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Electronic and Vibrational Spectroscopy of Perylene Diimide and Oligothiophene Triplet Excited States

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Publication Date
2015

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Electronic and Vibrational Spectroscopy of Perylene Diimide and Oligothiophene
Triplet Excited States

A dissertation submitted in partial satisfaction of the requirements for the degree
Doctor of Philosophy

in
Chemistry

by

Maria Angelella

Committee in Charge:

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Professor Judy E. Kim
Professor Melvin Y. Okamura
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Professor Charles L. Perrin

2015
The Dissertation of Maria Angelella is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

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Chair

University of California, San Diego

2015
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ACKNOWLEDGEMENTS

I acknowledge my encouraging advisor, Prof. Michael J. Tauber, who taught me how to be a scientist, a teacher, and a writer. I appreciate his availability to his students and unyielding insistence on quality.

I would also like to thank my thesis committee Prof. Judy Kim, Prof. Francesco Paesani, Prof. Charles Perrin, and Prof. Melvin Okamura for their encouragement throughout my studies. I thank Prof. Kim for taking time out of her busy days to help me set up UVRR experiments and for giving me opportunities to practice teaching.

I acknowledge my colleagues in Prof. Tauber’s research group. I was fortunate to work with a group of intelligent, relentless, amusing scientists: Chen Wang, Samantha J. Doyle, Megan Stone, Cyrus Rustomji, Christopher Berg, Shuwan Huang, Jennifer Daluz, Michael Frank, Yuelong Li, Brandon Connors, Steven Shimizu, Christina Stuart, and Sun Young Noh.

I also acknowledge Prof. Kim’s research group, especially Prof. Hannah Shafaat, Guipeun Kang, and Ignacio Lopez. I would be remiss if I did not thank, Brian Leigh for mentoring me in the laboratory. From chromatotrons to power supplies, I have found his expertise and generosity to be inexhaustible.

I acknowledge the chemistry facilities and their staff: Molecular Mass Spectrometry Facility (Yongxuan Su, Joshua Lee) and the NMR Facility (Anthony Mrse). Thank you to Rick Thomas, Facilities Director, for his help with building the Faraday cage.
Thank you to my early chemistry mentors. My high school teacher, Eileen Palmer, was the first educator to piqué my interest in the microscopic world. My college mentor, Prof. James Falcone, gave me the opportunity to conduct research in his laboratory. Thais Sielecki, my internship mentor, introduced me to synthetic chemistry and was patient with my questions about pursuing science as my career.

Chapter 2, in full, is a reprint of the material as it appears in the Journal of Physical Chemistry A, 2013, 117, pp 9196-9204, by Maria Angelella, Chen Wang, and Michael J. Tauber. The author of this dissertation was the primary experimentalist, and was a coauthor of the paper.

My work on perylene diimide is the result of collaboration with Prof. Boris Rybtchinski and Jonathan Baram at the Weizmann Institute of Science in Rehovot, Israel. Jonathan Baram synthesized the PDI dimer studied in Chapters 2 and 3 of this thesis. My femtosecond transient absorption data were acquired in collaboration with the Newport Corporation Technology & Applications Facility, with the help of Chun-Hung Kuo and Ruben Zadoyan. Chen Wang assisted with collection of Raman spectra and kinetics analysis.

My work on thiophene oligomers, Chapter 4, was a result of participation in the DOE-funded Energy Frontier Research Center (EFRC) at the University of Texas at Austin. Specifically, I acknowledge Prof. Peter J. Rossky and Prof. David A. Vanden Bout for their ideas and involvement. I acknowledge the students in the laboratory of Prof. Bradley J. Holliday who synthesized and purified the thiophene series: Kory Mueller, Sarah Moench, and John Lalande. Raman experiments were collected with the assistance of Samantha J. Doyle.
Finally, I acknowledge the support of my parents, Mary Jurchak Angelella and Francis M. Angelella, my sisters, Lisa Angelella and Valerie A. Evans, my brothers-in-law, Toby Veeder and Jeffrey Evans, and my partner, Barry J. Hatfield, Jr. Thank you all for your fresh perspectives and reassurances.
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PUBLICATIONS


ABSTRACT OF THE DISSERTATION

Electronic and Vibrational Spectroscopy of Perylene Diimide and Oligothiophene Triplet Excited States

by

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Doctor of Philosophy in Chemistry

University of California, San Diego, 2015

Professor Michael J. Tauber, Chair

The identification and characterization of excited states in conjugated organic molecules have been active areas of fundamental research for decades. Recent interest has been spurred by emerging applications in organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs). Among the most important fundamental questions are the diffusion rates of excited states in organic molecular materials, as well as the size (spatial extent) of excited states. Triplet excited states have been a particular
focus, in part because of the long lifetimes and transport distances of these species, as well as the fact that they are the products of singlet exciton fission.

In this dissertation, the structures and dynamics of excited states were probed in two important families of organic molecules: perylene-3,4,9,10-tetracarboxylic diimide (PDI), and oligothiophene. The vibrational spectrum of a PDI triplet excited state is reported for the first time. Several enhanced bands in the 1300–1600 cm$^{-1}$ region are readily distinguished from bands of the ground state, and the triplet spectrum is expected to be a useful reference for further studies of these excitons in PDI materials. Additionally, the diffusion constant and diffusion length (25 nm) for a singlet excited state in a PDI aggregate are derived from an analysis of exciton-exciton annihilation kinetics recorded by transient absorption spectroscopy.

The triplet excited states for a series of solvated oligothiophenes with 3 to 9 rings are probed with transient resonance Raman spectroscopy. The spectra evolve significantly up to a chain length of 7 units. This length is inferred to be the natural extent of the triplet excited state for long thiophene oligomers or polythiophene at room temperature in solution. The effect of substituents was also elucidated in this study.
Chapter 1 Introduction

There is a strong effort among researchers to probe conjugated organic materials for use in electronics and alternative energy production. Devices made of organic materials have several favorable qualities, including their low cost, simplicity of manufacture, and light weight.\textsuperscript{1,2} Pi-conjugated molecules are of interest because of their tunable electronic properties.\textsuperscript{3} Examples of these include pyrene, rylenes, acenes, thiophenes, phalocyanines, porphyrins, and fullerenes.\textsuperscript{4} Of the many dyes currently utilized for organic electronics and photovoltaic devices, perylene 3,4,9,10-tetracarboxylic diimide (perylene diimide, PDI) and oligothiophenes, are the focus of this dissertation.

Singlet and triplet excited states. This work includes studies of the lowest excited singlet state, $S_1$, for PDI and the lowest excited triplet state, $T_1$, for both PDI and oligothiophene. Excited states result from a molecule absorbing energy, and the lowest one can often be described in terms of an electron being promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The resulting configurations for $S_1$ and $T_1$ are $(\pi \uparrow)^1(\pi^* \downarrow)^1$ and $(\pi \uparrow)^1(\pi^* \uparrow)^1$, respectively, Figure 1.1.

The interconversion of triplet and singlet states is spin forbidden. A consequence is that the $T_1$ state has a significantly longer lifetime than $S_1$, because both its radiative and nonradiative decay to the ground state are disallowed transitions. Triplet excited states can be generated via intersystem crossing, charge recombination, or singlet fission. Singlet fission is the mechanism by which the energy of one $S_1$ state is partitioned into
two excited $T_1$ states. The overall spin is conserved in this process. My research on one molecular system, PDI, was partially motivated by the possibility of observing this mechanism, and thereby contributing to a very active area in photophysics.

Efficient excited state diffusion is important for energy harvesting in photovoltaic devices. The two states, $S_1$ and $T_1$, have different diffusion properties. Singlet excitons can diffuse quickly through crystals or strongly coupled aggregates via the relatively long-range Förster resonance energy transfer, or other mechanisms. Triplet excitons travel more slowly because their energy transfer can only occur through Dexter transfer, which is inherently a close-range process. Typical triplet exciton diffusion coefficients are nearly two orders of magnitude slower than those for singlet excitons. Conversely, the diffusion length, which is a function of the lifetime of the exciton, is much longer for triplet excitons. Triplet diffusion distances can exceed 1 µm, whereas those of singlet excitons are typically on the order of 100 nm.

Because of their long diffusion lengths, researchers have begun to utilize triplet excitons in devices. Triplet states are now being considered, in practice and in theory, for improved power conversion efficiencies in OPVs. It is important to note, that although triplet excitons can be beneficial, they are also associated with decreased device efficiency because they can be a product of charge recombination.
Figure 1.1. Vector diagram for singlet and triplet state spin configurations, modified from Turro. The corresponding spin wavefunctions are listed below each configuration. The singlet spin wavefunction is antisymmetric, and the triplet wavefunctions are symmetric with respect to exchange.

\[
\frac{1}{\sqrt{2}} (|\alpha_1 \beta_2 \rangle - |\beta_1 \alpha_2 \rangle) \quad |\alpha_1 \alpha_2 \rangle \quad \frac{1}{\sqrt{2}} (|\alpha_1 \beta_2 \rangle + |\beta_1 \alpha_2 \rangle) \quad |\beta_1 \beta_2 \rangle
\]
Perylene diimide and exciton coupling. Perylene diimide, Figure 1.2, is an ideal industrial dye because it is a strong absorber of visible light, and it is robust.\textsuperscript{14, 15} Researchers have attached substituents at the imide,\textsuperscript{16-19} bay region\textsuperscript{14, 16, 20} ( carbons 1, 6, 7, 12), more recently to the headland region ( carbons 2, 5, 8, and 11).\textsuperscript{21} The addition of substituents has several important outcomes. First, attachments such as alkyl chains\textsuperscript{16, 18} and tert-butyl groups\textsuperscript{22} make PDI soluble in organic solvents. Second, the addition of substituents can have significant effects on the electronic properties of monomeric PDI.\textsuperscript{16} Third, substituents influence the stacking of PDI molecules in extended solid systems (crystals, aggregates, and thin films). Offsetting the chromophores either by their long or short dimensions can change the absorption and emission properties of these materials.\textsuperscript{14, 23} Substituted variations of PDI span the majority of the visible spectrum.\textsuperscript{14, 16}
Figure 1.2. Molecular structure of perylene diimide. Positions 1, 6, 7, and 12 label the “bay region”.
Coupling can alter almost every aspect of a molecule’s excited state behavior. These effects can include changes in excited state energy, lifetime, decay pathways, and diffusion. For instance, interchromophore coupling allows singlet fission in a zeaxanthin aggregate and in a PDI polycrystalline thin film. This newly allowed mechanism results in a >100% triplet quantum yield in both cases. Those yields are especially significant compared to the <1% triplet quantum yields for both chromophores when in their monomeric form.

Kasha’s exciton model described the coupling of molecular electronic transitions. Exciton levels and allowed optical transitions for side-by-side (H) and end-to-end (J) coupled molecules are illustrated in Figure 1.3. Other researchers have extended the electronic transition model. Theoretical studies by Witkowski and Moffitt and Fulton and Gouterman described the effect of vibronic coupling in dimers. The shifts of vibronic bands after coupling can be complex. A more straightforward indicator of coupling geometry is the relative cross-section of the 0-0 and 0-1 vibronic bands. For an H-type interaction the cross-section of the 0-1 vibronic band is greater than 0-0, and vice versa for a J-type interaction.
Figure 1.3. (Upper) Diagram showing coupling of two electronic transition dipoles. Large arrows depict the electronic transition, and the smaller arrows represent the orientation of the transition dipole moments. Figure modified from Kasha. (Lower) Vibronic coupling diagram. Figure modified from Spano et al.
The most basic coupled unit is the covalent dimer. Many PDI dimers have been synthesized, including those connected cofacially with either open\textsuperscript{35-38} or closed\textsuperscript{39-41} architectures, and linearly connected at either the imide group\textsuperscript{42-46} or bay region (i.e. carbons 1, 6, 7, or 12).\textsuperscript{47, 48, 49-56} The vibronic coupling for these dimers results in significant changes to their UV-Vis absorption spectra. These changes are not only in the relative absorption cross-section of the vibronic bands but also the overall energies and width of the spectrum.\textsuperscript{54, 57} Excited state dimers, or “excimers,” are seen in these systems, with lifetimes that are significantly longer than monomeric PDI, \(\sim 20\) ns.\textsuperscript{36, 37} Chapter 2 of this dissertation is a vibrational study of a PDI dimer, molecule 1, that is attached in the bay region with an acetylene linker, Figure 1.4.

Important dynamic processes, including long-range charge transfer\textsuperscript{58} and exciton transport,\textsuperscript{7, 49} can be investigated in more extended structures, e.g. aggregates and thin films. There are numerous ways in which PDI can self-assemble,\textsuperscript{14, 58-60} and dimers and multimers of PDI tend to aggregate more readily than monomeric PDI.\textsuperscript{43, 46, 58, 61} In Chapter 3 of this dissertation, the excited state absorption and vibrational spectra of a PDI dimer in its aggregated form are reported. A modified second order kinetics model is applied to determine the excited state diffusion constant and diffusion length in the aggregate.
Figure 1.4. Molecule 1 studied in Chapters 2 and 3 of this dissertation.
**Thiophene.** Thiophene is widely used in organic electronics\textsuperscript{2,4,62} because of its facility for charge transport.\textsuperscript{63} Thiophene is often incorporated into these devices in polymeric form. Despite the prevalence of polythiophene, significant fundamental questions remain, such as the spatial extent of excited states in polymeric thiophene. The quantification of the spatial extent of the triplet exciton is important because it reports on the efficiency of exciton diffusion.\textsuperscript{64} Chapter 4 is a vibrational study on a series of thiophene oligomers in the T\textsubscript{1} state, Figure 1.5. By studying the Raman spectra for this series of thiophene oligomers, the triplet exciton size was determined. The spatial extent of the triplet-excited state measured with the oligomers is expected to also report on the excited state in polymeric thiophene.
Figure 1.5. Molecular structure of the oligothiophene series studied in Chapter 4 of this dissertation.
**Spectroscopic techniques.** Two primary techniques are used throughout this dissertation: transient absorption spectroscopy and resonance Raman spectroscopy. Absorption spectroscopy probes the electronic transitions of molecules. Transient absorption (TA) spectroscopy captures the absorbance spectra of photoexcited chromophores at a specific time after excitation. The kinetic data can be modeled to extract additional information, including exciton diffusion rates.\textsuperscript{7,49}

Resonance Raman spectroscopy probes the vibrational normal modes of a molecule using scattered light. Transient resonance Raman spectroscopy probes the vibrations of excited states, and reports on their structures.\textsuperscript{65} One challenge to spontaneous Raman spectroscopy is that it is sensitive to fluorescence.\textsuperscript{66,67} As part of the work reported in Chapters 2, 3, and 4, strategies to overcome this problem are discussed.

