{Number \text{ of singlet exciton}} = 0.7 \quad (17)$$

Similar measurements were carried out to determine the triplet extinction coefficient, number of triplet and SF yield for BDT-DPP₂. According to the calculation, BDT-DPP₂ shows triplet yields of 0.18 in the solid state.

NMR spectra of BDT-DPP₂

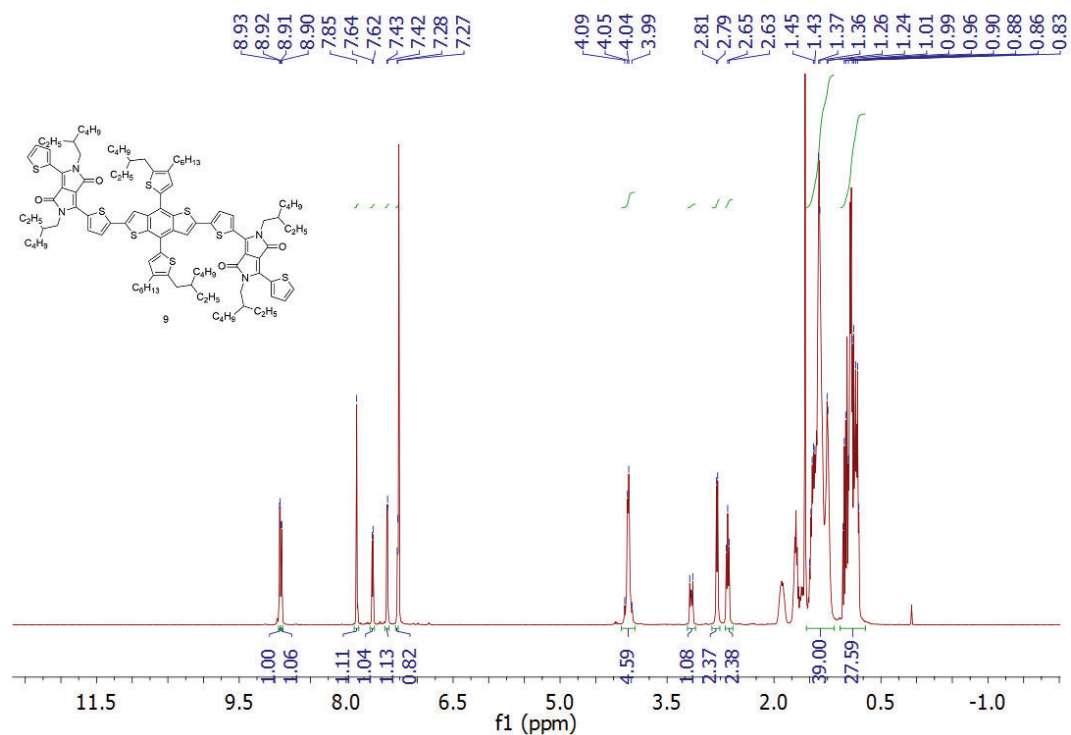


Figure S15. ¹H NMR of BDT-DPP₂

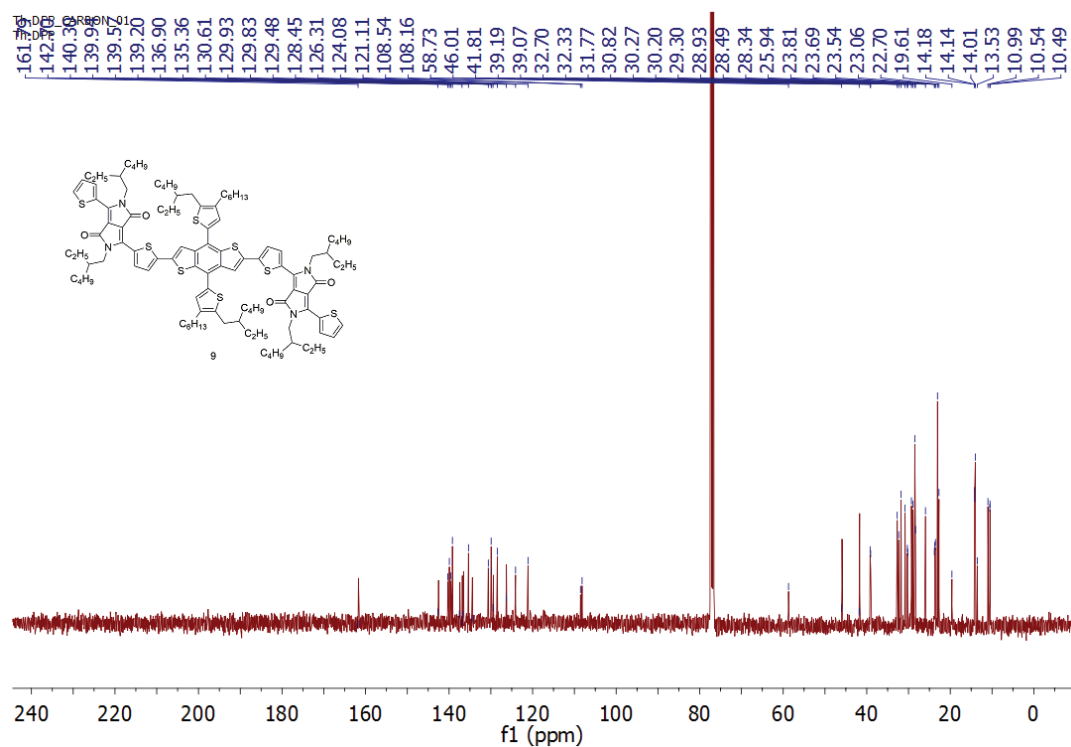


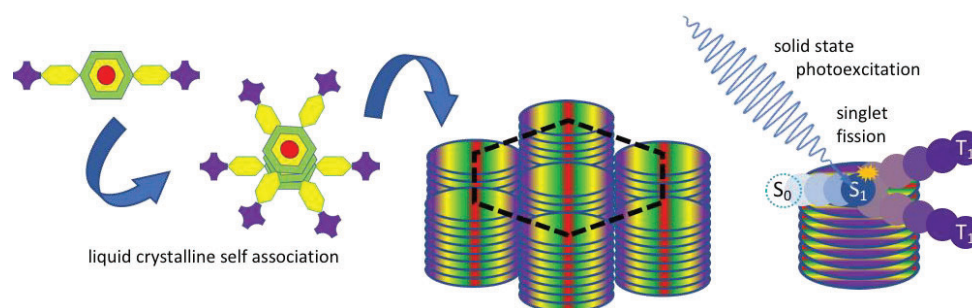
Figure S16. ^{13}C NMR of BDT-DPP₂

Reference

- [1] J. Snellenburg, S. Liptonok, R. Seger, K. Mullen, I. Van Stokkum, J. Stat. Softw. 2012, 49.
- [2] V. Gray, A. Dreos, P. Erhart, B. Albinsson, K. Moth-Poulsen, M. Abrahamsson, Phys. Chem. Chem. Phys. 2017, 19, 10931.

Chapter 5

Liquid Crystallinity as a Self-Assembly Motif for High-Efficiency, Solution-Processed, Solid-State Singlet Fission Materials



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5.1. Preface

The results of most of efficient SF systems demonstrate that a large degree of crystallinity is required, and the SF yield is highly sensitive to the nearest-neighbor coupling in these systems, the so called “local-order constraint”.¹ Therefore, the aims of this work were to develop a new class of solution processible SF materials that are more amenable to inclusion into solar cell devices through intra-molecular SF, and to remove the “local-order constraint”.

In Chapter 4, a new SF material, made by coupling two thienyl substituted diketopyrrolopyrroles (DPP) to the benzodithiophene core (BDT), (BDT(DPP)₂), was studied. However, triplet generation was low in the solid state in the molecular donor at 18% efficiency,

although results in solution suggested that the BDT(TDPP)₂ supported intra-molecular SF.² The results indicated two key issues with BDT(TDPP)₂; i) the S₁ energy was possibly too low at 1.89 eV, barely 2 x T₁ (T₁ = 0.95 eV), and ii) no evidence for self-association was observed. These results suggested that a stronger driver is required for self-association and a higher S₁ energy along with the two TDPP triplet host acceptors were needed to increase the SF yield. To address these two issues, we designed new chromophore with different core to organize the self-association and make the singlet state higher in energy which is studied in this chapter. In this study, the occurrence of SF in a hybrid material composed of hexa-peri-hexabenzocoronene (HBC) as a self-organizing electron donor attached to TDPP as an electron acceptor was investigated.

In this chapter, the use of hexa-peri-hexabenzocoronene (HBC) as a self-organizing core to promote singlet fission was investigated in amorphous films. HBC is a polycyclic aromatic hydrocarbon made up of thirteen fused six membered rings, which forms a mesophase. Soluble HBC derivatives show strong self-association in solution and discotic columnar structures with ordered morphology in films.³⁻⁴

Our interest in developing solution processible SF materials for use in the printed organic solar cells, led us to question, can the liquid crystallinity inherent in FHBC be used as a self-organizing motif and scaffold to pre-organize the DPP chromophore to promote intra-molecular SF in amorphous thin films? In this way, can the “local-order constraint”, inherent in known molecular SF materials, be removed?

In this chapter, a discotic liquid crystalline material FHBC(TDPP)₂, comprising a fluorenyl substituted hexabenzocoronene (FHBC) core and two pendant bithiophene-2,5-

dihydropyrrolo[3,4-c]pyrrole-1,4-dione (TDPP) groups is introduced and characterized for SF, and SF parameters are investigated using spectroscopic techniques such as time correlated single photon counting (TCSPC), ultrafast transient absorption (TA) and ns-transient absorption (ns-TA) measurements. The experimental results reported reveal new information on how to design a highly efficient, solution processible, solid state SF material.⁵

Time-dependent density functional theory with the Tamm–Dancoff approximation (TDA-DFT) and natural transition orbital (NTO) calculations have been performed and confirm the possibility of singlet fission in terms of the energetic landscape. The photophysical properties of FHBC(TDPP)₂ were fully characterized to study singlet fission in the solid state and in solution. The research results have been published in the following article:⁵

Saghar Masoomi-Godarzi, Maning Liu, Yasuhiro Tachibana, Valerie D. Mitchel, Lars Goerigk, Kenneth P. Ghiggino, Trevor A. Smith, and David J. Jones. Liquid Crystallinity as a Self-Assembly Motif for High-Efficiency, Solution-Processed, Solid-State Singlet Fission Materials. *Adv. Energy Mater.* 2019, 9, 1901069. DOI: [10.1002/aenm.201901069](https://doi.org/10.1002/aenm.201901069).

The experimental details are included in the Supplementary Information section following the main manuscript. Reprinted with the permission from Ref [5], copyright © 2019 Wiley.

Contribution of the candidate:

- All of the steady state spectroscopy
- Time correlated single photon counting (TCSPC) measurements
- Ultrafast transient absorption measurements

- Global target analysis
- Computational calculations in Gaussian

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Liquid Crystallinity as a Self-Assembly Motif for High-Efficiency, Solution-Processed, Solid-State Singlet Fission Materials

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Dedicated to Prof. Andrew Holmes on the occasion of his 75th birthday

Solution and solution-deposited thin films of the discotic liquid crystalline electron acceptor–donor–acceptor (A-D-A) p-type organic semiconductor FHBC(TDPP)₂, synthesized by coupling thienyl substituted diketopyrrolopyrrole (TDPP) onto a fluorenyl substituted hexa-*peri*-hexabenzocoronene (FHBC) core, are examined by ultrafast and nanosecond transient absorption spectroscopy, and time-resolved photoluminescence studies to examine their ability to support singlet fission (SF). Grazing incidence wide-angle X-ray (GIWAX) studies indicate that as-cast thin films of FHBC(TDPP)₂ are “amorphous,” while hexagonal packed discotic liquid crystalline films evolve during thermal annealing. SF in as-cast thin films is observed with an ≈150% triplet generation yield. Thermally annealing the thin films improves SF yields up to 170%. The as-cast thin films show no long-range order, indicating a new class of SF material where the requirement for local order and strong near neighbor coupling has been removed. Generation of long-lived triplets (μs) suggests that these materials may also be suitable for inclusion in organic solar cells to enhance performance.

1. Introduction

The dominant loss mechanism in single-junction photovoltaic (PV) devices following excitation with high-energy photons is the wasted excess energy above the bandgap that is emitted as heat (thermalization losses), leading to a maximum theoretical

efficiency of 32% for a single-junction PV; the Shockley–Queisser limit.^[1,2] A process that has the potential to increase this limit to 45% is to use high-energy photons to produce two electron–hole pairs following the absorption of a single photon. In organic materials, such a photophysical process is called singlet fission (SF), the spin allowed conversion of a singlet excited state into two triplets by an assembly of two or more chromophores.^[3] Although the mechanism of SF is not yet fully understood and is still the subject of intense research, it is generally accepted that the single excitation converts to a triplet pair state (¹TT), either coherently or incoherently, which later separates into two independent triplets ($2 \times T_1$).^[4,5] Recent studies show that the correlated triplet pair (¹TT) state may convert first to a spatially separated triplet pair intermediate (¹T...T) before it

undergoes dephasing or decorrelation into two independent triplets.^[4]

The design of a chromophore capable of supporting SF requires optimization of both energetics and intermolecular electronic coupling, so there are only a limited number of reported SF systems.^[6] For SF the energy of the singlet state ($E(S_1)$) should be greater than or equal to twice the energy of the triplet state ($E(T_1)$), i.e., $E(S_1) \geq 2E(T_1)$. Also, the electronic coupling between nearest neighbors must be optimized to have efficient SF. SF was first observed in crystalline anthracene, and has been extensively studied in this molecular system.^[2] SF has since been reported with high yields in polyacenes,^[7,8] such as tetracene, pentacene and their derivatives, oligophenyls,^[9] diphenylisobenzofuran,^[10] carotenoids,^[11,12] rylene-based chromophores,^[13] perylenediimides,^[14] diketopyrrolopyrroles (DPP) derivatives, and some conjugated polymers.^[15,16] Efficient SF has been reported mainly in condensed matter systems, e.g., crystals,^[17–20] polycrystalline films,^[21–23] amorphous films,^[24,25] nanoparticles and aggregates.^[12,26] Although SF has been reported in a limited number of partially disordered systems, highly efficient SF requires systems with a large degree of crystallinity and the SF yield is highly sensitive to the crystallinity of the film, crystal packing and intermolecular nearest-neighbor coupling

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in these systems; the so called “local-order constraint.”^[27] Theoretical calculations show that a slippage of only 2–3 Å along the main acene axis can significantly reduce orbital overlap reducing SF yields.^[28] It has been found that SF is suppressed in polymorphs with geometries that differ from their usual crystal packing arrangements.^[25] For example, no SF in pentacene is reported for films grown on a polymer substrate, whereas the vapor deposited pentacene films show efficient SF.^[29,30] During attempts to improve photovoltaic devices by inclusion of SF materials (tetracene and pentacene) external quantum efficiencies of over 100% have been reported, however, these efforts resulted in only modest improvements in the device efficiency.^[5] These results suggest the potential to enhance photovoltaic efficiency upon inclusion of SF materials, however, the sensitivity of device performance to the chromophore packing and the morphology of the active layer indicate new materials are required where the “local-order constraint” can be overcome. Recent studies using bridged acenes have demonstrated the key steric or conformational requirements for SF, and the need for spatially close chromophores that are electronically linked.^[31–34] However, most of these studies were carried out in solution and often no mention was made of their SF yield in the solid state, which is important for practical exploitation. As a result, finding a system capable of efficient SF in films with a degree of molecular disorder can make the future production of commercial SF-based organic photovoltaic (OPV) possible.

We aimed to develop a new class of solution processable SF materials that are more amenable to inclusion into solar cell devices through intramolecular SF, and removal of the “local-order constraint.” In this study, we investigate the use of hexa-*peri*-hexabenzocoronene (HBC) as a self-organizing core to promote singlet fission in amorphous films. HBC is a polycyclic aromatic hydrocarbon made up of thirteen fused six membered rings, which forms a mesophase. Soluble HBC derivatives show strong self-association in solution and discotic columnar structures with ordered morphology in films.^[35] The HBC core shows strong π – π intermolecular association and can show high charge mobilities ($\approx 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in certain silyl-substituted HBCs using pulse-radiolysis time resolved microwave conductivity measurements).^[36] Substitution of HBC with 9,9-dioctylfluorene (FHBC) imparts solubility and the ability to form mixtures with other conjugated molecules. The DPP family consists of a class of dyes that have strong visible absorption, high stability, are synthetically tunable, highly fluorescent, and also have high exciton mobilities.^[6] These properties make DPP derivatives good candidates for OPVs. Mauck et al. observed SF for the first time in DPP derivatives with a yield of up to 200% in polycrystalline films.^[6,37] Their studies on substituent variation in crystalline diketopyrrolopyrroles demonstrated that the torsion induced on substitution of thienyl (TDPP) by phenyl (PDPP) is sufficient to increase the π – π stacking distance and completely shut down SF, so SF in DPP is very sensitive to local-order (intermolecular coupling), which is not ideal for inclusion in OPV devices.^[37] Our interest in developing solution processable SF materials for use for printed organic solar cells, led us to question, can we use the liquid crystallinity inherent in FHBC as a self-organizing motif and scaffold to pre-organize the DPP chromophore to promote intramolecular SF in amorphous thin films? In this way can the

“local-order constraint,” inherent in known molecular SF materials, be removed?

The SF process has also been observed in a number of polymeric systems,^[34,38,39] however, we wished to avoid polymeric SF materials to better understand the SF process as systematic structural modifications in polymers were expected to be significantly more challenging than in more defined smaller molecules. A significant potential advance in the field was suggested by Busby et al. in 2015 where they suggested that electron acceptor–donor–acceptor (A–D–A) type molecules may be a class of materials that could promote SF.^[27] It was suggested that SF could be mediated in these systems through a charge transfer (CT) state, and by using intramolecular systems it may be possible to overcome the “local-order constraint.”^[27] They demonstrated the development of SF materials, both molecular and polymeric, albeit with low singlet fission yields for the molecular systems in solution (56%). We have published a number of analogous A–D–A materials, our benzodithiophene-X-thiophene-rhodanine (BXR) series, as p-type organic semiconductors in organic solar cells,^[40] however, calculations indicate that the triplet energy levels of these BXR materials are too high to support SF. Using this concept, we recently demonstrated that it was feasible to generate a new SF material by coupling two thienyl substituted diketopyrrolopyrroles (TDPP) to the benzodithiophene core (BDT), (BDT(TDPP)₂).^[41] However, triplet generation was low in the solid state in the molecular donor at 18% efficiency, although results in solution suggested that the BDT(TDPP)₂ supported intramolecular SF. The results indicated two key issues with BDT(TDPP)₂; i) the S₁ energy was possibly too low at 1.89 eV, barely 2 × T₁ (T₁ = 0.95 eV), and ii) no evidence for self-association was observed. These results suggested that a stronger driver is required for self-association and a higher S₁ energy along with the two TDPP triplet host acceptors were needed to increase the SF yield. In this study, the occurrence of SF in a hybrid material composed of FHBC as a self-organizing electron donor attached to TDPP as an electron acceptor was investigated.

We report here our studies on the discotic liquid crystalline material FHBC(TDPP)₂, comprising a fluorenyl substituted hexabenzocoronene (FHBC) core and two pendant bithiophene-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (TDPP) groups, for which we demonstrate a high SF yield in the solid state in as-cast and annealed films. We first reported FHBC(TDPP)₂ in 2012 as a p-type donor in organic solar cells.^[42] FHBC(TDPP)₂ shows strong self-association in solution, and the hexabenzocoronene core provides a strong driving force to form hexagonally packed discotic liquid crystalline structures in melt extruded fibers. Thin film grazing incidence wide-angle X-ray scattering (GIWAXS) studies on FHBC(TDPP)₂ indicated some π – π stacking, but little order other than this, suggesting strong self-association through the HBC units but little chance to order the pendant arms during spin coating, removing any local order between the TDPP units, **Figure 1**. The HOMO (highest occupied molecular orbitals) and LUMO (lowest unoccupied molecular orbitals) levels were reported at –5.40 and –3.40 eV respectively giving an energy gap of 2.00 eV. However, we did not report the triplet energy level of FHBC(TDPP)₂.

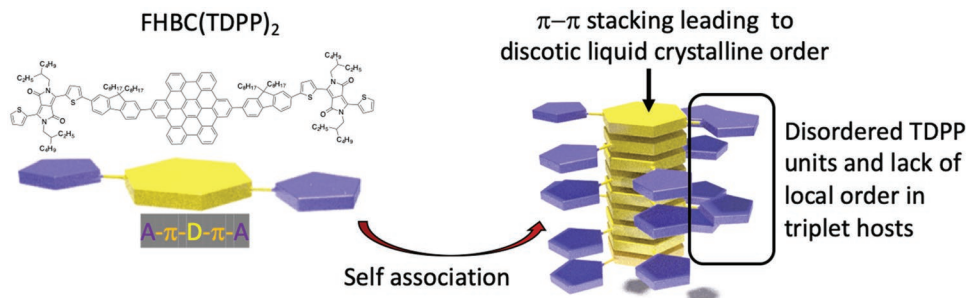


Figure 1. Chemical structure of FHBC(TDPP)₂ with a schematic representation of the A- π -D- π -A structure. The hexabenzocoronene (HBC, core D) provides strong self-association promoting discotic liquid crystalline order. The TDPP units, acting as triplet hosts, remain disordered removing any local order-based strong near-neighbor coupling for the dithienyldiketopyrrolopyrrole (TDPP, A) electron acceptor units.

2. Results and Discussion

2.1. Film Characterization

GIWAXS measurements were performed on as-cast and thermally annealed thin films of FHBC(TDPP)₂ to gain information about the crystallization behavior in these films and structural changes upon thermal annealing. The resulting scattering patterns (Figure 2) indicate little or no crystalline order in as-cast thin films of FHBC(TDPP)₂ with no significant peaks in the GIWAXS (Figure 2A), that is, the films are effectively amorphous. The thermally annealed film of FHBC(TDPP)₂ shows the π - π scattering peak along the out of plane axis at 0.34 nm due to FHBC stacking (Figure 2B), while the scattering attributed to the lamella are oriented in plane with d -spacing of 2.9, 1.7, and 1.5 nm that is in agreement with our previous result of 2D GIWAXS measurements of melt extruded fibers.^[42] The results suggest that FHBC(TDPP)₂ crystallites align in a face-on orientation. The crystallite dimensions for the thermally annealed film are summarized in Table S1 (Supporting Information).

2.2. Triplet Energy and Structural Character Calculation

Time-dependent density functional theory within the Tamm-Dancoff Approximation (TDA-DFT)^[43] with the CAM-B3LYP functional^[44] and natural-transition-orbital (NTO) analyses were conducted to investigate the photophysical properties and excited state energy levels in FHBC(TDPP)₂. The structure of FHBC(TDPP)₂ is shown in Figure S1 (Supporting Information) and its xyz coordinates are reported in Table S2 (Supporting Information). The fluorene that is attached to the HBC core and thiophene ring is twisted at a dihedral angle of 40° relative to the core. The results show that the first and second singlet excited states (S_1 and S_2) are quasi degenerate with vertical excitation energies of 2.84 and 2.86 eV and have oscillator strengths of 1.71 and 1.61, respectively. For these two singlet states, HOMO-1 $\rightarrow$ LUMO & LUMO+1 and HOMO $\rightarrow$ LUMO & LUMO+1 excitations (Figure 3) are the respective dominant contributions with multiple minor contributions to the excitation energies stemming from other MOs. The HOMO is delocalized over the entire molecule, and the LUMO and LUMO+1 are localized on the DPP units and mostly located

on the electron rich nitrogen and sulfur atoms. On the other hand, the HOMO-1 is located on the fluorene and DPP units. To find more information on the distribution patterns of electron and hole, the electron and hole NTO patterns for the S_1 state are demonstrated in Figure S2 (Supporting Information). The singlet state shows two main pair contributions where the electron and hole are mostly located on the fluorene and DPP units (Figure S2A, Supporting Information), and a minor component where the electron is delocalized over the whole molecule (Figure S2B, Supporting Information). These calculations suggest that the smaller atomic-orbital coefficients in the HBC core, and hence the lower contribution to the HOMO, might be due to the twist between the core and fluorene units. The NTO electron and hole pairs of the T_1 state are localized within the DPP unit (Figure S3, Supporting Information). Moreover, the first triplet excited state (T_1) has a vertical excitation energy of 1.38 eV, so FHBC(TDPP)₂ meets the energy level requirement for SF, i.e., $2^*E(T_1) \leq E(S_1)$. Overall, however, the charge-transfer character of these excitations seems low. The same trends were confirmed with the ω B97X functional^[45] (see Figure S4, Supporting Information).

2.3. Optical and Electrochemical Properties

Steady state absorption and fluorescence spectra of FHBC(TDPP)₂ were recorded for dilute chloroform solutions and in thin films (Figure 4). The absorption spectrum comprises a strong band at 365 nm, which can be assigned to the π - π^* transition of the FHBC component of the material, and a π - π^* intramolecular charge transfer absorption band at 580 nm. The absorption spectra of FHBC, TDPP, and FHBC(TDPP)₂ in chloroform solution were also compared, see Figure S5 (Supporting Information). The absorption spectrum of FHBC has a similar π - π^* transition band to FHBC(TDPP)₂ at 365 nm and the CT band in FHBC(TDPP)₂ shows a redshift of only 30 nm (550–580 nm) compared to free TDPP. FHBC(TDPP)₂ has a fluorescence quantum yield of about 30% in chloroform solution. In the photoluminescence emission spectrum, a sharp peak is seen at 627 nm in solution. We could not study the ionic character in the CT state in various solvents due to the solubility issue.

In a thin film of FHBC(TDPP)₂ there is a slight broadening of the absorption bands, with a small redshift of the

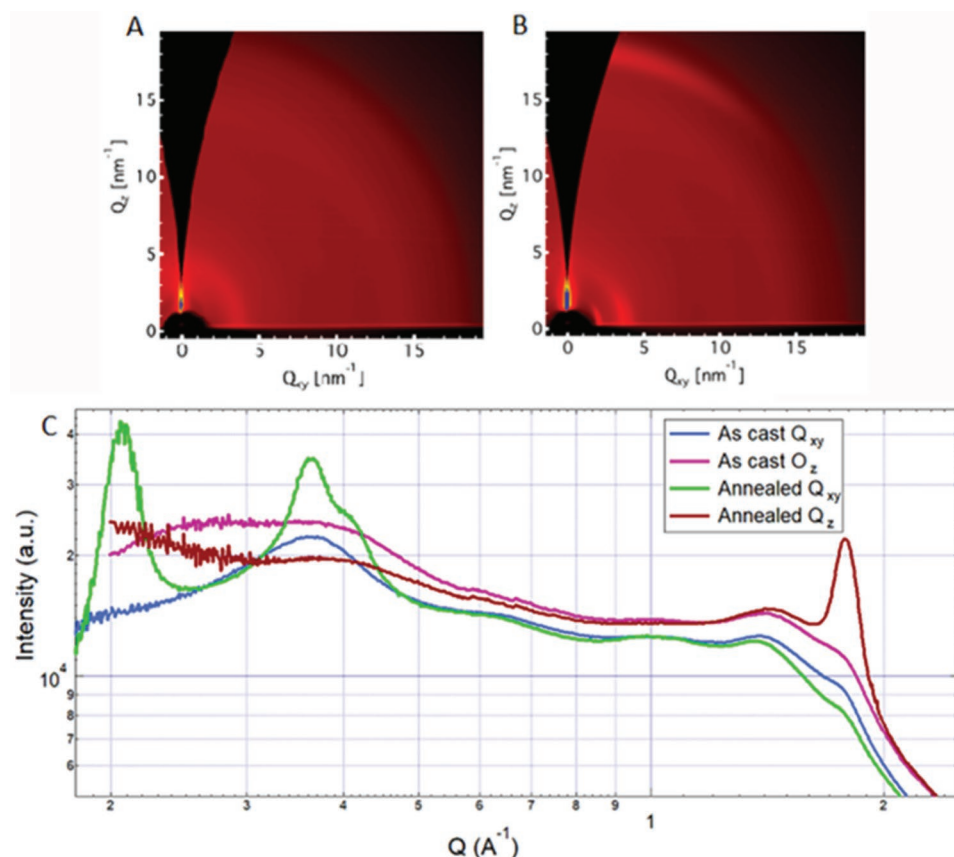


Figure 2. GIWAXS diffraction patterns of FHBC(TDPP)₂ A) as-cast and B) thermally annealed films, and C) line cuts along the Q_{xy} and Q_z axes.

charge transfer band (≈ 20 nm) and the band at 365 nm becomes less featured. This suggests some aggregation in the thin film. It is known that FHBC(TDPP)₂ strongly associates in solution, and the small change in the FHBC π - π^* transition on film formation suggests aggregates form that are not crystalline enough to show in the GIWAXS analysis.