The work in this dissertation provides insights into the structure of the lowest excited triplet state in two important families of conjugated molecules. Additionally, the spectroscopic study of excited states in an aggregate of a conjugated molecule reports upon the rate of energy transfer, and other aspects of the coupling of excitons to their surroundings.
References


Chapter 2 Resonance Raman Spectra of a Perylene Bis(dicarboximide) Chromophore in Ground and Lowest Triplet States

2.1 Introduction

The utilization of triplet excited states in organic molecular photovoltaics is a topic of growing interest.\textsuperscript{1-4} Triplet excitons have long (typically microsecond) excited-state lifetimes, and therefore exhibit diffusion lengths that are orders of magnitude greater than those of singlet excited states.\textsuperscript{4} These advantages could improve the efficiency of various organic photovoltaics (OPVs), such as those based on a bilayer design. The focus on triplet excitons in photovoltaics has sharpened because of a renaissance of research on singlet fission.\textsuperscript{5-7} In this mechanism, two triplet excited states form on neighboring molecules from one singlet excited state. A chromophore that is an outstanding candidate for the efficient generation of triplet excitons by fission is perylene bis(dicarboximide) (PDI).\textsuperscript{8, 9} PDI dyes elicit special interest because they have large absorption cross-sections, and are unusually robust and tunable.\textsuperscript{10-13} A PDI derivative was incorporated in the first organic molecular photovoltaic,\textsuperscript{14} and this family of dyes continues to play an important role in the search for new OPVs.\textsuperscript{3, 15-17}
In experimental studies, it would be advantageous to utilize a variety of methods for probing triplet excited states of PDI (\(^3\text{PDI}^*\)). The first spectroscopic characterization of \(^3\text{PDI}^*\) was by transient absorption (TA) spectroscopy.\(^{18}\) The \(T_1 \rightarrow T_n\) transition in the visible was found to have a cross-section that was only slightly less than that of \(S_0 \rightarrow S_1\), and these absorption bands were closely overlapped. Since the pioneering report of Ford and Kamat, TA spectroscopy continues to be a useful probe of \(^3\text{PDI}^*\).\(^{19-25}\) Electron paramagnetic resonance (EPR) and optically-detected magnetic resonance (ODMR) spectroscopy are powerful techniques for identifying and characterizing triplet states of organic molecules, and their application to \(^3\text{PDI}^*\) has been demonstrated.\(^{26-31}\) Surprisingly, the vibrational spectroscopy of \(^3\text{PDI}^*\) is largely unexplored. Among the few studies of PDI excited states by vibrational spectroscopy,\(^{32-35}\) only one has recently identified several IR absorption bands of a triplet excited state.\(^{34}\) Here, we report resonance Raman spectra of a PDI dimer 1 (Scheme 2.1) in its ground and lowest triplet states. The spectra of the \(S_0\) and \(T_1\) states of 1 are analyzed by comparison with vibrational normal mode calculations of model compounds, including PDI monomers 2 and 3.
Scheme 2.1. PDI dimer 1 is investigated experimentally. The polyethylene glycol (PEG) substituents have 13-15 repeat units. Monomers 2 and 3 are two model compounds explored with computations.
2.2 Experimental

Dimer 1 was synthesized as described previously. The product was purified by column chromatography with silica 60-200 µm in diameter, and a 1:1 (v/v) acetone/methanol eluent. The purity was checked by analysis of 1H NMR spectra of concentrated solutions of 1 in CDCl₃, and by absorption and fluorescence spectroscopy. Samples were rinsed with methanol or hexane to reduce grease impurities, if indicated by broad peaks at ~1.25 and ~1.68 ppm in the NMR spectrum. The dimer was recrystallized in methanol (Fisher Scientific, HPLC grade) prior to measurement of the reported Raman spectra.

For µs–TA spectroscopy of the triplet excited state, zinc tetraphenylporphyrin (ZnTPP) was used as a triplet sensitizer. A toluene solution of 1 (~8 µM) and ZnTPP (~4 µM) was prepared in a glovebox, and loaded in a sealed cuvette. The spectra were acquired with a homebuilt system. The pump wavelength was 431 nm, where the strong Soret transition of ZnTPP accounted for more than ~80% of the absorbed photons. For steady-state Raman spectroscopy of the triplet excited state, a toluene solution of 1 (~30 µM) with ZnTPP (~14 µM) was prepared in an oxygen-free environment and contained in a sealed cuvette. ZnTPP was photoexcited with 405 nm pulses at 88 MHz (quasi-CW). The Raman probe wavelengths consisted of either a 488.0 or 496.5 nm continuous-wave beam from an argon/krypton ion laser. Spectra were acquired with a 90 degree scattering geometry. The resolution of the spectrograph was ~4 cm⁻¹. Degradation of samples was less than 5% during the course of the experiments, as monitored by UV-Vis absorption spectroscopy. The Raman spectrum of the ground state was acquired with a toluene solution of 1, a probe
wavelength of 488.0 nm, and the same detection system as used for the spectroscopy of the triplet excited state.

A new correction procedure was implemented to overcome column-to-column variation in the sensitivity of the CCD. The spectra of 1 benefited from this correction particularly when residual impurities elevated the fluorescence background in the spectral window. In brief, the procedure incorporated the pump-induced emission from the sample as part of the instrument response. Emission from the probed area was more effective than diffuse white light in reducing artifacts caused by the detector. The instrument response spectrum (IRS\textsubscript{sample}) relates to one typically acquired with a calibrated white light (IRS\textsubscript{wl}) as follows:

\[
IRS_{sample} = \frac{(pump\, only)}{(pump\, only)_{smoothed}} (IRS_{wl}) \quad (2.1)
\]

The correction procedure avoids the need for spectral reconstruction from derivative features, as in shifted-excitation Raman difference spectroscopy (SERDS), or subtracted shifted Raman spectroscopy\textsuperscript{38,39} Final spectra reported in Figures 2.2 and 2.4 benefited only marginally from the new procedure, because they were acquired with highly purified samples with low fluorescence background.

Computations were performed with density functional theory (DFT) using Gaussian 09W software\textsuperscript{40} All calculations employed the B3LYP functional and a 6-31G(d) basis set. Frequencies of normal modes and computed spectra were scaled by 0.972. The triplet state computations were obtained by restricting the spin of the molecule. Normal mode diagrams were prepared using Jmol\textsuperscript{41} Additional description of experiments and computations is provided in the Appendix.
2.3 Results and discussion

Our study focuses on dimer 1 in toluene for two reasons. First, the dimer is soluble and stable in toluene under the conditions of pump-probe and other optical spectroscopy. In general, solubility is important for triplet sensitization. A second reason is that the fluorescence quantum yield of 1 is unusually low (less than 10%) for a solvated PDI molecule.\textsuperscript{36} Low fluorescence emission is important for the acquisition of spontaneous Raman spectra with visible excitation.

The visible absorption spectrum of 1 in toluene (Figure 2.1) differs significantly from that of typical PDI monomers.\textsuperscript{13} The differences are an expected consequence of the electronic communication of two PDI units via the ethyne linker.\textsuperscript{36, 42} Some characteristics of the absorption and fluorescence spectra of 1 suggest that it may self-assemble in toluene; conversely, other evidence does not support aggregation. Our results lead us to favor an intramolecular explanation for solvent-dependent changes (see Appendix). However, if aggregation were to occur, it would have little impact on the present work because the wavefunction of the triplet exciton is expected to be localized (i.e. on a single molecule).\textsuperscript{2, 43-45}
Figure 2.1. Normalized absorption and emission spectra of 1 in toluene. (Solid black curve) Absorption spectrum of ground state. (Dashed black curve) Absorption spectrum of the triplet excited state, $^31^*$ (see Appendix). Vertical arrows indicate the Raman probe wavelengths. (Red curve) Fluorescence spectrum.
**Resonance Raman spectroscopy of the ground \( (S_0) \) state of PDI.** The experimental resonance Raman spectrum of 1 in toluene is illustrated in Figure 2.2. The spectrum generally corresponds to published resonance Raman spectra of PDI.\(^{46-48}\) However, Raman spectra of PDI with substituents attached to the perylene core have not been reported previously. Substituents attached to the bay regions of 1 lower the local symmetry of each PDI moiety, and cause significant changes in the resonance Raman spectrum. The analysis of the experimental spectrum of 1 relies upon DFT/normal mode calculations of three model PDI systems. The calculated off-resonance Raman spectrum of an asymmetric PDI monomer with ethoxy and ethyne substituents attached to its bay positions, 2, is a good match to the experimental spectrum of 1 in the 1000-1800 cm\(^{-1}\) window (Figure 2.2).
Figure 2.2. Raman spectrum of dimer 1 in the S₀ state, compared with calculated spectra of model monomers 2 and 3. (A) Experimental spectrum acquired with 488.0 nm excitation in toluene. Portions of the spectrum are fitted with Gaussian functions (red). An asterisk (*) denotes imperfect subtraction of a Raman band of the solvent. (B) Calculated spectrum of asymmetrically substituted PDI monomer, 2. (C) Calculated spectrum of PDI monomer with no substituents, 3. The symmetry of each mode in the D_{2h} point group of 3 is indicated. Calculated spectra have frequencies scaled by a factor of 0.972. Color-coding of bands indicates correlation of normal modes between model compounds 2 and 3, or between S₀ and T₁ states (Figure 2.4).
The computed spectrum of a model monomeric PDI without substituents at the bay positions and only H-atoms at the imide groups, 3, is not as good of a match to experiment. Nonetheless, one can identify normal modes of 3 that have similar frequencies and patterns of vibration, relative to the asymmetrically substituted molecule (Figure 2.3). Furthermore, molecule 3 has high symmetry ($D_{2h}$ point group), which simplifies its vibrational structure and assists in the understanding of more complex molecules 1 and 2. The unsubstituted monomer 3 has 114 normal modes, of which 77 are in-plane. A subset of 39 modes has even ($gerade$) symmetry upon inversion, as required for Raman scattering in the $D_{2h}$ point group. Of the 20 vibrational normal modes with $A_g$ symmetry, there are 10 with frequencies in the range 1000-1800 cm$^{-1}$, 3 are C-H or N-H stretches with higher values, and all remaining modes are less than 1000 cm$^{-1}$. Of the 19 modes with $B_{1g}$ symmetry, there are 11 with frequencies in the range 1000-1800 cm$^{-1}$, 2 are C-H stretches with higher values, and all others are less than 1000 cm$^{-1}$.

Calculations were also performed on a third model compound with two PDI units linked by an ethyne group, and two ethoxy substituents at the outer bay positions (4, see Appendix). Despite the similarity of 4 to the experimental dimer, its calculated Raman spectrum does not improve upon that of 2 in matching the experimental spectrum. These results indicate that the asymmetry of each PDI moiety of 1, rather than the electronic coupling of the two chromophores, has the most significant effect on its Raman scattering.

The vibrational normal modes of PDI molecules 1-3 can be divided into four sections within the 1000-1800 cm$^{-1}$ spectral window. In the 1000-1300 cm$^{-1}$
subsection, the normal modes are dominated by CH in-plane bends (equivalently, CH rocks). From the match of frequencies it is expected that the experimental bands of 1 at 1077 and 1253 cm$^{-1}$ are well-described by the calculated normal modes of 2 at 1063 and 1256 cm$^{-1}$, respectively (Figure 2.2). These modes correlate well with the 1054 and 1271 cm$^{-1}$ modes of 3 (Figure 2.3 and Appendix). These two vibrations, like others in the 1000-1300 cm$^{-1}$ range, exhibit relatively small displacements of carbon atoms in the perylene core compared with the prominent CH bending motions. The carbon atoms with the most displacement are the interior ones of PDI, e.g. carbons of the central ring or along the centerline of perylene, or those to which the diimide groups are attached (C3, C4, C9, C10). Neighboring carbon atoms tend to move along trajectories that are somewhat parallel; this pattern imparts a breathing or collective characteristic to the motion of these modes.
Figure 2.3. (Left column) Normal modes of model monomer 2 that have a close correspondence in frequency with representative experimental bands of 1 in the $S_0$ state. (Right column) Normal modes of model monomer 3 in the $S_0$ state that are the closest match to those of 2.
The 1300-1500 cm\(^{-1}\) subsection of the spectrum (denoted here as perylene core I) is generally characterized by modes with diminished C-H rocking and enhanced carbon motion relative to those found in the lower frequency window. The carbon atoms with greatest displacements tend to be interior ones of PDI (described above), and again the motion has a bending/breathing characteristic. The pair of bands centered at 1332 and 1351 cm\(^{-1}\) in the experimental spectrum of 1 nearly coincide with calculated bands of 2 at 1336 and 1349 cm\(^{-1}\). Such a correspondence suggests that these normal modes of monomer 2 depict the motions of 1 for this pair of bands. However, the vector displacements for these modes of 2 do not correspond well with those of the unsubstituted monomer 3 at similar frequencies (1304, 1366, and 1382 cm\(^{-1}\)). For example, only some aspects of the 1349 cm\(^{-1}\) mode of 2 match the 1366 cm\(^{-1}\) mode of 3, as illustrated in Figure 2.3. The displacement vectors are better matched between substituted and unsubstituted PDIs for modes at 1433 cm\(^{-1}\) (2) and 1436 cm\(^{-1}\) (3). The combination of central ring distortion and CH rocks of these modes are expected to characterize the motion for either the 1442 or 1457 cm\(^{-1}\) bands of 1.

The 1500-1620 cm\(^{-1}\) subsection, denoted perylene core II, includes modes that have the greatest extent of carbon motion and the least CH in-plane bending. The modes of 2 at 1549, 1592, and 1607 cm\(^{-1}\) (Figure 2.3 and Appendix), as well as the corresponding ones of 3 at 1571, 1594, and 1612 cm\(^{-1}\), exhibit vectors of neighboring atoms that tend to be antiparallel in an obvious stretching motion. These modes of 2, including a fourth with frequency 1565 cm\(^{-1}\), are expected to depict the motion associated with experimental bands of 1 at 1551, 1572, 1593, and 1612 cm\(^{-1}\).
In the high-frequency window (1620-1800 cm\(^{-1}\)), a pair of weak C=O stretching bands of 1 are centered at 1662 and 1702 cm\(^{-1}\). These bands correspond to ones calculated for 2 at 1683 cm\(^{-1}\) (asymmetric stretch) and 1720 cm\(^{-1}\) (symmetric stretch), or a pair at 1736 and 1741 cm\(^{-1}\) for 3. The only significant band in the region from ~1800-2200 cm\(^{-1}\) is the ethyne stretch. It is observed at 2178 cm\(^{-1}\) in the experimental spectrum, at 2146 cm\(^{-1}\) for 2, and 2200 cm\(^{-1}\) for the model dimer 4 (see Appendix).

Several aspects of the band intensities suggest that the A-term mechanism of resonance enhancement\(^49\) is the most important one for the experimental resonance Raman spectrum of 1. First, we note that resonance Raman intensities of perylene-based pigments have been previously connected to the magnitude of excited-state displacements of their A\(_g\) modes.\(^{50,51}\) The prior work provides strong support for the A-term mechanism as the basis for resonance enhancement in this family of chromophores. Second, we find that the strongest bands of the PDI dimer 1 (e.g. 1551, 1593 cm\(^{-1}\)) are correlated with fully symmetric modes of the parent molecule 3. Although this correlation is not proof of A-term resonance enhancement, it is consistent with that mechanism. Any fully symmetric vibration in the D\(_{2h}\) point group of 3 can have an excited state displacement. It is reasonable to expect that an analogous normal mode in a lower point group (e.g. for asymmetrically substituted PDI) will also sustain a displacement upon excitation, and contribute to A-term Raman scattering. Third, weaker bands of 1 in the same frequency region (1572, 1612 cm\(^{-1}\)) are correlated to modes of 3 that are not fully symmetric. The 1612 cm\(^{-1}\) band of the experiment correlates to a calculated mode of 3 with B\(_{1g}\) symmetry at the same
frequency. A mode of 3 with B$_{1g}$ symmetry is an unlikely candidate for A-term scattering, because a frequency change in the excited state or Duschinsky rotation would be required for that mechanism in the D$_{2h}$ point group. Nonetheless, weak A-term enhancement is possible for an analogous normal mode of 1, because B$_{1g}$ character in D$_{2h}$ translates to A$_g$ character in the lower C$_{2h}$ point group of 1. Along similar lines, the mode at 1572 cm$^{-1}$ in the experiment correlates with the 1565 cm$^{-1}$ mode calculated for 2 (see Appendix). The overall character of the 1565 cm$^{-1}$ mode strongly suggests ungerade symmetry from the standpoint of the perylene core, and closely resembles one calculated at 1584 cm$^{-1}$ for 3 with B$_{3u}$ symmetry. The mode is expected to be IR active, but of course Raman-forbidden in the D$_{2h}$ point group. In short, the lowered symmetry of molecule 1 allows significant scattering from some normal modes that are identified as non-totally symmetric in the D$_{2h}$ point group of the parent molecule 3. However, the intensities of these bands of 1 are not as strong as those that derive from A$_g$ modes of 3.