The steady state photoluminescence emission of the film is also broad and red-shifted compared to in solution, which suggests coupling between chromophores in the solid state. The broadened peak appears at 670 nm in thin film. The fluorescence quantum yield of the thin film is only about 1% indicating that there is an additional pathway for excited

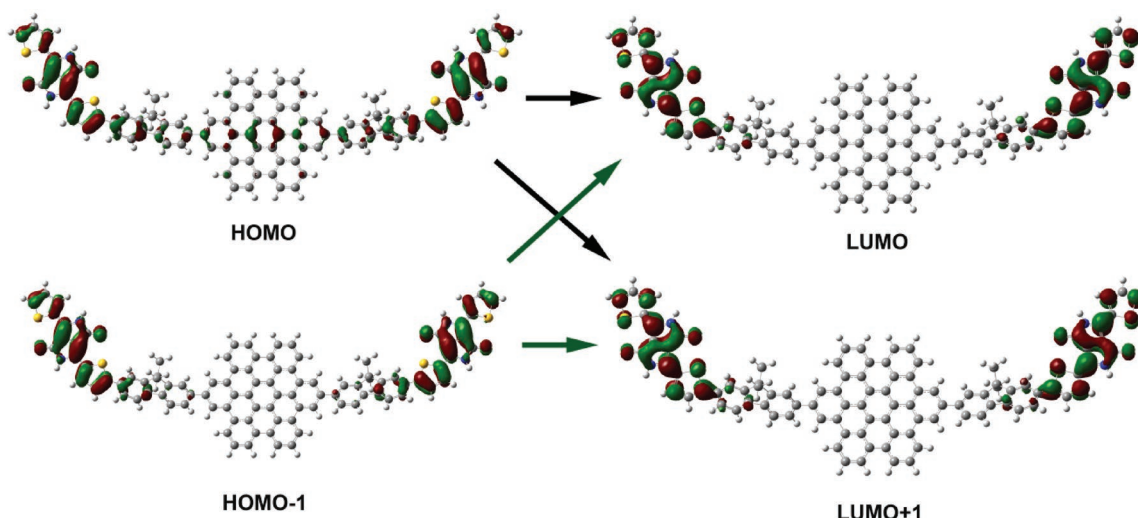


Figure 3. Representation of the main transitions in FHBC(TDPP)₂ where the HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital.

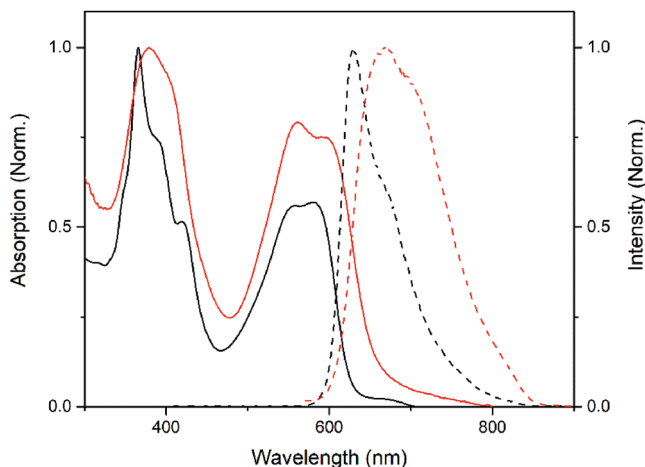


Figure 4. Normalized absorption (solid line) and fluorescence (dashed line) spectra of FHBC(TDPP)₂ in chloroform solution (black line) and thin film (red line).

state quenching in the solid state that is not present in the solution. The absorption and fluorescence spectra of the thermally annealed film were recorded for comparison (see Figure S6A,B, Supporting Information). The bands narrow slightly in the annealed film with a 10 nm blueshift of the CT band compared to the as-cast film. This suggests that upon formation of a more ordered discotic liquid crystalline structure on annealing, as evidenced by the GIWAXS pattern (Figure 2B), there is no significant change in the FHBC environment, however, a less ordered TDPP environment is generated or there is less CT state coupling. On the other hand, the emission spectrum for the annealed film is quite similar to the as-cast film.

The optical bandgaps were calculated as 2.05 and 1.97 eV for FHBC(TDPP)₂ in the solution and thin film, respectively, from the intersection of the normalized absorption and emission spectra, see Figure 4.

The strong self-association, and optical bandgap of ≈ 2.0 eV^[42] suggested this might be a good SF material, if the T_1 energy was in the range of 0.95–1.0 eV. Theoretical calculations show the S_1 and T_1 energy levels of 2.84 and 1.38 eV, respectively. The emission of FHBC(TDPP)₂ in thin film at room temperature and 77 K in the spectral region of 650–1400 nm and 900–1600 nm (with >1200 nm highpass filter) are shown in Figure S7 (Supporting Information). By decreasing the temperature to 77 K, the non-radiative loss pathways are frozen out,^[46] and a peak appears at 1200–1400 nm (0.95 eV) which is assigned to the triplet state. It suggests that FHBC(TDPP)₂ has a T_1 energy level appropriate for SF.

It is expected that in a material that promotes SF, the photo-induced S_1 state will have a short lifetime as it undergoes SF to generate a correlated triplet pair. For the correlated T_1 states, the reverse triplet-triplet annihilation process will be fast unless the $E(S_1)$ energy is significantly above the energy of $2 \times E(T_1)$ state. Therefore, in an active SF material the T_1 state lifetime will be short when compared to a triplet generated through triplet sensitization experiments.

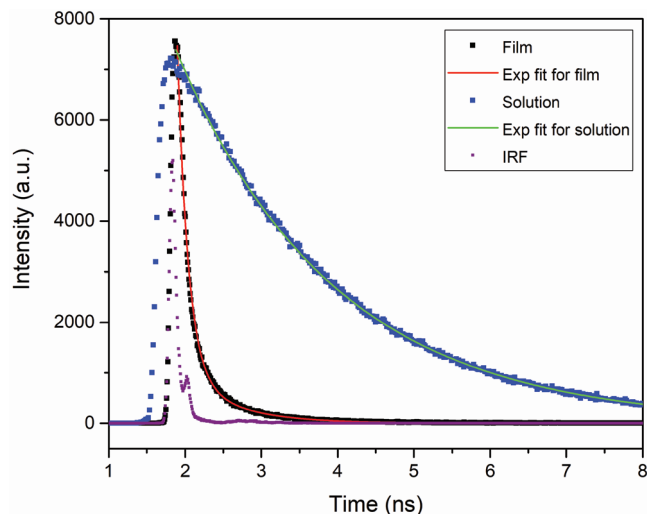


Figure 5. The instrument response function (IRF) and fluorescence decay curves recorded by TCSPC, monitored at 650 nm following excitation at 400 nm for both thin film and dilute chloroform solution; the solid lines are the best fits using bi- and single-exponential decay functions, respectively.

2.4. Time-Resolved Photoluminescence of FHBC(TDPP)₂ in Solution and Thin Film

To provide more information about the decay kinetics of the singlet state the as-cast thin film and a dilute chloroform solution of FHBC(TDPP)₂ were characterized using time correlated single photon counting (TCSPC) measurements, see Figure 5. Following excitation at 400 nm, the fluorescence decays of FHBC(TDPP)₂ in the as-cast thin film and dilute chloroform solution show bi-exponential and single exponential decay behavior, respectively. The fluorescence of FHBC(TDPP)₂ in thin film decays very rapidly with $\tau_1 \approx 100$ ps and $\tau_2 \approx 600$ ps. On the other hand, the emission from FHBC(TDPP)₂ in dilute chloroform solution decays exponentially with a lifetime of ≈ 2 ns, indicating that there is an excited deactivation pathway in the solid state that is not present in the solution.

2.5. Femtosecond and Nanosecond Transient Absorption in Thin Film and Dilute Solution

Femtosecond transient absorption (TA) measurements were undertaken to probe the excited state dynamics of FHBC(TDPP)₂ in dilute chloroform solution and thin film to better understand the contribution of uni- or bimolecular interactions. The TA spectra and kinetic traces of FHBC(TDPP)₂ in both the visible (Vis) and near-infrared (NIR) regions following excitation at 600 nm in a dilute chloroform solution are shown in Figure 6A,B, respectively. A negative ground-state bleach (GSB) signal was monitored in the region of 500–700 nm, mirroring the steady state absorption spectral features while positive transient absorption peaks at 760, 830, and 870 nm were recorded as PIA1, PIA2, and PIA3, respectively. The kinetics of PIA2 and 3 show biexponential decay kinetics with a rapid component and a slow component that decays over the nanosecond

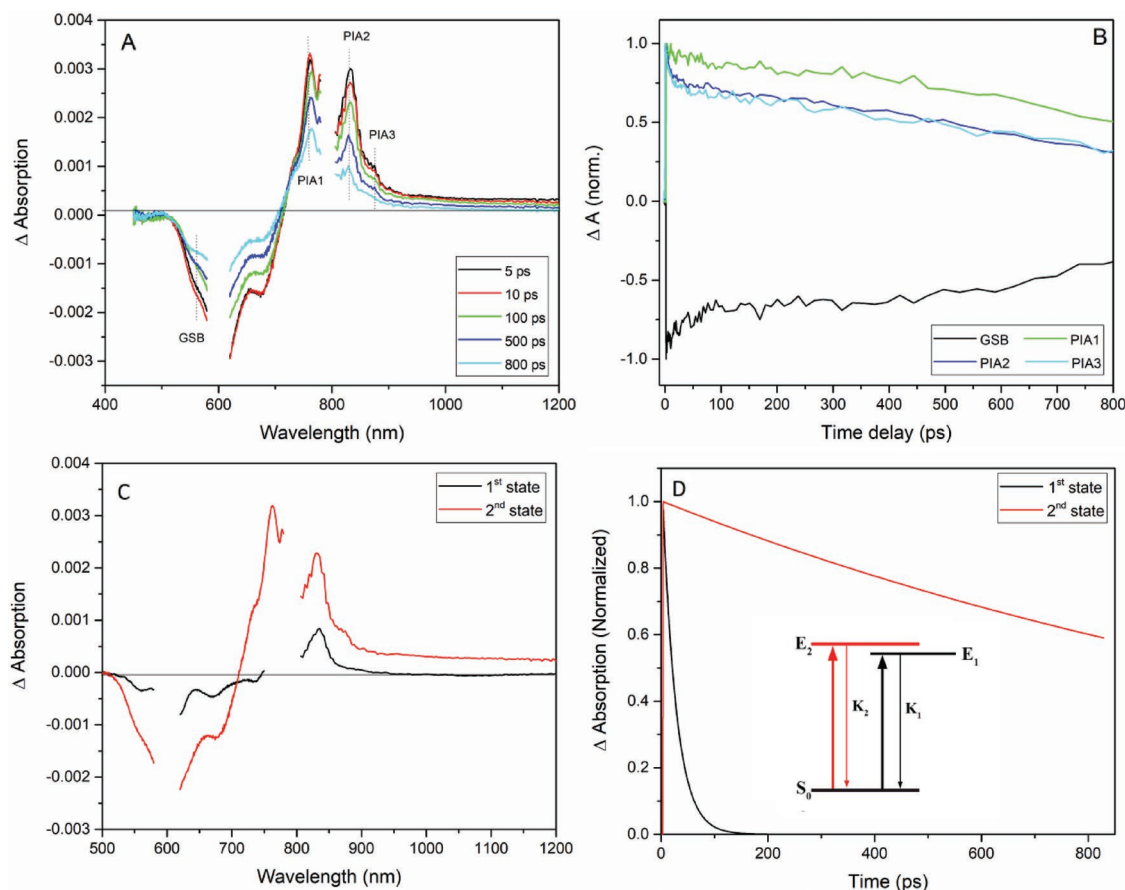


Figure 6. A) Transient absorption spectra at time delays of 5, 10, 100, 500, and 800 ps, and B) kinetic traces at 580, 760, 830, and 870 nm of FHBC(TDPP)₂ in a chloroform solution after exciting at 600 nm with a fluence of 10 $\mu\text{J cm}^{-2}$. C) The associated spectra and D) concentration profiles versus time for E_1 and E_2 from the global target analysis. The inset of graph (C) shows the extracted kinetic model.

time window. The decay of PIA1 only shows the slow component. The transient signal of the GSB effectively mirrors the kinetics of PIA2 and 3 suggesting that a parallel two species process ($E_1 \rightarrow \text{GS}$ and $E_2 \rightarrow \text{GS}$) is occurring in the solution of FHBC(TDPP)₂. To better understand the relationship between the PIA signals, we have completed a global target analysis (GTA) on the TA data to help identify the individual features and their population variation with time. The global analysis of the transient absorption data of FHBC(TDPP)₂ in the solution using a parallel two species process ($E_1 \rightarrow \text{GS}$ and $E_2 \rightarrow \text{GS}$) returned the extracted spectra and kinetics of each species shown in Figure 6C,D, respectively. The extracted spectrum with a sharp peak at 850 nm (E_1 from GTA) decays with a time constant of ≈ 30 ps. The extracted spectrum with an extra peak at around 760 nm (E_2 from GTA) decays over the nanosecond timescale. The results indicate that both E_1 and E_2 are generated upon excitation and relax back to the ground state with different rates. We assign E_2 to the S_1 state as the results show the same kinetics for the ground state recovery (nanosecond transient absorption (ns-TA)) and the time-resolved fluorescence (TCSPC). E_1 is assigned to an excimer state, which is a short-lived component. The known π - π stacking of the FHBC core can lead to the formation of dimers even in a dilute solution of FHBC(TDPP)₂.

ns-TA measurements were conducted to monitor the recovery of the ground state in FHBC(TDPP)₂ in solution. The kinetic trace at 650 nm following excitation at 600 nm, see Figure S8 (Supporting Information), shows a single exponential decay with a time constant of about 3 ns, which matches the fluorescence decay profile from the TCSPC measurement. These results are consistent with the dominant mechanism in solution of FHBC(TDPP)₂ being a singlet state decay process back to the ground state with a competing parallel process, which also recovers the ground state with a much faster time constant. That is, no singlet fission is observed in solution.

To investigate the effect of the charge transfer state and chromophore association in solution, TCSPC measurements of solutions of FHBC(TDPP)₂ in various solvents and concentrations were performed. The fluorescence decay of FHBC(TDPP)₂ in solvents with various dielectric constants from toluene, chloroform, tetrahydrofuran and dichloromethane ($\epsilon = 2.4, 4.8, 7.5$, and 9.1, respectively) are shown in Figure S9 (Supporting Information). Similar decay profiles were obtained for all of the solvents suggesting that no intrinsic pathway for rapid singlet state quenching in these solvents is observed, which is inconsistent with the expected fast depopulation of the S_1 state when SF is the dominant process. The fluorescence decay of FHBC(TDPP)₂ in chloroform solution with concentrations in

the range 10×10^{-6} to 500×10^{-6} M are shown in Figure S10 (Supporting Information). The results show no evidence for SF even at high concentration.

Femtosecond transient absorption (TA) measurements were performed on a thin film of FHBC(TDPP)₂ and the spectra extracted at time delays of 5, 10, 100, 500, 700, and 800 ps are shown in Figure 7A, along with decay traces for the GSB at 550 nm and positive photoinduced absorption at 760 (PIA1) and 900 nm (PIA2) (Figure 7B). The PIAs at 760 and 660 nm are expanded to 100 ps, inset Figure 7B, to highlight the difference in the initial transient behavior of these species. The GSB does not relax back to zero during the time-window of the experiment. The PIA2 has a rapid decay within the time region of 0–100 ps, while PIA1 has an initial fast decay similar to the PIA2 kinetics followed by a slower decay, Figure 7B. The kinetic trace of the GSB mirrors the kinetics of PIA1. Also, there is a growth of a positive transient signal at 660 nm following the initial decay of PIA1, inset Figure 7B. This evidence supports a sequential two-species process ($E_1 \rightarrow E_2 \rightarrow \text{GS}$) in the thin

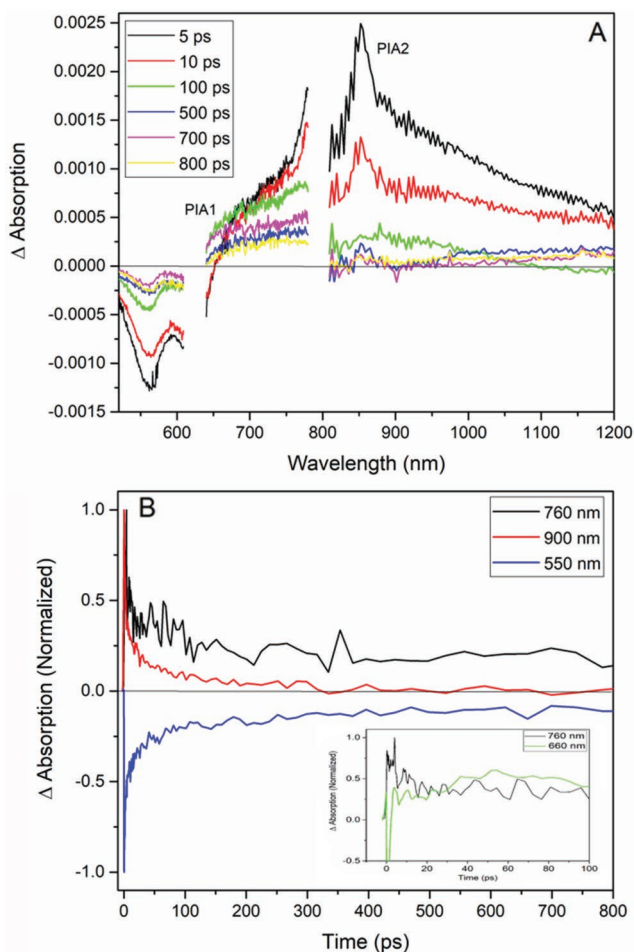


Figure 7. A) Transient absorption spectra at time delays of 5, 10, 100, 500, 700, and 800 ps, and B) kinetic traces at 550, 760, and 900 nm of FHBC(TDPP)₂ in thin film after exciting at 620 nm with a fluence of $10 \mu\text{J cm}^{-2}$. The inset of (B) shows PIAs at 760 and 660 ps expanded to 100 ps.

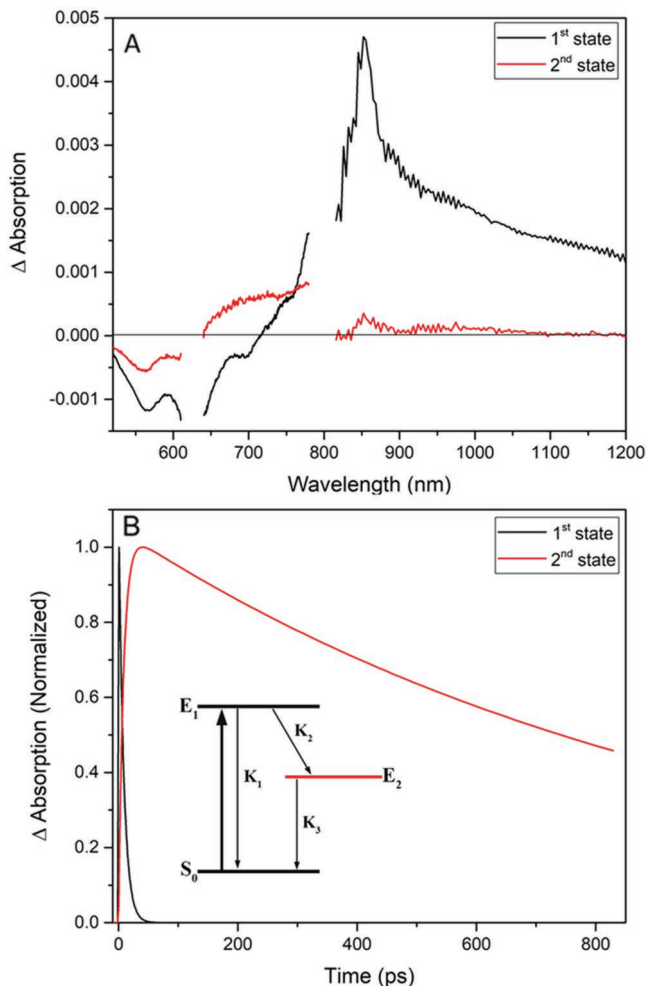


Figure 8. A) The associated spectra and B) concentration profiles versus time for E_1 and E_2 from the global target analysis for FHBC(TDPP)₂ in the thin film. The inset of (B) shows the extracted kinetic model for FHBC(TDPP)₂ in thin film.

film of FHBC(TDPP)₂ so global target analysis was performed to help identify the individual features in the next section.

GTA was performed on the transient absorption data of FHBC(TDPP)₂ in the thin film using a simple, sequential two-species model ($E_1 \rightarrow E_2 \rightarrow \text{GS}$) as two independent species were recognized by a singular value decomposition (SVD) analysis. The extracted spectra and kinetics of the individual species are shown in Figure 8A,B, respectively. The broad extracted spectrum with a peak at 850 nm (E_1 from GTA, see inset Figure 8B) shows a rapid rise with a time constant of ≈ 1 ps and decay with a time constant of ≈ 10 ps. The extracted spectrum with a peak at around 760 nm (E_2 from GTA, see inset Figure 8B) has a delayed rise concomitant with the fall of the E_1 signal. Our GTA indicates a linear process with E_1 generated upon excitation, followed by population of the E_2 state with a slow relaxation to the ground state. We tentatively assign E_1 to the S_1 state and E_2 to the T_1 state following SF, however, to confirm this assignment we need to demonstrate that the E_2 spectrum corresponds to the FHBC(TDPP)₂ triplet state and the generated triplet pair lifetime is shorter than the isolated triplet.

2.6. Triplet Characterization

Triplet sensitization experiments have been undertaken to independently populate the triplet state and to find the excited triplet state absorption spectrum and isolated triplet lifetime in order to confirm that the long-lived species (E_2 from the GTA) formed after excitation of FHBC(TDPP)₂ is due to a triplet state. Palladium octaethylporphyrin (PdOEP) was chosen as the triplet sensitizer. Since PdOEP has two narrow and isolated absorption bands at 400 and 550 nm and they both overlap with the absorption band of FHBC(TDPP)₂, the sensitizer cannot be excited selectively. As a result, the sensitized transient absorption spectrum is a linear combination of the PdOEP, FHBC(TDPP)₂ triplet, and the nonsensitized FHBC(TDPP)₂ species. The TA spectra of PdOEP in a thin film show a narrow, negative GSB at 550 nm and no positive photoinduced absorption following excitation at 400 nm (Figure S11, Supporting Information). As a result, the sensitized transient absorption spectrum is the combination of the nonsensitized spectrum and triplet energy transfer from the sensitizer to FHBC(TDPP)₂. To find the excited triplet state absorption, GTA was performed on the transient absorption data set of a FHBC(TDPP)₂:PdOEP blended film. The TA spectra of PdOEP

sensitized FHBC(TDPP)₂ thin films (50:50 weight ratio) following excitation at 400 nm are shown in Figure 9A at different time delays. The kinetic traces of the sensitized and nonsensitized FHBC(TDPP)₂ films at selected wavelengths of 660 and 900 nm are shown in Figure 9B. The difference between the kinetic traces of PIA1 at 660 nm in the sensitized and nonsensitized FHBC(TDPP)₂ cases show that the triplet excited state of FHBC(TDPP)₂ gets repopulated over a time period of about 100 ps, and this is attributed to triplet energy transfer from the PdOEP to FHBC(TDPP)₂. The T_1 -induced absorption spectrum extracted from GTA of the sensitization data (see Figure S12, Supporting Information) is very similar to the long-lived species found in the pure FHBC(TDPP)₂ film (Figure 9C) suggesting that the long-lived species is a triplet rather than an excimer or any other long-lived, charge separated state. In conclusion, we confirm that triplets are formed on an ultrafast timescale following excitation of the FHBC(TDPP)₂ in the solid state.

The fast triplet formation (<50 ps) in FHBC(TDPP)₂ as-cast films suggests SF rather than intersystem crossing (ISC) as the main mechanism of triplet formation, because in most cases ISC on such a short timescale is only observed in systems with heavy atoms.^[27] To compare and provide more detail about the dynamics of the sensitizer-generated triplet

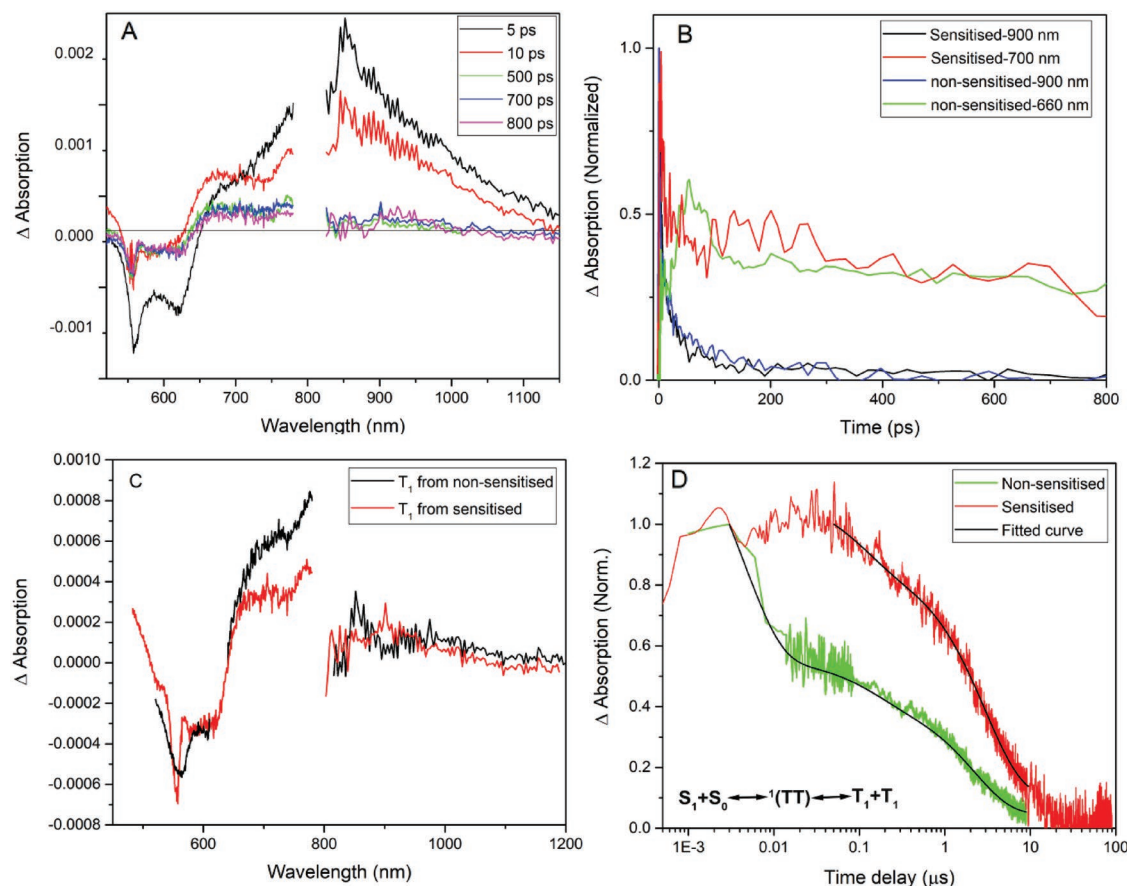


Figure 9. A) Transient absorption spectra of sensitized FHBC(TDPP)₂ thin film at various time delays and B) transient absorption decays at selected wavelengths (700 and 900 nm) of the sensitized and (660 and 900 nm) of nonsensitized thin films of FHBC(TDPP)₂. C) T_1 -induced absorption spectrum of the FHBC(TDPP)₂ derived from the triplet sensitization technique and associated spectrum of the 2nd excited state species from GTA. D) Nanosecond transient absorption decays of sensitized and nonsensitized thin films of FHBC(TDPP)₂ monitored at 730 nm following excitation at 550 nm with excitation density of 30 $\mu\text{J cm}^{-2}$.

species in FHBC(TDPP)₂ and triplets formed in the neat FHBC(TDPP)₂ film, ns-TA measurements were conducted on both FHBC(TDPP)₂ and FHBC(TDPP)₂:PdOEP blend films with excitation at 550 nm. The triplet absorption decays for both FHBC(TDPP)₂ and FHBC(TDPP)₂:PdOEP blend films were recorded at 730 nm (Figure 9D). The decay of the triplet transient signals for both films follow nonexponential kinetics. For FHBC(TDPP)₂, a three-component decay model, interpreted in terms of three separate states, provided the best fit to the data (Figure 9D). The lifetimes of the first and second triplet states were determined to be 5 and 140 ns, while the long-lived species has a lifetime of 2.5 μ s. Two mechanisms have been proposed for triplet state formation through SF. First, the correlated triplet production can occur within two timescales, then it undergoes decorrelation to form individual triplets with 2 μ s lifetime. The major population of the correlated triplet appears on the picosecond timescale after photoexcitation followed by a slower triplet growth over a few ns. According to the previous report of SF in a disordered film,^[25] some of the chromophore dimer pairs have a favorable geometry that promotes SF. A singlet state around these sites can undergo SF whereas singlet excitons at other sites in the film can diffuse to those pairs forming a secondary diffusion-limited triplet production. The second mechanism, based on the suggestion made by Pensack et al.,^[4] is that the separation of the triplet pair requires the inclusion of an additional correlated intermediate. We assigned the first and second triplet states to two distinct correlated triplet pair intermediates as suggested by Pensack, whereas the third state is assigned to the decorrelated individual triplets.

The FHBC(TDPP)₂:PdOEP blend film also shows a biexponential decay with lifetimes of 100 ns and 3 μ s. However, at the wavelength used, the FHBC(TDPP)₂ is excited directly as well as via the sensitizer, leading to two decay components. The triplet species with the longer time constants are attributed to the sensitizer generated individual triplets, which have similar lifetime to the slow decay component in the neat film. The rapidly decaying species are assigned to the correlated triplet formed by direct excitation of FHBC(TDPP)₂. A faster recombination rate for the triplet pairs generated from SF is due to the enhanced contribution of spin-allowed geminate triplet-triplet annihilation, which is confirmed by monitoring the delayed fluorescence compared to the sensitizer-generated single triplets, with a slower recombination rate. We recorded a long-lived emissive state at 620 and 750 nm that is assigned to delayed fluorescence as a result of geminate triplet-triplet annihilation, see Figure S13 (Supporting Information). The emission decays on the nanosecond timescale, well beyond the major excited singlet decay component of $\approx$ 100 ps. The results are strongly suggestive that singlet fission occurs in the thin film of FHBC(TDPP)₂. The triplet yields for FHBC(TDPP)₂ in thin film were determined using the singlet depletion method, one of the well accepted methods of triplet yield determination. A triplet yield of 150% was calculated. This method has been used to calculate the triplet yield in various DPP derivatives, and has been shown to be comparable with triplet sensitization methods (more detail about the triplet yield calculation is provided in the Supporting Information).