The weak intensity of the carbonyl stretching modes of 1 provides further support for an A-term mechanism of resonance enhancement. The bond order of the C=O groups does not change with the HOMO→LUMO excitation. Therefore one would not expect significant Franck-Condon displacement along modes involving carbonyl stretches.

We note that B-term scattering is another mechanism for enhancement in resonance Raman spectroscopy.$^{52}$ The term depends upon vibronic coupling of two excited electronic states that are nearby in energy. As one example, in the model D$_{2h}$ point group, a B$_{1g}$ mode could couple the S$_1$ state (B$_{3u}$ symmetry with axes selected as
in Scheme 2.1) with any excited state that has B_{2u} symmetry because the direct product B_{3u} \otimes B_{1g} \otimes B_{2u} is fully symmetric. However, modes that transform as B_{1g} in the D_{2h} point group of the parent PDI molecule 3 are totally symmetric in the lower point group of 1. In short, we find no reason to extend beyond the Albrecht A-term to explain the resonance Raman bands of 1 in its ground state.

One intriguing observation is that the intensity pattern of the experimental spectrum [1253m; (1332m, 1351s); (1551s, 1572m, 1593s, 1612m)] tracks with the calculated intensities of 2 [1256m; (1336s, 1349s); (1549s, 1565m, 1592s, 1607m)] where m and s denote medium- and strong- intensity bands, respectively. The agreement is surprising because the relative intensities of the experimental resonance Raman bands depend upon mode-specific displacements that are not included in the calculations. One qualitative explanation relates to the symmetry arguments described above, where the strongest experimental bands appear to have a close connection with fully symmetric modes in the D_{2h} point group, and less intense bands correlate to modes that are not totally symmetric. Similarly, the calculated Raman intensities (polarizability derivatives) are generally greatest for modes of 2 that correlate with fully symmetric modes of 3 in the parent D_{2h} point group. Although the match of relative band intensities between experiment and computation is good over the 1200-1620 cm\(^{-1}\) window, there is less agreement for the carbonyl region, and the ethyne stretch. A quantitative match over the full experimental window would require calculations of the excited state displacement for each mode.
**Resonance Raman spectroscopy of the triplet excited state (³PDI*).** Raman spectroscopy of the triplet excited state of 1 relied upon the formation of a steady-state population of ³1*. The sensitizer was ³ZnTPP*. The buildup of ³1* population was favored with its long 140 µs lifetime (see Appendix). The Raman probe wavelengths, 488.0 and 496.5 nm, were selected to be resonant with the strong visible absorption band of ³1* (Figure 2.1). The Raman spectra of the T₁ excited state of 1 are illustrated in Figure 2.4. Given the low signal-to-noise ratio, a comparison of these two spectra acquired with different wavelengths is a useful check of the reliability of each band. The quality of these T₁ spectra is not as good as the ground-state spectrum, for three reasons. First, the steady-state concentration of the T₁ excited state is only 15-20% that of the ground state. Second, the pump beam causes the background fluorescence in the probe window to approximately double in intensity relative to the probe-only (see Appendix), therefore, the shot noise is worse by a √2. A third factor is revealed upon inspection of the excited-state Raman difference spectra (see Appendix). The amplitudes of the most positive T₁ Raman signals are only a fraction (∼1/4th) of the most negative S₀ bands. This finding was unexpected, because the probe wavelengths were selected for resonance with the strong T₁→Tₙ absorption band.
Figure 2.4. Comparison of Raman spectra of dimer 1 in the T₁ excited state, versus calculated spectra of model compounds 2 and 3. (A) Resonance Raman spectrum of ³₁ in toluene with 488.0 nm probe. The spectrum is fitted with Gaussian functions (red) and labeled frequencies are their center positions. An asterisk (*) denotes imperfect subtraction of the toluene Raman scattering. (B) Same as (A), but with 496.5 nm probe. (C) Calculated spectrum of asymmetrically substituted PDI monomer, 2. (D) Calculated spectrum of PDI monomer with no substituents at the bay positions, 3. The symmetry of each mode in the D₂h point group of the PDI core is indicated. Calculated spectra have their frequency axes scaled by a factor of 0.972. Color-coding of bands indicates correlation of normal modes between model compounds 2 and 3, or between T₁ and S₀ states (Figure 2.2).
Four prominent \( T_1 \) bands of \( 1 \) are fitted with Gaussian functions centered at \(~1324, 1507, ~1535\) and \( 1596\) cm\(^{-1}\). A fifth band at \(~1160\) cm\(^{-1}\) is likely, although it is hardly evident in the spectrum with 488.0 nm excitation. Among the calculated bands of the asymmetrically substituted model molecule \( 2 \), five are a good match to the observed experimental bands. This correspondence is important for assigning experimental bands to normal modes of vibration (Figures 2.4 and 2.5). Following the analysis of the \( S_0 \) state, the modes of the \( T_1 \) Raman spectra in the frequency range \( 1000-1800\) cm\(^{-1}\) can be partitioned into four subsections: \( 1000-1300\) cm\(^{-1}\), \( 1300-1500\) cm\(^{-1}\), \( 1500-1620\) cm\(^{-1}\), and \( 1620-1800\) cm\(^{-1}\). The \( 1160\) cm\(^{-1}\) band in the one experimental spectrum matches a weak band calculated for \( 2 \) at \( 1157\) cm\(^{-1}\). The mode of \( 2 \) consists primarily of CH in-plane bends, as expected in this subsection. If one overlooks the bay-region substituents, the vectors indicate that the parent mode in the \( D_{2h} \) point group has \( B_{1g} \) symmetry. A mode of monomer \( 3 \) with that symmetry has a frequency of \( 1173\) cm\(^{-1}\) (Figure 2.5). The \( 1324\) cm\(^{-1}\) band in the experimental spectrum corresponds to the \( 1328\) cm\(^{-1}\) mode of \( 2 \), and consists mainly of CH in-plane bends, CC stretches at the bay-region, and central ring-breathing. The displacement vectors suggest that the symmetry of this mode would be \( A_{1g} \) in the \( D_{2h} \) point group (i.e. if substituents were not considered). The mode of \( 3 \) closest in frequency with that symmetry is found at \( 1361\) cm\(^{-1}\), and there is some overlap of vector displacements for molecules \( 2 \) and \( 3 \). Next, the \( 1507\) cm\(^{-1}\) band in the experiment is a close match to one calculated at identical frequency for \( 2 \), and at \( 1520\) cm\(^{-1}\) for \( 3 \). The normal mode of \( 3 \) is totally symmetric, and includes stretches of the CC single bonds of the perylene core, as well as outer diagonal CC bonds (C2C3, C4C5, C8C9, C10C11). The 1535
cm$^{-1}$ band in the experiment probably correlates with the 1541 cm$^{-1}$ mode calculated for 2, and the 1550 cm$^{-1}$ mode (B$_{1g}$) for 3. The dominant motions of both modes are out-of-phase longitudinal stretches of the outer CC bonds of perylene that are parallel to the long axis (C1C2, C5C6, C7C8, C11C12). Finally, the experimental band at ~1597 cm$^{-1}$ is correlated to the 1591 cm$^{-1}$ in-phase longitudinal stretch of 2, and the 1603 cm$^{-1}$ mode (A$_{1g}$) of 3. The experimental and calculated modes are summarized in Table 1.
Figure 2.5. (Left column) Normal modes of the model PDI monomer 2 that have a close correspondence in frequency with experimental bands of 1 in the $T_1$ excited state. (Right column) Normal modes of model monomer 3 in the $T_1$ state that are the closest match to those of 2.
The generalization described above about Raman intensities for the $S_0$ state appears to hold true for the $T_1$ state: the strongest resonance enhancements are associated with modes that correlate with fully symmetric ones in the $D_{2h}$ point group. The two bands that are strongest in both spectra (1507, 1597 cm$^{-1}$), as well as the 1319 cm$^{-1}$ band (third most intense with 496.5 nm excitation), are correlated with $A_{1g}$ modes of the parent $D_{2h}$ point group. The $\sim$1160 cm$^{-1}$ band is weak in the experimental spectra, and it correlates to a mode with $B_{1g}$ symmetry in the $D_{2h}$ point group. Along the same lines, a band that is predicted in the off-resonance calculations at 1226 cm$^{-1}$ for 2 does not appear above the noise level of the experimental spectra. The vectors of this mode suggest that it would have $B_{1g}$ symmetry in $D_{2h}$, therefore the excited-state displacement of the equivalent mode in the lower (approximately $C_{2h}$) point group of 1 is probably insufficient for A-term enhancement. The calculated spectrum also predicts a strong Raman band (CO stretch) at 1694 cm$^{-1}$, whereas no band in that region is observed in our experimental spectra. Analogous to the $S_0 \rightarrow S_1$ excitation of the ground state, it is likely that the bond order of the carbonyl groups does not change upon $T_1 \rightarrow T_n$ excitation. Therefore a small Franck-Condon displacement is one explanation for the mismatch between the experimental resonance Raman spectrum and the off-resonance calculation.

In the analysis above, we have assumed that the best model system for the $T_1$ excited state of 1 is an asymmetric monomer, 2. The use of 2 was suggested by the successful match of its calculated bands in the $S_0$ state, to the experimental ground-state vibrational spectrum of 1. However, for the $T_1$ state, one must consider an additional question that is unrelated to the ground state: How delocalized is the triplet
excited-state wavefunction? The calculated molecular orbital isosurfaces of 1 implies that the T\textsubscript{1} excited state is distributed equally over both chromophores. The comparison of experimental and simulated Raman spectra of the T\textsubscript{1} state leads to a different conclusion. The spectrum calculated for model dimer 4 is an inferior match to the experimental T\textsubscript{1} spectra of dimer 1, in comparison with the spectrum of the asymmetric monomer 2 (see Appendix). The findings based upon experimental Raman bands and the corresponding calculations support the picture of a T\textsubscript{1} excited state wavefunction that is localized on a single PDI moiety of dimer 1, on the femtosecond timescale for resonance Raman scattering.

The localized T\textsubscript{1} state inferred from resonance Raman spectroscopy is also consistent with our results from transient absorption spectroscopy (Figure 2.1). We note that the T\textsubscript{1}→T\textsubscript{n} absorption maximum of 1 at ~530 nm is significantly blue-shifted relative to its ground-state absorption band. This blue shift is unlike the more closely matched triplet and ground state absorption bands that have been reported for monomeric PDI.\textsuperscript{18,20} The unusual transient spectrum of the dimer could be explained by a T\textsubscript{1} excited-state wavefunction that is localized on half of the molecule. It is possible that solvent fluctuations cause the loss of symmetry (and collapsed wavefunction) that is inferred by electronic and vibrational spectroscopy. Triplet excited states have been found to localize on a single unit in other conjugated systems,\textsuperscript{53} including ethyne-linked porphyrin oligomers that are analogous to 1.\textsuperscript{54-56} The fact that triplet excitons are localized in the latter systems on the relatively slow timescale of EPR spectroscopy implies that localization on the faster (fs) timescale of resonance Raman scattering is even more probable.
Comparison of $S_0$ and $T_1$ Raman spectra. Further insights into the nature of the $T_1$ excited state can be gained by comparison of the normal modes of the $T_1$ excited state of model molecule 2 with similar modes of the $S_0$ state. The compilation in Table 2.1, and the color coding of Figures 2.2 and 2.4, aid in this comparison. The relevant normal modes of 2 are pictured in Figures 2.3 and 2.5, and the SI. The best match of the 1328 cm$^{-1}$ mode ($T_1$) is the pair of modes at 1336/1349 cm$^{-1}$ ($S_0$). The ~1507 cm$^{-1}$ mode of $T_1$ is a poor match to nearby $S_0$ modes at 1508 or 1522 cm$^{-1}$; however some aspects resemble the 1592 cm$^{-1}$ mode of $S_0$. The 1541 cm$^{-1}$ mode ($T_1$) compares well with 1522 cm$^{-1}$ ($S_0$). The 1591 cm$^{-1}$ mode of $T_1$ correlates with the 1549 cm$^{-1}$ mode of $S_0$. Overall, the correspondences between the two states are not straightforward, and the frequency shifts between $S_0$ and $T_1$ are not in the same direction for all modes. The reason is that excitation from $S_0$ to $T_1$ causes changes in bond orders (see Appendix for data on HOMO isosurfaces for the two electronic states). These changes result in a normal mode structure in the $T_1$ excited state that is mixed relative to the ground state (Duschinsky rotation). In the $T_1$ excited state, the bonds that lengthen 0.03-0.04 Å are the outer diagonal CC bonds (C2C3, C4C5, C8C9, and C10C11) and the four CC bonds in the interior bay region. Their force constants are expected to decrease. Consistent with that change, modes that involve a significant proportion of the outer diagonal or bay region CC bonds are lower in frequency for the $T_1$ state of 2 versus $S_0$ (e.g. 1507 cm$^{-1}$ of $T_1$ versus 1592 cm$^{-1}$ of $S_0$). In contrast, bonds that shorten by 0.03-0.04 Å upon excitation to the $T_1$ excited state are C1C2, C5C6, C7C8, and C11C12, and the pair of C-C single bonds that hold the naphthalene units together. Normal modes of 2 that consist primarily of stretches of
the shortened bonds should be higher in frequency for the T\textsubscript{1} state, e.g. the 1591 cm\textsuperscript{-1}
mode for the T\textsubscript{1} state of 2, versus the 1549 cm\textsuperscript{-1} of its S\textsubscript{0} state.
Table 2.1. Experimental and computed Raman frequencies (cm\(^{-1}\))

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<th>Ground state, (S_0)</th>
<th>Triplet State, (T_1)</th>
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<td>3 (calc.)(^b)</td>
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\(^a\)Raman frequencies (cm\(^{-1}\)) for 1 or \(3^1\) solvated in toluene. \(^b\)DFT calculations for asymmetrically substituted PDI 2, and unsubstituted PDI 3. \(^c\)Likely band, but not observed with both excitation wavelengths. All implied correlations indicated within each row are best matches for normal modes of model compounds 2 and 3, or between \(S_0\) and \(T_1\) states. Calculated frequencies are scaled by 0.972.
2.4 Conclusions

In the above sections we have described and analyzed the first Raman spectrum of a triplet exciton in the PDI family. We conclude with three points.

First, the bands of the T\textsubscript{1} excited state are distinguishable from those of the ground (S\textsubscript{0}) state. The bands of the T\textsubscript{1} state are also distinguishable from spontaneous resonance Raman or femtosecond-stimulated Raman spectra of PDI anions\textsuperscript{33,58} or PDI in its lowest singlet (S\textsubscript{1}) excited state\textsuperscript{32,33}. The use of different excitation wavelengths in resonance Raman spectroscopy can provide an additional level of selective identification, apart from unique bands for each state. For example, with 1064 nm excitation, signatures from PDI anions are amplified relative to those of the neutral species.\textsuperscript{58} Similarly, with visible excitation near \sim 500 nm, the signals of \textsuperscript{3}PDI\textsuperscript{*} state are expected to be significantly enhanced over other species, such as the S\textsubscript{1} excited state (\textsuperscript{1}PDI\textsuperscript{*}) or the ground-state anion (PDI\textsuperscript{−}).

Second, it is useful to generalize the results here for an experimental dimer, and predict the key resonance Raman bands for a triplet state (T\textsubscript{1}) PDI monomer without substituents attached to the bay region. The three most prominent bands in our experimental spectrum of 1 in the T\textsubscript{1} state (~1324, 1507, and 1597 cm\textsuperscript{−1}) match those computed for the asymmetric monomer 2 (1328, 1507, and 1591 cm\textsuperscript{−1}). These three vibrational modes of PDI 2 resemble totally symmetric (A\textsubscript{g}) modes calculated for unsubstituted PDI 3 at 1361, 1520, and 1603 cm\textsuperscript{−1}, respectively. Therefore, we predict that the triplet excited state of PDI without bay substituents will have resonance Raman bands centered near 1361, 1520, and 1603 cm\textsuperscript{−1}. Additional bands are likely at
1262, 1288, and 1412 cm\(^{-1}\), based upon calculations of \(A_g\) normal modes with those frequencies for 3 in the \(T_1\) state.

Third, we note that singlet fission is an expected mechanism for generating triplet excitons of PDI chromophores, if they are packed appropriately.\(^8\),\(^9\) Given that the chromophore is generally much less fluorescent when crystalline or aggregated than when solvated,\(^10\) resonance Raman spectroscopy would be well-suited for these studies. The technique could be readily employed for non-transmissive solid samples with a backscattering geometry.

In short, resonance Raman spectroscopy is capable of specifically identifying the \(T_1\) excited state of PDI. The technique could play a significant role in probing solid samples where singlet fission is expected. The comparative analysis of \(S_0\) and \(T_1\) states described in the present work can facilitate such studies.

**Acknowledgement**

Chapter 2, in full, is a reprint of the material as it appears in the Journal of Physical Chemistry A, 2013, 117, pp 9196-9204, by Maria Angelella, Chen Wang, and Michael J. Tauber. The author of this dissertation was the primary experimentalist, and was a coauthor of the paper.
References


Appendix of Chapter 2

A2.1. Absorption and fluorescence spectra of PDI dimer 1: effect of solvent, filtration, and concentration

Figure A2.1. Absorption spectra (solid lines) and fluorescence spectra (dashed lines) of 1 in chloroform (top panel) and in toluene (bottom panel). The fluorescence quantum yield (FQY) of 1 in each solvent is listed.
State of 1 in toluene: aggregated or not?

The relative amplitude of the 0-0 vibronic band (identified as a peak or shoulder at approximately 620 nm) of 1 is greater when dissolved in toluene than in chloroform (Figure A2.1). This change can be taken as evidence for J-aggregation. Consistent with that hypothesis, the fluorescence quantum yield of 1 in toluene (7%) is higher than in chloroform (4%), and its emission spectrum is narrower in the former solvent. However, other evidence does not support aggregation in toluene. The toluene solution passes through 0.2 µm pores of a PTFE filter with almost no loss of PDI (Figure A2.2). Therefore, if 1 self-assembled in toluene, its aggregates would be much smaller than those that form in binary aqueous/THF solvents.

Furthermore, ~200 nM and ~30 µM solutions of 1 in toluene have UV-Vis spectra with the same vibronic profile (Figure A2.3). It is unlikely that a 150-fold change in concentration would have no effect on aggregation. Thus, the concentration dependence provides additional reason to question aggregation as the origin for the relatively strong 620 nm absorption band in toluene.

Based on the preceding lines of evidence, we favor an intramolecular explanation for the changes in spectroscopy of 1 in each solvent. It is possible that the solvent could influence the relative orientation of the two PDI halves of 1 and therefore alter its fluorescence and absorption characteristics.
Figure A2.2. Absorption spectra of dimer 1 in toluene before (red) and after (blue) filtration through a PTFE filter with 0.2 µm pores. The concentration of 1 did not decrease significantly after filtration.
Figure A2.3. Normalized absorption spectra of dimer 1 with concentrations 0.2 µM (blue) and ~30 µM (red) in toluene.
A2.2. Transient absorption spectroscopy of PDI dimer 1 in the triplet excited state

![Graph](image)

**Figure A2.4.** TA spectra of $^31^*$ solvated in toluene, sensitized by $^3$ZnTPP*. The ZnTPP is photoexcited at 431 nm. The dashed line is the ground state absorption of 1 in toluene, inverted and scaled for comparison with the transient spectra. Arrows depict the Raman excitation wavelengths used to probe $^31^*$. (Inset) Kinetic decay of $^31^*$ at 500 nm, fitted with a single exponential function.
Transient absorption spectra were acquired with a system described previously. Pump pulses were centered at 431 nm. The pulses were ~6 ns in duration and the repetition rate was 20 Hz. At the sample the excitation energy was 0.2 mJ/pulse and beam diameter was approximately 4-5 mm.

The lowest triplet excited state of dimer 1 was generated through triplet sensitization by ZnTPP*. The photoexcitation of ZnTPP is expected to generate ZnTPP* in high (~0.9) yield and within 2 nanoseconds after absorption of a photon. The triplet lifetime of ZnTPP in toluene without oxygen or other quenchers is 1.25 ms. The ns-TA spectra (Figure A2.4) indicated that in the presence of PDI dimer 1, triplet-triplet energy transfer caused the formation of 1*. The lifetime (~140±10 µs) is similar to other T1 lifetimes of PDI reported in the literature. No evidence of charge-separated species was found, as would be expected if ZnTPP were covalently bound to the PDI.

The spectrum shown in Figure 2.1 is of the main paper is simulated by adding a fraction of the ground state to the transient spectrum at 80 µs.
A2.3. Raman spectroscopy of PDI dimer 1 in the triplet excited state

A2.3A. Experimental setup

The sample solution was prepared in a glovebox and contained in a sealed 1×1 cm cuvette, and stirred with a magnetic stir bar during the experiment. The 405 nm pump was generated by second-harmonic generation of the 810 nm light from a Ti:sapphire oscillator (Spectra-Physics Mai Tai). The pulse repetition rate was 88 MHz (quasi-CW). The wavelength of the pump excitation was tuned slightly post-resonant of the Soret band, so that the absorbance of the solution was less than 0.3 over a ~2 mm length of sample that was photolyzed and probed. The absorption by ZnTPP accounted for approximately 50% of the total pump photons that were absorbed by the sample. The 488.0 and 496.5 nm probe beams were continuous-wave from an argon/krypton ion laser (Laser Innovations Innova-70C). The pump and probe beams were combined collinearly with a beamsplitter, and both were directed vertically through the bottom of the cuvette. The beams were focused with 75 and 150 mm focal length (f.l.) cylindrical lenses. The slightly elliptical beam profiles were measured at 10% and 90% attenuation points with a razorblade. The areas of the beams are equivalent to circles with radii of 50±10 µm for the pump, and 40±10 µm for the probe. The focal point was located close (1.0 - 1.5 mm) to the bottom and front surfaces of the cuvette to minimize artifacts from self-absorption. The pump power at the sample was 5.5 mW, and the probe power was 1.2 mW.

Raman scattering was collected at 90 degrees relative to the propagation of the excitation beam, using an F/1.2 camera lens (Canon FD, f.l. 55 mm). Rayleigh scattering was blocked by either a 488 nm edge filter (Semrock) or a 496 nm notch
filter (Iridian). The Raman light was focused onto the entrance slit of a spectrograph (Horiba Jobin Yvon iHR-320, 1200 groves/mm) with an F/4, 200 mm f.l. achromatic doublet lens. The entrance slit width was 50 μm (~4 cm⁻¹ resolution). The detector was a back-illuminated CCD (Andor Newton DU920N-BU), thermoelectrically cooled to -80 °C.
A2.3B. Steady-state model

The following mechanism describes the generation of triplet excitons of \( 1^* \), \( 3^1 \),
\[
\begin{align*}
\text{ZnTPP} + \text{hv} & \rightarrow \text{ZnTPP}^* \rightarrow 3\text{ZnTPP}^* \quad k_{Ex} \\
3\text{ZnTPP}^* + I & \rightarrow \text{ZnTPP} + 3I^* \quad k_{ET} \\
3I^* & \rightarrow I \quad k_D \\
3I^* + 3I^* & \rightarrow 1I^* + I \quad k_{TT}
\end{align*}
\]

The rate of intersystem crossing for ZnTPP \( (5.8 \times 10^8 \ s^{-1})^4 \) is much faster than
the rate of photoexcitation. Therefore the formation of \( 3\text{ZnTPP}^* \) can be expressed as:
\[
\begin{align*}
k_{Ex} = I(\lambda)\sigma(\lambda)\Phi(\lambda)
\end{align*}
\]
where \( I(\lambda) \) is irradiance, \( \sigma(\lambda) \) is absorption cross section of ZnTPP at the pump
wavelength (405 nm), and \( \Phi(\lambda) \) is the triplet quantum yield, 0.9 \( 11 \). The irradiance is
multiplied by a factor of 0.5 because ZnTPP accounted for only half of the absorbed
pump photons. The value obtained for \( k_{Ex} \) is 11,000 \( s^{-1} \). The bimolecular rate
constants for energy transfer, \( k_{ET} \), and triplet-triplet annihilation, \( k_{TT} \), are assumed to be
close to the diffusion limit, \( 10^9 \ M^{-1}s^{-1} \). \( 12 \) The first-order rate constant for the decay of
\( 3I^* \), \( k_D = 7,100 \ s^{-1} \), was determined from transient absorption spectroscopy (Figure
A2.4).

The following two equations result from the mechanism above under steady-
state conditions:
\[
\begin{align*}
\frac{d[3I^*]}{dt} &= 0 = k_{ET}[3\text{ZnTPP}^*]I - k_D[3I^*] - k_{TT}[3I^*]^2 \\
\frac{d[3\text{ZnTPP}^*]}{dt} &= 0 = k_{Ex}[\text{ZnTPP}] - k_{ET}[3\text{ZnTPP}^*]I
\end{align*}
\]
Additional experimental constraints are:

\[ [I]_{tot} = [I] + [^3I^*] = 30 \mu M \quad (A2.4) \]
\[ [ZnTPP]_{tot} = [ZnTPP] + [^3ZnTPP^*] = 14 \mu M \quad (A2.5) \]

The solution to equations A2.2-A2.5 leads to estimated steady-state concentrations of 7 \( \mu M \) for \([^3\text{I}^*]\), and 5 \( \mu M \) for \([^3\text{ZnTPP}^*]\). The concentration of \(^3\text{I}^*\) derived from the steady-state analysis is similar to the 5 \( \mu M \) determined from the experimental observation of a 15-20% decrease in the bands of the ground state of \textbf{I}.

The omission of \(^3\text{ZnTPP}^*\) triplet-triplet annihilation from the mechanism is justified because the concentration of \textbf{I} is four-fold greater than that of \(^3\text{ZnTPP}^*\). Therefore the rate of \(^3\text{ZnTPP}^*\) triplet-triplet annihilation is small relative to triplet sensitization of \textbf{I},

\[
^3\text{ZnTPP}^* + ^3\text{ZnTPP}^* \quad \text{Rate} = k_{\text{Diff}} \left[^3\text{ZnTPP}^*\right]^2 = 0.025 M \cdot s^{-1}
\]
\[
^3\text{ZnTPP}^* + I \quad \text{Rate} = k_{\text{Diff}} \left[^3\text{ZnTPP}^*\right][I] = 0.12 M \cdot s^{-1}
\]

To further identify the species observed by the steady-state resonance Raman experiment, two control experiments were carried out with the same excitation/probe conditions as described in the main manuscript. First, a solution of pure ZnTPP yielded no signs of known \(^3\text{ZnTPP}^*\) Raman bands at 1594, 1236 and 1181 cm\(^{-1}\).\(^{13,14}\) Although the steady state concentration of \(^3\text{ZnTPP}^*\) was appreciable (0.02 mM) in the control experiment, the result was expected because the Raman cross-section of \(^3\text{ZnTPP}^*\) is small. Previous studies of \(^3\text{ZnTPP}^*\)\(^{13,14}\) employed much higher ZnTPP concentrations (~1 mM), and a time-resolved resonance Raman experiment. The approach of prior studies greatly increased the probed triplet population relative to a
steady-state experiment. Additionally, the probe wavelengths of the prior work were shorter and more resonant with $^3\text{ZnTPP}^*$, and the average pump and probe powers (where specified)$^{13}$ were many times higher than powers employed in our experiments.

A second control experiment employed a pure solution of 1 in toluene. When photoexcited and probed under the same conditions as described above, the spectra showed no signs of ground-state bleach or positive excited-state signals. The two control experiments reassured us that the steady-state spectroscopy of the solution with ZnTPP and 1 had contributions only from the Raman bands of $^3\text{I}^*$ without signals from $^3\text{ZnTPP}^*$ or any other photoproducts of 1.
A2.3C. Data acquisition and pretreatment

Three spectral components: (pump+probe), (probe only) and (pump only), were collected with alteration every 10 or 20 min, Figure A2.5. A (solvent only) spectrum was also acquired. The total integration time for each spectrum was 120 min.

Figure A2.5. Spectral components for the triplet sensitization experiment with 405 nm pump and 488.0 nm probe after self-absorption and instrument response correction. The (pump+probe) spectrum contains Raman signals from both ground state and dimer 1 in the triplet excited state. The (pump only) spectrum is dominated by sample fluorescence. The (probe only) spectrum records the ground state Raman scattering of 1 and the solvent. The dotted lines label the position of the main Raman bands of 1 in the ground state.
Raman shifts were calibrated by recording a spectrum of a standard toluene/acetonitrile sample with known Raman assignments. A constant background (740 readout counts per acquisition) was subtracted from each spectral component before any other steps. (Pump+probe), (pump only), and (probe only) spectra were corrected for self-absorption using measured absorption spectra of the sample solution. The effective pathlength of the Raman scattering through the sample was determined from ratios of the solvent band intensities in the sample solution versus the neat solvent.
A2.3D. Instrument response correction

The fluorescence background in the triplet sensitization Raman experiment has three contributing factors. First, there is significant emission caused by the pump beam. Second, the ground state absorption of 1 is significant at the probe wavelengths, so emission from the lowest excited singlet state will be enhanced. Third, the probe is close to the high-energy side of the main emission band.

The typical instrument response spectrum based on a calibrated white-light lamp, IRS\(_{wl}\), corrects for relatively broad changes in the spectral response of the collection optics, spectrograph, or detector. To obtain the IRS\(_{wl}\), a white-light spectrum was acquired with a calibrated tungsten lamp (Acton Research TDS-429) that was scattered off of a PTFE block (LabSphere, Spectralon). The IRS\(_{wl}\) was computed as:

\[
IRS_{wl} = \frac{\text{(measured lamp spectrum)}}{\text{(standard lamp spectrum)}}
\]  
(A2.6)

A portion of the IRS\(_{wl}\) is shown in Figure A2.6. Correction with IRS\(_{wl}\) removes the smoothly varying curved background, but fixed-pattern artifacts caused by variation in column-to-column response of the CCD detector are still present. It was found that acquiring IRS\(_{WL}\) from a white light source that was distant from the focal plane of the collection lens helped to reduce the artifacts. This fixed-pattern is not a problem for the final triplet spectra because most of the artifacts cancel out when taking the difference spectra as described in section 2.3E. However, for the ground state spectrum, which is dominated by the probe-induced fluorescence background, the effect is observed in the final spectrum, as shown in Figure A2.7.
Instrument response spectra. IRS$_{wl}$ refers to the standard instrument response correction that is generated from a calibrated tungsten lamp. IRS$_{sample}$ refers to the curve that was adjusted using the (pump only) spectrum, equation A2.7. The inset shows the comparison of the column-to-column fine structure between IRS$_{wl}$ and IRS$_{sample}$. The use of the IRS$_{sample}$ results in a two-fold improvement in the signal-to-noise ratio for the final Raman spectrum of the triplet excited state, compared with the IRS$_{wl}$ correction.
The final instrument response spectrum, $IRS_{\text{sample}}$, was generated from the (pump only) spectrum by,

$$ IRS_{\text{sample}} = \frac{(\text{pump only})_{IRS_wl}^{\text{smoothed}}}{(\text{pump only})_{IRS_wl}} $$ (A2.7)

As shown in Figure A2.6, the $IRS_{\text{sample}}$ curve has the same overall profile as $IRS_{w_l}$, and thus accounts for the variation of the spectrograph and detector efficiency as a function of wavelength. Moreover, the use of the pump beam allows this method of correction to compensate for the column-to-column variation that is impressed in the strong fluorescence caused by the probe.