2.7. Femtosecond and Nanosecond Transient Absorption in a Thermally Annealed Thin Film

To provide details about SF in the more crystalline film, TA measurements were performed on a thermally annealed thin film of FHBC(TDPP)₂. TA spectra at various time delays and extracted kinetic traces at 660 and 760 nm for the thermally annealed thin film of FHBC(TDPP)₂ are shown in Figure 10A,B, respectively. GTA was completed on the TA data of the thermally annealed thin film of FHBC(TDPP)₂ using a simple sequential two-species model ($S_1 \rightarrow T_1 \rightarrow GS$). The induced absorption peak at 700 nm, which is assigned to T_1 for the annealed thin film of FHBC(TDPP)₂, is slightly broader compared to the as-cast film. The results indicate that singlet fission occurs in the thermally annealed thin film of FHBC(TDPP)₂ with a triplet yield of 170% as measured by the singlet depletion method (details about the triplet yield calculation are provided in the Supporting Information). Also, the thermally annealed thin film undergoes singlet fission with a faster rate constant of 0.2 ps⁻¹ than the as-cast film with a rate constant of 0.1 ps⁻¹. The results suggest that increased stacking of FHBC units after annealing results in faster and more efficient SF.

3. Conclusions

We have demonstrated the formation of SF-generated triplets in an “amorphous” as-cast FHBC(TDPP)₂ thin film, and evidence of de-coalescence of SF-generated triplet pairs is presented. We designed SF materials with an electron A-D-A structure to promote SF using liquid crystallinity as a self-organizing motif to pre-organize TDPP chromophores in amorphous films. It is suggested that the directed self-assembly through the HBC core and formation of discotic liquid crystalline domains, pre-organizes the TDPP chromophores (triplet hosts) in the solid state, placing them in close proximity but not allowing crystalline order; that is we have removed the “local-order constraint.” The proximity allows Dexter energy transfer, and a potential route to the SF generated correlated triplet pair. Although GIWAX evidence suggests the as-cast films are amorphous, we have previously shown that FHBC(TDPP)₂ strongly associates in solution and therefore we suggest that aggregates form during drying, however, these aggregates are too small to strongly diffract. The rate of SF (0.1–0.2 ps⁻¹), the SF yield (150–170%), and molecular order are all improved upon annealing the film. We observe no evidence of SF in solution.

We believe that the use of liquid crystallinity as the self-assembly motif to drive self-organization for SF chromophores is a new pathway to new materials capable of singlet fission. Based on this idea, FHBC(TDPP)₂, comprising a hexabenzocoronene-fluorene (FHBC) core and two pendant bithiophene-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (TDPP) groups, with a low triplet energy level, was investigated for singlet fission. TDA-DFT calculations show that the first triplet excited state has an energy of about half of the first singlet excited state. The steady state photophysical measurements also confirm that this compound meets the energy level requirements for singlet fission. TCSPC, femtosecond and nanosecond transient

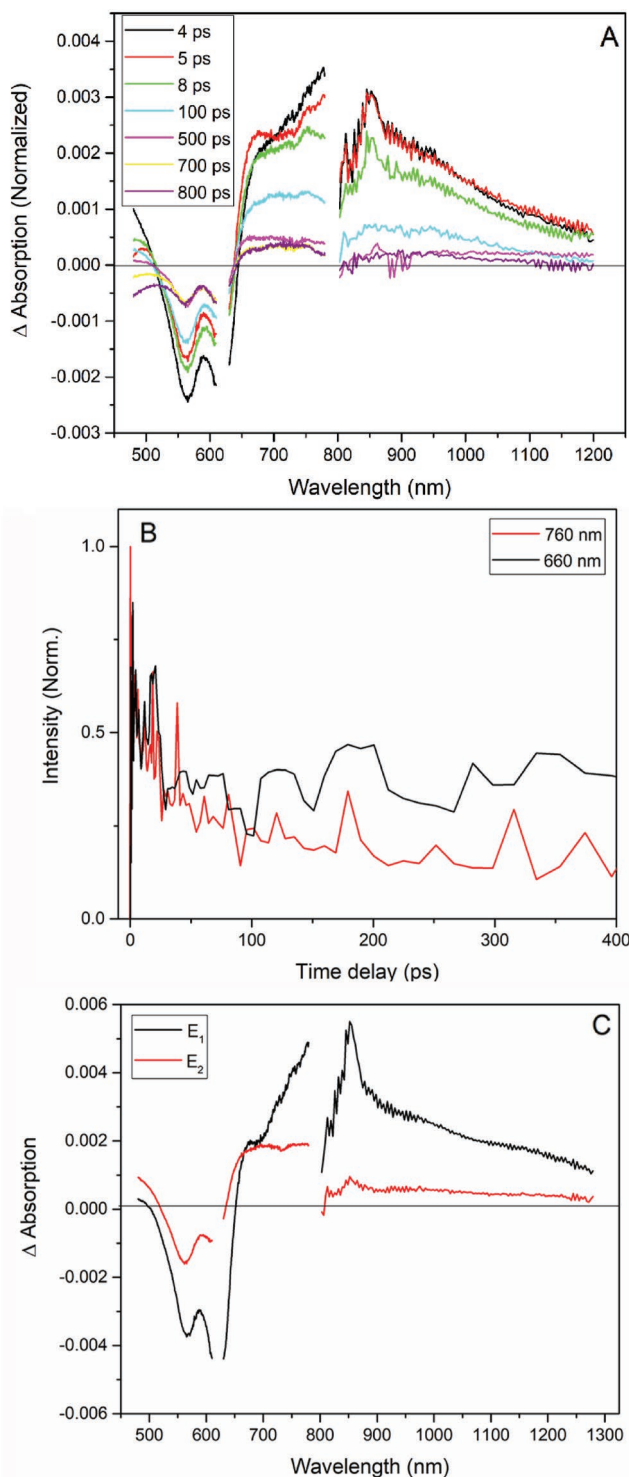


Figure 10. A) Transient absorption spectra at various time delays and B) transient decays at selected wavelengths of 660 and 760 nm of a thermally annealed FHBC(TDPP)₂ thin film. C) The associated spectra for E_1 and E_2 from the global target analysis for the thermally annealed FHBC(TDPP)₂ thin film.

absorption spectroscopy measurements were used to investigate the excited state dynamics in FHBC(TDPP)₂ in solution and film. Fast formation of the triplet state, short lifetimes of

the triplet pairs and delayed fluorescence in FHBC(TDPP)₂ in thin film suggest singlet fission is operating. The triplet pair lifetimes and the triplet yields are ≈ 500 ns and 150%. GiWAXS measurements show well developed π - π stacking peaks due to FHBC stacking but there is no apparent order in the TDPP moieties indicating a new class of SF material. This suggests that enhanced triplet harvesting may be possible in solar cell devices containing these materials and these device studies are currently in progress. We expect the results of this work can lead to the development of a new class of SF materials suitable for application in third generation optoelectronic devices and we are currently completing structure property studies to better understand the generation of triplets in these systems.

4. Experimental Section

Material Synthesis: The commercially available chemicals were purchased from Sigma-Aldrich, Boron Molecular, Matrix Scientific, Ajax Finechem, Univar, Luminescence Technology Corp., and Suna Tech Inc. and all chemicals were used as received. FHBC(TDPP)₂ were prepared according to published procedures.^[42]

Film Preparation: Glass substrates with dimensions of 2.5 cm $\times$ 2.5 cm $\times$ 0.1 cm were cleaned by sonicating sequentially in acetone, isopropanol, and chloroform. Before thin film casting, the substrates were dried with a strong flow of nitrogen and then subjected to UV/ozone treatment for 30 min. Solutions of FHBC(TDPP)₂ were prepared by dissolving the samples into chloroform with a concentration of 5 mg mL⁻¹. To prepare blend films for sensitized experiments, solutions of FHBC(TDPP)₂ in chloroform mixed with palladium octaethyl porphyrin (PdOEP) were prepared by dissolving the compounds with mass ratio of 50:50. Finally, thin films were cast onto clean glass substrates via spin coating at 1000 rpm s⁻¹ and spun for 1 min. The thermally annealed film was prepared by putting the as cast film on the top of a plate with the temperature of 120 $^{\circ}$ C for 10 min then the film was allowed to cool down to room temperature slowly.

Thin Film Characterization: Samples for grazing incidence wide angle X-ray scattering transmission measurements were prepared by loading the materials onto silicon wafers. The samples were analyzed at the SAXS/WAXS beamline at the Australian synchrotron^[47] with an X-ray energy of 10 keV. A Pilatus 200K detector was used for wide-angle measurements. The substrates were silicon wafers that had been sonicated in acetone and isopropanol for 30 min each followed by 30 min of UV/ozone treatment. The beamline has a range of incident angles from $\Omega = 0.02$ – 0.35 in 0.005 increments to allow signal optimization near the critical angle of the film but below the critical angle of the substrate. Data from GIWAXS experiments were analyzed using a customized version of NIKA 2D based in IgorPro.^[48,49]

Steady State Spectroscopy: Absorption spectra were recorded for FHBC(TDPP)₂ using a Varian Cary 50 UV-vis spectrophotometer. Fluorescence spectra were recorded on a Varian Eclipse spectrofluorimeter using an excitation wavelength of 550 nm and excitation and emission bandwidths of 5 nm for solution and 10 nm for film measurements.

Photoluminescence (PL) spectra in the near-IR region were recorded with a spectrometer (Horiba Jobin Yvon iHR320) and an amplified InGaAs photodetector (Electro-Optical System). The excitation source was a supercontinuum laser (NKT Photonics, SuperK Extreme) for wavelengths tunable across the 450–750 nm region. The excitation beam was mechanically chopped and the detector output was fed into a lock-in amplifier synchronized to the chopper frequency. A 1200 nm high pass filter was used to remove the second order of the excitation and fluorescence. PL experiments at cryogenic temperatures were carried out in a liquid nitrogen cryostat (Oxford Instruments, Optistat DN).

Time Correlated Single Photon Counting: As described previously,^[50] the excitation source was a mode-locked and cavity dumped Ti:Sapphire

laser (Coherent Mira 900F/APE PulseSwitch) pumped by a Coherent Verdi-10 DPSS Nd:YVO₄ laser. The laser output (880 nm wavelength, 5.4 MHz repetition rate) was frequency doubled to provide an excitation wavelength of 440 nm. The individual fluorescence decay curves were collected using a time-correlated single photon counting (TCSPC) module (SPC-150, Becker & Hickl, Berlin, Germany). The fluorescence decay parameters were extracted from the decay profiles using FAST software (Edinburgh Instruments Ltd) and a sum of exponentials analysis.

Sub-Nanosecond Transient Absorption Spectroscopy: A mode-locked Ti:sapphire oscillator (Coherent, Mira Seed) seeded a Ti:sapphire regenerative amplifier system (Coherent, RegA 9050) to produce pulses of about 50 fs duration at a repetition rate of 92 kHz and a wavelength centered at 800 nm. A portion of the light was used to generate the 400 nm pump beam using a β -BBO (β -barium borate) crystal, and the 630 and 730 nm pump beams were generated with an optical parametric amplifier (OPA9450, Coherent). The pump beam was mechanically chopped at ≈ 3.5 kHz, and the arrival time of the pump pulses relative to the probe was manipulated using a variable optical delay line (Newport, UTS150PP with ESP 300 controller). The broadband probe was derived from the residual 800 nm beam focused onto a 3 mm sapphire substrate (Crystal Systems) for measurements in the visible region (450–800 nm) and a 5 mm undoped YAG substrate (Crystal Systems) for the infrared region (800–1400 nm). After passing through the sample, the probe beam was detected with a CMOS-equipped spectrometer (Ultrafast Systems) at 7077 spectra s⁻¹, and the excess 800 nm laser fundamental was blocked using low- and high-pass filters for the visible and IR regions, respectively. The relative orientation of the pump and probe polarization was 54.7° and all spectra were corrected for the chirp of the supercontinuum probe. Dry nitrogen was blown over films for all measurements.^[51]

Nanosecond Visible Transient Absorption Measurements: ns-TA spectroscopy was employed to monitor the triplet excited state lifetime. The measurements were conducted by a home-built transient absorption spectrometer with a N₂ laser (LTB Lasertechnik Berlin GmbH, MNL 202-C) pumped dye laser (LTB Lasertechnik Berlin GmbH, ATM200, 700 ps pulse duration) as an excitation source. Transient absorption was probed by a Xe lamp (Photon Technology International) light through two monochromators (Acton, Princeton Instruments), and detected by a Si based nanosecond detection system (Unisoku Co., Ltd., TSP-2000SN, time resolution: 1.2 ns (FWHM), monitoring wavelengths: 400–1100 nm) with a fast oscilloscope (Tektronix, TDS 3052C, Digital Phosphor Oscilloscope 500 MHz 5 GS s⁻¹).^[52] Transient data were collected with 550 nm excitation with a repetition rate of 2 Hz at 22 °C. The pulse excitation intensity was adjusted to 30 μ J cm⁻². Decay curve fitting was performed using FLASH software (Edinburgh Instruments Ltd.) and an exponential components analysis.

Computational Details: The geometry optimization of the ground state was carried out using Turbomole version 7.3^[53] with the efficient hybrid-DFT model PBEh-3c^[54] under inclusion of the continuum solvation model COSMO^[55] to simulate the effects of chloroform as a solvent. In order to reduce computational costs, we have replaced the long side chains in the compound by methyl groups, as the length of the alkyl chains has no significant impact on the optical properties.^[56] Vertical excitation energies were calculated via TDA-DFT^[43] using the CAM-B3LYP^[44] range-separated hybrid functional approximation and the 6-311G**^[57] atomic-orbital basis set based on the optimized geometry with the Gaussian09 program Rev. E.01.^[58] A range-separated density functional approximation was chosen to ensure that potential CT states could also be appropriately treated. Moreover, it has been shown that this method is one of the most accurate hybrid functional approximations with an expected accuracy of 0.18 eV for medium-sized and large chromophores.^[59] The pairs of hole and electron NTOs^[60] for the S₁ and T₁ states were also calculated with Gaussian09 Rev. E.01.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

liquid crystalline, organic photovoltaics, photophysics, self-assembly core, singlet fission

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Supporting Information

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Liquid Crystallinity as a Self-Assembly Motif for High-Efficiency, Solution-Processed, Solid-State Singlet Fission Materials

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GIWAXS measurements

Table S1. Summary of GIWAXS scattering data for FHBC(TDPP)₂ thermally annealed film.

	Q ($\text{\AA}^{-1}$)	D-spacing ($\text{\AA}^{-1}$)
In-plane	0.21	29.2
In-plane	0.37	17.0
In-plane	0.41	15.0
Out-of-plane	1.81	3.4

Ground state optimized structure of FHBC(TDPP)₂



Figure S1. The PBEh-3c ground state optimized structure of FHBC(TDPP)₂

Table S2. Coordinates (Å) of the PBEh-3c ground state optimized structure of FHBC(TDPP)₂

Atom	X	Y	Z
C	0.698737	-0.84489	0.12402
C	1.397241	-2.06807	0.213505
C	0.699519	-3.29073	0.111514
C	-0.6976	-3.29017	-0.08439
C	-1.39641	-2.06701	-0.17172
C	-0.69928	-0.84438	-0.06559
C	-1.41124	-4.53646	-0.19298
C	-2.80917	-4.54275	-0.39393
C	-3.52641	-3.28184	-0.4965
C	-2.82026	-2.06639	-0.37373
C	1.413725	0.401491	0.222482
C	2.81446	0.407975	0.402904
C	3.531391	-0.85291	0.507453
C	2.821559	-2.06859	0.412137
C	-1.41579	0.402395	-0.14641
C	-0.72364	1.628434	-0.03862
C	0.719688	1.628085	0.13492
C	-3.531	-0.85029	-0.45586
C	-2.81626	0.409742	-0.32877
C	3.529314	-3.28481	0.516923
C	2.81253	-4.54506	0.403699
C	1.414224	-4.53761	0.205431
C	0.721678	-5.76373	0.100898
C	-0.71806	-5.76316	-0.10014

C	4.906922	-0.87959	0.710784
C	5.609002	-2.0697	0.822486
C	4.904673	-3.25951	0.721852
C	-1.42984	-6.95673	-0.20321
C	-2.7957	-6.95636	-0.39439
C	-3.47771	-5.76121	-0.48963
C	3.481822	-5.76405	0.486886
C	2.800282	-6.95858	0.381276
C	1.434224	-6.95785	0.191463
C	1.434252	2.82175	0.214775
C	2.803254	2.821566	0.382324
C	3.485586	1.626575	0.477292
C	-4.9006	-3.2552	-0.70897
C	-5.60537	-2.06483	-0.79956
C	-4.90523	-0.8756	-0.66808
C	-3.48936	1.628326	-0.3826
C	-2.80899	2.822625	-0.26694
C	-1.44002	2.822158	-0.09916
C	-7.06209	-2.06265	-1.02965
C	7.067264	-2.06884	1.042601
C	-7.88412	-1.15202	-0.35833
C	-9.24429	-1.16099	-0.587
C	-9.80701	-2.07139	-1.48542
C	-9.00453	-2.98132	-2.15903
C	-7.63881	-2.96953	-1.92467

C	-10.3076	-0.28041	0.034801
C	-11.5543	-0.807	-0.64434
C	-11.2458	-1.84952	-1.52265
C	-12.8574	-0.39145	-0.47805
C	-13.8817	-1.01522	-1.20199
C	-13.5579	-2.05387	-2.08442
C	-12.2503	-2.47776	-2.24613
C	-15.2715	-0.6031	-1.04857
S	-15.669	0.984888	-0.51925
C	-17.3625	0.65265	-0.59816
C	-17.5888	-0.63634	-1.0269
C	-16.4055	-1.34567	-1.28118
C	-18.3291	1.642783	-0.2509
C	-18.1754	2.926112	0.207469
C	-19.4605	3.493737	0.407117
C	-20.4591	2.509215	0.050907
N	-19.685	1.40823	-0.3403
C	-17.1771	3.907754	0.568771
N	-17.9516	5.006737	0.966196
C	-19.3069	4.77325	0.873542
C	-20.2752	5.763771	1.228894
C	-20.046	7.036751	1.698767
C	-21.2359	7.749095	1.950395
C	-22.3495	7.010424	1.66891
S	-21.9705	5.449858	1.098691

C	7.883568	-1.14923	0.376563
C	9.24557	-1.1608	0.593838
C	9.815844	-2.08243	1.475893
C	9.01896	-3.00059	2.144995
C	7.651369	-2.98639	1.9218
C	10.30373	-0.27316	-0.02673
C	11.55634	-0.80949	0.633566
C	11.25514	-1.86244	1.501943
C	12.85822	-0.39343	0.459524
C	13.88881	-1.02691	1.165904
C	13.5724	-2.07588	2.03875
C	12.266	-2.50032	2.208063
C	15.27753	-0.61449	1.003527
S	15.67179	0.979247	0.489332
C	17.36548	0.643041	0.544155
C	17.59436	-0.65124	0.955207
C	16.41273	-1.36157	1.214616
C	18.32977	1.635071	0.195975
C	18.17315	2.92451	-0.24388
C	19.45692	3.491764	-0.45325
C	20.45769	2.500273	-0.12366
N	19.68615	1.395988	0.263327
C	17.17255	3.913083	-0.57894
N	17.94445	5.016029	-0.97051
C	19.3002	4.77776	-0.90043

C	20.26615	5.770121	-1.25718
C	20.0338	7.050072	-1.70611
C	21.22203	7.762213	-1.96633
C	22.33738	7.016365	-1.7123
S	21.96225	5.44933	-1.15752
O	-15.9636	3.881054	0.562763
O	-21.672	2.536366	0.055665
C	-10.376	-0.47949	1.552231
C	-10.0738	1.195826	-0.30046
C	10.35741	-0.45262	-1.54718
C	10.07448	1.198815	0.329798
O	15.95922	3.8886	-0.55841
O	21.67055	2.524607	-0.14461
H	5.459015	0.041909	0.81819
H	5.463363	-4.18127	0.784092
H	-0.92808	-7.90964	-0.13506
H	-3.33189	-7.89263	-0.46928
H	-4.54579	-5.79862	-0.63876
H	4.55014	-5.80238	0.63424
H	3.337003	-7.89525	0.446777
H	0.932969	-7.91033	0.114177
H	0.932586	3.774466	0.143184
H	3.341557	3.757848	0.439724
H	4.556102	1.664695	0.608498
H	-5.45809	-4.17659	-0.78611

H	-5.45736	0.046738	-0.76796
H	-4.55997	1.666858	-0.5129
H	-3.34882	3.758882	-0.30816
H	-0.93986	3.774365	-0.01184
H	-7.45223	-0.46265	0.358573
H	-9.42541	-3.68724	-2.8641
H	-7.00494	-3.66042	-2.46605
H	-13.0894	0.400073	0.226525
H	-14.3381	-2.52291	-2.66924
H	-12.0266	-3.28116	-2.93658
H	-18.5714	-1.07101	-1.14591
H	-16.3885	-2.378	-1.59886
H	-20.1018	0.548491	-0.65985
H	-17.5353	5.869053	1.279442
H	-19.0622	7.454622	1.861039
H	-21.2669	8.762057	2.322884
H	-23.3806	7.311847	1.770595
H	7.445661	-0.4507	-0.32771
H	9.445621	-3.71475	2.838189
H	7.022069	-3.68418	2.459661
H	13.08441	0.405682	-0.23835
H	14.35781	-2.55296	2.609996
H	12.04802	-3.31179	2.890904
H	18.57748	-1.08879	1.058305
H	16.39755	-2.39751	1.520411

H	20.10511	0.530407	0.563779
H	17.52616	5.88395	-1.26506
H	19.04904	7.47308	-1.84747
H	21.25056	8.780118	-2.32529
H	23.36777	7.315998	-1.82592
H	-9.44664	-0.15876	2.025232
H	-11.1867	0.110127	1.983034
H	-10.5436	-1.52567	1.808325
H	-9.13974	1.54755	0.140306
H	-10.0225	1.355366	-1.3775
H	-10.8797	1.814993	0.096522
H	9.423794	-0.12518	-2.00707
H	11.16439	0.142009	-1.97806
H	10.52177	-1.49549	-1.8184
H	9.13661	1.556954	-0.09756
H	10.03345	1.34445	1.409257
H	10.87716	1.822417	-0.06672

Natural transition orbitals (NTOs) of S_1 and T_1 with the CAM-B3LYP functional

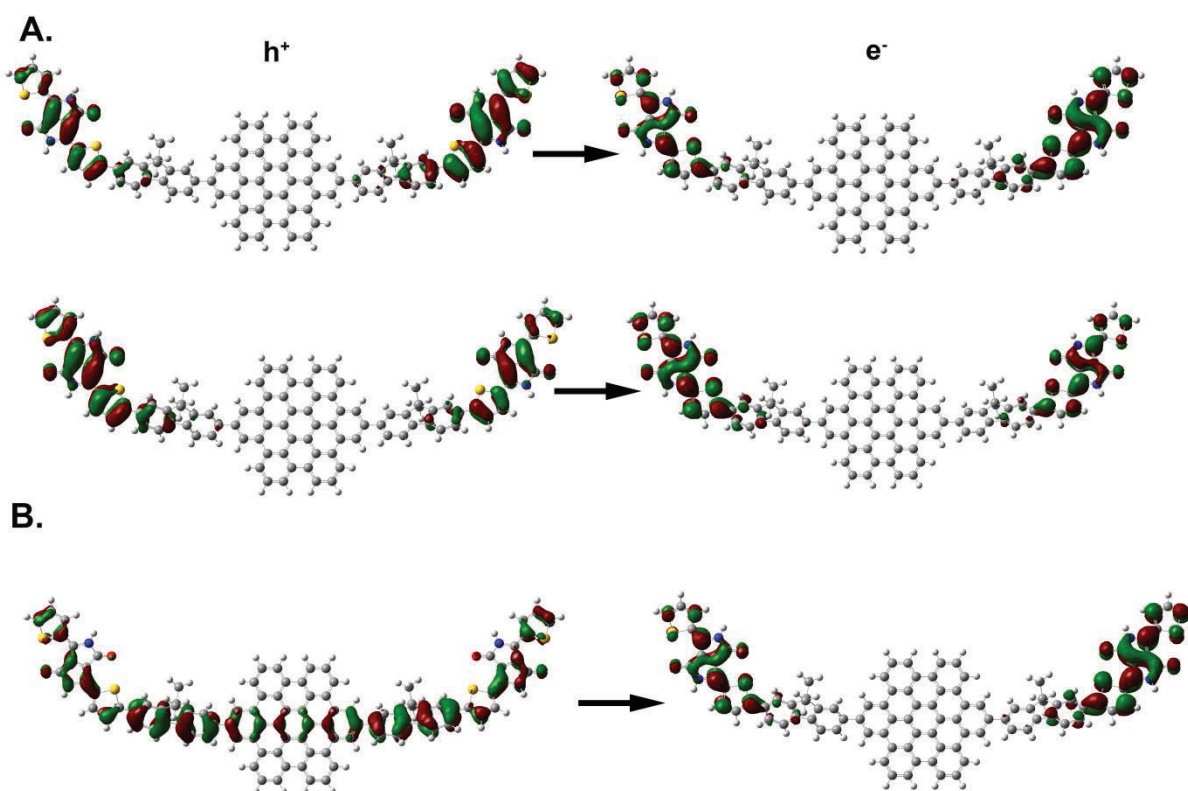


Figure S2. (A) The two main NTO electron-hole pair contributions for the S_1 state with 45% and 44%, (B) the minor NTO electron-hole pair contributions for the S_1 state with 11%.

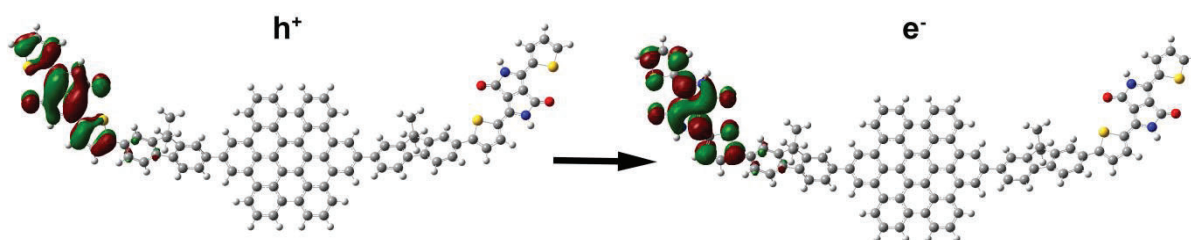


Figure S3. (A) The dominating NTO electron and hole pairs for the T_1 state

The results of TDA-DFT calculation using the ω B97X functional

The results show that the first and second singlet excited states (S_1 and S_2) are quasi degenerate with vertical excitation energies of 2.99 and 3.00 eV and have oscillator strengths of 1.27 and 1.57, respectively. For these two singlet states, HOMO-1 $\rightarrow$ LUMO & LUMO+1 and HOMO $\rightarrow$ LUMO & LUMO+1 excitations (Figure S4) are the respective dominant contributions. The results are consistent with the result of CAM-B3LYP functional. The first triplet excited state (T_1) has a vertical energy of 1.42 eV.

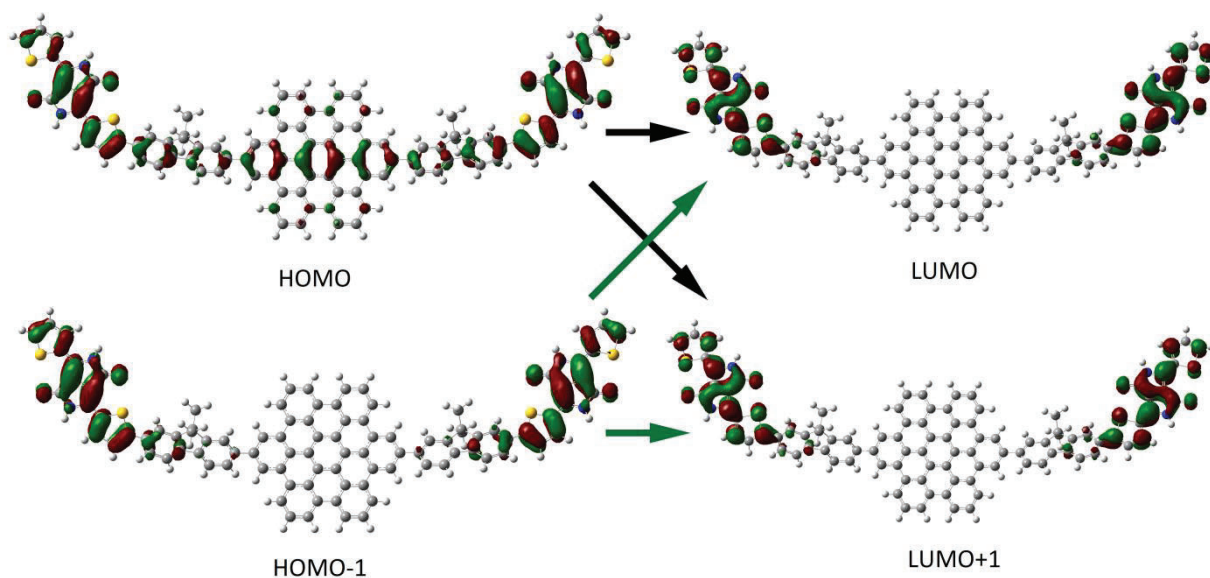


Figure S4. Molecular orbital representation of the main transitions of FHBC(TDPP)₂ using the ω B97X functional.