A detailed comparison shown in the inset of Figure A2.6 reveals the subtle differences between the fine structure of $IRS_{w_l}$ and $IRS_{\text{sample}}$. Correction with $IRS_{\text{sample}}$ helps to reduce the artifacts in the ground state spectrum by a factor of two. To be consistent, all raw spectra were divided by $IRS_{\text{sample}}$ before further processing.

Our method can be applied when a pump beam is present with a similar or identical beam-path as the probe, and when the pump excitation causes sufficient fluorescence background signals without imprinting Raman features in the window. It is important to note that the $IRS_{\text{sample}}$ procedure resulted in only incremental improvement in the signal-to-noise of the Raman spectra pictured in the main manuscript. This result is due to two factors: (1) the samples used for the spectra in the manuscript were recrystallized in methanol, removing residual fluorescent impurity, (2) for the $^3\text{I}^*$ spectra, pixel-to-pixel fluctuations were mostly removed during the subtractions described in section 2.3E.
Figure A2.7. Raman spectra of ground-state 1 in toluene acquired with 488 nm excitation. The sample used for this experiment was not purified by recrystallization in methanol. The strong fixed pattern artifacts caused by the high fluorescence background help to demonstrate the effect of the instrument response correction procedure. The spectra shown have the solvent Raman scattering removed (equation A2.8). The specific spectra are: (blue) divided by IRS_{wl}; (red) divided by IRS_{sample}. Following the correction with IRS, a background was removed from these spectra by subtracting a baseline generated by a spline fit.
A2.3E. \( T_1 \) spectra workup

After the treatment described in sections 2.3C and 2.3D, the final \( ^3I^* \) resonance Raman spectrum was obtained by the following procedure:

1. The ground state spectrum of 1 was obtained by subtracting the (solvent only) spectrum from the (probe only) spectrum.

\[
S_0 \text{ spectrum} = \text{(probe only)} - \text{(solvent only)} \quad (A2.8)
\]

2. The pump-induced background was removed by taking the difference D1,

\[
D1 = \text{(pump + probe)} - a \times \text{(pump only)} \quad (A2.9)
\]

where the subtraction factor \( a \) was determined by matching the background level of the difference D1 to that of the (probe only) spectrum. The factor \( a \) was typically 0.8-0.9.

3. Spectrum D1 consisted of signals from both the ground state and the triplet excited state. The ground-state signal was removed by subtracting the (probe only) spectrum.

\[
D2 = D1 - b \times \text{(probe only)} \quad (A2.10)
\]

The subtraction factor \( b \) was determined by optimizing the subtraction of the solvent bands, and was typically 1.00. Variations of up to 2% were sometimes required to compensate for fluctuations in the probe power.

The pixel-to-pixel variation is mostly cancelled out during the subtraction in steps 2 and 3. At this point the quality of the spectrum is primarily affected by the shot noise.

4. A fraction of the \( S_0 \) spectrum was added to spectrum D2 to compensate for the loss of ground state caused by the pump pulse:

\[
T_1 \text{ spectrum} = D2 + c \times (S_0 \text{ spectrum}) \quad (A2.11)
\]
The smallest addition fraction ($c$) yielding a reconstructed spectrum that was (1) free of a negative dip in the ~1300 cm$^{-1}$ and 1500-1600 cm$^{-1}$ region and (2) free of positive features from the ground state, was considered optimal (Figure A2.8).

(5) The final spectrum was obtained after subtracting a baseline generated by a spline fit.
Figure A2.8. Fractional addition of the $S_0$ spectrum to the difference spectrum D2. The optimum scalar addition of the $S_0$ spectrum was selected as 0.20 in this example. Dotted lines mark the positions of the ground state Raman bands. A scaled ground state spectrum (0.20) is also shown for comparison.
A2.4. Results from DFT calculations and normal mode analysis

A2.4A. Model molecules, and bond lengths of perylene core in S₀ and T₁ states

**Figure A2.9.** Asymmetrically substituted PDI monomer 2 and acetylene-linked PDI dimer 4.
**Figure A2.10.** Bond lengths of perylene core for unsubstituted PDI 3 in the ground state (left) and excited $T_1$ state (right). Bond lengths are colored green if there is no significant change from $S_0$ to $T_1$; red (blue) if increased (decreased) significantly for $T_1$. Atom numbers are included in black.
A2.4B. Frontier molecular orbitals

**Figure A2.11.** Wavefunctions for the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) for asymmetrically substituted PDI 2 (top row), acetylene-linked PDI dimer 4 (middle row), and unsubstituted PDI, 3 (bottom row). The columns are divided as follows: $S_0$ HOMO (left column), $S_0$ LUMO (middle column) and $T_1$ HOMO (right column). The isovalue for all wavefunctions is 0.02.
A2.4C. Calculated Raman spectra and comparison to experiment

Frequencies are found from a harmonic analysis at stationary points in the geometry optimization using Gaussian 09W software. Raman intensities are predicted from polarizability derivatives, without taking into account resonance with an electronic transition.

Peak positions of the multiple bands in the experimental spectra were determined by fitting the region of interest to Gaussian functions. A minimum number of Gaussian components were chosen in order to represent every local maxima as well as shoulders appearing in the experimental spectra. The initial peak positions were set to the experimental peak maxima, but they were allowed to change freely during the fitting. The bandwidths of each fit were controlled to limit the ranges of broadening among each component in the same spectral region to less than 10%.
Figure A2.12. Ground state Raman spectra. (A) Experimental spectrum of 1 in toluene with 488.0 nm excitation. An asterisk (*) denotes imperfect subtraction of a toluene Raman band. (B) Calculated Raman spectrum of the asymmetrically substituted PDI monomer 2. (C) Calculated spectrum of the acetylene-linked PDI dimer 4. (D) Calculated spectrum of the unsubstituted PDI monomer 3. The frequency axes of the calculated spectra are multiplied by 0.972.
Figure A2.13. Triplet excited state Raman spectra. (A) Experimental spectrum of $^11^*$ in toluene with 488.0 nm probe. An asterisk (*) denotes imperfect subtraction of a toluene Raman band. (B) Same as (A) but with 496.5 nm probe. (C) Calculated spectrum of asymmetrically substituted PDI monomer 2. (D) Calculated spectrum of the acetylene-linked model PDI dimer 4. (E) Calculated spectrum of unsubstituted PDI monomer 3. The frequency axes of the calculated spectra are multiplied by 0.972.
A2.4D. Normal mode diagrams

The diagrams below were prepared using Jmol.17

Figure A2.14. Normal mode diagrams for the ground state ($S_0$) of unsubstituted PDI monomer 3. All ten $A_g$ modes that have calculated frequencies (after scaling ×0.972) within the range 1000-1800 cm$^{-1}$ are shown. Three of the eleven $B_{1g}$ modes (1245, 1612, and 1736 cm$^{-1}$) in the same window are also included. These $B_{1g}$ modes are selected because of their likely connection to Raman bands recorded for dimer 1. The $B_{3u}$ mode at 1584 cm$^{-1}$ is also included as a comparison to the 1565 cm$^{-1}$ mode calculated for model molecule 2, both of which are possibly correlated with the experimental band at 1572 cm$^{-1}$.
Figure A2.15. Normal mode diagrams for the first triplet excited state (T₁) of unsubstituted PDI monomer 3. All ten Aᵣ modes that have calculated frequencies (after scaling ×0.972) within the range 1000-1800 cm⁻¹ are shown. Six of the eleven B₁₉g modes (1173, 1249, 1371, 1430, 1550, and 1703 cm⁻¹) in the same window are also included. The B₁₉g modes are selected because of their possible connection to the observed bands of dimer 3¹⁺.
Figure A2.16. Normal mode diagrams for the ground state (S\textsubscript{0}) of the asymmetrically substituted PDI monomer 2. Modes are shown if they are considered a possible match to one of the fifteen bands observed in the experimental spectrum of dimer 1 within the spectral range 1000-2200 cm\textsuperscript{-1}.
Figure A2.17. Normal mode diagrams for the triplet excited state (T_1) of the asymmetrically substituted PDI monomer 2. Modes in the spectral range of 1000-2200 cm^{-1} are shown if they are considered potentially relevant to the five bands that are observed in the experimental spectrum of ^3I*, or for comparison with modes of the S_0 state.
References


Chapter 3 Excited state dynamics of a perylene diimide dimer and its aggregate

3.1 Introduction

Perylene 3,4,9,10-tetracarboxylic diimide (PDI) is one of the most important synthetic building blocks in the dye industry, and in fundamental research.\textsuperscript{1-3} Electronic coupling between PDI units is well known to affect many of its properties, including optical absorption and fluorescence emission.\textsuperscript{4-7} Covalent dimers are the most elementary coupled unit; PDI dimers with various structures have been the focus of considerable theoretical\textsuperscript{8-11} and experimental research.\textsuperscript{12-32} Dimers or other multimers of PDI tend to self-assemble more readily than monomers.\textsuperscript{6, 23, 26, 33} The additional level of interaction brought about by self-assembly opens opportunities to explore varied architectures and chromophore-chromophore interactions.\textsuperscript{23, 34-36} In turn, the coupling brought about by self-assembly can have a strong effect on physical properties that are most relevant to applications, for example charge delocalization and exciton transport.\textsuperscript{1, 6, 37-39}

The ethynyl-linked dimer of PDI with polyethylene glycol (PEG) substituents (1, Figure 3.1) illustrates the above points. The dimer readily self-assembles to form micrometer-length nanofibers in binary aqueous/organic solution.\textsuperscript{40} A remarkable aspect of this system is its reversibility: chemical reduction causes the nanofibers to
disassemble into solvated dimers, and oxidation causes their reformation.\textsuperscript{40} The absorption and emission properties change substantially upon aggregation. Preliminary results from ultrafast spectroscopy revealed annihilation of excitons in the aggregated state, however a quantitative analysis was not performed.\textsuperscript{40} Fast diffusion of excitons was highlighted in other self-assembled PDI systems.\textsuperscript{1, 34, 35, 37} For example, a self-assembled PDI J-type aggregate was found to have an exciton diffusion length of almost 100 nm,\textsuperscript{37} similar to those found for crystalline acenes.\textsuperscript{41}

The optical spectroscopic studies of self-assembled dimer 1 reported herein were motivated by our interest in gaining a more complete and quantitative understanding of the exciton dynamics within this unique system. We were also driven by a specific interest in singlet fission, whereby a singlet excited state separates into a pair of triplet excited states on neighboring chromophores.\textsuperscript{42, 43} Computations indicate that PDI has energy levels that can support this mechanism, specifically $E(S_1) \cong 2E(T_1)$; additionally the relative orientation of the interacting molecules was predicted to have a strong impact on triplet yield by singlet fission.\textsuperscript{44, 45} Triplet yields of $140\pm20\%$ were found in an experimental study of slip-stacked PDI.\textsuperscript{46} The two alkyne-linked PDI units of 1 are expected to have a delocalized singlet excited state. We speculated that a dimeric unit within a larger self-assembled structure could enhance the initial energy partitioning to form two triplet-excited states. Furthermore, the short columns that were proposed\textsuperscript{40} as a structural element of aggregated 1 could also facilitate the prompt separation of a nascent triplet pair.

We report transient absorption (TA) and vibrational spectra of 1 in its solvated and aggregated forms. Excited–state TA spectra suggest that a large population of
triplet excitons is created on a sub-picosecond timescale after excitation. However, other evidence, including rapid annihilation, is more consistent with singlet exciton dynamics.
Figure 3.1. Molecule 1. The polyethylene glycol (PEG) length distributions are centered in the range of $n=14\pm 6$. 
3.2 Experimental

**Preparation of samples and steady-state characterization.** The synthesis of dimer 1 was described previously. The number of \((\text{CH}_2\text{CH}_2\text{O})_n\) units in each polyethylene glycol (PEG) substituent was 14±6 units, averaged over multiple preparations of 1. The sample purity was checked with \(^1\text{H} \text{NMR}, \text{absorption, and fluorescence spectroscopy.} \) Dimer 1 was recrystallized in methanol (Fisher Scientific, HPLC grade) as part of the preparation for the fluorescence and Raman measurements.

Water for aggregate samples was deionized (Barnstead, model D11911). Tetrahydrofuran (THF) was inhibitor-free, spectroscopic-grade (Fisher Scientific). Toluene was HPLC grade (Alfa-Aesar). Solvents were deoxygenated by refluxing under dry \(N_2\) (water, toluene) or by several freeze-pump-thaw cycles (water, THF). Solutions of 1 in various solvents were prepared in a nitrogen- or argon-filled glovebox (MBraun, UniLab), with a concentration of oxygen that was less than 1 ppm. Aggregates were formed in binary organic-aqueous solutions. Water was added to a \(~0.4 \text{ mM}\) solution of 1 dissolved in THF, until the ratio of water:THF was 4:1 (v/v). The solution of aggregated 1 was sonicated for 30 minutes, and aged for approximately 10 hours at room temperature prior to experiments. The stability of the aggregate solutions was found to improve if the THF was passed through a column of alumina (50–200 \(\mu\)m diameter, Acros Organics) immediately before their preparation, presumably because of the removal of trace peroxides.

Absorption spectra were collected with a UV-Vis spectrophotometer (Shimadzu, UV-3600) with 1 nm bandpass, and samples were contained in quartz
cuvettes with a 0.2 cm pathlength. The molar absorption coefficients for 1 in chloroform were determined over the 300–800 nm spectral region (see Appendix). Molar absorption coefficients for 1 dissolved in THF, or aggregated in water:THF (4:1), were determined by the ratio of absorption spectra in these solvents versus a spectrum of an equal amount of 1 in chloroform.

Fluorescence spectra were acquired with a spectrofluorimeter (Horiba Jobin Yvon, model Fluorolog-3 FL3-11) with 1 nm bandpass. Samples were contained in a 1×1 cm quartz cuvette and excited with 550 nm light in a 90 degree geometry. The absorbance over a 1 cm pathlength was less than 0.1 at the excitation wavelength to minimize artifacts from self-absorption. The fluorescence quantum yield for 1 in chloroform was determined relative to sulforhodamine 101 (Exciton) in ethanol, which has a fluorescence quantum yield of 0.95±0.02.47

**Femtosecond Transient Absorption Spectroscopy.** The dimer was dissolved in THF (~30 µM) for femtosecond transient absorption (fs-TA) spectroscopy of the solvated molecule. The concentration of 1 was ~80 µM in water/THF for the aggregate studies. These concentrations maintained the sample absorption at the pump wavelengths in the range of 0.1–0.3 over the 2 mm cuvette pathlength. The solutions were open to atmosphere, and stirred with a small magnetic stir-bar. The wavelength of the pump was either 395 or 530 nm; the excitation energies varied from 0.5 to 3.0 µJ/pulse; and the 1/e² radii of the pump beam at the sample were 330 ± 20 µm at 395 nm, and 270 ± 20 µm at 530 nm. TA spectra were acquired in the spectral range of 370–750 nm and 850–1400 nm using calcium fluoride and sapphire crystals, respectively, for the generation of white-light continuum. The white light probe had a
$1/e^2$ radius of 130±20 µm at the sample. The pump and probe beams intersected at ~10 degrees, and their relative polarization was 54.7 degrees (magic angle). Further details of the transient absorption system are described elsewhere.\textsuperscript{48}

The TA spectra were corrected for variation in the position of zero-time (chirp) across the visible spectrum by analyzing the solvent-only response. Instrument response times were 150 fs (395 nm excitation) and 100 fs (530 nm excitation), assessed by fitting the stimulated Raman band of the solvent to a Gaussian function.