Absorption spectra of FHBC, DPP and FHBC(TDPP)₂

The absorption spectra of FHBC, TDPP and FHBC(TDPP)₂ in chloroform solution are shown in Figure S5.

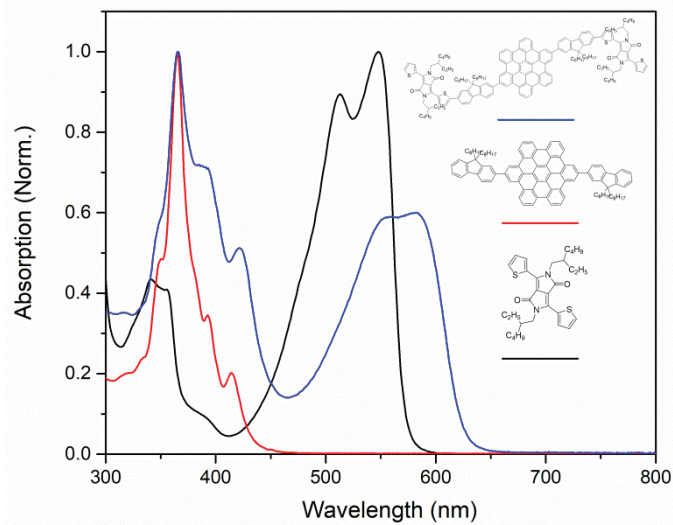


Figure S5. Absorption spectra of FHBC, TDPP and FHBC(TDPP)₂ in chloroform solution

Absorption and fluorescence spectra of FHBC(TDPP)₂ after annealing

The steady state absorption and fluorescence spectra of FHBC(TDPP)₂ were recorded for as-cast and thermally annealed thin films at 120° C for 10 min, see Figure S6 A and B.

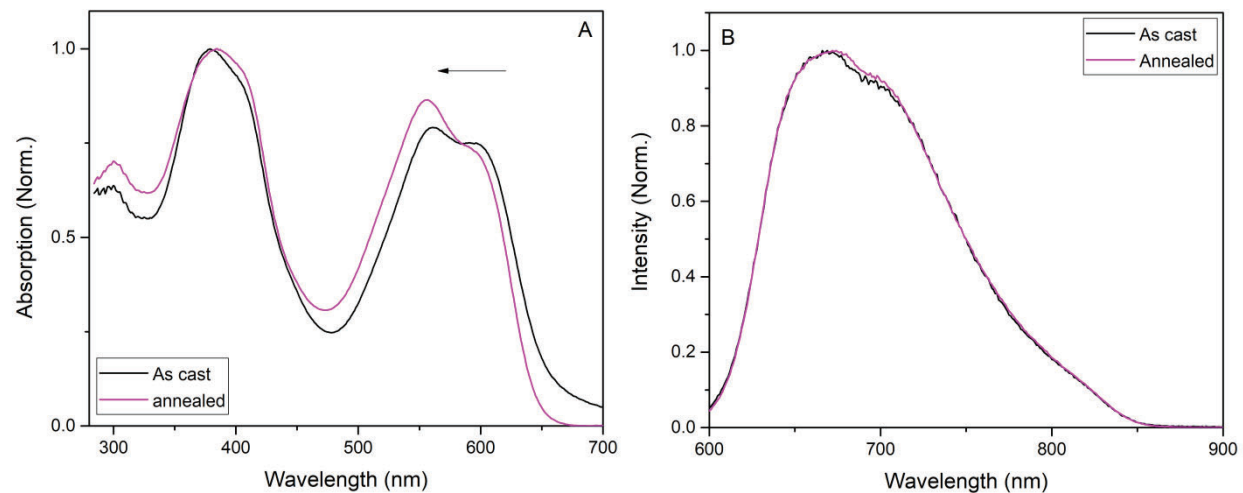


Figure S6. (A) The absorption spectra and (B) fluorescence spectra of FHBC(TDPP)₂ for the as-cast film and thermally annealed thin films.

Phosphorescence spectra of FHBC(TDPP)₂

Figure S7 compares the emission spectra of FHBC(TDPP)₂ in a thin film at room temperature and 77 K in the spectral region of 650-1400 nm without any optical filter and 900-1600 nm with >1200 highpass

filter. When the temperature is lowered to 77 K, a peak is observed at about 1300 nm (0.95 eV), which is assigned to emission from the triplet state.

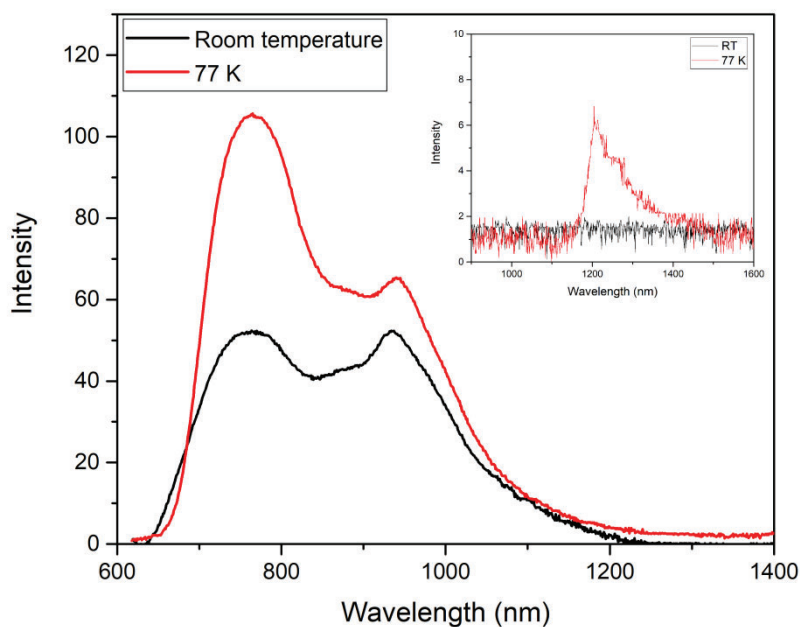


Figure S7. The emission of FHBC(TDPP)₂ in thin film at room temperature and 77 K in the spectral region of 650-1400 nm without any optical filter and the inset shows the emission at 900-1600 nm with >1200 highpass filter.

Nanosecond transient absorption decay profile of chloroform solution of FHBC(TDPP)₂

Figure S8 shows transient absorption kinetic trace at 650 nm, the fitted curve and instrument response function (IRF). The emission decays exponentially with a time constant of about 3 ns.

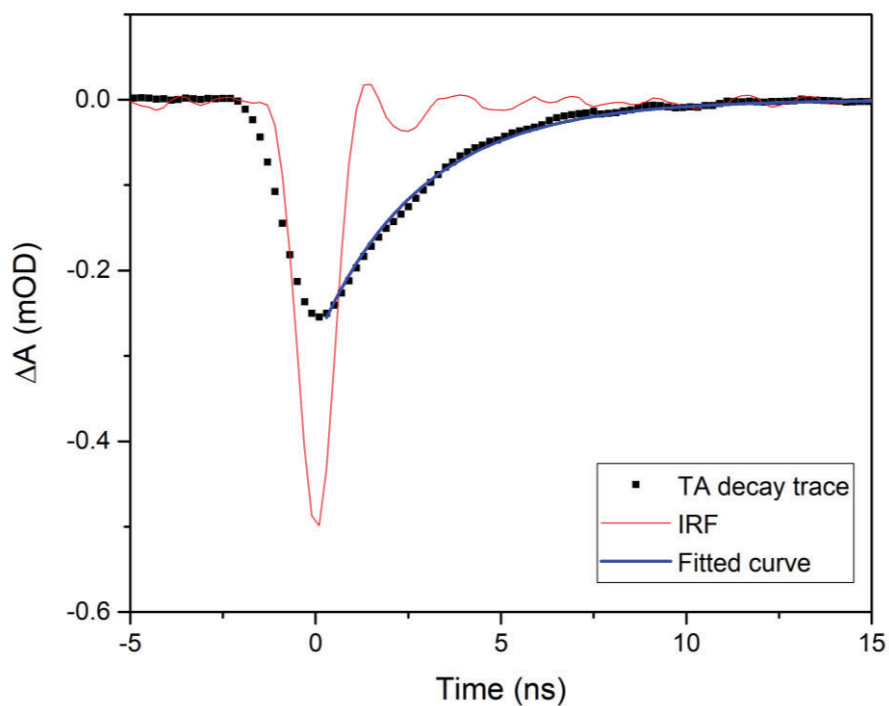


Figure S8. Nanosecond TA decay curve of chloroform solution of FHBC(TDPP)₂ monitored at 650 nm following excitation at 600 with excitation density of 30 $\mu\text{J}/\text{cm}^2$.

TCSPC of FHBC(TDPP)₂ in different solvents

The fluorescence decay profile of FHBC(TDPP)₂ by TCSPC measurements in solvents with varied dielectric constants from toluene, chloroform, tetrahydrofuran and dichloromethane ($\epsilon = 2.4, 4.8, 7.5$ and 9.1 , respectively) are shown in Figure S9.

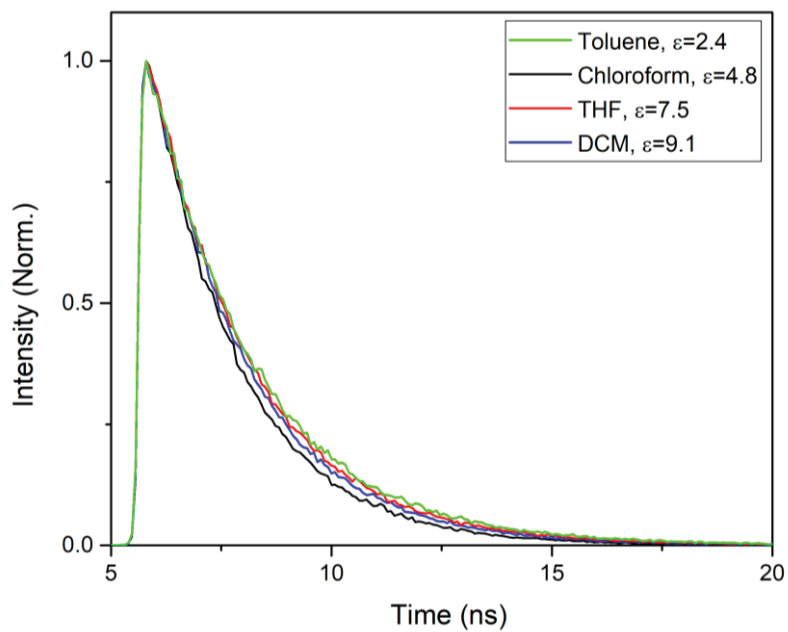


Figure S9. TCSPC measurements of FHBC(TDPP)₂ in different solvents.

TCSPC of FHBC(TDPP)₂ as a function of concentration

The fluorescence decay profile of FHBC(TDPP)₂ recorded by TCSPC measurements with different concentration of 10, 50, 100 and 500 μM are shown in Figure S10.

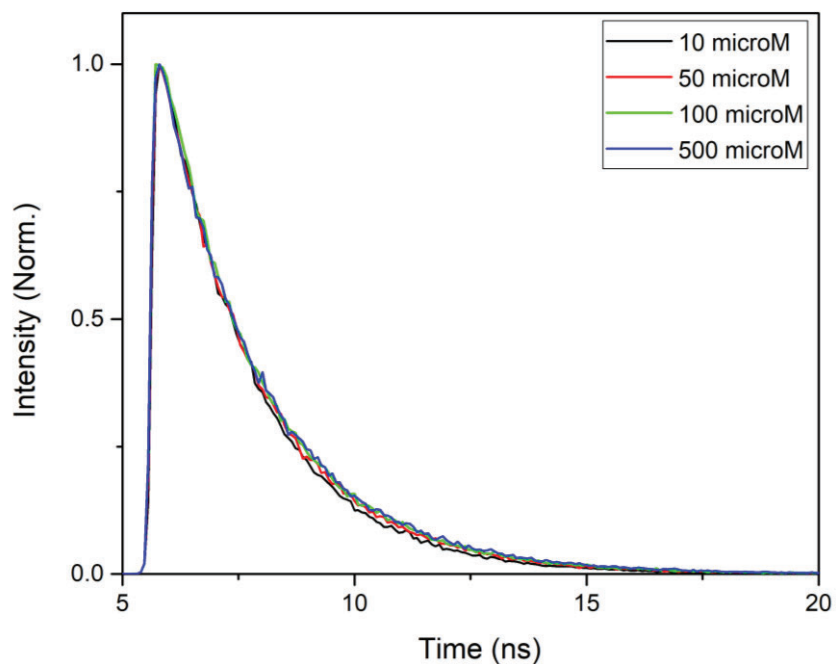


Figure S10. TCSPC measurements of FHBC(TDPP)₂ as a function of concentration.

Transient absorption spectra (TA) of PdOEP

The thin film TA spectra of PdOEP in the spectral region of 500-1300 nm following excitation at 400 nm are shown in Figure S11 showing a narrow, negative ground state bleach (GSB) at 550 nm, assigned to the Q band in the steady state absorption, at time delays of 100 and 800 ps, and no positive photoinduced absorption features following excitation at 400 nm.

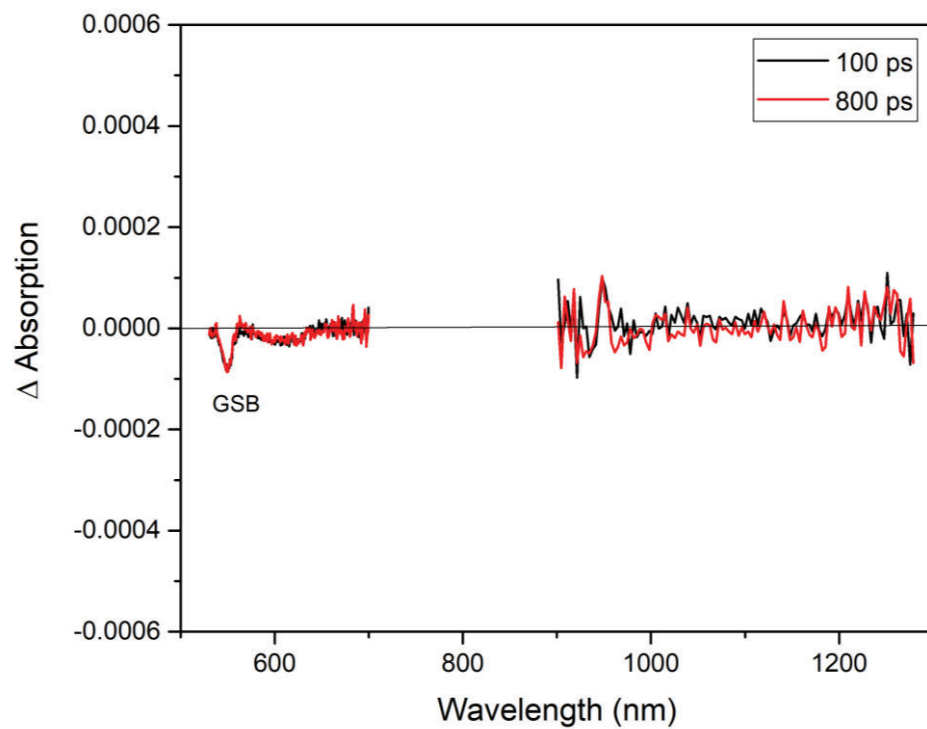


Figure S11. TA spectra of PdOEP in thin film at time delays of 100 and 800 ps excited at 400 nm with fluence of $10 \mu\text{J}/\text{cm}^2$.

Global target analysis of FHBC(TDPP)₂: PdOEP blend film

To study the mechanism from a large transient absorption data set, advanced modeling and data analysis techniques such as global and target analysis are needed to derive models and decompose spectra into their overlapping component spectra. Specifically, Global Target Analysis (GTA) is an approach based on differential equations that is employed to analyze multidimensional data sets for kinetic modeling and spectral interpretation. In our study, the program Glotaran¹, which is an easy-to-use modeling and data analysis tool, was used for such analysis. This approach starts with a simple model with a defined number of components and a set of starting values for the rate constants describing the kinetic connectivity between the components. The whole transient absorption data set is fitted by generating the time dependent population evolution of spectral intensities from a set of first order differential equations. Then, the parameters are optimized by re-adjusting the starting values based on the resulting model. The quality of the fit can be judged from the fitted spectra and time traces as well as residual matrices. Any residual structure in the singular vectors displays a potential misfit and the need for another component in the proposed model. After checking and accepting the fitted model, the program generates kinetic traces, the evolution of populations and spectra of each component. GTA was used to separate the overlapping features and generate the population profiles for each component versus time.

To find the triplet absorption spectrum, global target analysis was performed on the FHBC(TDPP)₂:PdOEP blend film. A simple two species model was considered and the resulting associated spectra and concentration profile versus time for each species which are assigned to the S_1 and T_1 are shown in Figure S12 A and B, respectively.

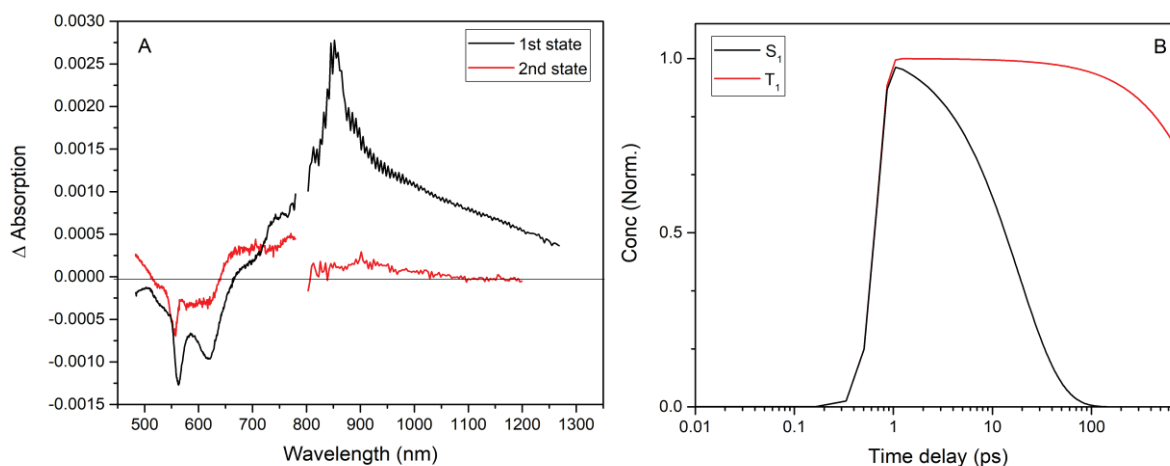


Figure S12. (A) The extracted associated spectra and (B) concentration profile versus time for S_1 and T_1 from the global target analysis for FHBC(TDPP)₂:PdOEP blend system.

Delayed Fluorescence of FHBC(TDPP)₂ in thin film

The delayed fluorescence decay of FHBC(TDPP)₂ in thin film at two different wavelengths of 620 and 750 nm were measured with the fluence of 30 $\mu\text{J}/\text{cm}^2$, Figure S13.

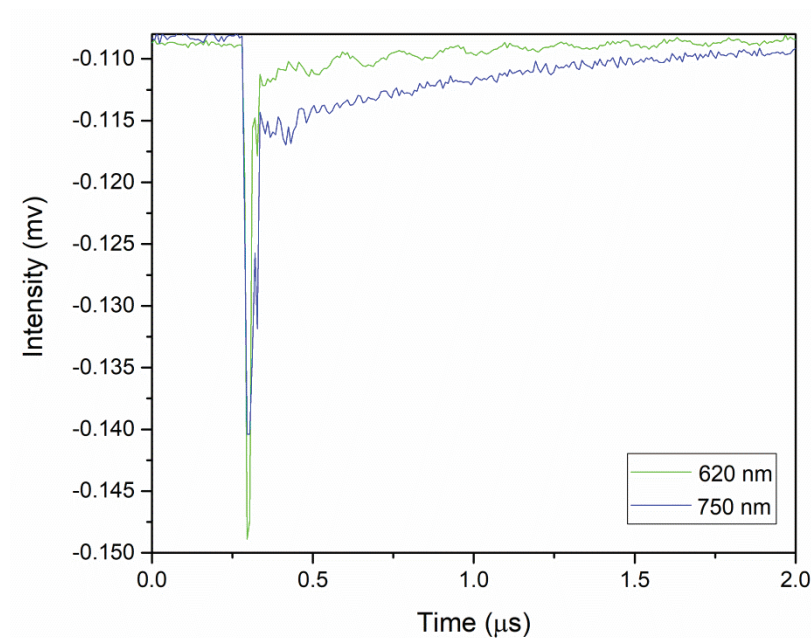


Figure S13. The fluorescence decay of FHBC(TDPP)₂ in thin film at two different wavelengths of 620 and 750 nm.

Singlet fission yield calculation based on the singlet depletion method

The singlet depletion method is one of the well accepted methods of triplet yield determination which has been used to calculate the triplet yield in various DPP derivatives and has been shown to be comparable with triplet sensitization methods². This method is based on two assumptions:

- (1) that the triplet and singlet state do not absorb in the same region, i.e. their peak maxima may lie close to one another but are not identical,
- (2) and that all photoexcited molecules return to the ground state or form the triplet state.

To obtain the triplet-triplet absorption, it is assumed that:

$$A(T_1) = \Delta A_{800\text{ps}} + [\phi_T \times A(S_0)] \quad (1)$$

where $A(T_1)$ is triplet-triplet absorption, $A(S_0)$ is the expected GSB for one singlet depleted per triplet, and $\Delta A_{800\text{ps}}$ is the fsTA spectrum of the film at 800 ps, after which the singlet state should be fully converted into the triplet state. As the singlet should be completely converted to triplet states by the end of the fsTA experiment, we restrict our yield analysis to the end of the fsTA spectra. Therefore, the singlet GSB spectrum is added to the fsTA ΔA spectrum until a singlet ground state peak (initially appearing as negative ΔA signal) is removed, and the region of the peak becomes linear in the $A(T_1)$

spectrum. By adding multiples of this spectrum (i.e., $\Phi_T = 10\%$ – 200%) to the ΔA fsTA spectrum of FHBC(TDPP)₂ film at 800 ps, we estimate the triplet yields for the annealed and as cast films.

To measure this for the as-cast film of FHBC(TDPP)₂, we choose a region of the transient spectrum (ΔOD) centered around a peak of the ground state absorption spectrum (565 nm) in the range of 15 nm each side, as shown in Figure S14.

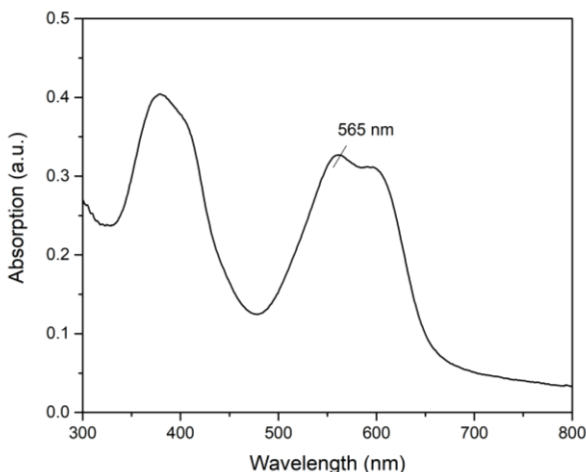


Figure S14. Steady state absorption spectra for as-cast film of FHBC(TDPP)₂

The expected ground state bleach signal was calculated, based on the molecular density from each crystal structure, the thickness of each film, and the energy of excitation, using the following equation:

The number of excitons per cm³ is calculated based on the thickness of the film (L) that is measured from profilometer and the energy of excitation (E) using the following equation:

$$\xi = \frac{E \lambda K(1-10^{-A})}{IL} = 2.1 \times 10^{18} \text{ exciton/cm}^3 \quad (2)$$

Dividing ξ (in excitations per cm³) by the number density of molecules in the film (molecules per unit cell N divided by the total volume V of the unit cell) gives the percentage of molecules in the film that are excited, which is about 5% for FHBC(TDPP)₂. Therefore, the expected ΔOD at 565 is 0.015.

The expected ground state bleach (GSB) is then multiplied by 10-200% and added to the transient signal. A baseline subtraction, defined by the endpoints of the specified region, allows a comparison of the linearity of each GSB addition multiple, performed in increments of 10% as shown in Figure S15.

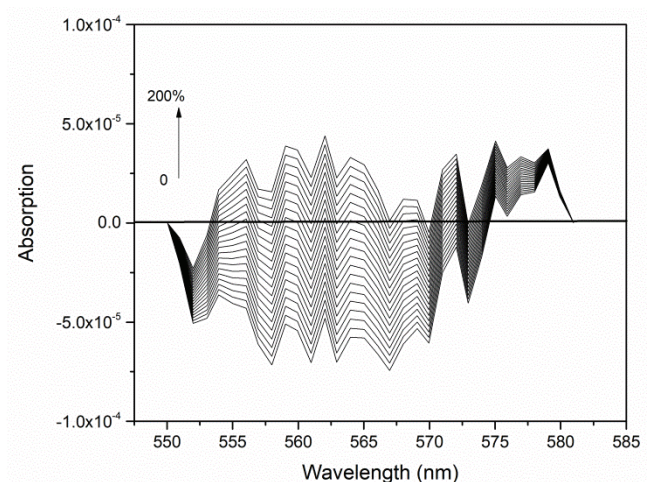


Figure S15. Linear analysis centered around 565 nm

By integration over the resulting linearized curves, the GSB total area can be plotted as shown in Figure S16. Where this line crosses $y = 0$, we obtain our triplet quantum yield, Φ_T . A similar calculation was performed for the annealed film and results in triplet yields of 150% and 170% for as-cast and annealed film, respectively. The triplet yield error bars are $\pm 20\%$ which are due to the number density of molecules in the film and excitation density calculation.

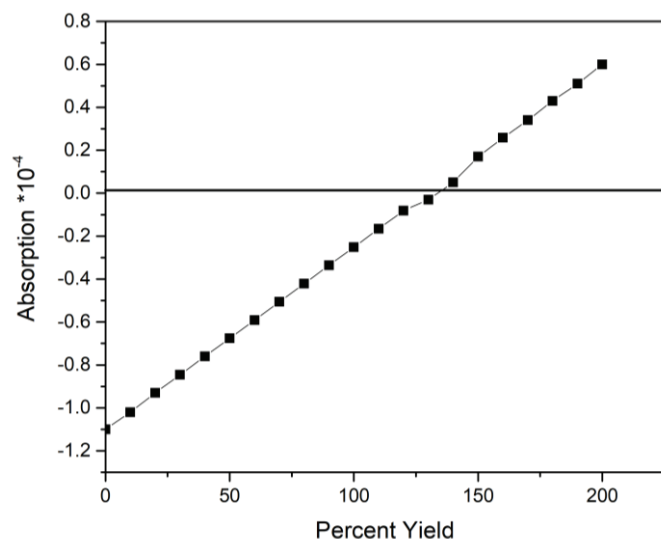


Figure S16. Area vs. percent yield. Triplet yield is estimated from the location of crossing $y = 0$.

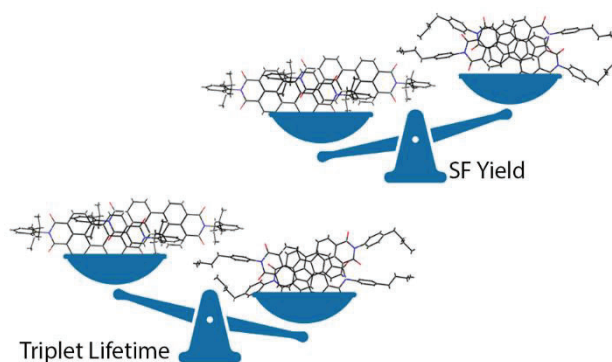
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Chapter 6

Competitive triplet formation and recombination in crystalline films of perylenediimide derivatives: implications for singlet fission



Scheme 6.1. The structures of the selected PDI derivatives that are studied for SF in this chapter

6.1. Preface

Several studies have shown that the rate of SF is highly sensitive to the intermolecular coupling and even minor variations in the relative position of chromophores in a solid can make a significant change in the efficiency of the SF process.¹⁻² As a result, it is necessary to develop rules for favorable orientation of the coupled chromophores. This information also helps us to design efficient intramolecular SF as it helps clarify the mechanism of SF. For this purpose, various numerical calculations have been reported on the pairs of chromophores in a crystalline material using a simplified model with some assumptions and approximations to calculate the SF rate.³⁻⁵ These assumptions can cause errors and make the calculations unreliable and at

variance with the experimental findings.⁶ In addition, it has been found that for a prediction of desirable packing patterns in crystalline solids, it is necessary to consider the geometrical arrangements of a larger number of molecules simultaneously.⁷ The better alternative to define these rules more accurately is making the crystal pairs by crystal engineering or by preparation of covalent dimers and comparing their SF behavior. PDI derivatives form well-ordered, π -stacked structures with a packing geometry that can be tuned by functionalizing the PDIs with different substituents. When the PDIs are functionalized at their imide positions, the functional groups have little impact on the electronic properties of the molecule compared to other positions.⁸ However, in crystals, the functional groups allow control over the relative orientation of neighboring molecules, providing a mechanism for control over the intermolecular interactions.

In this paper, we map the relationship between various crystal pairs of PDI derivatives and the SF efficiency. For this purpose, the ability of four PDI derivatives that are shown in Scheme 6.1 to undergo SF was studied. All four PDI derivatives (PDI1-4) are based on the same PDI core but are substituted differently at their imide positions; PDI1 by 4-butylphenyl, PDI2 by 5'-butyl-1,1':3,1''-terphenyl, PDI3 by 2,6-diisopropylphenyl and PDI4 by mesityl.

Calculations show that upon progression from a perfectly stacked pair arrangement, which is unfavorable for SF, and one chromophore is slipped along the direction of the HOMO-LUMO transition moment, fast SF results.⁴ The effect of slipping distance on the efficiency of singlet fission has been investigated using models based on Marcus^{1, 9} or Redfield^{23, 28} theories of slip-stacked pairs. To the best of our knowledge, the effect of rotating one chromophore

with respect to its neighbor around one of its axes in the crystal motif has not been investigated previously, either experimentally or theoretically, and this is one objective of this study. The other important factor for inclusion of SF materials in photovoltaic devices is the triplet lifetime of the SF material. The triplet should last long enough for charge extraction. The triplet lifetime has been investigated for all four PDI derivatives.

In this work, thin films of the four PDIs (1-4) have been evaluated with respect to their ability to support SF, using ultrafast transient absorption, flash photolysis and time-resolved fluorescence techniques to map the relationship between stacking geometry and SF parameters in a direct SF mechanism. This study will help guide the design of an ideal geometry with a fast SF rate and low recombination rate, which is essential for light harvesting applications. The research results have been submitted to the Journal of Physical Chemistry C and the article is under review:

Saghar Masoomi-Godarzi, Christopher R. Hall, Bolong Zhang, Mark A. Gregory, Jonathan M. White, Wallace W. H. Wong, Kenneth P. Ghiggino, Trevor A. Smith, and David J. Jones. Competitive triplet formation and recombination in crystalline films of perylenediimide derivatives: implications for singlet fission. J. Phys. Chem. C, In progress.¹⁰

The experimental details are included in the Supplementary Information section following the main manuscript.

Contributions of the candidate:

- All of the steady state spectroscopy

- Time correlated single photon counting (TCSPC) measurements
- Ultrafast transient absorption measurements
- Global target analysis
- Computational calculations

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10. Saghar Masoomi-Godarzi, C. R. H., Bolong Zhang, Mark A. Gregory, Jonathan M. White, Wallace W. H. Wong, Kenneth P. Ghiggino, Trevor A. Smith, and David J. Jones. , Competitive Triplet Formation and Recombination in Crystalline Films of Perylenediimide Derivatives: Implications for Singlet Fission. *J. Phys. Chem. C, In Progress*.

Competitive Triplet Formation and Recombination in Crystalline Films of Perylenediimide Derivatives: Implications for Singlet Fission

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Abstract

Developing photostable compounds that undergo quantitative SF is a key challenge. As singlet fission necessitates electron transfer between neighboring molecules, the SF rate is highly sensitive to intermolecular coupling in the solid state. We investigate singlet fission in thin films for a series of perylenediimide (PDI) molecules. By adding different substituents at the imide positions, the packing of the molecules in the solid state can be changed. The relationship between SF parameters and the stacked geometry in PDI films is investigated, with two-electron direct coupling found to be the main SF mechanism. Time-resolved emission and transient absorption (TA) data show that all of the PDI films undergo SF although with different rates and yields varying from 35 to 200%. The results show that PDI1 and 2, which are stacked PDI pairs twisted out of alignment along the HOMO to LUMO transition dipole, exhibit faster and more efficient SF up to 200% yield. We demonstrate that both triplet formation and decay rates are highly sensitive to the ordering of the molecules within a film. The results of this study will assist the design of optimized structures with the large SF rate and low recombination rate that are required for useful light harvesting applications.

1. Introduction

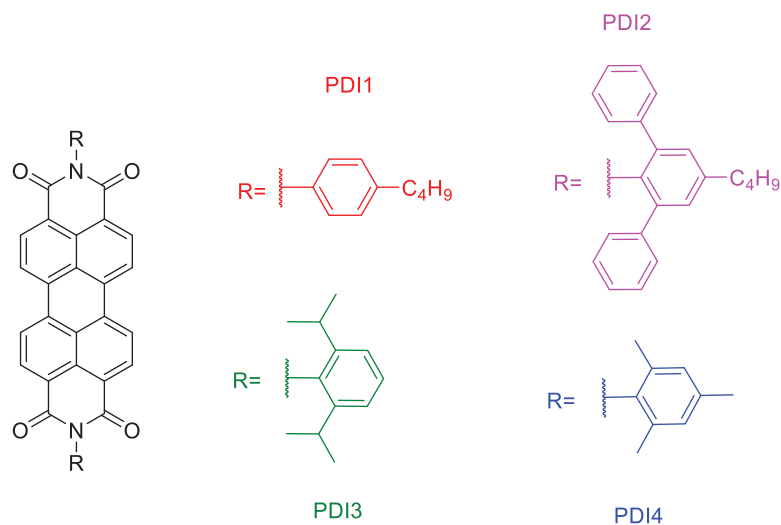
Singlet fission (SF) is a photophysical process that occurs in coupled organic molecules where the first singlet state has at least twice the energy of the corresponding triplet state i.e. $E(S_1) \geq 2 \times E(T_1)$. In this energetic configuration SF can generate two triplet excitons on absorption of a single high energy photon, and thereby has the potential to increase the theoretical photoconversion efficiency limit of photovoltaic (PV) devices from 32% to 46% and mitigate thermalization losses.¹⁻³ SF was first reported in anthracene crystals half a century ago, and has been reported since then with high yields in polyacenes,⁴⁻⁵ such as tetracene, pentacene and their derivatives, oligophenyls,⁶ diphenylisobenzofuran,⁷ carotenoids,⁸⁻⁹ rylene-based chromophores,¹⁰ perylenediimides,¹¹ diketopyrrolopyrroles derivatives and conjugated polymers.¹²⁻¹³ However, most of our understanding of the SF process relies on the experimental and computational work on the acene family. Perylenediimides (PDIs), in contrast to the acenes, have many properties that make them suitable for light harvesting applications.¹⁴ They are photostable, resistant to photooxidation, have low production costs and display large molar extinction coefficients in the range of $5-10 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in the visible region.¹⁵⁻¹⁹ They also meet the energy level requirement for SF with reported triplet energy levels around 1.1 eV, suggesting PDIs as ideal chromophores for SF-based light harvesting applications.^{15-16, 20}

Theoretical calculations demonstrate two distinct pathways for the formation of triplets through singlet fission. The first is a two-step, one electron mechanism where a charge transfer (CT) state acts as an intermediate species for the triplet formation.²¹ These CT states can be real or virtual intermediates. It has been reported that this CT-mediated mechanism can efficiently support SF where the energy of the CT state is low and the different intermolecular coupling is sufficiently large.²²⁻²³ The other mechanism is a one-step, two electron mechanism that does not involve any intermediate states.^{21, 24-26} In this study, the energy of the CT state is too high to be populated by the initial excited state so two-electron direct coupling is the main mechanism for SF in these series of compounds.¹⁴

Several studies have shown that the rate of SF is highly sensitive to the intermolecular coupling and even minor variations in the relative position of chromophores in a solid can have a

significant affect on the efficiency of the SF process.^{25, 27} As a result, it is necessary to develop rules for favorable orientation of the coupled chromophores. For this purpose, various numerical calculations have been performed on the pairs of chromophores in a crystalline material using a simplified model with some assumptions and approximations to calculate the SF rate.^{3, 21, 28} Some computational studies revealed that the intermediate multiexciton ¹(ME) state intersects the singlet S_1 state at smaller intermolecular distances using multireference Møller–Plesset perturbation theory (MRMP). They showed that π -orbital overlap between the two adjacent chromophores occurs via excimer formation resulting in an intersection between the S_1 and ¹(ME) states.²⁹ This can drive SF through the formation of a correlated triplet pair via an excimer state, i.e. an excimer-mediated SF. However, in the case of CT-mediated SF, the crystal packings with a weak cofacial motif are efficient for SF as they hold the highest degree of singlet exciton CT character and thermodynamic driving force. However, these assumptions can cause errors and make the calculations unreliable and at variance with the experimental findings.²⁸ In addition, it has been found that for a prediction of desirable packing patterns in crystalline solids, it is necessary to consider the geometrical arrangements of a larger number of molecules simultaneously.³⁰ The better alternative to define these rules more accurately is making the crystal pairs by crystal engineering or by preparation of covalent dimers and comparing their SF behavior.

PDI derivatives form well-ordered, π -stacked structures with a packing geometry that can be tuned by functionalizing the PDIs with different substituents. When the PDIs are functionalized at their imide positions, the functional groups have little impact on the electronic properties of the molecule compared to other positions.³¹ However, in crystals, the functional groups allow control over the relative orientation of neighboring molecules, providing a mechanism for control over the intermolecular interactions. In this paper, we map the relationship between various crystal pairs of PDI derivatives and the efficiency of the one step direct mechanism of SF. For this purpose, the ability of four PDI derivatives (Scheme 1) to undergo SF was studied. All four PDI derivatives (PDI1-4) are based on the same PDI core but are substituted differently at their imide positions; PDI1 by butylbenzene, PDI2 by butyl-terphenyl, PDI3 by diisopropylbenzene and PDI4 by mesitylene.



Scheme 1. The structures of the selected four PDI derivatives

Calculations show that in progressing from a perfectly stacked pair arrangement, which is unfavorable for SF, and slip one chromophore along the direction of the HOMO-LUMO transition dipole moment, fast SF results. The effect of slipping distance on the efficiency of singlet fission has been investigated using models based on Marcus^{10, 25} or Redfield^{23, 28} theories in the slip-stacked pairs. Both models predict a large variation in SF rates as one chromophore is slipped with respect to its neighbor in their long and short axes. However, the two models predict different chromophore pair geometries that maximize SF efficiency. To the best of our knowledge, the effect of rotating one chromophore with respect to its neighbor around one of its axes in the crystal motif has not been investigated, either experimentally or theoretically, and this is one objective of this study. The other important factor for inclusion of SF materials in photovoltaic devices is the triplet lifetime of the SF material. The triplet should last long enough for charge extraction. We have investigated the triplet lifetime for all four PDI derivatives.

In this work, thin films of the four PDIs (1-4) have been evaluated with respect to their ability to support SF, using ultrafast transient absorption, flash photolysis and time-resolved fluorescence techniques to map the relationship between stacking geometry and SF parameters in a direct SF mechanism. Our results show that both triplet formation and decay rates are highly sensitive to the ordering of the molecules within a film.

This study will help guide the design of an ideal geometry with a fast SF rate and low recombination rate, which is essential for light harvesting applications. The results demonstrate that the structure with more orbital overlap between neighboring molecules and smaller $r_{\pi-\pi}$ shows faster SF. We demonstrate a fast and efficient SF process in the PDI pairs when the direct two electron mechanism is dominant.

2. Experimental Methods

Material synthesis

The synthesis procedures of PDIs (1-4) have been reported elsewhere.³²⁻³⁴ Palladium octabutoxyphthalocyanine (PdPc(OBu)₈) was synthesized following the literature procedure as described in the supplementary information (SI).³⁵ All chemicals were used as received from suppliers.

Film preparation

Glass substrates with dimensions of 2.5 cm × 2.5 cm were cleaned by sonicating sequentially in acetone, isopropanol and chloroform. Before thin film casting, the substrates were dried with a strong flow of nitrogen. Solutions of PDIs were prepared by dissolving the samples into chloroform at a concentration of 5 mg/mL. The films were prepared under ambient condition. To prepare blend films for sensitized experiments, solutions of PDI mixed with PdPc(OBu)₈ were prepared by dissolving PDI and PdPc(OBu)₈ with mass ratio of 50:50 in chloroform at 5 mg/mL. Finally, thin films were cast onto clean glass substrates via spin coating at 1000 rpm/s and spun for 1 min. The crystalline film was treated by solvent vapor annealing (SVA) whereby chloroform was injected into a 30 mm glass Petri dish. The Petri dish was closed for 1 min to let the vapor saturate the treatment chamber. Then as-cast films were attached on the backside of the Petri dish lid, which was quickly swapped with the lid covering the solvent-containing Petri dish. The film was about 1 cm above the solvent level during the SVA. The optimal duration of SVA treatment used in this study was 60 s.³⁶

Crystal structure determination

Single crystals of PDIs were grown by slow diffusion of methanol or isopropanol vapor into the solution of chloroform with the concentration of 10 μ M. The single-crystal X-ray data for PDI3 were collected at 100 K on the MX1 beamline at the Australian Synchrotron.³⁷ The structures of PDI1 and PDI4 were collected at 100K on a Rigaku Synergy diffractometer. The structures were solved by direct methods and difference Fourier synthesis. Thermal ellipsoid plots were generated using the program ORTEP-3 integrated within the WINGX suite of programs. The crystal data for PDI2 were published in our previous report.³² Structures for PDI1, PDI3 and PDI4 have been deposited at the CSD and assigned CCDC deposit codes are 1949528, 1958260 and 1958261, respectively.

Thin film characterization

Samples for grazing incidence wide angle X-ray scattering transmission measurements were prepared by loading the materials onto silicon wafers. The samples were analyzed at the SAXS/WAXS beamline at the Australian Synchrotron with an X-ray energy of 10 keV.³⁸ A Pilatus 200K detector was used for wide-angle measurements. The substrates were silicon wafers that had been sonicated in acetone and isopropanol for 30 min each followed by 30 min of UV/ozone treatment. The beamline has a range of incident angles from $\Omega = 0.02$ – 0.35 in 0.005 increments to allow signal optimization near the critical angle of the film but below the critical angle of the substrate. Data from GIWAXS experiments were analyzed using a customized version of NIKA 2D using IgorPro.³⁹⁻⁴⁰

Steady state spectroscopy

Absorption spectra were recorded for PDI derivatives using a Varian Cary 50 UV–vis spectrophotometer. Fluorescence spectra were recorded on a Varian Eclipse spectrofluorimeter using an excitation wavelength of 550 nm and excitation and emission bandwidths of 5 nm for solution and 10 nm for film measurements. Photoluminescence (PL) spectra in the near-IR region were recorded with a spectrometer (Horiba Jobin Yvon iHR320) and an amplified InGaAs photo-detector (Electro-Optical System). The excitation source was a supercontinuum laser (NKT Photonics, SuperK Extreme& Varia) for excitation wavelengths tunable across the 450-750 nm region. The excitation beam was mechanically chopped and the detector output was fed into a

lock-in amplifier synchronized to the chopper frequency. A 750 nm high pass filter was used to remove the second order of the excitation and fluorescence. PL experiments at cryogenic temperatures were carried out in a liquid nitrogen cryostat (Oxford Instruments, Optistat DN).

Time correlated single photon counting

As described previously,³² the excitation source was a mode-locked and cavity dumped Ti:Sapphire laser (Coherent Mira 900F/APE PulseSwitch) pumped by a Coherent Verdi-10 DPSS Nd:YVO₄ laser. The laser output (880 nm wavelength, 5.4 MHz repetition rate) was frequency doubled to provide an excitation wavelength of 440 nm. The individual fluorescence decay curves were collected using a time-correlated single photon counting (TCSPC) module (SPC-150, Becker & Hickl, Berlin, Germany). The fluorescence decay times were extracted from the decay profiles using non-linear least square iterative deconvolution software (FAST, Edinburgh Instruments Ltd) and a sum-of-exponentials analysis.

Sub-nanosecond transient absorption spectroscopy

A mode-locked Ti:sapphire oscillator (Coherent, Mira Seed) seeded a Ti:sapphire regenerative amplifier system (Coherent, RegA 9050) to produce pulses of about 50 fs duration at a repetition rate of 92 kHz and a wavelength centered at 800 nm. A portion of the light was used to generate the 400 nm pump beam using a β -BBO (β -barium borate) crystal, and the 630 and 730 nm pump beams were generated with an optical parametric amplifier (OPA9450, Coherent). The pump beam was mechanically chopped at $\sim$ 3.5 kHz, and the arrival time of the pump pulses relative to the probe was manipulated using a variable optical delay line (Newport, UTS150PP with ESP 300 controller). The broadband probe was derived from the residual 800 nm beam focused onto a 3 mm sapphire substrate (Crystal Systems) for measurements in the visible region (450–800 nm) and a 5 mm undoped YAG substrate (Crystal Systems) for the infrared region (800–1400 nm). After passing through the sample, the probe beam was analyzed with a CMOS detector (Ultrafast Systems) at 7077 spectra/s, and the excess 800 nm laser fundamental was blocked using low- and high-pass filters for the visible and IR regions, respectively. The relative orientation of the pump and probe polarization was 54.7° and all spectra were corrected for the chirp of the supercontinuum probe. Dry nitrogen was blown over films during all measurements.⁴¹

Flash photolysis

Flash photolysis was employed to monitor the triplet excited state lifetime. The measurements were conducted on a home built transient-absorption apparatus. The 5 ns duration pump pulses are generated by a Nd:YAG laser/OPO (Ekspla, NT340, 10 Hz repetition rate), centered at 550 nm. A pulsed white light LED (Thorlabs, MCWHLP1) was used for the probe, synchronized to the laser pump source. The trigger pulse timing and duration are controlled with a BNC (Model 7010) delay generator and BK Precision 4064 waveform generator. The electronic trigger pulse train is connected to the modulation input of the Thorlabs LED controller (DC2200). The pump and probe beams are focused to a 0.5 cm FWHM spot at the sample position. After the sample, the probe beam is collimated and re-focused onto the entrance slit of a spectrometer (SpectraPro-300i, Acton Research Corporation, 0.3 meter spectrograph, 150 l/mm grating blazed at 500 nm). A photomultiplier tube (1P28, Hamamatsu) detected the spectrometer output at a given probe wavelength. The PMT analogue voltage is acquired with a digitizing oscilloscope (Teledyne LeCroy WaveSurfer 10). The signal kinetics were analyzed using FLASH software (Edinburgh Instruments Ltd).

Global target analysis

To study the mechanism from a large transient absorption data set, advanced modeling and data analysis techniques such as global and target analysis are needed to derive models and decompose spectra into their overlapping component spectra. Specifically, Global Target Analysis (GTA) is an approach based on differential equations that is employed to analyze multidimensional data sets for kinetic modeling and spectral interpretation. In this study, the program Glotaran⁴² was used for the analysis. This approach starts with a simple model with a defined number of components and a set of starting values for the rate constants describing the kinetic connectivity between the components. The whole transient absorption data set is fit by generating the time dependent population evolution of spectral intensities from a set of first order differential equations. Then, the parameters are optimized by re-adjusting the starting values based on the resulting model. The quality of the fit can be judged from the fitted spectra and time traces as well as residual matrices. Any residual structure in the singular vectors displays

a potential misfit and the need for another component in the proposed model. After checking and accepting the fitted model, the program generates kinetic traces, the evolution of populations and spectra of each component. GTA was used to separate the overlapping features and generate the population profiles for each component versus time.

3. Results

Structural characterization

All four PDI derivatives (PDI1-4) are based on the same core but are substituted differently at their imide positions; PDI1 by 4-butylphenyl, PDI2 by 5'-butyl-1,1':3',1''-terphenyl, PDI3 by 2,6-diisopropylphenyl and PDI4 by mesityl (Scheme 1). This has a significant impact on their intermolecular interaction and crystal packing (Figure 1). The molecules PDI1 and 3 pack in the monoclinic crystal system in the $P2_1/c$ and $P2_1/n$ space groups with one molecule in the unit cell whereas PDI2 and 4 pack in the triclinic and cubic crystal systems in the $P1$ and $I23$ space groups with two molecules in the unit cell. The crystallographic parameters of PDI1-4 are summarized in Tables S1 in the supporting information.

In all four PDI molecules, the PDI core is roughly flat with dihedral angles, Θ_1 , for the four carbons comprising the bay position as shown in Figure S1 ranging from 0.43° to 2.63° , which are listed in Table 1. In addition, the phenyl groups at the imide position are twisted by $\Theta_2 = 117^\circ - 118^\circ$ out of the PDI plane. The molecules PDI1 and PDI2 show herringbone packing with π - π overlap between neighboring molecules, whereas PDI3 packs in π -stacking columns in a lamellar arrangement and PDI4 forms a hollow circle with π - π stacked pairs as building blocks (Figure 1). For PDI4, when the solvent is completely removed, the gross crystal structure collapses, however, the PDI pairs that are the building blocks might remain intact. In order to investigate the intermolecular interaction for each PDI, the structures of the two nearest neighboring units from the crystal packing of the four PDI derivatives (PDI1-4) are shown in Figure 2. The PDI3 molecules form slip-stacked pairs with π - π stacking distances ($r_{\pi-\pi}$) of $5.2 \text{ \AA}$ and slipping distances of $6.3 \text{ \AA}$ in the x axis (Δx), and $1.2 \text{ \AA}$ in the y axis (Δy) (Figure 2). On the other hand, PDI1, 2 & 4 form π - π stacked PDI pairs twisted out of alignment as shown in Figure 2. These molecules show different rotational angles against their neighboring chromophore through the xy plane, Θ_3 , ranging from

PDI4 with a largest rotational angle of about 110° to PDI2 and 1 with rotational angles of about 90° and 45°, respectively. The measured π - π stacking distance ($r_{\pi-\pi}$) is 3.5 Å for PDI1 and 4.5 Å for PDI2 & 4, respectively. The values for $r_{\pi-\pi}$, Δx , Δy , Θ_1 and Θ_2 are summarized in Table 1. All four molecules show strong intermolecular interactions. PDI3 has the largest π - π distance of 5.2 Å and PDI1 displays the shortest π - π distance of 3.5 Å. PDI3 displays the least overlap between the neighboring chromophores compared to the other derivatives of PDI, which leads to a weaker intermolecular interaction. PDI1, with the twist angle of 45° and the shortest π - π distance, has the strongest intermolecular interaction among the other derivatives.

Table 1. The structural parameters for the associated dimers of the four PDI derivatives including π - π stacking distance $r_{\pi-\pi}$, displacement distance along the x axis (Δx) and y axis (Δy), the dihedral angles of the four carbons (Θ_1), the torsion angle of phenyl (Θ_2) and rotation angle (Θ_3)

	$r_{\pi-\pi}$ (Å)	Δx (Å)	Δy (Å)	Θ_1 (degrees)	Θ_2 (degrees)	Θ_3 (degrees)
PDI1	3.5	-	-	1.26	117	45
PDI2	4.5	-	-	2.63	118	90
PDI3	5.2	6.3	1.2	0.43	117	110
PDI4	4.5	-	-	2.25	117	-

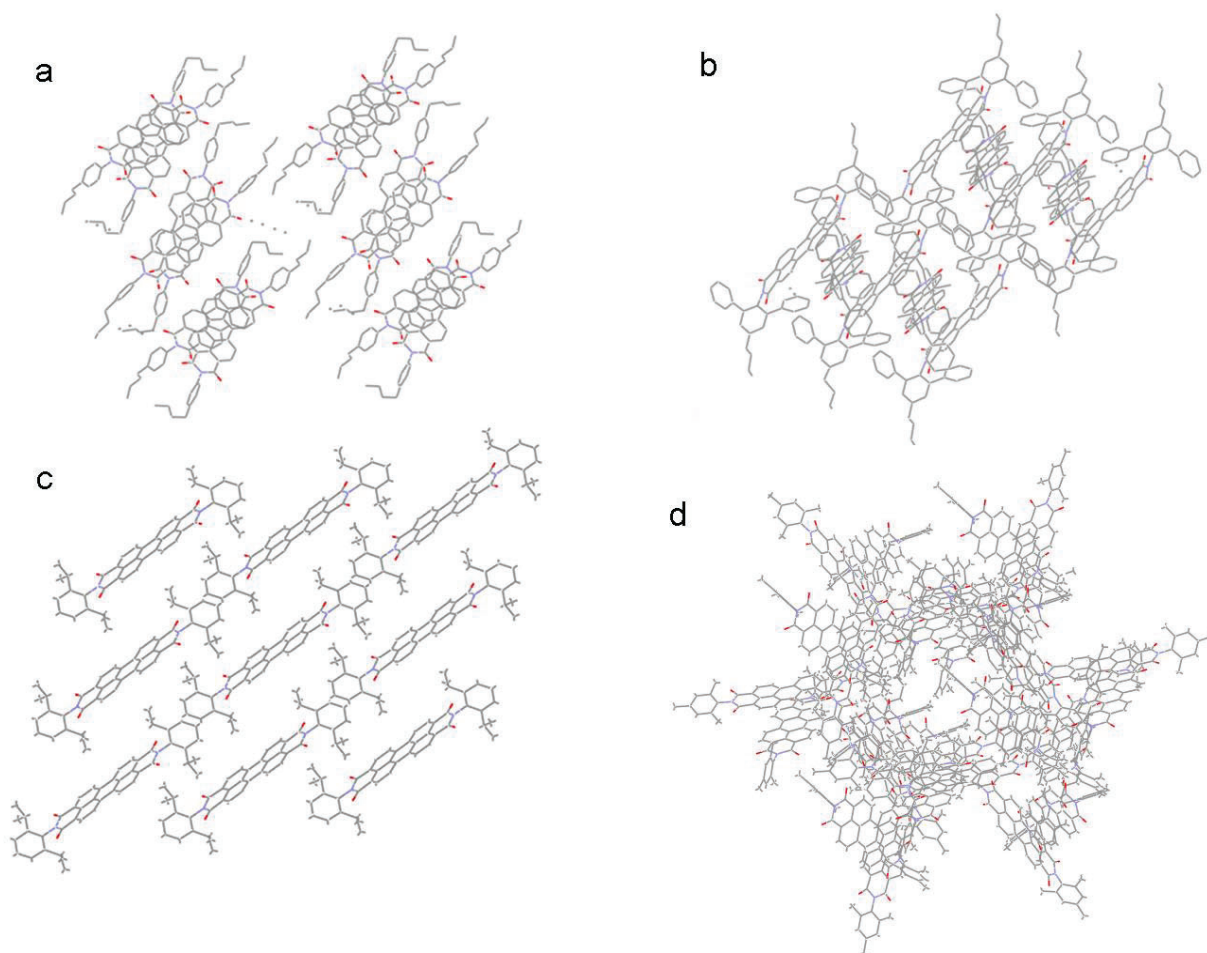


Figure 1. The lattice packing of (a) PDI1, (b) PDI2, (c) PDI3 and (d) PDI4.

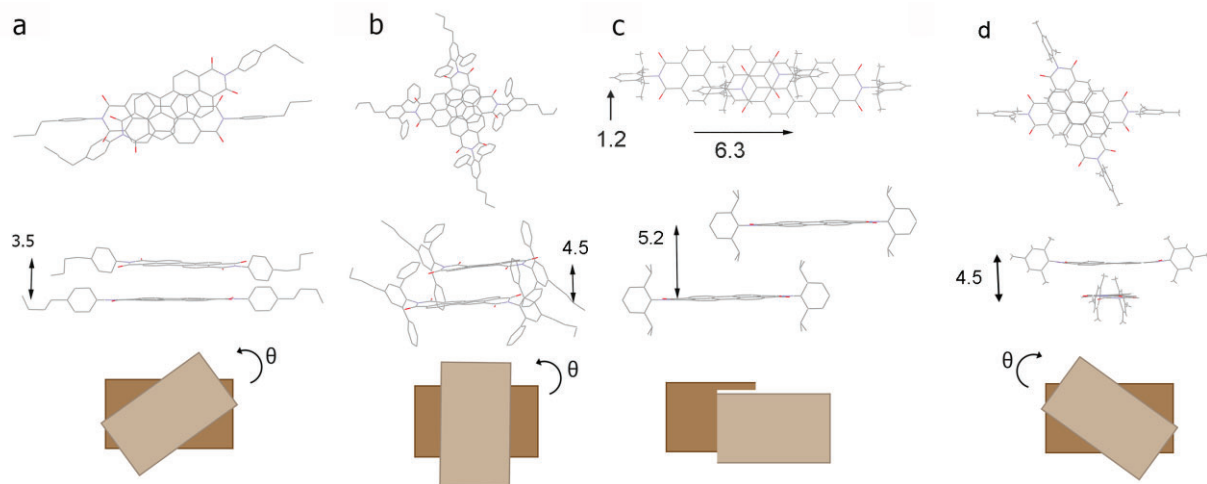


Figure 2. The associated pair units from the crystal packing of (a) PDI1, (b) PDI2, (c) PDI3 and (d) PDI4. Top view (upper row) and side view (middle row) and representation of pairs plane units (lower row). The distance units are in Å.

Thin film characterization

Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed on the as-cast and solvent vapor annealed (SVA) thin films of all PDI derivatives. The resulting scattering patterns of PDI1-4 are shown in Figure S2A-D. GIWAXS data contain information about the structural changes upon annealing and the results of the SVA film can be compared to the reported crystal structure for each PDI molecule. For PDI1, the scattering patterns for both the as-cast and SVA film indicate speckled rings suggesting long range crystalline order and the scattering rings in the as-cast film are more isotropic (Figure S2A1-2). The PDI2 as-cast and SVA film shows no crystalline order with no peak detected in the GIWAXS, see Figure S2B1-2. The scattering pattern for PDI3 shows two closely spaced rings in the as-cast film which is indicative of a small amount of isotropic crystallinity and after annealing the crystallinity is increased dramatically indicating isotropic long range order (Figure S2C1-2). The scattering pattern indicates little or no crystalline order in the as-cast thin film of PDI4 with no significant peaks in the GIWAXS (Figure S2D1) indicating that the films are effectively amorphous. However, the PDI4 SVA film shows speckled rings and crystalline order (Figure S2D2). The results suggest that the crystallinity of the film is increased consistently by solvent vapor annealing the as-cast film. Line-cuts from the in-plane and out-of-plane GIWAXS patterns for the SVA thin films are compared to the corresponding powder patterns simulated from the single crystal structures and the line-cuts are compared to find a preferred orientation (Figure S3). For PDI1 and 3, the linecuts of GIWAXS spectra for the SVA film match with the reported single crystal structures indicating that the key single crystal structural interactions are present in SVA thin films. However, for PDI4, the linecuts of GIWAXS spectra for the SVA film do not match with the reported single crystal structures and therefore the interpretation for PDI4 may be adversely influenced.