Kinetic traces for solvated 1 in THF were fitted with a function that included a sum of two or three exponential terms, convolved with a single Gaussian function to account for the instrument response. Fits to kinetic traces for aggregated 1 are described in the Results section. The optimal kinetic parameters and amplitudes were determined by the Levenberg-Marquardt nonlinear least-squares minimization algorithm in Igor Pro (Version 6).

**Nanosecond Transient Absorption.** Nanosecond-to-microsecond TA spectra were collected using a custom system.\textsuperscript{48} Pump pulses with a wavelength of 525 nm were generated by an optical parametric oscillator (OPOTEK Inc., Magic Prism) pumped with the 355 nm third harmonic of a Nd:YAG laser (Quantel, Brilliant). The pump pulses had a repetition rate of 20 Hz and were ~6 ns in duration. At the sample the energy per pulse was ~0.2–0.3 mJ, and the beam diameter was 4–5 mm. The time response of the system was <50 ns. The probe was scanned from 400 to 800 nm with 10 nm step-size. The signals at each wavelength were averaged for 4,000 shots.

Significant RF noise associated with the Quantel Brilliant YAG laser Q-switch electronics was problematic for measuring small (milli-OD) transients. The noise was
substantially reduced by enclosing the detection apparatus in a housing constructed with an aluminum frame and lined with RF-shielding fabric (Less EMF Inc., High Performance Silver Mesh Fabric). The laser head and power supply were also enclosed in aluminum frames lined with copper mesh.

Kinetic parameters were determined at various wavelengths by fitting the data to a function that included one or two exponential terms, and a least-squares algorithm.

**Raman Spectroscopy.** The continuous wave (cw) resonance Raman experiment was described previously. Briefly, the excitation beam for ground state measurements was 488.0 nm light from an argon/krypton ion laser (Laser Innovations, Coherent Innova-70C). The Raman scattered light was collected at 90 degrees relative to the propagation of the excitation beam, using an F/1.2 camera lens (Canon, FD, f.l. 55 mm). A 488 nm edge filter (Semrock) blocked the Rayleigh scattering. The Raman scattering was dispersed with a spectrograph (Horiba Jobin Yvon, iHR-320), with 1200 grooves/mm grating and entrance slit 150 μm (bandpass ~15 cm⁻¹). The detector was a back-illuminated CCD with thermoelectric cooling (Andor, Newton DU920N-BU). Sample degradation was less than 5%.

Picosecond time-resolved resonance Raman spectra of aggregated 1 were acquired with a system that was described elsewhere. The pump and probe wavelengths were 405 and 488 nm, respectively. The cross-correlation time of the pump and probe pulses was 5.6 ps, and spectra were acquired at delay times of 6, 30, and 200 ps. A water/THF solution of the aggregate (8–12 mL total volume with 70–100 μM concentration of 1) was circulated continuously through a 2×2 mm quartz
capillary at the sample point. The solution was exposed to air during these pump-probe experiments. The cross-sections of the beams at the sample point were elliptical, with the longer dimension parallel to the optical axis of the collection lens. The axis lengths measured by a razor blade and 10–90% energy cutoffs were (350 ± 5 µm) × (75 ± 5 µm) for the pump, and (330 ± 5 µm) × (70 ± 5 µm) for the probe. The beam dimensions were increased for the 200 ps time delay spectrum, to diminish exciton-exciton annihilation: the pump axis lengths were (700 ± 5 µm) × (130 ± 5 µm), and the probe axis lengths were (682 ± 5 µm) × (63 ± 5 µm). Estimates of the excitation percentage (Equation 1) were based upon computed radii of spherically symmetric Gaussian beams that had equivalent cross-sectional areas as the pump and probe ellipses. Additionally, a factor of 1.561 was used to convert a beam size measured with 10–90% energy cutoffs to a 1/e² diameter for a TEM₀₀ Gaussian beam.⁵⁰ The pump pulse energies were 0.7–1.3 µJ. Approximately 10–25% of the molecules were photoexcited with each pump pulse (Eq 3.1). A probe pulse energy of 0.4 µJ was selected to limit excitation of the ground state to ≤10%. Both of the excitation ratios were computed with the simplifying assumption that each excited state within the aggregate is localized to a single molecule of 1 (vide infra). The spectrograph/detection system was the same as for the cw-Raman experiment. Spectra with (pump+probe), (pump only), and (probe only) conditions were collected with alternation every 10 or 20 minutes. The integration time for each sub-spectrum was 120 seconds. The total integration time for each of the three conditions was 240 min (for 6 and 200 ps delay), and 360 min (for 30 ps delay). UV-Vis spectra showed degradation of less than 25% at the end of the TRRR experiments.
Artifacts from cosmic rays were identified by overlay of at least five of the 120 second sub-spectra, and removed manually before summation. Raman spectra were corrected for self-absorption effects using the absorption spectra of the sample solution. The effective pathlength of the Raman scattering through the sample was determined from ratios of the solvent band intensities in the sample solution versus the neat solvent. Raman shifts for the steady-state and TRRR experiments were calibrated by recording spectra of standard toluene/acetonitrile samples with known Raman assignments.51

The direct excitation TRRR experiment was not conducted for solvated 1 because of relatively high sample fluorescence in the 600−750 nm spectral window.

Determining percent excitation. Quantification of the excited state concentration was an important part of the transient absorption and transient resonance Raman experiments of the aggregated samples. The number of excited states of 1 per unit volume of solution, or number density of 1• in solution, is denoted \( n_{\text{soln}}(1^•) \). An estimate of \( n_{\text{soln}}(1^•) \), averaged over the probed region, is readily derived for Gaussian pump and probe beams:

\[
n_{\text{soln}}(1^•) = N_{\text{pump}} \left[ 1 - 10^{-A(\lambda_{\text{pump}})} \right] \left[ 1 - e^{-\left(\frac{2r_{\text{probe}}^2}{r_{\text{pump}}^2}\right)} \right] \left[ \frac{1}{\pi r_{\text{probe}}^2 l} \right] (3.1)
\]

In equation 3.1, \( N_{\text{pump}} \) is the number of pump photons per pulse. The first bracketed term approximates the fraction of pump photons absorbed by 1. The actual fraction absorbed from the high-irradiance pulses is expected to be slightly less than extrapolated from the absorbance \( A(\lambda_{\text{pump}}) \) measured with continuous wave UV-Vis spectroscopy. The second bracketed term quantifies the fraction of pump photons,
with $1/e^2$ beam radius $r_{\text{pump}}$, that impinge upon the circular area defined by the $1/e^2$ beam radius of the probe, $r_{\text{probe}}$. The third bracketed term is the reciprocal of the probed volume. The volume is assumed to be pumped along the full internal pathlength, $l$, of the cuvette, which is a reasonable approximation because of the small crossing angle of the beams. The result from equation 3.1, when divided by the total concentration of 1 in solution, $n_{\text{solv}}(1^*)/n_{\text{solv}}(1)$, yields the percentage of excited molecules for the TA and TRRR experiments.

Equation 3.1 yields an estimate for the number of excitons per volume of solution, which is appropriate when studying solvated samples. However, for aggregates and other solid samples, it is useful to compute the number density of excitons per unit solid volume, denoted $n_{\text{agg}}(1^*)$. In turn, $n_{\text{agg}}(1^*)$ depends upon the number density of ground-state dimers 1 within the aggregates, denoted $n_{\text{agg}}(1)$. From cryogenic transmission electron microscopy (cryo-TEM) and small-angle X-ray scattering (SAXs) data, $n_{\text{agg}}(1)$ is approximately $6 \times 10^{20}$ cm$^{-3}$. This value for a PDI dimer with bulky substituents is less than half the number densities reported for PDI monomers within crystals, as expected. The ratio of number densities of $1^*$ for solid and solution phases is equal to the ratio of number densities for the ground-state of 1:

$$
\frac{n_{\text{agg}}(1^*)}{n_{\text{solv}}(1^*)} = \frac{n_{\text{agg}}(1)}{n_{\text{solv}}(1)}
$$

(3.2)
3.3 Results

Steady-state Absorption/Emission Spectroscopy. The absorption spectra of the solvated and aggregated PDI dimer (Figure 3.2) are significantly red-shifted and broadened relative to monomeric PDI.\textsuperscript{1, 7, 40} The lowest energy absorption band of aggregated 1, with maximum at \(\sim 650\) nm is bathochromically shifted \(\sim 0.12\) eV relative to the lowest energy band of solvated 1. The maximum absorption coefficient in the visible region decreases by nearly a factor-of-two when aggregated. However, the integrated absorption cross-section of the aggregate over the visible region is at least 80\% that of solvated 1. The fluorescence quantum yield (FQY) of solvated and aggregated 1 are much lower than those for monomeric PDI. The yield from 1 solvated in chloroform is \((4 \pm 1)\%\), and when aggregated, it is 0.1\% or less. The fluorescence emission lacks the mirror-image appearance that is typical of monomeric PDI.\textsuperscript{53}
Figure 3.2. UV-Vis absorption spectra of 1 solvated in THF (blue) and aggregated in water:THF, 4:1 v/v (red). Fluorescence spectra are shown as dashed lines. The emission spectrum of the aggregate was multiplied by 8-fold for ease of comparison.
Femtosecond-to-microsecond Transient Absorption Spectroscopy.

Solvated dimer. Fs-TA spectra of solvated 1, excited with 530 nm, 1 μJ pulses are presented in Figure 3.3A. Similar spectra are observed with 395 nm excitation. Decreased absorption (or, bleach) from ~490 to ~620 nm is observed after excitation, portions of which resemble the (inverted) ground state absorption spectrum. The absorption changes are otherwise positive. There are at least two absorption bands in the range 620−800 nm, and the strongest has a maximum at ~730 nm (1.7 eV). The 730 nm band decays biexponentially with time constants 40±10 ps (~5% amplitude) and 730±40 ps (95%) (Figure 3.4A). Other apparent maxima in the transient spectra at ~390, 440, and 475 nm are likely caused by minima and maxima of the ground state absorption (GSA) that are impressed upon a relatively featureless excited state absorption (ESA). The decay of the 430 nm band occurs primarily with a time constant of 860±50 ps.

Nanosecond-microsecond transient absorption spectra of solvated 1, excited with 525 nm light, are shown in Figure 3.5A. The maximal transient absorption is at ~500 nm, and weaker absorption is observed from ~640 to 800 nm. These TA bands decay with a single exponential time constant of 150±30 μs.
Figure 3.3. Transient absorption spectra of I. (A) Solvated in THF, with excitation at 530 nm, 1 µJ/pulse. The region near 530 nm is not shown because of scattering artifacts from the pump. The dashed spectrum is the ground-state (GS) absorption, inverted and scaled for comparison with the transient spectra. (B) Aggregated I in water:THF (4:1 v/v), with pump excitation at 395 nm, 1 µJ/pulse. The region 750-850 nm in the transient spectra is not shown because of the uneven white light in this spectral range.
Figure 3.4. Transient absorption kinetics of 1. (A) Solvated in THF, with pump excitation at 530 nm and probe at 730 nm. Energy per pulse is 0.5 µJ (blue), 1.0 µJ (red), and 1.5 µJ (green). The data points and fits are normalized to illustrate overlap and offset for clarity. (B) Aggregated in water:THF (4:1 v/v), with pump excitation at 530 nm and probe at 497 nm. Kinetic decays obtained with energy per pulse 0.5 µJ (blue), 1.0 µJ (red), and 3.0 µJ (green), fitted with a time-dependent second order model. (Inset) Kinetics at early times.
Figure 3.5. Microsecond transient absorption spectra. (A) Direct excitation of solvated 1 in toluene, excited with 525 nm light, ~0.2 mJ/pulse. (dotted line) Triplet excited solvated 1 in toluene, sensitized with $^3\text{ZnTPP}$. Spectrum is reprinted from an earlier publication.\textsuperscript{32} (B) Direct excitation of aggregated 1 in water:THF (4:1 v/v), with 525 nm excitation, ~0.3 mJ/pulse. Regions near the excitation wavelength are deleted due to scattering artifacts.
**Aggregated Dimer.** Fs-TA spectra of aggregated 1, excited with 395 nm, 1 µJ pulses are presented in Figure 3.3B. Similar spectra are found with 530 nm excitation, but scattering at this wavelength interferes with an important ESA band. The strongest ESA band for aggregated 1 is centered at ~500 nm, and reaches its maximum amplitude within 0.5 ps. Previously reported TA spectra of aggregated 1 showed a ~500 nm band that was significantly smaller. The difference is possibly caused by an optical artifact of the earlier experiment. Nevertheless, the kinetic behavior reported previously is the same as found in the present study. Specifically, the decay of the transients at 500 nm (Figure 3.4B) and other wavelengths in the red and near-IR are strongly dependent on the energy of the pump excitation. Datasets of either study yield similar decay constants, using equations and fitting methods that are described below.

Three wavelengths (472, 570 and 682 nm) are near-isosbestic points for the aggregate TA spectra. Isosbestic points are consistent with relaxation of one excited-state species back to the ground state; or possibly simultaneous decay of a transient pair (e.g. cation and anion, via charge recombination). To better characterize the excited state or intermediate species, the ESA of aggregated 1 was simulated for a select time delays by adding small fractions of GSA to the transient difference spectra. The simulated ESA was considered optimum when the smallest fraction of GSA was added, and when the spectrum was positive at all wavelengths. Addition of ~5% GSA to the 500 fs transient difference spectrum was sufficient to generate positive ESA at that time delay (Figure 3.6).
The nanosecond transient spectrum for aggregated 1 was acquired with 525 nm excitation (Figure 3.5B). Bands at 490 nm and 700–800 nm decay exponentially with a 100±40 µs time constant, and no power-dependence was found.
Figure 3.6. (Upper) Excited state absorption (ESA) for 1 aggregated in water:THF (4:1, v/v) at 0.5 ps delay. The ESA spectra are simulated by the addition of the ground state absorption (GSA) spectrum (dashed line) in the indicated proportions to the raw fs-TA spectrum (red line). The optimum addition of GSA is 5.2%. (Lower) Comparison of aggregate ESA to the T1 ESA. The T1 ESA was generated from addition of GSA to the triplet sensitized spectrum of 1 solvated in toluene.32
**Modeling Excited State Annihilation.** The power-dependence found for the aggregate of 1 (Figure 3.4) is characteristic of a bimolecular process. The simplest equation for modeling the decay is

\[
\frac{dn}{dt} = -\gamma_0 n^2 - \frac{n}{\tau}
\]  

(3.3)

where \( \gamma_0 \) is the second order rate constant, \( n \) is the exciton population, and \( \tau \) is the intrinsic first order lifetime. This simple model assumes a homogeneous exciton density and isotropic exciton mobility. However, the kinetics do not fit well to this model (Figure 3.7).
Figure 3.7. Transient absorption kinetics of $1$ aggregated in water:THF, with pump excitation at 530 nm (1.0 µJ) and probe at 497 nm. Data fitted with second-order rate law with time-independent rate constants of $0.7 \times 10^{-9}$ cm$^3$/s (dotted), $1 \times 10^{-9}$ cm$^3$/s (solid), and $3 \times 10^{-9}$ cm$^3$/s (dashed). The red trace is the time-dependent non-Markovian fit, as shown in Figure 3.4.
Instead, the aggregate excited state decays are better fit to a modified bimolecular model that is appropriate for exciton-exciton annihilation.\(^5^4\)

\[
\frac{dn}{dt} = - \frac{f \gamma n^2}{\sqrt{t}} - \frac{n}{\tau}
\]

(3.4)

The factor \(\gamma\) is termed the annihilation constant (units \(\text{cm}^3 \text{s}^{-1/2}\)). The factor \(f\) is a scalar that depends on the number of excitons that remain after each annihilation event. If both excitons return to the ground state, then \(f = 1\). For typical singlet-singlet annihilation, one singlet excited state remains and \(f = 1/2\).\(^5^5\) The long-time kinetics (500–2500 ps) of aggregated 1 decay were fitted with an exponential \(\tau\) of \(-0.8\) ns at both 497 and 705 nm. The first order decay time is uncertain, partly because the amplitude of this decay component was small in our TA experiments, and because the maximum delay time was limited to 2.5 ns.