Steady state optical properties

Figure 3A-D shows the solution and SVA thin film absorption and fluorescence spectra of the four PDI molecules (PDI1-4). For comparison, the corresponding spectra of the four PDI derivatives in as-cast thin films are also shown in Figure S4 in the Supplementary Information. The similarity of these spectra in solution suggests that the substitutions at the imide position have only minor

effects on the photophysical properties of the PDIs in solution, but influence their solid state packing. For all of the studied PDI derivatives in solution, the fluorescence spectra mirror their absorption features and show small Stokes shifts. For all the PDI derivatives both the absorption and fluorescence spectra are different to one another in the solid state and compared to when in solution, which is attributed to different extents of intermolecular association. PDI1 in the film shows a broader and blue-shifted absorption band with loss of vibronic features compared to its monomeric form (assumed from the solution), features characteristic of H-type aggregation as mentioned in our previous report.³² PDI2 and 3 in films show broader and slightly red-shifted absorption spectra (relative to the solution case) with similar or slightly smaller A_1/A_2 ratios (A_1 and A_2 are the main absorption peaks as illustrated in Figure 3), which is attributed to a mixture of H and J aggregates as mentioned in our previous report for PDI2.³¹ PDI4 shows a slightly broader and red-shifted absorption spectrum with different A_1/A_2 ratio in the film compared to its monomer. Minor changes in the absorption and fluorescence spectra of the PDI derivatives are observed upon solvent vapor annealing (SVA) due to changes in the orientation and coupling of the chromophores in the more crystalline film induced by SVA, compared to the amorphous films. On the other hand, no change in the spectrum of PDI1 is observed upon SVA.

It was reported that both short-range charge transfer (CT) coupling and long range coulombic coupling are simultaneously present in the π -stacking molecules that are associated with the formation of H and J-aggregates.⁴³ Spano and coworkers demonstrated that the absorption spectra of PDI derivatives comprise features that result from competition between short and long range couplings. They showed how the relative sign and magnitude of these two interactions affect the absorption spectrum by representing the total coupling between neighboring molecules as the sum of $J_{\text{coul}} + J_{\text{CT}}$. For PDI1, the broadening of the absorption spectrum and loss of vibronic features in the film relative to its monomer with a greatly attenuated A_1/A_2 ratio, are characteristics of H-aggregates where the sum of coulombic and CT-mediated coupling is positive ($J_{\text{coul}} + J_{\text{CT}} > 0$). For PDI2 and 3, the solid-state absorption spectrum strongly resembles the monomer with a small red-shift, which is characteristic of a H/J null aggregate. This is due to the coulombic coupling being of opposite sign and similar magnitude as the CT-mediated coupling, so the sum is zero ($J_{\text{coul}} + J_{\text{CT}} = 0$). For PDI4, the solid state absorption spectrum shows a red-shift

and an increase in the A_1/A_2 ratio relative to the monomer, which is characteristic of J/H aggregates, so the sum of the coulomb and CT-mediated coupling is negative ($J_{\text{coul}} + J_{\text{CT}} < 0$).

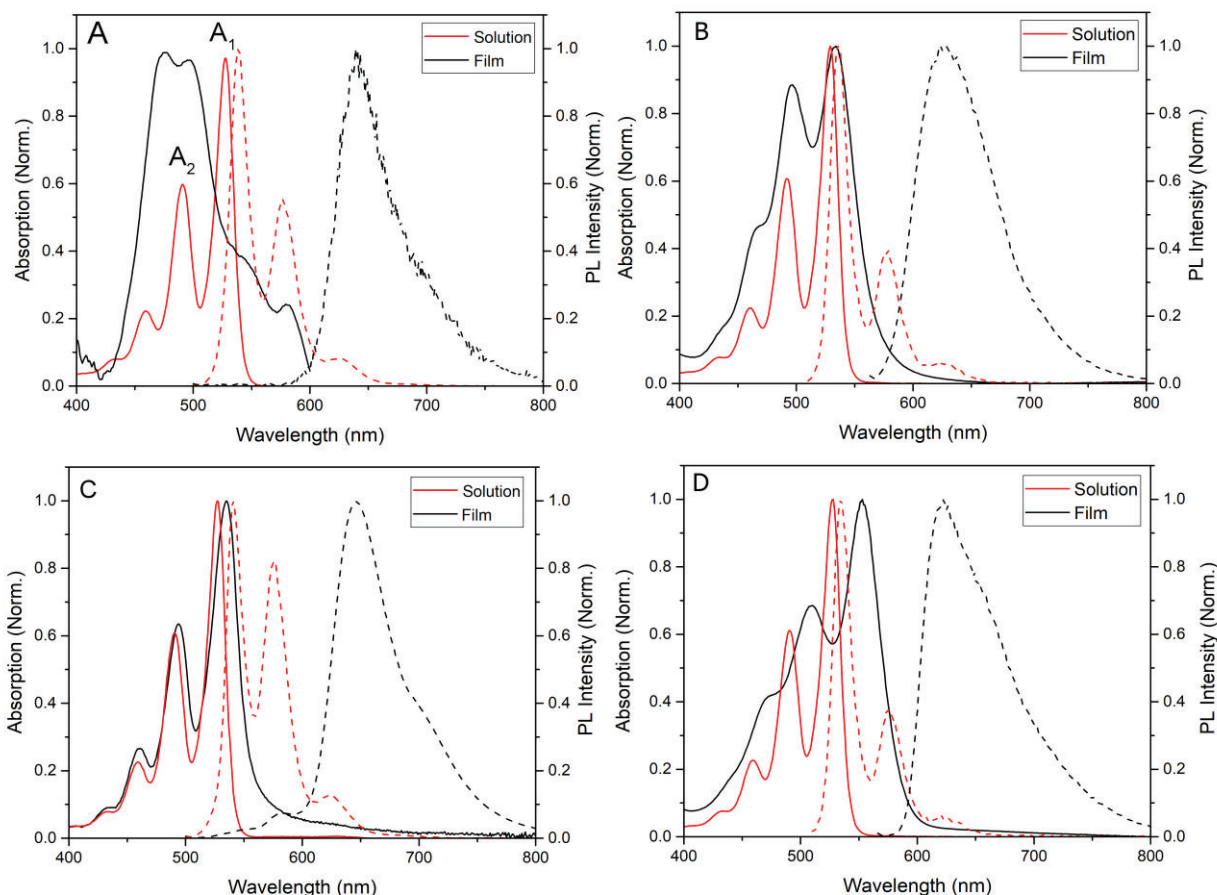


Figure 3. Steady state absorption (solid lines) and emission spectra (dashed lines) of dilute chloroform solutions (red) and SVA thin films (black) of (A) PDI1, (B) PDI2, (C) PDI3 and (D) PDI4.

Time-resolved photoluminescence of PDI derivatives

The fluorescence decay profiles, acquired by time correlated single photon counting (TCSPC) (see Figure S5), of PDI2-4 in SVA films show bi-exponential decay behavior upon excitation at 400 nm. The fluorescence of PDI1 was too weak to be measured at 650 nm. For PD2, PDI3 and PDI4 the shorter decay component has a time constant of 0.59, 0.27 and 0.22 ns while the longer second component has a time constant of 2.15, 2.02 and 1.7 ns, respectively. The fluorescence decay of the PDI4 SVA film is compared with the as-cast thin film and a dilute chloroform solution in Figure S6. The fluorescence decay of PDI4 in as-cast thin films decays (with time constants of $\tau_1=0.45$ ns and $\tau_2=1.7$ ns) faster than in solution (with decay time of 4.9 ns) indicating additional pathways

are available to depopulate the excited state in the more condensed state of the film, possibly including excimer formation. In addition, the fluorescence decay of PDI4 in the annealed film differs from the as-cast film with decay times of $\tau_1=0.22$ ns, $\tau_2=1.7$ ns. The reduced value for τ_1 indicates an additional quenching pathway for fluorescence in the annealed film which is not present in the as-cast film, or the formation of different crystalline phases which exhibit different fluorescence decay characteristics to the more amorphous regions.

Ultrafast transient absorption spectroscopy

Ultrafast transient absorption spectroscopy (TA) was performed for PDI1-4 in chloroform solution, and the as-cast and SVA thin films. The samples were excited at 540 and 550 nm with low pump energy of 1 nJ/pulse and fluence of 10 $\mu\text{J}/\text{cm}^2$ to avoid multi-exciton affects. Kinetic traces at 580 and 700nm of PDI4 in solution are shown in Figure S7A and B, respectively. A ground state bleach (GSB, 450-650 nm) and a photoinduced absorption band (PIA1, > 650 nm) are apparent. The decay of the PIA1 band is concomitant with the ground state recovery (Figure S7B) and there is no sign of triplet formation. PDIs 1-3 also show the same kinetic and spectral behavior in dilute chloroform solution (data not shown).

The TA spectra and kinetic traces at 500 and 650 nm of PDI1-4 in as-cast films are shown in Figure 4 and S8, respectively. A GSB and a positive photoinduced absorption band (PIA1, beyond 550 nm) with similar but mirrored kinetics are observed for all PDI2-4 compounds and no sign of triplet formation is observed. PDI3 shows the fastest decay and PDI2 shows the slowest decay to the ground state. However, different excited state dynamics are seen in the SVA PDI films (Figure 5 and S9). Besides the GSB and PIA1 features, the evolution of a new positive absorption band stretching from 550 nm to 650 nm (PIA2) appears in the TA spectra of the SVA PDI2-4 films with the concomitant decay of the PIA1 (Figure 5). The kinetic traces at selected wavelengths for the SVA thin films of the PDI2-4 samples are shown in Figure S9. Comparison between Figures S8 and S9 shows the effect of annealing on the excited-state kinetics. In PDI2, the extracted kinetic traces at 500 and 670 nm corresponding to GSB and PIA1 consist of short and long-lived features in the SVA film (Figure S9A), whereas the as-cast film shows mono-exponential decay (Figure S8B). The extracted decay curve at 600 nm (PIA2) indicates a growth of PIA2 concomitant with the decay

of PIA1. In PDI3 and 4, the kinetic traces in SVA films (Figure S9B-C) also show different kinetics from the as-cast films (Figure S8B-C) and the formation of a new feature. This suggests that the PDIs' singlet exciton decay follows the growth of another feature with different rates for each PDI sample in SVA films. This is in agreement with time-resolved photoluminescence data which show exciton quenching in the SVA film which is not present in the as-cast film.

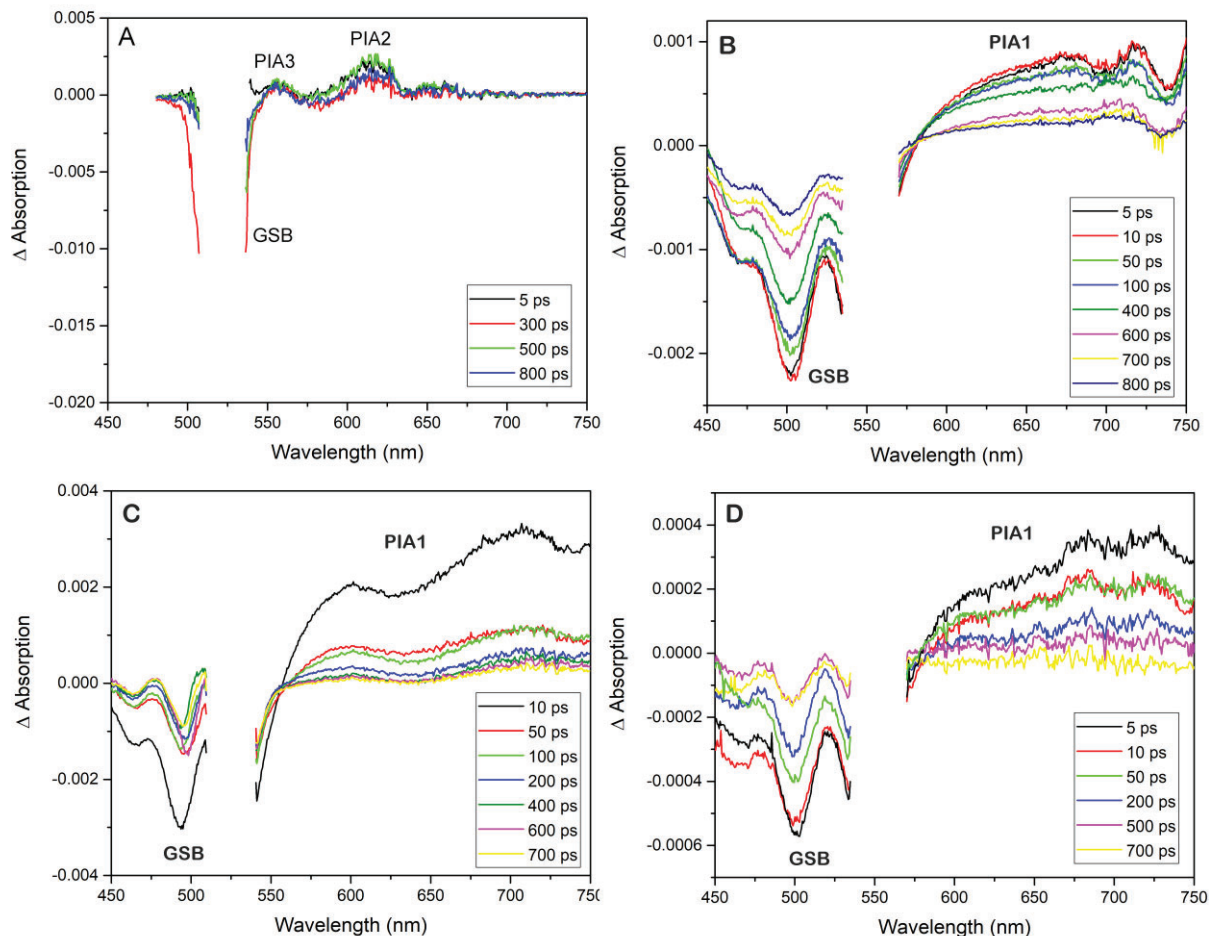


Figure 4. Transient absorption spectra of as-cast A) PDI1, B) PDI2, C) PDI3 and D) PDI4 films at different time delays in the range of 0-800 ps.

The TA spectra of PDI1 look different from the other three samples showing the formation of PIA2&3 at very early time delays and no PIA1 (singlet exciton) can be detected. This suggests that the singlet exciton decays quickly to another electronic state with absorption bands assigned PIA2&3 which could not be detected within the time resolution of this technique. Also, PDI1 shows the same dynamics in both as-cast and SVA films presumably due to the high crystallinity

of the PDI1 sample in both films as confirmed from GIWAX data. Unfortunately, the high crystallinity and subsequent heterogeneous nature of PDI1 films causes a low signal to noise ratio and the kinetic data cannot be used.

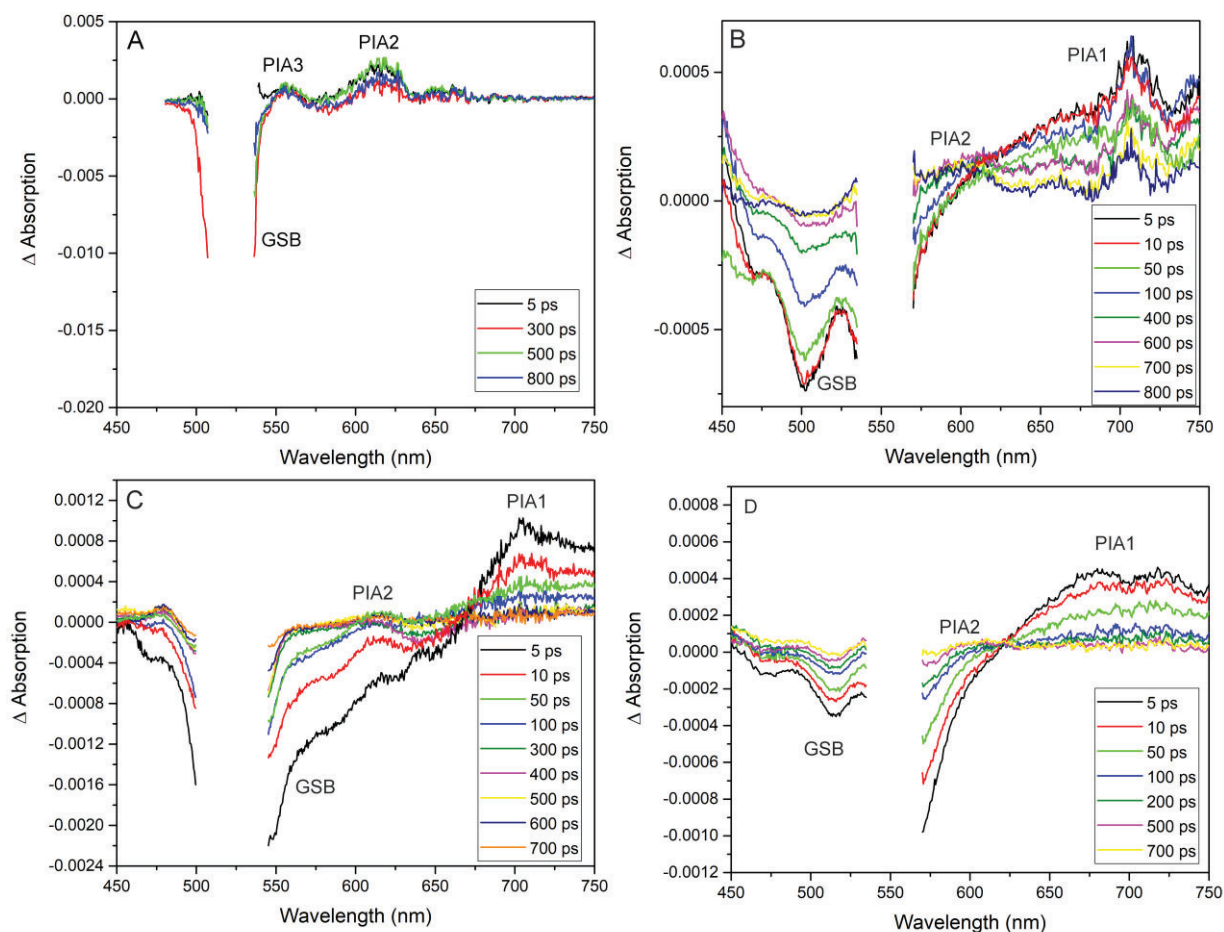


Figure 5. Transient absorption spectra of A) PDI1, B) PDI2, C) PDI3 and D) PDI4 in SVA films at different time delays in the range of 0-800 ps.

The TA spectra and the kinetics of SVA PDI2-4 films were analyzed by singular value decomposition (SVD) and global target analysis (GTA) to identify the species associated spectra (Figure S10) and kinetic parameters (Table 2). The time constants that result from the fit ($k_1=1/\tau_1$) are summarized in Table 2. The first excited state decays with a time constant of k_1 to state B that is identical to the triplet absorption signal of PDI previously reported in the literature.^{11, 14} This state then decays to the ground state. The assignment of the triplet absorption spectra will be discussed in the next section in more detail. From the global analysis, a direct conversion

mechanism ($S_1 \rightarrow T_1$) shows the best fit to the TA data of all the PDI derivatives in SVA films suggesting that either no intermediate state is formed or it cannot be detected in this spectral region with the available time resolution. The fast formation of triplets can be indicative of SF in the annealed PDI films. The results suggest that SF in SVA PDI films is highly sensitive to the intermolecular coupling and crystallinity of the films since it is not observed in the amorphous films. The role of intermolecular coupling and its effect on SF parameters will be discussed in detail below.

Triplet Characterization

To obtain the triplet absorption spectrum of PDI and to prove that the species B in the TA spectra of the PDI SVA films is due to the triplets and not any other long-lived species, a triplet sensitization experiment was performed. PdPc(OBu)₈ was chosen as the triplet sensitizer because it undergoes rapid intersystem crossing and has two narrow absorption bands at 370 and 730 nm (Figure S11) which makes the direct excitation of PDI derivatives possible, and a triplet energy level of 1.1 eV (see Figure S12) that is higher than the PDI triplet energy level. The TA spectra of PdPc(OBu)₈ in a thin film excited at 730 nm, show a GSB at 650-750 nm and a PIA in the spectral region of 500-650 nm that decays to the ground state and is assigned to the triplet excited state (Figure S13). The transient absorption spectra of PdPc(OBu)₈:PDI4 are shown in Figure S14. Although PdPc(OBu)₈ was excited selectively, the GSB from PDI4 is observed in the spectral region of 480-560 nm showing triplet energy transfer takes place from PdPc(OBu)₈ to PDI4 so the photoinduced absorption peak at about 600 nm is due to the PDI4 triplet absorption which is consistent with the literature. To provide more information about the dynamics of the triplet decay in PDI4, laser flash photolysis measurements were performed on the PdPc(OBu)₈:PDI film. The photoinduced absorption decay curve is shown in Figure S15, following excitation at 650 nm showing a bi-exponential decay with one time constant of 300 ns and slower time constant of 5.2 μ s which might be due to the presence of PdPc(OBu)₈ triplet. The T_1 -induced absorption peak obtained from the sensitization experiments is similar to the absorption spectrum of the 2nd species extracted from the GTA of the SVA PDI films. This confirms that the 2nd species (PIA2) in the SVA PDIs are triplets rather than any other long-lived state. As a result, we confirm that

triplets are formed on an ultrafast time scale following excitation of the SVA PDI films, but are not observed in the as-cast films or solutions.

Flash photolysis spectroscopy of PDI films

The triplet decays in the SVA PDIs thin films were measured by laser flash photolysis. The GSB recoveries in both the as-cast and SVA films of PDI1-4 at 500 nm are shown in Figure 6A and B, following excitation at 550 nm. The weak GSB signal in PDI1 is due to the low quality and highly crystalline nature of the film. The GSB kinetics of the PDI2-4 as-cast films show single fast components with kinetics limited to the instrument response function (IRF). The annealed thin films of PDI2-4 and PDI1 show much slower kinetics, with bi-exponential character, fitting with fast time constants of 100, 95, 120 and 55 ns and slower time constants of 0.6, 0.8, 1.05 and 1.2 μ s for PDI1-4, respectively. The sensitizer-generated isolated triplets are long-lived, of about 5 μ s. PDI1 shows the fastest triplet decay and PDI4 the slowest triplet decay. The change in the dynamics of the GSB recovery in the PDI thin films upon annealing, in combination with the ultrafast TA results, suggest fast triplet formation via singlet fission following different triplet dynamics from the sensitized film. The two triplet lifetimes suggest that triplets decay with different rates in different crystalline regions in films of a given compound.⁴⁴ A faster recombination rate for the triplet pairs generated in PDI1-4 via SF is due to the enhanced contribution of spin-allowed geminate triplet-triplet annihilation. The fast triplet formation ($\sim$ 100 ps) in PDI1-4 suggests SF is the dominant process of triplet formation rather than intersystem crossing (ISC), because in most cases ISC on such a short timescale is only observed in systems with heavy atoms.⁴⁵

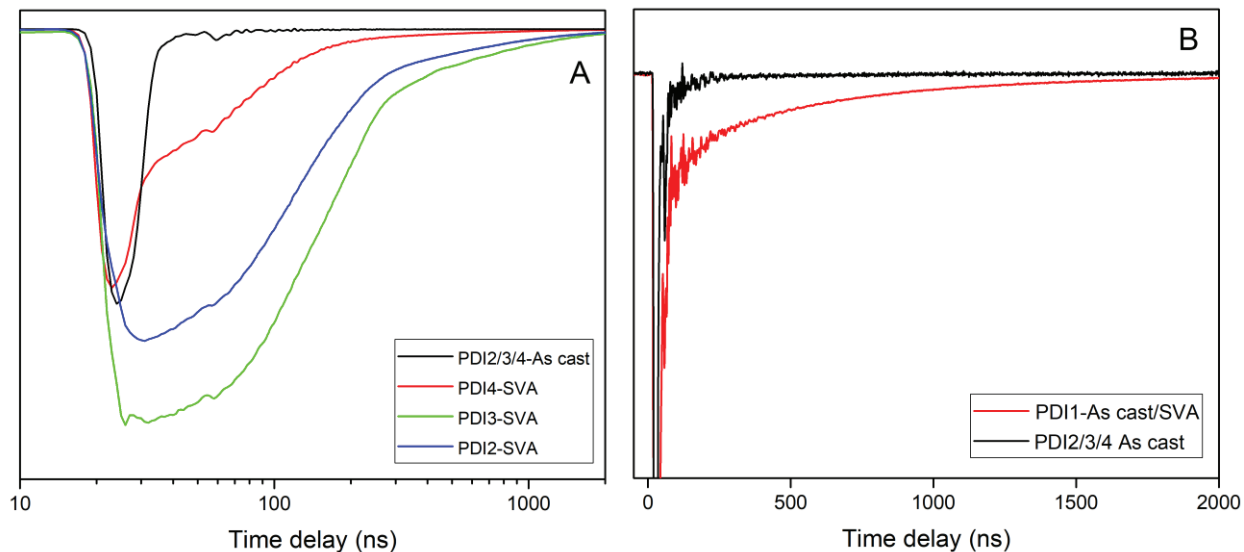


Figure 6. Ground state bleach recoveries of (A) SVA and as-cast thin films of PDI2-4 and (B) thin film of PDI1 and as-cast films of PDI2-4 monitored at 500 nm following excitation at 550 nm with excitation density of $30 \mu\text{J}/\text{cm}^2$.

Triplet yield calculation

In an ideal singlet fission chromophore, two triplets can be formed per absorbed photon. To determine the triplet yield, which is the main characteristic of SF, different methods are employed. One of the most reliable and accurate methods is the triplet sensitization technique in which a suitable triplet sensitizer undergoes energy transfer to the triplet states of the SF chromophore. In this method, the triplet extinction coefficient for the SF molecule is first determined using a triplet sensitizer with known triplet extinction coefficient. The numbers of triplets contributing to the triplet-triplet absorption band of the PDI SVA film are then quantified using the PDI triplet extinction coefficient. The excitation density of the sample is calculated and used to determine the number of singlet excitons generated during the experiments. Finally, the triplet yield is measured as the ratio of the number of triplets per singlet. The triplet extinction coefficient ($\Delta\epsilon_{\text{PDI}}$) for the PDI4 thin film is measured to be $\Delta\epsilon_{\text{PDI}} = 3850 \text{ cm}^{-1} \text{ M}^{-1}$ at 600 nm (further details of this calculation are given in the Supplementary Information). To determine the concentration of singlet excitons, the excitation density of the sample is calculated using:

$$\xi = \frac{E\lambda K(1 - 10^{-A})}{la}$$

where E is the pump energy, λ is the pump wavelength, $K= 5.034 \times 10^{-15} \text{ J}^{-1} \text{ nm}^{-1}$, A is the absorbance of the sample at the pump wavelength, l is the sample thickness and a is the spot size of the pump pulse. The excitation density then is used to calculate the percentage of molecules in the film that are excited and finally the concentration of singlet excitons that are formed is calculated. The triplet yield and lifetime from flash photolysis measurements and SF rate derived from the GTA are summarized in Table 2. The details of the triplet yield calculation are described in the Supplementary Information. The SF time constants were determined from the rate constant of the second step of modelling from GTA.

Table 2. Triplet yield, lifetime and SF rate of PDI1-4 SVA films

Sample Name	Triplet yield (%) $\pm 50\%$	Triplet lifetime		SF time constant (ps^{-1})
		1 st time constant (ns)	2 nd time constant (μs)	
PDI1	200	100	0.6	> 0.1
PDI2	180	95	0.8	0.02
PDI3	35	120	1.05	0.004
PDI4	60	130	1.2	0.005

4. Discussion

We have studied singlet fission in four PDI molecules which pack differently in the thin film state. The molecules of PDI3 form the slip-stacked pairs with their nearest neighboring chromophore with π - π stacking distances ($r_{\pi-\pi}$) of 5.2 Å and slipping distance of 6.3 Å in the x axis (Δx), and 1.2 Å in the y axis (Δy). On the other hand, PDI1 and 2 form π - π stacked PDI pairs twisted out of alignment with different rotational angle against their neighboring chromophore through the xy plane. The time-resolved emission, TA and flash photolysis data show that all of the PDI films undergo SF in SVA films although with different rates and yields. PDI1 and PDI2 show faster and more efficient SF compared to PDI3 suggesting that the chromophores with more orbital overlap between neighboring molecules and smaller π - π stacking distances ($r_{\pi-\pi}$) show faster SF. Marcus^{10, 25} and Redfield^{23, 28} demonstrated how the variation in SF rate of PDI pairs can be predicted with the change in the degree of slip displacement through the x and y axis in the packing arrangement of chromophores. However, unfortunately, there is no model available to predict the effect of rotating one chromophore with respect to its neighbor in one of its axes in

the crystal motif on SF rate and it can be useful to have this information to correlate the experimental results with theory in the future.

Calculations for PDI molecules have shown that the energy of the CT state is about 4.5 eV using a Weller-like relation, which is about 2 eV above the S_1 energy level.²⁵ In addition, PDI molecules in thin films and molecular crystals tend to pack closely in cofacial arrangements with an interplanar distance of about 3.5 Å, which induces significant orbital overlap between neighboring molecules. This in turn produces strong charge resonance interactions that can facilitate one step, two electron exchange between neighboring molecules.¹⁴ In addition, it is reported by Ayan Datta and coworkers⁴⁶⁻⁴⁷ that the energy of the CT state remains high irrespective of the configuration of the anthracene dimer. As a result, due to the relatively high energy of CT states and strong charge resonance interactions, SF mediated by the CT state can safely be ruled out. For SF by direct coupling, the intrinsic SF rate is proportional to the square of the Hamiltonian matrix element $\langle S_1 S_0 | H_{el} | T_1 T_1 \rangle$. Michl et. al.³ have calculated this matrix element as the difference between the two electron repulsion integrals of $\langle l_A l_B | e^2 / r_{12} | h_B l_A \rangle$ and $\langle h_A h_B | e^2 / r_{12} | l_B h_A \rangle$ (l_1 and l_2) where l_A , l_B , h_A and h_B are the LUMO and HOMO orbitals of two chromophores A and B. They demonstrated that if the stacking is perfect, there is as much attraction as there is repulsion, and two integrals (l_1 and l_2) cancel each other. However, if the stacked molecules are mutually shifted in the direction of the HOMO to LUMO transition moment, the cancellation is no longer perfect and the two integrals differ in sign, which results in a nonzero integral. The distribution patterns of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are demonstrated in Figure S16. These suggest that the two PDI pairs of 1 and 2 that stacked in parallel planes slipped along the direction of the $h \rightarrow l$ transition, which is of importance for fast SF and that might be the reason why PDI1 and 2 show faster and more efficient SF compared to the other compounds.