The kinetic decays of aggregated 1 are fit with the integrated solution to Eq 4,\(^5^4\)

\[
A(t) = \frac{A_0 \exp(-t/\tau)}{1+k \cdot \text{erf} \left( \frac{t}{\sqrt{\tau}} \right)} + y
\]

(3.5)

\[
k = f \cdot \gamma \cdot n_{agg}(1^*) \cdot \sqrt{\pi \cdot \tau}
\]

(3.6)

where \(A_0\) is the \(t = 0\) absorption amplitude, and \(y\) is the residual amplitude at long times. The calculated number densities of excitons within the aggregates, \(n_{agg}(1^*)\) is determined from Equations 3.1 and 3.2, and the values vary from \(2 \times 10^{19}\) to \(14 \times 10^{19}\) \(\text{cm}^{-3}\), depending on excitation energy. The annihilation constant that results from fits to the set of decay curves at both 497 and 705 nm is \(\gamma = (7 \pm 2) \times 10^{15} \text{ cm}\(^3\) \text{s}^{-1/2}\). The values are all within \(3 \times 10^{-15} \text{ cm}\(^3\) \text{s}^{-1/2}\) of each other, when surveyed across the range of
exciton densities. Also, the values of gamma did not vary much if $\tau$ were greater than 0.8 ns (see Appendix).

The inverse dependence on time in equation 3.4 arises from the depletion of excitons.$^{41}$ The specific exponent $t^{-1/2}$ is appropriate for two situations.$^{56}$ First, it can describe exciton diffusion and collision in one dimension. Second, annihilation via Förster resonance energy transfer (FRET) can also have the $t^{-1/2}$ term. In a 1D diffusion scenario, the diffusion coefficient, $D$, is related to the annihilation constant,$^{55}$

$$D = \frac{\pi \cdot (\gamma \cdot n_{agg})^2}{8}$$

(3.7)

where $a$ is the lattice constant equal to 3.5 Å,$^{7,9}$ and $n_{agg}(1)$ is the density of 1 in the aggregate equal to $6 \times 10^{20}$ cm$^{-3}$. Based on equation 3.7, $D = 0.008 \pm 0.005$ cm$^2$ s$^{-1}$. The large error is a result of the squared dependence on $\gamma$. The diffusion length, $L_D$, is determined by,$^{57}$

$$L_D = \sqrt{D \cdot \tau}$$

(3.8)

The experimentally determined $L_D$ for aggregated 1 is $25 \pm 9$ nm.

Annihilation can otherwise occur through FRET interactions in three dimensions.$^{58,59}$ The Förster radius ($R_F$) for annihilating excitons in aggregated 1 is determined by,

$$R_F = \left(\frac{3 \gamma}{2 \pi} \sqrt{\frac{\tau}{\gamma}}\right)^{1/3}$$

(3.9)

Based on the values of $\gamma$ and $\tau$ mentioned above, $R_F$ is equal to $4 \pm 1$ nm.
3.3 Raman Spectroscopy.

**Raman spectroscopy of aggregated 1 in the ground state.** The ground state Raman spectrum for aggregated 1 is shown in Figure 3.8. The mode assignments are divided into five regions based on our previous work with solvated 1.32

1) 1000-1300 cm\(^{-1}\) contains mostly CH rocks;
2) 1300–1500 cm\(^{-1}\) contains collective CC stretches of the perylene core;
3) 1500–1620 cm\(^{-1}\) contains CC stretches of the perylene core, but with less collective movement and more nodes,
4) 1620-1750 cm\(^{-1}\) is attributed to carbonyl stretches; and
5) 2100–2200 cm\(^{-1}\) is assigned to the ethyne stretch.

The experimental Raman spectrum for the ground state of aggregated 1 in water:THF (4:1, v/v) has band positions that are in most cases within 1–4 cm\(^{-1}\) of the solvated 1 spectrum. The main spectral change caused by aggregation is a 20 cm\(^{-1}\) downshift of the ethynyl stretch, from 2178 cm\(^{-1}\) for solvated 1 to 2158 cm\(^{-1}\) for aggregated 1. The downshift is likely caused by structural flattening of 1 in the aggregate. A similar phenomenon was observed for polydiacetylene.60
Figure 3.8. Raman spectra of 1. (A) Ground state, solvated in toluene, 488.0 nm probe. (B) Ground state, aggregated in water:THF (4:1 v/v), 488.0 nm probe. (C) Triplet excited state, in toluene with ZnTPP sensitizer and 405 nm pump, 488.0 nm probe. (D) Same as (C), except with 496.5 nm probe. (E) Excited state of aggregated 1 in water:THF (4:1, v/v) with 405 nm pump, 488 nm probe at 6, 30, and 200 ps delay.
**Picosecond TRRR of aggregated 1.** The time-resolved resonance Raman (TRRR) spectra for aggregated 1 at 6, 30, and 200 ps delay are shown in Figure 3.8. The vibrational bands do not change significantly for these time delays, which supports their assignment to an excited electronic state, rather than a vibrationally hot species. Most bands of the TRRR spectra are downshifted ~10 cm$^{-1}$ relative to the strongest ones of the ground state (~1590, ~1540, ~1320, ~1240 cm$^{-1}$ vs. 1596, 1549, 1334, 1252 cm$^{-1}$). The largest spectral shift is a nearly 30 cm$^{-1}$ downshift of the ethynyl stretch (~2130 vs. 2158 cm$^{-1}$).
3.4 Discussion

A wide range of excited state dynamics is possible for the dimer of PDI and its aggregate. All of the same photophysical processes that are available to crystals, thin amorphous films, and aggregates of PDI are, at least in principle, available to the system studied here. To understand the dynamics of our system, we take the following approach: We first discuss the excited-state behavior of the solvated dimer, and make comparisons to monomers and dimers of PDI as well as other dye dimers that are bound by a single ethynyl group. Next, we focus our attention on the cw and transient electronic spectra of the aggregate of 1. Comparisons to the cw and transient spectra of aggregates, thin films, and crystalline PDI and perylene systems are made. We then summarize the power-dependent kinetic behavior of the aggregate, and compare these findings to other relevant systems. Next, we compare the picosecond Raman spectra of the aggregate with other systems. Finally, we discuss triplet excited state formation in dimers and aggregates of PDI and other organic systems.

Solvated Dimer. Steady-state absorption shows that the two PDI moieties in solvated 1 are strongly coupled through the ethynyl linkage. The lowest energy band of solvated 1 in THF, with maximum at \(~610\) nm, is red-shifted \(~0.25\) eV \((2000\ \text{cm}^{-1})\) relative to the 0-0 vibronic transition of a PDI monomer with two phenoxy substituents.\(^{12,15}\) An acetylene-linked PDI dimer without bay region substituents has its lowest energy absorption band at 582 nm.\(^{29}\) Similar to 1, that dimer is red-shifted 1870 cm\(^{-1}\) relative to the 0-0 absorption band of unsubstituted, monomeric PDI.\(^{29}\) The smaller transition energy of the dimers is attributed to delocalization of the HOMO and LUMO orbitals over both chromophores.
The solvated 1 fs-TA spectrum is dominated by a strong band at ~720 nm and a smaller absorption band in the region 400–480 nm, Figure 3.3. The features are maximum after vibrational cooling, ~10 ps. This absorption profile is similar to the absorption of other PDI molecules in the excited S₁ state. Figure 3.3 shows how the ~700 nm band changes shape between 12 and 52 ps. At this time, the ~700 nm band begins to flatten, the shoulder at ~640 nm becomes stronger, and the maximum at 440 nm red-shifts. These changes occur with a time constant of 40±10 ps. The explanation for the spectral evolution on the <50 ps timescale, whether it involves changes in the extent of excited-state delocalization, or perhaps a charge-transfer process, is uncertain.

The principle decay time is 730±40 ps. A Strickler-Berg analysis of the absorption and fluorescence spectra yields an estimate of 8 ns for the radiative lifetime (see Appendix). The ratio of the 730 ps lifetime to the 8 ns radiative lifetime, gives a predicted ~9% fluorescence quantum yield. This yield is similar to the measured FQY. The match supports the viewpoint that the 730 ps time constant is a decay time for an emissive state.

The relaxation of the excited state to the ground state is faster than most PDI excited states of monomers and dimers. It is likely that the internal conversion is accelerated by the flexibility of the linker, via the free rotor effect. A similar increase in the rate of internal conversion was reported for acetylene linked zinc porphyrin dimers. Those dimers have an S₁ lifetime of 0.45–1.13 ns, which is 3 to 6 times shorter than the S₁ lifetime for monomeric zinc porphyrin.
The ns-TA spectra of solvated 1 (Figure 3.5A) have a strong band at 500 nm. The triplet state of 1 is known from sensitization experiments to have its most prominent absorption in the visible region, centered at ~500 nm.\textsuperscript{32} Similarly, for other PDI derivatives, absorption in the 400–500 nm region is typical of the $T_1 \rightarrow T_n$ transition.\textsuperscript{53, 61, 62} The long exponential decay, $150\pm30 \, \mu$s, observed for the 500 nm band is the same as the $T_1$ lifetime of 1 measured by triplet sensitization, $140\pm10 \, \mu$s.\textsuperscript{32} The small triplet quantum yield, 1-10\%, indicates that the time constant for $T_1$ formation is on the order of 10–100 ns.

**Aggregated Dimer.** Significant changes in the absorption spectrum are observed for the aggregate compared to solvated 1, Figure 3.2. The most prominent change is a ~1000 cm\textsuperscript{-1} red-shift in the lowest energy vibronic band. The shift cannot be attributed to J-type exciton coupling because typical J-type aggregates have a strong, narrow, red-shifted absorption.\textsuperscript{67, 68} Therefore, the red-shift in aggregated 1 is likely caused by non-resonant dispersion interactions (gas-to-crystal shifts).\textsuperscript{69} Red-shifted absorption maxima have been predicted and observed for many different stacking geometries of PDI crystal packing.\textsuperscript{52}

Previously this aggregate was shown to be aligned in a transverse slipped stack (along its short end),\textsuperscript{40} and the steady-state spectroscopy shown here corroborates that model. In the absorption spectrum, the intensity of the 0→1 vibration is larger than the 0→0 mode, which shows up as a shoulder. This vibrational progression is consistent with H-type coupling.\textsuperscript{10} Further, the reduction in fluorescence quantum yield for aggregated 1 is consistent with the quenched fluorescence observed in systems with strong H-type interactions, such as solid PDI\textsuperscript{7} and crystalline perylene.\textsuperscript{70}
**Excited State Identification and Exciton Mobility.** The most prominent band in the aggregated 1 TA spectra has a maximum at ~500 nm, which suggests an assignment to the triplet excited state.\textsuperscript{30, 32, 53} A comparison of the fs-TA ESA spectrum at 500 fs to the triplet sensitized ESA spectrum supports this correlation (Figure 3.6). However, compared to T\textsubscript{1}, the fs-TA spectra for aggregated 1 have a much stronger absorption in the region between 580 and 750 nm. That absorption is more consistent with the S\textsubscript{1} or delocalized S\textsubscript{1} state.\textsuperscript{15, 23} A charge-separated state is ruled out because of the strong absorption at 500 nm, which is absent in the chemically reduced spectrum of aggregated 1. Therefore, the fs-TA spectra support the identification of the excited state as either the T\textsubscript{1} or S\textsubscript{1} state.

The strong power dependent kinetic decays for aggregate 1 are consistent with S\textsubscript{1}−S\textsubscript{1} annihilation. The annihilation constant measured for aggregated 1 lies within the range of values measured for singlet-singlet annihilation in thin films of PTCDA.\textsuperscript{55} The diffusion coefficient, 0.008±0.005 cm\textsuperscript{2}s\textsuperscript{-1}, measured for aggregated 1 is consistent with S\textsubscript{1} diffusion in other PDI assemblies. Singlet excited state diffusion in a PDI J-aggregate and PTCDA thin film, are ~0.01 and 0.04±0.01 cm\textsuperscript{2}s\textsuperscript{-1}, respectively.\textsuperscript{37, 55} Self-assembled crystalline nanosheets of PDI dimers and trimers were recently reported to have 1D excited singlet state diffusion coefficients equal to 0.08±0.02 and 0.016±0.005 cm\textsuperscript{2}s\textsuperscript{-1}, respectively.\textsuperscript{34} The diffusion length, \(L_D\), 25±9 nm, is within the normal range for singlet excitons in organic solids. For instance, singlet excitons in PTCDA thin films have a \(L_D\) equal to 10.4 nm,\textsuperscript{71} and PDI J-aggregates have a diffusion length equal to ~100 nm.\textsuperscript{37} Singlet excitons in naphthalene, tetracene, and perylene crystals have diffusion lengths equal to 50, 12, and 2 nm, respectively.\textsuperscript{41}
Furthermore, the measured Förster radius, is similar to values reported for singlet excited states in other PDI and perylene dianhydride assemblies.\textsuperscript{37, 55}

Conversely, the ultrafast second order decay is not consistent with T\textsubscript{1} behavior. In general, triplet-triplet annihilation within low-molecular weight organic systems cannot occur via a FRET mechanism because of the extremely weak oscillator strength for the T\textsubscript{1}→S\textsubscript{0} transition. The low oscillator strength is certainly true for \textsuperscript{3}PDI*, and it is only recently that the first reports of phosphorescence from such a system appeared.\textsuperscript{46, 72, 73} Thus, if the excited state species is in the triplet excited state, then the mechanism of energy transfer must be short-range (Dexter, diffusion-limited). However, the measured diffusion coefficient for aggregated \textbf{I} is much faster than tabulated T\textsubscript{1} diffusion coefficients. Triplet excited states in crystalline pyrene, naphthalene, and anthracene have $D$ equal to $0.30\times10^{-4}$, $0.33\times10^{-4}$, and $1.50\times10^{-4}$ cm$^2$s$^{-1}$, respectively.\textsuperscript{69} Therefore, the kinetics model confirms that the excited aggregate populates the S\textsubscript{1} state.

The $D$ and $L_D$ calculations assume that the exciton is localized on one dimer. The cw absorbance spectrum for aggregated \textbf{I} shows evidence that the dimers are strongly coupled to one another when aggregated, and therefore, the exciton is delocalized over more than one dimer. Other researchers have shown that excitons in strongly coupled aggregates are delocalized.\textsuperscript{37, 74, 75} The lattice coefficient can be considered an estimate of exciton size if localized to one molecule,\textsuperscript{37} and the value used in Eq 3.7 is 3.5 Å. If the excited states are delocalized over two dimers, then $a$ would double.\textsuperscript{37} Carrying this increased exciton size through the calculations would result in an $L_D$ equal to 50 nm if the exciton is distributed over two dimers ($a$ = 7.0 Å).
and 75 nm if distributed over three dimers ($a=9.5$ Å). Further measurements would need to be carried out to determine the extent of exciton delocalization. With our inconclusive understanding of the exciton size, we can report that the exciton diffusion length is equal to or greater than 25 nm.