Once triplet pairs are formed via SF, they are coupled and can either decay to the ground state quickly or re-encounter each other and recombine to higher triplet or singlet excited states (K_{TTA1}). Also, they can diffuse apart before recombination and undergo slow non-radiative decay to the ground state (K_{TTA2}) which is an important step for device applications. The schematic

diagram of energy levels and the kinetic model for SF dynamics of the PDI molecules are shown in Figure 7. The energy level of the first excited triplet state was reported previously ($T_1=1.05$ eV)^{15-16, 20} and the higher triplet state is derived from TA measurements ($T_2=3.05$ eV, $\Delta T(T_2-T_1)=2$ eV, 620 nm). Triplet pairs that recombine can only form singlet excitons as triplet recombination to form higher energy triplet states is energetically forbidden. The kinetic decay of the triplet species also varies with the change in the packing arrangement of the chromophores in the film. PDI1 shows the shortest and PDI4 the longest-lived triplet states in the film suggesting that the chromophore with more orbital overlap with its neighboring molecules shows faster triplet recombination rates. The binding energy can be considered to explain this effect. The binding energy can be defined as the reinforcement of intermolecular interactions.²⁹ When the intermolecular interaction between two chromophores is very strong like in PDI1, the binding energy is high which strengthens the interaction in the excited state structure. As a result, the high binding energy can increase the formation rate of the ME state and facilitate the first step of singlet fission. On the other hand, a high binding energy decreases the rate of the second step of singlet fission i.e. separating the ME state into triplet states.⁴⁸ Also, it implies that the ME states are more stabilized in PDI1 so the formation rate of a correlated triplet pair is faster. However, this suggests that the energetic barrier of PDI1 for separating into two triplet states from the ME state increases and the rate of the second step of singlet fission decreases. In conclusion, there is a trade-off between correlated triplet formation and triplet separation. It has been shown that the recombination rate of the triplets depends highly on the three-dimensional spatial diffusion of triplet excitons in the film.⁴⁹ Also, The results show that both triplet formation and decay rates are highly sensitive to the ordering of the molecules within a film and finding an ideal geometry with a fast SF rate and low recombination rate is still a challenge. One of the issues in employing SF chromophores in photovoltaic devices is the limited amount of time that the triplet excitons are available to be utilized for light harvesting applications. The ideal system for a SF capable photovoltaic application not only needs strongly coupled chromophore pairs to allow SF to occur but also needs weakly coupled chromophore pairs to allow triplet pairs to diffuse apart.

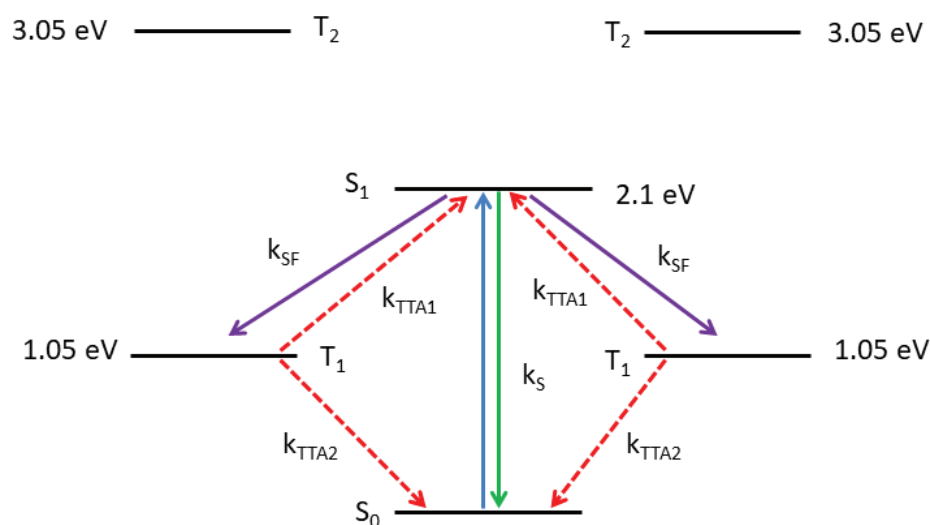


Figure 7. Schematic diagram of energy levels and the kinetic model for SF dynamics of PDI molecules

5. Conclusion

Due to their high stability, synthetic accessibility and high extinction coefficient, PDIs are potentially useful chromophores for SF-based applications. In this study, four PDI derivatives were investigated comprising the same PDI core but with different substituents at their imide positions, 4-butylphenyl, butyl-terphenyl, diisopropylphenyl and mesityl, which display distinct molecular geometries with varied intermolecular π - π interactions. The ultrafast TA, time-resolved fluorescence and flash photolysis spectroscopic studies show that SF occurs with different rates and yields in SVA thin films of all the PDI derivatives but not in disordered PDI aggregates or in solution. By comparing structural information from single crystal diffraction, the triplet lifetime and SF rate and yield of each derivative can be related to intermolecular electronic coupling and orientations of the adjacent PDI chromophore. The X-ray crystal structures show that PDI3 form slip-stacked pairs with their nearest neighboring chromophore. On the other hand, PDI1 and 2 form π - π stacked PDI pairs twisted out of alignment along the HOMO to LUMO transition. The ultrafast TA results demonstrate that PDI1 with more orbital overlap between neighboring molecules and smaller $r_{\pi-\pi}$, shows faster SF. The flash photolysis data show that PDI1 has the shortest and PDI4 the longest-lived triplet species in the films suggesting that the

chromophore with more orbital overlap with its neighboring molecules shows the shorter-lived triplets, i.e. faster triplet recombination rate. This study affords a better understanding to identify the packing motifs that enhance SF efficiency in chromophores having two-electron direct coupling as the main SF mechanism. These results confirm that where there is a high SF yield, this comes with a shorter triplet lifetime, and therefore, a lower probability to potentially harvest the triplets. New approaches are required to find optimized geometries that will allow the generated triplets to be harvested effectively.

Supporting information

Details of crystal structures, X-ray data, molecular synthesis, optical characterization techniques and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Acknowledgements

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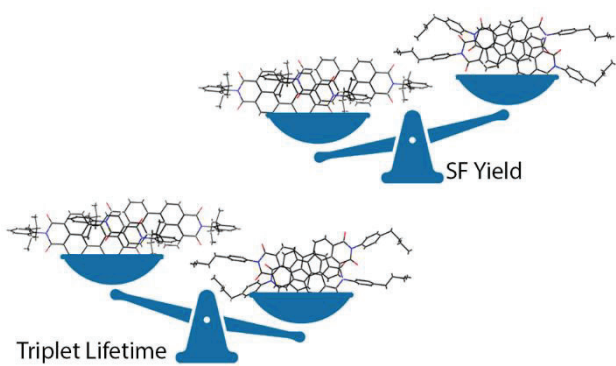
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TOC Graphic



Supplementary information for

Competitive Triplet Formation and Recombination in Crystalline Films of Perylenediimide Derivatives: Implications for Singlet Fission

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Crystal structure

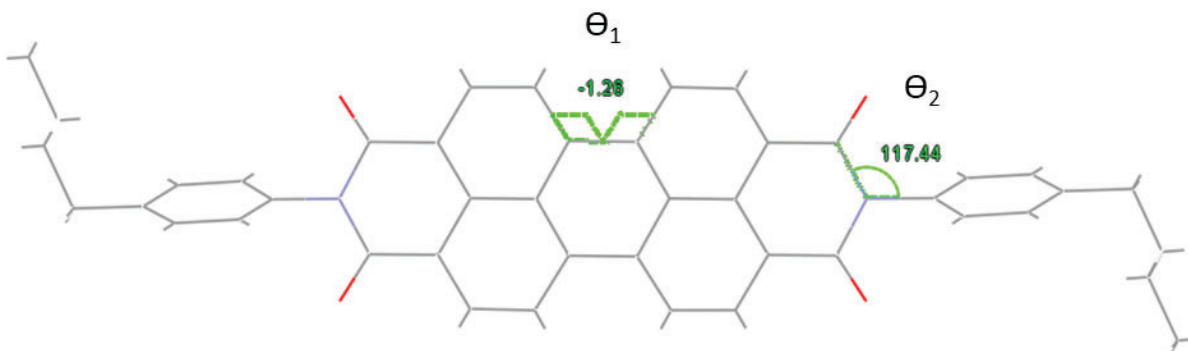


Figure S1. The structure of PDI1 molecule showing the dihedral angel of Θ_1 and twisting angle of Θ_2

Table S1. Summary of crystallographic parameters for PDI1-4

	PDI1	PDI2	PDI3	PDI4
a (Å)	22.11	16.94	10.94	22.79
b (Å)	6.97	17.24	15.95	22.79
c (Å)	21.54	20.31	13.01	22.79
α	90°	81.27°	90°	90°
β	102.84°	73.96°	106.42°	90°
γ	90°	64.79°	90°	90°
V (Å ³)	3239	5154	2178	11846.6
Z	4	2	4	6

GIWAXS data

Grazing incidence wide-angle X-ray scattering (GIWAXS) measurement was performed on the as-cast and solvent vapor annealed thin films of all PDI derivatives and the resulting patterns are shown in Figure S2. The in-plane and out-of-plane patterns of SVA films are compared to the simulated powder patterns (Figure S3). For PDI1 and 3, although the simulated X-ray patterns at $2\theta < 5^\circ$ is missed, the linecuts of GIWAXS spectra for SVA film match with the reported single crystal structures.

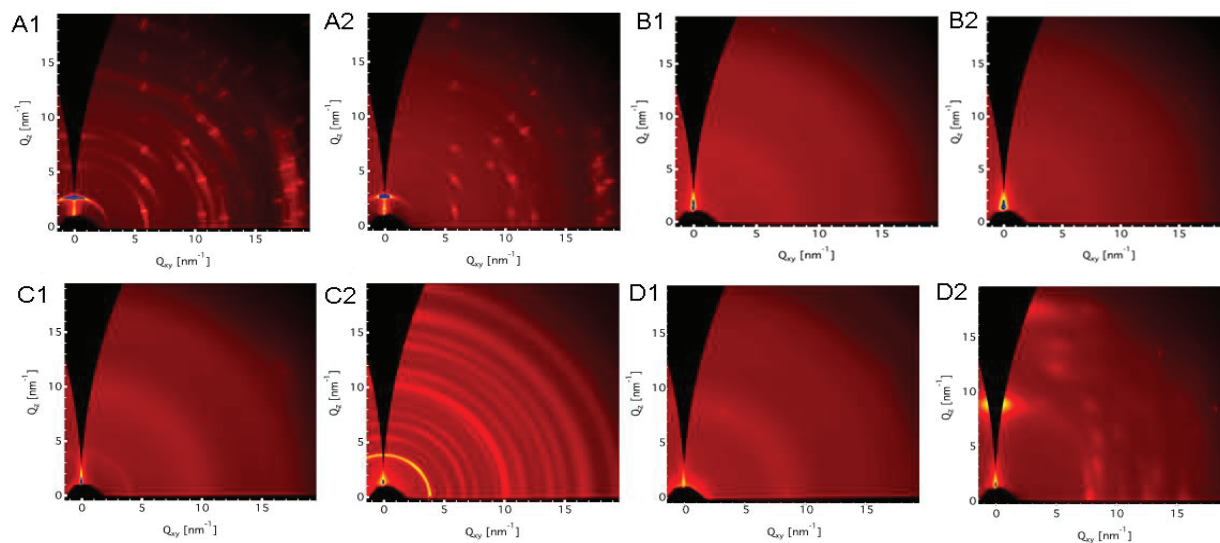


Figure S2. GIWAXS diffraction patterns of A) PDI1, B) PDI2, C) PDI3 and D) PDI4 in as cast (1) and SVA films (2)

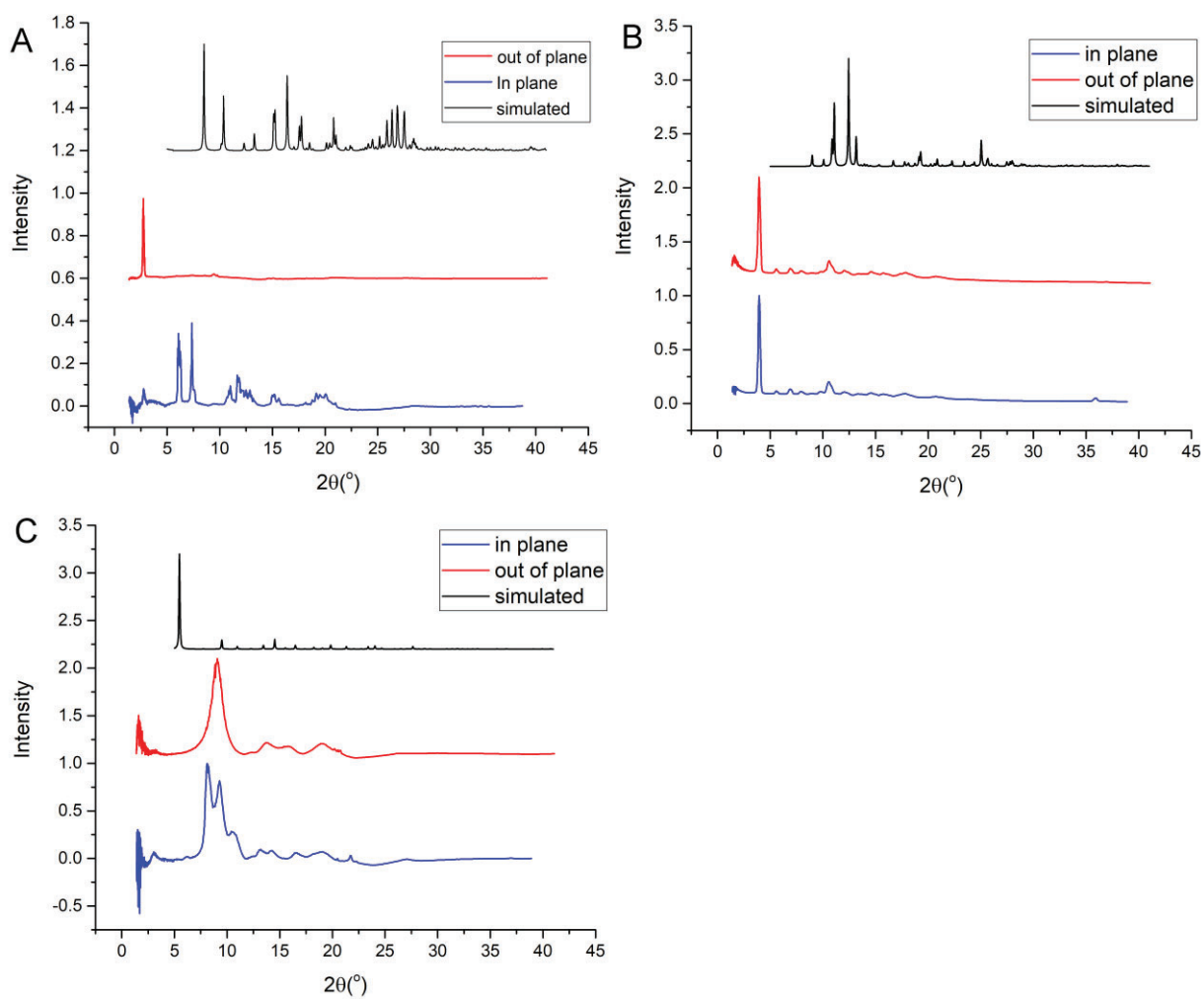


Figure S3. The in-plane and out-of-plane patterns of SVA thin film and the single crystal simulated powder patterns of A) PDI1, B) PDI3 and C) PDI4

Steady state optical properties

Figure S4 shows as-cast thin film absorption and fluorescence spectra of the four PDI derivatives. PDI1 shows a broader absorption spectrum with loss of vibronic features compared to the other PDIs. Also, PDI4 has the broadest emission spectrum whereas PDI1 shows the narrowest emission bandwidth in the film.

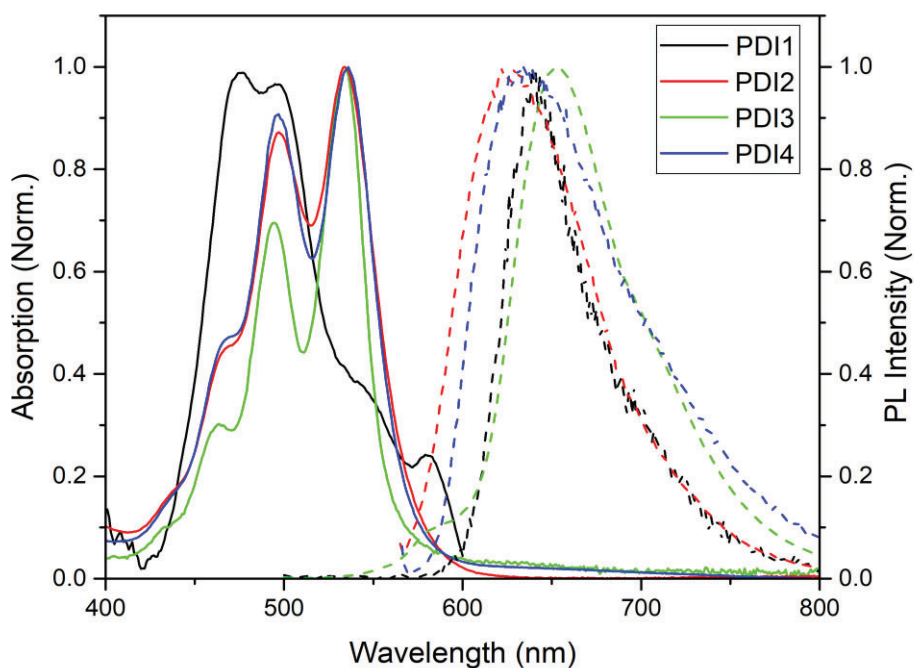


Figure S4. The as-cast thin film steady-state absorption (solid lines) and emission spectra (dashed lines) of PDI1-4

Time-resolved photoluminescence of SVA PDI derivatives

Figure S5 shows the fluorescence decay of SVA PDI2-4, recorded by time correlated single photon counting (TCSPC) to compare the decay kinetics of PDIs.

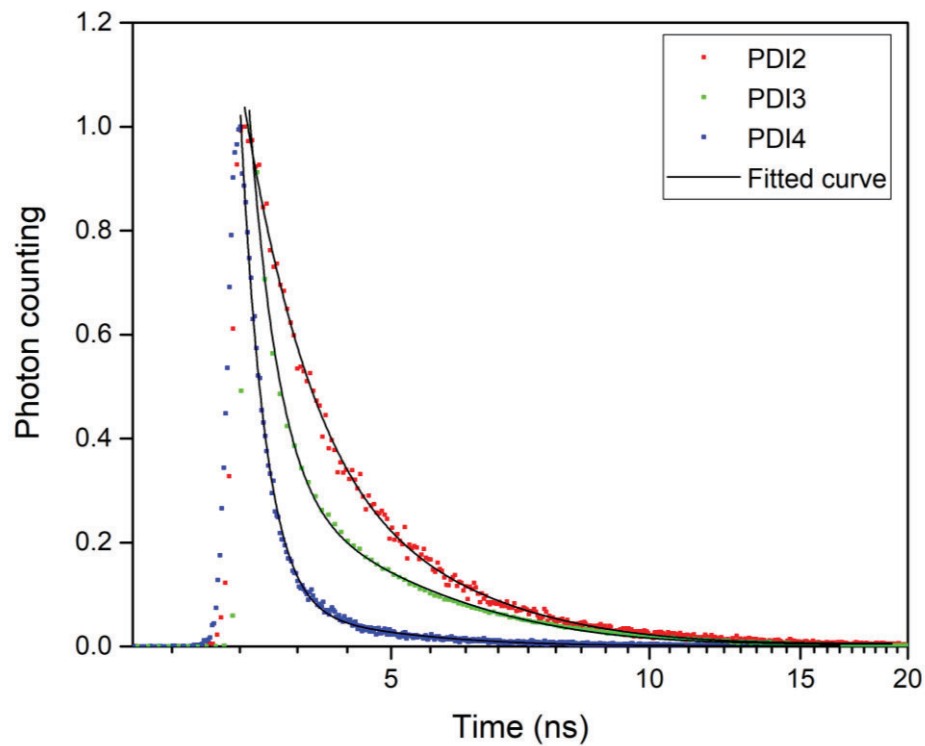


Figure S5. Fluorescence decay curves of SVA PDI2-4 recorded at 650 nm following excitation at 400 nm; the solid lines are the best fits using bi-exponential decay functions.

The fluorescence decay of the PDI4 SVA film is compared with the as-cast thin film and a dilute chloroform solution in Figure S6.

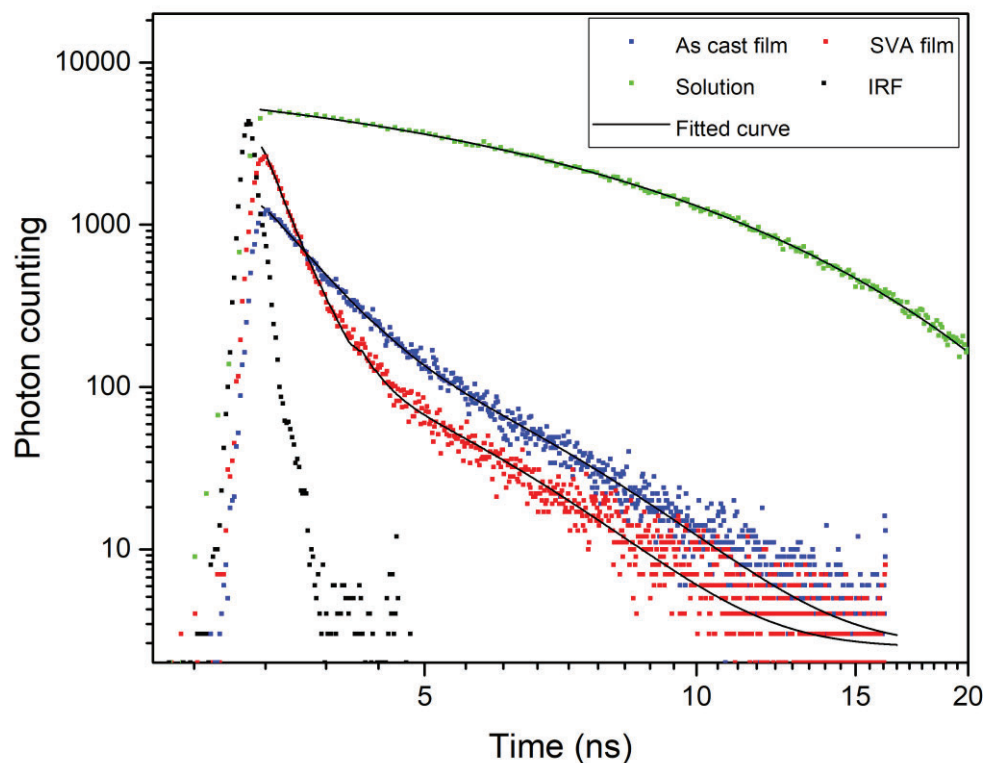


Figure S6. Fluorescence decay curves for SVA, as-cast film and dilute chloroform solution of PDI4 recorded by TCSPC at 650, 650 and 520 nm following excitation at 400 nm. The solid lines are the best fits using bi-, bi- and single exponential decay functions, respectively.

Ultrafast transient absorption spectroscopy of PDI4 in solution

The TA spectra in the visible region and kinetic traces at 580 and 700nm of PDI4 in solution are shown in Figure S7A and B, respectively. A ground state bleach (GSB, 450-650 nm) and a photoinduced absorption band (PIA1, beyond 650 nm) are apparent. The PIA1 band decays monoexponentially to the ground state which is consistent with the ground state recovery decay.

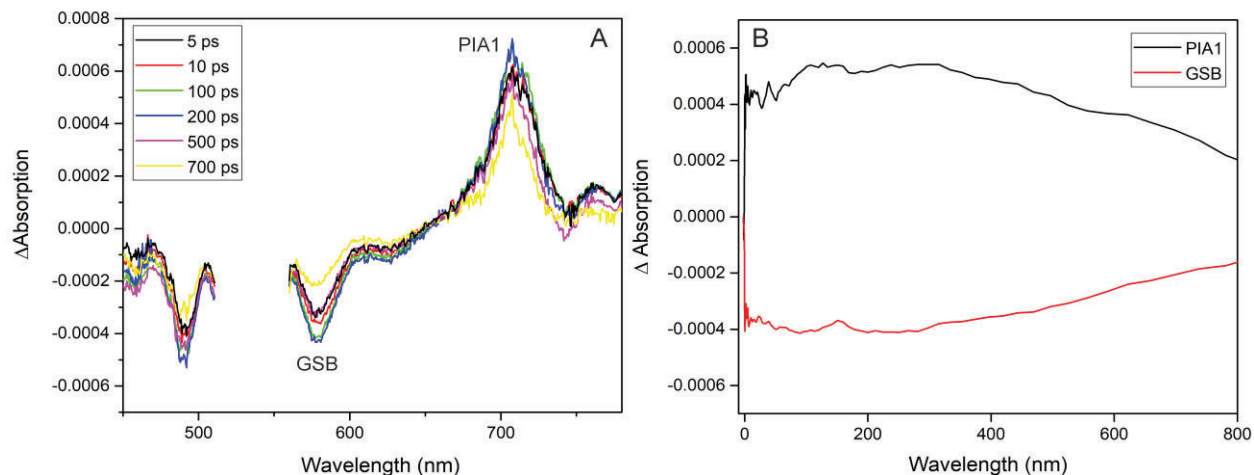


Figure S7. (A) Transient absorption spectra at different time delays in the range of 0-800 ps and (B) kinetic traces at 580 (ground state bleach) and 700 nm (photoinduced absorption 1) of PDI4 in dilute chloroform solution following excitation at 540 nm.

Kinetic traces of as-cast PDIs

The kinetic traces at 500 and 650 nm of as-cast PDI2-4 are shown in Figure S8. The GSB and positive photoinduced absorption band show similar but mirrored kinetics. The results suggest that the PDIs singlet exciton decays directly to the ground state.

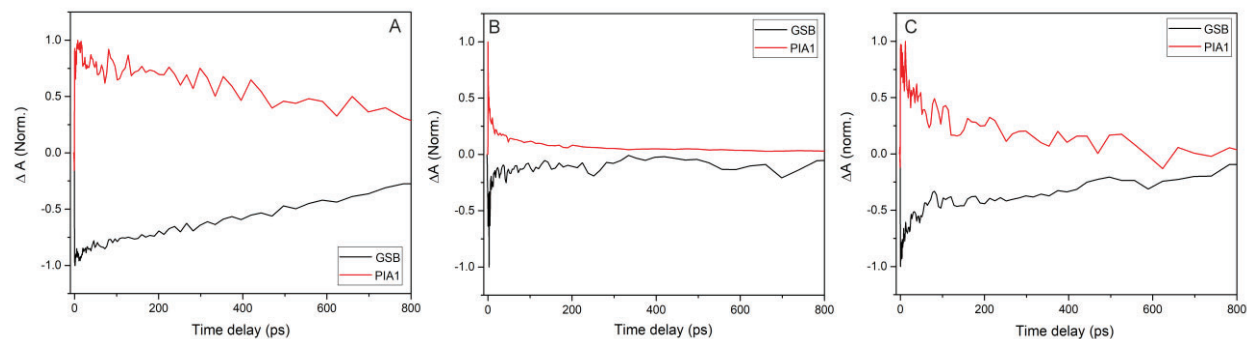


Figure S8. The kinetic traces of as-cast A) PDI2, B) PDI3 and C) PDI4 at 500 and 650 nm

Kinetic traces of SVA PDIs

The kinetic traces at selected wavelengths of SVA PDI2-4 are shown in Figure S9.

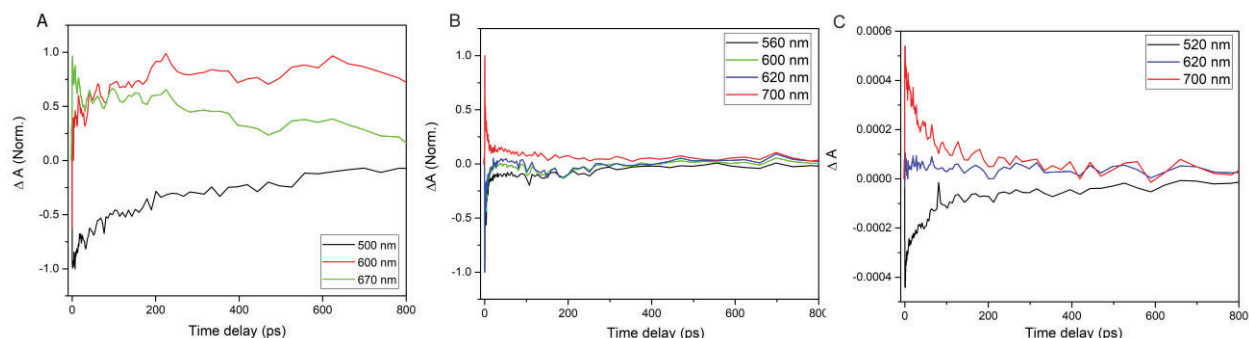


Figure S9. The kinetic traces of A) PDI2, B) PDI3 and C) PDI4 in SVA films at selected wavelengths.

Global target analysis of PDIs

The TA spectra and the kinetics of SVA PDI2-4 films were analyzed by singular value decomposition (SVD) and global target analysis (GTA) to identify the species associated spectra (Figure S10). The data were best fit by a two species sequential $A \rightarrow B \rightarrow GS$ model.

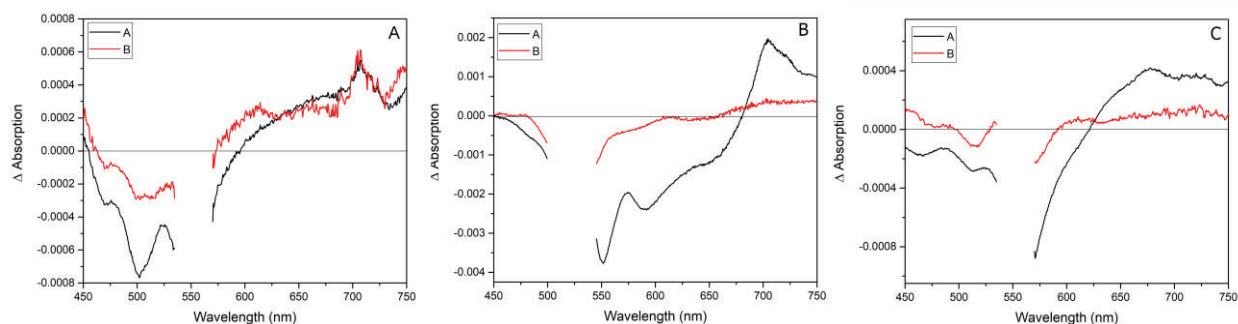


Figure S10. The species-associated spectra resulting from global target analysis of the TA data of SVA films of A) PDI2, B) PDI3 and C) PDI4. All data sets were fit using a two species sequential model.

Absorption and photoluminescence of $\text{PdPc}(\text{OBu})_8$

$\text{PdPc}(\text{OBu})_8$ has two isolated absorption bands at 370 and 730 nm (Figure S11). The longer wavelength absorption band does not have overlap with the absorption spectrum of any PDI derivatives so it can be excited selectively in the presence of the PDIs.

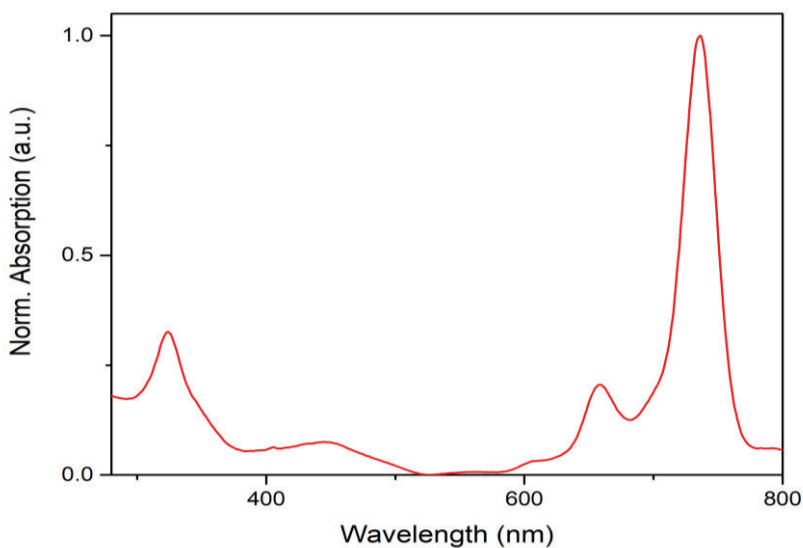


Figure S11. Steady-state absorption of PdPc(OBu)₈ in a dilute solution of THF

Figure S12 shows the photoluminescence spectra of PdPc(OBu)₈ in a dilute MTHF solution before degassing at room temperature and after degassing at 77 K. In the presence of oxygen, fluorescence at about 880 nm (1.4 eV) and a weak emission at ~1130 nm (1.1 eV) are observed. Also, emission from singlet oxygen is obvious (~1270 nm) showing that the triplet of PdPc(OBu)₈ is quenched by oxygen. In the absence of oxygen, the fluorescence appears in the same spectral region but with more vibronic structure due to the lower temperature. The peak at 1130 nm increases in the absence of oxygen suggesting that it is phosphorescence, indicating that PdPc(OBu)₈ has a triplet energy level of 1.1 eV.

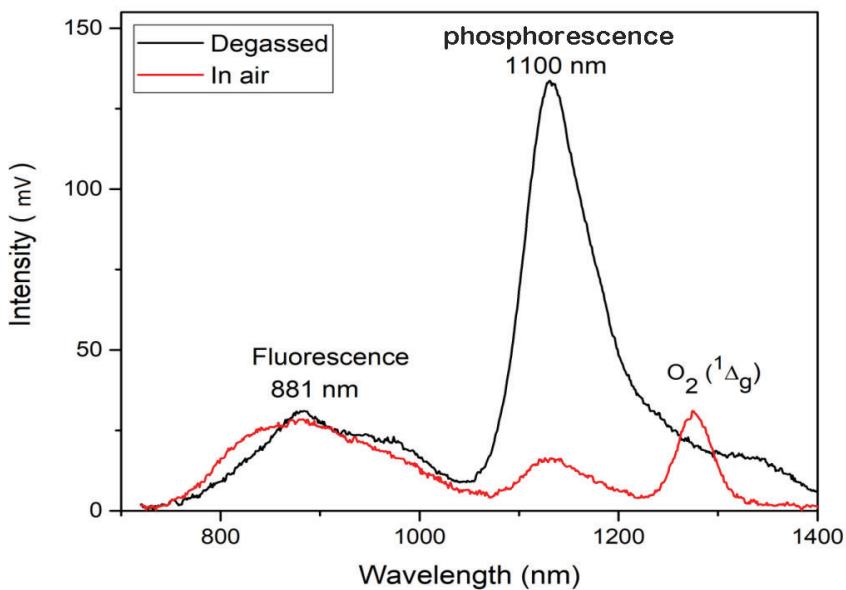


Figure S12. The photoluminescence of PdPc(OBu)₈ in a dilute solution of MTHF before degassing at room temperature and after degassing at 77 K

Ultrafast transient absorption spectroscopy of PdPc(OBu)₈ in film

The TA spectra of thin film PdPc(OBu)₈ after excitation at 730 nm are shown in Figure S13 in the visible spectral region at different time delays in the range of 0-800 ps.

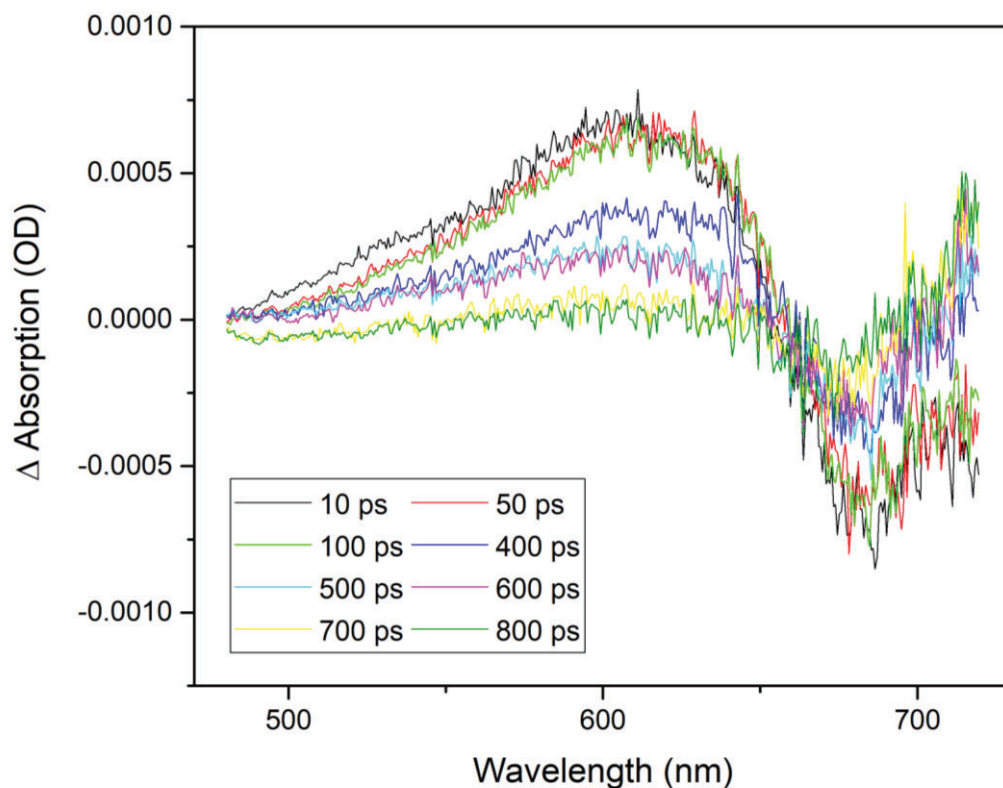


Figure S13. The TA spectra of PdPc(OBu)₈ in a thin film at different time delays of 10, 50, 100, 400, 500, 600, 700 and 800 ps

TA spectra of PdPc(OBu)₈:PDI4 thin film

The TA spectra of thin film PdPc(OBu)₈:PDI4 after excitation at 730 nm are shown in Figure S14 in the visible spectral region at different time delays in the range of 0-800 ps.

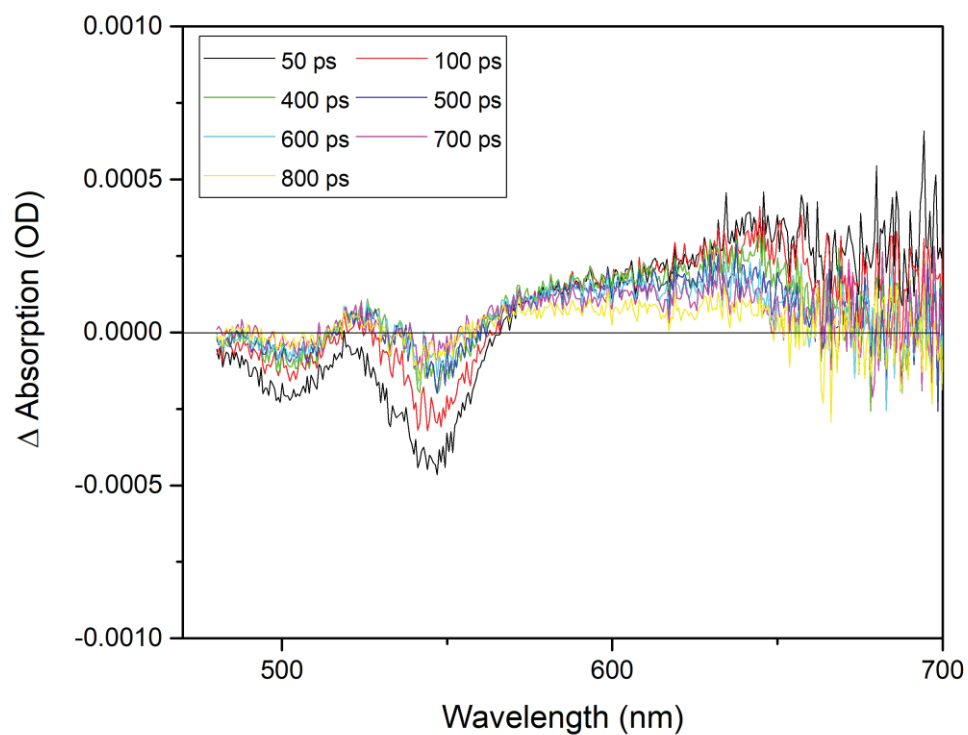


Figure S14. Transient absorption spectra of sensitized thin film of PDI4 with PdPc(OBu)₈ at PDI4: PdPc(OBu)₈ ratio of 70:30 at various time delays.

The kinetics of the sensitized PDI film

Figure S15 shows the photoinduced absorption decay curve of PIA2 in PdPc(OBu)₈:PDI film, following excitation at 650 nm.

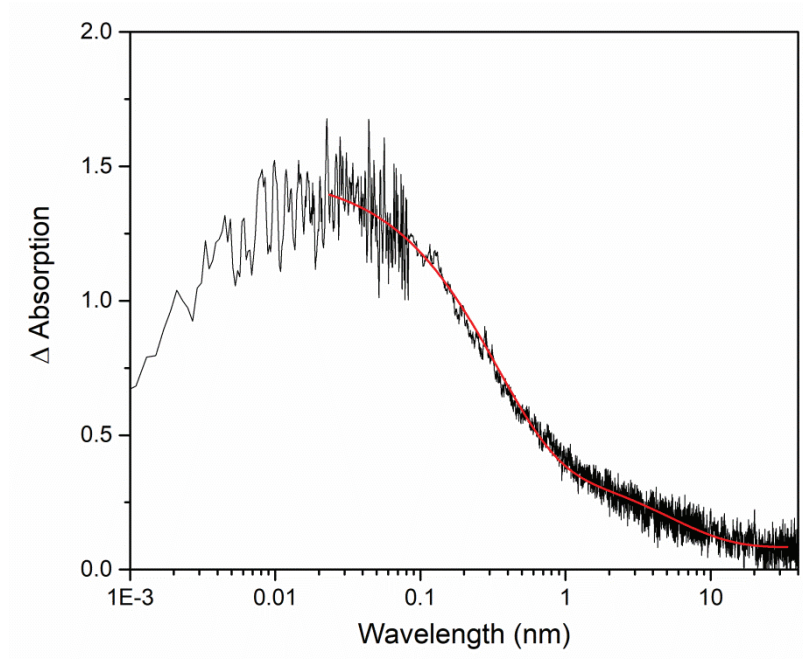


Figure S15. The decay kinetic curve of PDI4: PdPc(OBu)₈ with mass ratio of 70:30.

Triplet yield calculation using the triplet sensitization method

The triplet extinction coefficient of PDI ($\varepsilon_{PDI}^{\lambda}$) was calculated from the known extinction coefficient of PdPc(OBu)₈ ($\varepsilon_{PdPC}^{\lambda}$) using the following equation:

$$\varepsilon_{PDI}^{\lambda} = \frac{\Delta OD_{PDI}^{\lambda} \times \varepsilon_{PdPC}^{\lambda}}{QY_{TT} \times \Delta OD_{PdPC}^{\lambda}}$$

where $\Delta OD_{PDI}^{\lambda}$ and $\Delta OD_{PdPC}^{\lambda}$ are the triplet absorption intensities of PDI and PdPc(OBu)₈ at 600 nm after a time delay of 800 ps, which are derived from the ultrafast TA measurements. The previously reported triplet extinction coefficient of PdPc(OBu)₈ ($\varepsilon_{PdPC}^{\lambda}=28000 \text{ M}^{-1}\text{cm}^{-1}$) is used to calculate $\varepsilon_{PDI}^{\lambda}$. QY_{TT} is the triplet energy transfer yield from PdPc(OBu)₈ to PDI, which can be determined from the late time delays in the TA data (Figure 7) where there is no sign of the triplet or ground state depletion of PdPc(OBu)₈ assuming that all of the triplets transfer energy to the PDI molecules so the triplet energy transfer yield is 100%. Using the derived values $\varepsilon_{PDI}^{\lambda}$ is calculated as:

$$\varepsilon_{PDI}^{\lambda} = \frac{8.8 * 10^{-5} * 28 * 10^3}{1 * 6.4 * 10^{-4}} = 3850 \text{ M}^{-1}\text{cm}^{-1}$$

Using this value, the triplet concentration for each of the PDIs can be determined from their triplet absorption intensities in the ultrafast TA measurement as follows and the resulting concentrations are given in Table S2.

$$conc_{PDI}^{triplet} = \frac{\Delta OD_{PDI}^{\lambda}}{\varepsilon_{PDI}^{\lambda} * l}$$

where l is the sample thickness.

Table S2. The triplet concentration of each PDI derivatives

Sample Name	Triplet concentration (M)
PDI1	0.0032
PDI2	0.0027
PDI3	0.000658
PDI4	0.000381

The excitation density of the sample is calculated using the following equation using the thickness of the film, l , and the energy of excitation, E :

$$\xi = \frac{E\lambda K(1 - 10^{-A})}{la}$$

where $E = 7.61 \times 10^{-6}$ mJ, $\lambda = 550$ nm, $K = 5.034 \times 10^{-15}$ J⁻¹ nm⁻¹, $A = 1.5$, $l = 150$ nm and $a = 265$ μm² so the measured ξ is 7.5×10^{17} cm⁻³ and the singlet concentration is 1.2×10^{-3} M. Finally, the triplet yields are determined as the ratio of triplet to singlet concentration and are summarized in Table 2.

Computational study on PDI

The calculations were performed with the Gaussian16 program.¹ The geometry optimization of the ground state was carried out using dispersion-corrected density functional theory (DFT) at the TPSS-D3(BJ)² /6-311G(d)³ level of theory. In order to reduce computational costs, we have removed the substituted group, as the length of the alkyl chains has no significant impact on the optical properties. Vertical excitation energies and HOMO/LUMO distribution patterns of the electronically states were calculated via time dependent density functional theory within the Tamm-Dancoff Approximation (TDA-DFT)⁴ using the CAM-B3LYP⁵ range-separated hybrid functional approximation and the 6-311G**atomic-orbital basis set. The distribution patterns of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are demonstrated in Figure S16.

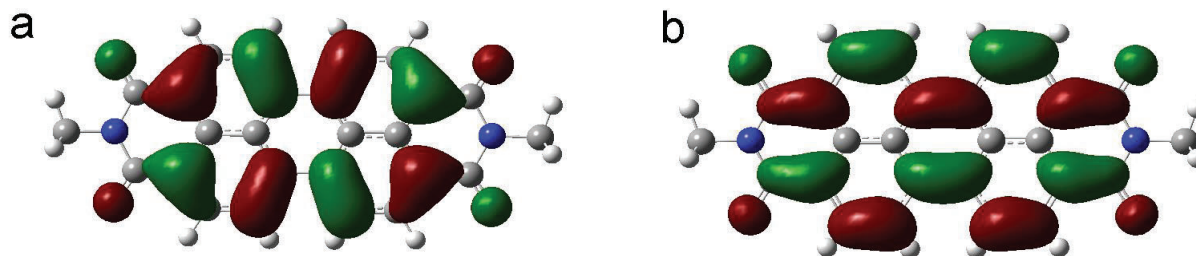
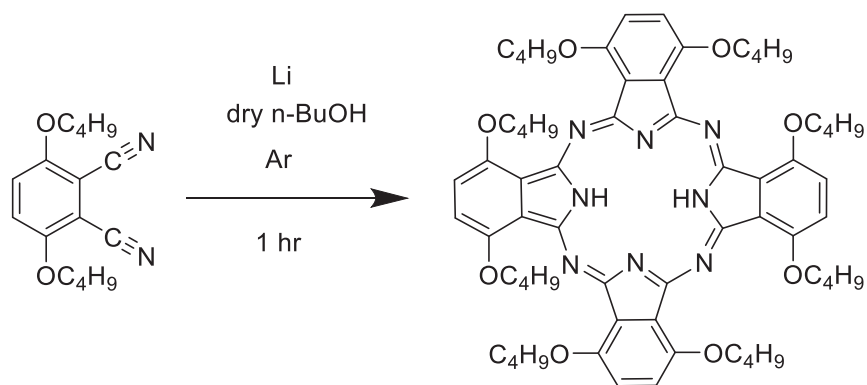


Figure S16. (a) Representation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)

Material synthesis

^1H NMR spectra were recorded on a Varian Inova-400 (400 MHz) spectrometer.

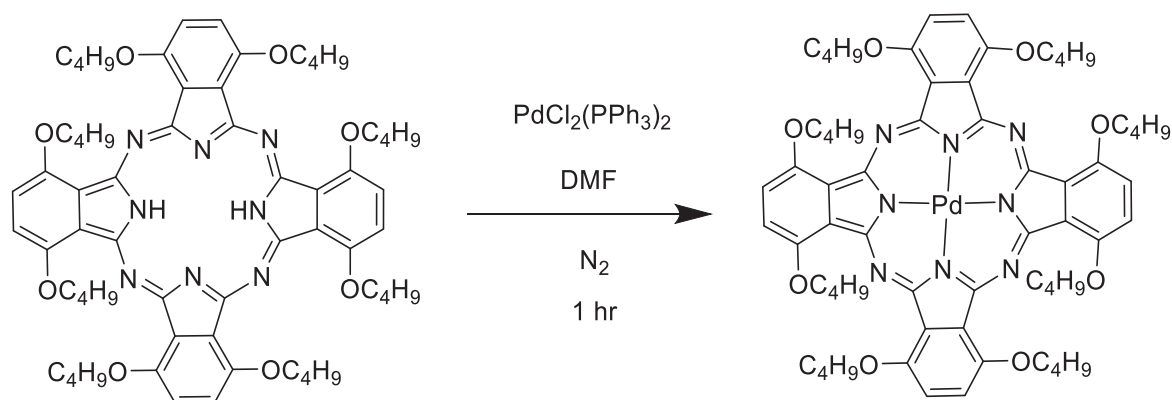
$\text{H}_2\text{Pc}(\text{OBu})_8$: Li was added to a refluxing solution of 1,4-dibutoxy-2,3-dicyanobenzene in dry 1-Butanol under Ar. The mixture was refluxed for 1 h then cooled to room temperature. The resulting mixture was then diluted with glacial acetic acid and stirred for 1 h. Finally, it was evaporated to dryness. The residue was washed with dilute HCL and water and then evaporated to dryness. The solid was purified by column chromatography (Al_2O_3 , pyridine) and recrystallized in DCM-Methanol solution to afford $\text{H}_2\text{Pc}(\text{OBu})_8$ in 20% yield as a green powder.⁶ ^1H NMR (400 MHz, CDCl_3) δ 7.53 (s, 2H), 4.91 (t, 2H), 2.20 (m, 2H), 1.70 (m, 2H), 1.03 (t, 3H), 0.08 (s, 1H).



Scheme S1. The detail of $\text{H}_2\text{Pc}(\text{OBu})_8$ synthesis.

$\text{PdPc}(\text{OBu})_8$: A mixture of $\text{H}_2\text{Pc}(\text{OBu})_8$, $\text{PdCl}_2(\text{PPh}_3)_2$ and dimethylformamide was refluxed under N_2 for 1 h and then cooled to room temperature. The resulting solution was diluted with DCM and washed with dilute HCl and water, then dried over MgSO_4 , and evaporated to dryness. The solid was purified by column chromatography (Bio-Beads, toluene) to afford $\text{PdPc}(\text{OBu})_8$ in 40% yield as a green powder.¹

^1H NMR (400 MHz, CDCl_3) δ 7.53 (s, 2H), 4.91 (t, 2H), 2.20 (m, 2H), 1.70 (m, 2H), 1.03 (t, 3H).



Scheme S2. The detail of PdPc(OBu)₈ synthesis.

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Chapter 7

Conclusion and Future Directions

7.1. Conclusion

The objective of this thesis was to develop a new class of solution processible SF materials that are more amenable to inclusion into solar cell devices through intra-molecular SF, and removal of the “local-order constraint” as for most highly efficient SF systems, a large degree of crystallinity is required. A number of novel organic chromophores were designed and synthesized, and their photophysical properties were investigated. Also, Time-dependent density functional theory with the Tamm–Dancoff approximation (TDA-DFT) and natural transition orbital (NTO) calculations were performed and confirmed the possibility of singlet fission in terms of the energetic landscape.

In chapter 1, the Introduction, the motivation and aim of study and an overview of the thesis were described.

In chapter 2, the background and history of singlet fission and potential of using singlet fission in photovoltaic were fully explained. The reported SF materials in the literature were listed and required criteria for efficient SF was described based on the literature.

In Chapter 3, the general methodology and experimental approaches used in the thesis is described, which includes the information of synthesis, computational details, and spectroscopy analysis.

In chapter 4, to overcome the issue of “local-order constraint” that is observed in most of SF materials; new class of material should be designed and synthesized. One method is using A-D-A motif for designing highly efficient iSF material. This model not only takes the advantage of providing an excited electronic state with significant charge-transfer character but also allows us to choose units based on the energy level requirement. An organic molecule (BDT(DPP)₂) and polymer (p-BDT-DPP) based on a donor–acceptor framework comprising BDT as electron rich and DPP as electron deficient were designed, synthesized, and investigated for singlet fission. Fast formation of the triplet state (<100 ps) in p-BDT-DPP in thin film suggests singlet fission is operating, but there is no sign of triplet formation in the solution. On the other hand, singlet fission occurs in BDT(DPP)₂ in both thin film and in dilute solution, suggesting that the SF mechanism is more probably intramolecular. The triplet pair lifetimes and the triplet yields in p-BDT-DPP and BDT(DPP)₂ in thin film are about 150, 1 ns and 70%, 20%, respectively.

In chapter 5, the results of previous chapter indicated two key issues with BDT(TDPP)₂; i) the S₁ energy was possibly too low at 1.89 eV, barely 2 x T₁ (T₁ = 0.95 eV), and ii) no evidence for self-association was observed. These results suggested that a stronger driver is required for self-association and a higher S₁ energy along with the two TDPP triplet host acceptors were needed to increase the SF yield. In this work, the formation of SF-generated triplets in an as-cast FHBC(TDPP)₂ thin film was demonstrated, and evidence of de-coalescence of SF-generated triplet pairs is presented. The rate of SF (0.1–0.2 ps⁻¹), the SF yield (150–170%), and molecular order are all improved upon annealing the film. We observe no evidence of SF in solution.

In chapter 6, Due to their high stability, synthetic accessibility and high extinction coefficient, PDIs are potentially useful chromophores for SF-based applications. In this study, four PDI derivatives were investigated comprising the same PDI core but with different substituents at their imide positions, 4-butylphenyl, butyl-terphenyl, diisopropylphenyl and mesityl which display distinct molecular geometries with varied intermolecular π - π interactions. The ultrafast TA, time-resolved fluorescence and flash photolysis spectroscopies show that SF occurs with different rates and yields in SVA thin films of all the PDI derivatives but not in disordered PDI aggregates or in solution.

The work described in this thesis has developed new methodology to design SF material that is solution processible, solid state and more applicable to inclusion in photovoltaic device. Besides, it revealed information on the rules of SF material organization in the crystal to promote SF.

7.2. Future direction

7.2.1. Structural properties relationship

Other FHBC derivatives can be synthesised to fully understand the structural property relationship with SF parameters and the ability to separate SF triplets from dephasing of the correlated triplet pair formed.

7.2.2. SF-enhanced PV device

The next step in this study is using these SF materials in photovoltaic devices to check if an increase in PCE will occur or not. SF-enhanced PV can be achieved in three ways: charge

transfer, energy transfer and photon multiplier.¹ In the charge transfer method, the SF generated triplets are dissociated at a heterojunction between SF material and the inorganic semiconductor and electron and holes are collected at the electrodes.¹ Approach two is inspired by Dexter theory where the SF generated triplets undergo triplet energy transfer to an inorganic semiconductor where charge generation and collection occur (Figure 7.1a).¹ Although Felix Castellano et. al.² demonstrate that the triplets can be transferred from organic molecule to inorganic QDs but no study has been done on the energy transfer from SF material to the bulk inorganic semiconductors which is one of our aims.

In the third, or SF photon multiplier, the SF generated triplet energy is transferred to an emissive intermediate, thereby generating two low energy photons from a single high energy photon (Figure 7.1b). The intermediate should take the dark triplet states, and through spin inversion makes an emissive bright state through, i) a thermally activated delayed fluorescence (TADF) materials, ii) a metal organic framework, or iii) quantum dots. The efficiency limit of SF photon multiplier matches the efficiency limit for a two-junction tandem solar cell. However, this method is more stable against changing irradiation, spectral change and temperature than tandem solar cells. Bruno Ehrler et. al. demonstrate that for a silicon solar cells with PCE of 26.6%, the photon multiplier has the potential to increase the efficiency by up to 4.2% absolute in a realistic case, however directly coupling the SF to the silicon PV was still projected to increase the efficiency up to 38%.³

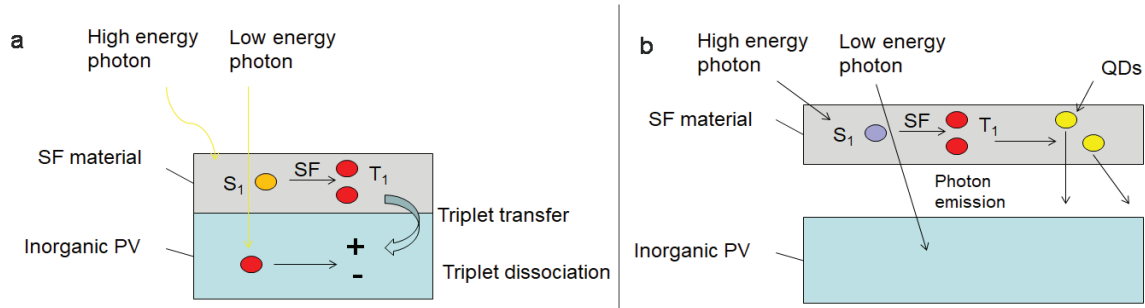


Figure 7.1. Schematic illustration of a) SF-enhanced PV through energy transfer, b) SF photon multiplier system

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3. Moritz H. Futscher, Akshay Rao, and Bruno Ehrler, The potential of singlet fission photon multipliers as an alternative to silicon-based tandem solar cells *ACS Energy Lett.* **3**, 2587 (2018).