The identity of the excited state population changes at long times. The $T_1$ and charge separated states are both populated in the nanosecond-to-microsecond regime. The 500 nm feature is assigned to the triplet-excited state. The second transient species is likely a charge transfer state, with a broad absorption $>670$ nm.

**Excited State Raman Spectra.** Here we summarize the few reports of PDI excited state Raman spectra.\textsuperscript{18, 32, 76, 77} The bands are labeled as strong (s), medium (m), or weak (w) strength relative to the other bands in the spectrum. Femtosecond stimulated Raman spectroscopy (FSRS) was used to collect the $S_1$ spectra for two different PDI monomers\textsuperscript{76, 77} and a cofacial PDI dimer.\textsuperscript{18} The first PDI monomer, PDI-C8, has octyl chains attached to its imide groups. The $S_1$ Raman spectrum for PDI-C8 has bands at 1728(s), 1595(s), 1544(m), 1516(m), 1442(m), 1401(m), and 1301(m) cm$^{-1}$.\textsuperscript{77} The second PDI monomer, PDI-Xy, has a xylene group and a heptyloctyl group attached to either of its imide ends. The $S_1$ Raman bands for PDI-Xy are 1677(w), 1593(s), 1525(m), 1474(w), 1419(w), 1367(m), 1298(m) cm$^{-1}$.\textsuperscript{76} Finally, the cofacial PDI dimer has $S_1$ Raman bands at 1523(s) and 1588(s) cm$^{-1}$.\textsuperscript{18} The $S_1$ Raman spectrum for aggregated 1 has perylene core stretches at $\sim$1590(s), 1540(s), 1320(s), and 1240(w) cm$^{-1}$, Figure 3.8.

There are significant differences between the documented $S_1$ Raman spectra. For instance, even a comparison of the two monomeric PDI FSRS spectra yields
several dissimilarities: (1) PDI-C8 has a strong band at 1728 cm\(^{-1}\) and medium strength band at 1442 cm\(^{-1}\) that are both absent for PDI-Xy, (2) PDI-Xy has a medium strength band at 1367 cm\(^{-1}\) that is absent for PDI-C8. Furthermore, the aggregated \(\mathbf{1}\) \(S_1\) spectrum has a strong band at 1320 cm\(^{-1}\) that is absent in the \(S_1\) spectra of the other molecules. Despite the differences, one can at least conclude from all four \(S_1\) spectra, that the \(S_1\) state has a strong band at 1590±5 cm\(^{-1}\). However, that ~1590 cm\(^{-1}\) band is not unique to the \(S_1\) state. FSRS spectra of the PDI anion monomer\(^{76}\) or a cofacial dimer\(^{18}\) have a strong band at 1588 cm\(^{-1}\).

One significant source of the inconsistencies between the \(S_1\) Raman spectra is made apparent from the different ESAs for the molecules studied. For instance, the ESA for aggregated \(\mathbf{1}\) has significantly more absorption strength in the region below 650 nm than do the other PDI derivatives compared here. It follows then, that the delocalized \(S_1\) state for aggregated \(\mathbf{1}\) is different than the \(S_1\) state for monomeric PDI. Therefore, it is not surprising the “\(S_1\)” Raman spectra are also different. More studies of the \(S_1\) excited state of PDI will need to be carried out to better understand this complicated spectrum.

Rather than just comparing the absolute band frequencies, one can also compare the shift in band frequencies between the ground state and \(S_1\) spectra. Excited monomeric PDI and perylene have average downshifts of ~30 cm\(^{-1}\);\(^{76,78}\) whereas, the average downshift for aggregated \(\mathbf{1}\) is ~10 cm\(^{-1}\). The (unusual) behavior for aggregated \(\mathbf{1}\) is firstly attributed to the delocalization of the LUMO over the two PDI moieties in the dimer. The delocalization results in smaller bond length changes, i.e.
frequency shifts, (compared to $S_0$) when the excited state is shared over two chromophores.

In a previous publication from our group, we collected the triplet sensitized resonance Raman spectrum of 1 solvated in toluene.\textsuperscript{32} We found that the $T_1$ state has Raman bands at 1596±1(s), 1535(m), 1506±1(s), 1322±3(m), and 1155±5(m) cm\textsuperscript{-1}, Figure 3.8. The comparison between $S_1$ and $T_1$ spectra is limited to the aggregated $S_1$ and solvated $T_1$ spectra (Figure 3.8).\textsuperscript{32} This limitation arises because the solvated spectrum is too fluorescent for TRRR, and we were unable to triplet sensitize aggregated 1. We observe two significant differences between the spectra: 1.) The $T_1$ bands have a larger average downshift compared to $S_0$ than does $S_1$ (~20 vs 10 cm\textsuperscript{-1}) 2.) The separation between the two high energy bands changes. For the $S_1$ (TRRR) spectrum it is 50 cm\textsuperscript{-1} (~1540–1590 cm\textsuperscript{-1}), compared to 40 cm\textsuperscript{-1} for the solvated ground state (~1550–1590 cm\textsuperscript{-1}), and 90 cm\textsuperscript{-1} for the triplet sensitized spectrum (~1510–1600 cm\textsuperscript{-1}). Overall, when compared to the ground state spectrum, the $T_1$ spectrum changes more significantly than does the $S_1$ spectrum. Unfortunately, because we are comparing an aggregated sample with a solvated one, we cannot tease out if these differences are due primarily to the different excited states or because of exciton delocalization in the aggregate.

In the TRRR spectra a shoulder is observed in the acetylene feature at ~2100 cm\textsuperscript{-1}. The broad acetylene feature (FWHM ~50 cm\textsuperscript{-1}) can possibly be attributed to excimer-like interactions. Excited state delocalization can cause a downshift of the acetylene vibrational frequency by giving the triplet bond more double bond character.
The broadness of the acetylene band might be a result of variable degrees of excimer-like interactions,\textsuperscript{74} where stronger coupling leads to a larger downshift.

**Triplet state formation in solvated and aggregated PDI.** Strongly coupled PDI dimers can have near unity triplet state quantum yields. For instance, \(T_1\) is formed via a charge transfer intermediate in high yields, up to 94\%, in a xanthene-bridged cofacial dimer.\textsuperscript{61} Another PDI dimer has increased spin-orbit coupling as a result of a nonplanar structure. This dimer is fused at the bay region with three parallel single bonds, and has a \(T_1\) yield greater than 90\%.\textsuperscript{72} Solvated dimer 1 has a \(\leq 10\%\) triplet yield. As a result of excited state delocalization, the \(S_1\) energy for dimer 1 is 2.0 eV, which is \(-0.4\) V lower than monomeric PDI.\textsuperscript{53} This excited state lowering increases the energetic barrier to formation of a charge transfer state, and therefore, the pathway for \(T_1\) generation through charge recombination is less favorable. Furthermore, while the dimer can move freely about the acetylene linker, the perylene cores are not distorted, as is the case in the example above. Finally, a singlet fission mechanism is unlikely for solvated 1 because the yield is \(<100\%\) and the triplets are generated at late times (> 2.5 ns).

For some chromophores, such as carotenoids,\textsuperscript{49, 79, 80} aggregation can enable the singlet fission pathway. For PDI molecules specifically, slipped stacked alignment of the planar pi-systems have been predicted\textsuperscript{43} and shown\textsuperscript{46} to facilitate singlet fission. Despite the strong exciton coupling observed for aggregated 1, we did not observe singlet fission. Ratner et. al\textsuperscript{45} showed through simulations that the promotion of the singlet fission mechanism is sensitive to chromophore coupling. Studies on polycrystalline thin films of 1,3-diphenylisobenzofuran (DPBF) demonstrate this
Two crystal packing arrangements of DPBF were studied, α and β. The α crystal packing promoted efficient singlet fission with a quantum yield of 140%. However, the more strongly coupled β packing resulted in a quenching of triplet state formation and instead promoted formation of the excimer state. Lastly, the relative $E(S_1)$ and $E(T_1)$ energies of 1 were impaired by self-assembly of 1. The energy of the $S_1$ state decreases to 1.9 eV, and the $T_1$ energy is expected to be unaffected by aggregation.
3.5 Conclusions

The excited state dynamics for solvated and aggregate 1 are summary in Figure 3.9. The delocalized $S_1$ state is the primary excited state for solvated 1 at early times. This state decays primarily through fast internal conversion. An observable portion (1–10%) of the $S_1$ state decays into the $T_1$ state. Self-assembled 1 forms H-type aggregates in water:THF (4:1). Aggregated 1 populates a delocalized excited $S_1$ state. The Raman spectra of aggregated 1 shows smaller spectral shifts between the $S_0$ and $S_1$ states compared to other literature because of the delocalization of the excited state over the two PDI chromophores. At the excitation densities studied here, the majority of excited states decay via singlet-singlet annihilation. This annihilation can occur through 1D diffusion or FRET. In the future, pump-probe polarization studies could be used to determine which model is dominant.\textsuperscript{37}
Figure 3.9. Summary of excited state dynamics for (left) solvated and (right) aggregated 1.
References


Appendix of Chapter 3

A3.1. Determination of molar absorption coefficient.

The molar decadic absorption coefficients of solvated 1 in the 300-700 nm spectral window were determined in chloroform, a solvent which was known to minimize its aggregation. Small quantities of 1 with masses in the range of 0.1 to 0.3 mg were measured with a microbalance (Cahn C-31, accuracy 0.0005 mg). Quantities of chloroform sufficient for 3 to 20 µM solutions of 1 were measured with an analytical balance (Mettler-Toledo AB204). Absorption spectra were collected in a 2 mm quartz cuvette with a UV-Vis spectrometer (Shimadzu, UV-3600). The molar decadic absorption coefficient at the maximum in the spectral window (537 nm) was determined from the slope of a least-squares fit to a plot of $A(537 \text{ nm})$ versus concentration (Figure A3.1-A). The absorption coefficient values in THF and in water:THF (4:1 v/v) were determined relative to the values in chloroform.
Figure A3.1. (A) Determination of the molar decadic absorption coefficient of 1 solvated in chloroform at its maximum (537 nm). (B) Comparison of the molar absorption coefficients of 1 in chloroform, THF, and aggregated in water:THF (4:1 v/v).
The maximum absorption coefficient of aggregated 1 in water:THF in the visible region decreases by nearly a factor-of-two compared to solvated 1. However, the integrated area of the absorption coefficient/wavenumber vs. wavenumber for the aggregate, i.e. oscillator strength, is 80% that of solvated 1.
Figure A3.2. Absorption spectra divided by wavenumber for 1 (A) solvated in THF and (B) aggregated in water:THF (4:1, v/v) plotted on an energy axis. The ratio of the integrated areas, i.e. oscillator strengths, is 1.2:1.
A3.2. Determination of the radiative lifetime for solvated 1.

The radiative lifetime, $\tau_{rad}$, of solvated 1 was estimated using the Strickler-Berg relationship,

$$\frac{1}{\tau_{rad}} = 2.880 \times 10^{-9} \cdot \eta^2 \cdot \frac{\int I(v) dv}{\int I(v) v^{-3} dv } \cdot \int \frac{\varepsilon(v)}{v} dv$$

(A3.1)

where $\eta$ is the refractive index of the solvent, $I(v)$ is the emission intensity as a function of wavenumber, $v$ is wavenumber, and $\varepsilon(v)$ is the absorption coefficient as a function of wavenumber. Using this relationship, the radiative lifetime, $\tau_{rad}$, is estimated as 8.25 ns.

Figure A3.3 shows the area of the absorption spectrum used for the calculation. The Strickler-Berg analysis is most accurate within the limitation that there is “mirror image” symmetry between the absorption and emission spectra. That symmetry is absent for solvated 1 for two reasons: (1) the strongly allowed absorption to higher lying singlet states above $S_1 (>20,000 \text{ cm}^{-1})$ and (2) the delocalization of the excited state over the two PDI chromophores in the dimer. As shown below, the area of the absorbance spectrum chosen for the integration is as close to a “mirror image” to the emission spectrum as is possible. The ~8 ns radiative lifetime calculated with this relationship should be considered an estimate.
Figure A3.3. Normalized absorbance and fluorescence spectra for solvated 1 in THF.
A3.3. Steady-state absorbance spectra of chemically reduced 1.

Reduction of 1 in either solvated or aggregated forms was performed via a photochemical method, utilizing triethylamine (TEA) as the electron donor. TEA (Acros) was purified by passing it through a silica column, and two or three drops were added to several milliliters of aggregated or solvated solutions of 1 in a glovebox. The concentration of TEA in solution was 150–250 mM. The oxygen-free samples were loaded into a sealed cuvette and exposed to 45–50 mW of 568 nm cw-laser light from an argon/krypton ion laser. The beam was defocused along one axis with a cylindrical lens. The photolytic reduction occurred for up to one hour, and the progress was monitored by acquiring UV-Vis absorption spectra every several minutes.

The steady-state absorption spectrum of photochemically reduced 1 in THF shows an increase in absorption coefficient at approximately 728 and 1032 nm and a decrease from ~550–650 nm, compared to neutral 1. This result is similar to other reduced PDI monomer and dimer systems that report a steady-state anion absorption at ~600–800 nm. The reduction of aggregated 1 produces a broad increase in absorption in the near-IR with maxima at 752, 837, and 1052 nm, and no significant increase in absorption was observed at 500 nm.
Figure A3.4. Photochemical reduction of 1 with triethylamine as the reducing agent and 568 nm photolysis. (Upper panel) Solvated dimer in THF. (Lower panel) Aggregated 1 in water:THF (4:1 v/v).
A3.4. Fs-TA spectra and kinetics.

Additional femtosecond transient absorption spectra and kinetic decays for solvated and aggregated 1 are included in this section as complements to the data shown in the main paper. The excited state absorption spectra of solvated 1 at 10 ps and 2.5 ns are also included.
Figure A3.5. Transient absorption spectra of dimer 1, acquired with complementary excitation wavelengths relative to the results shown in Figure 3.3. (Upper panel) Solvated in THF with pump excitation at 395 nm, 0.5 µJ/pulse. The dashed line depicts the ground-state (GS) absorption spectrum of the dimer, inverted and scaled for comparison with the transient spectra. (Lower panel) Aggregated in water:THF (4:1 v/v) with pump excitation 530 nm, 1 µJ/pulse. The dashed line is the inverted GS spectrum of the aggregate. The gap near 530 nm is caused by scattering from the pump laser. The gap 750-850 nm is caused by instability of the white light near the 800 nm wavelength of the fundamental.
Figure A3.6. Fs-TA decay kinetics for solvated 1 in THF with 530 nm excitation. Residuals for each fit are shown in red.
<table>
<thead>
<tr>
<th>Probe nm</th>
<th>Pulse Energy (µJ)</th>
<th>% Ex</th>
<th>$\tau_1$ ps</th>
<th>$\tau_2$ ps</th>
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<td>0.5</td>
<td>12%</td>
<td>810±40</td>
<td>--</td>
</tr>
<tr>
<td>430</td>
<td>1.0</td>
<td>23%</td>
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<td>34%</td>
<td>910±30</td>
<td>--</td>
</tr>
<tr>
<td>730</td>
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<td>12%</td>
<td>40±10</td>
<td>700±40</td>
</tr>
<tr>
<td>730</td>
<td>1.0</td>
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<tr>
<td>730</td>
<td>1.5</td>
<td>34%</td>
<td>40±4</td>
<td>760±20</td>
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Figure A3.7. Second order kinetic decays, fit with equation 3.5, for aggregated 1 in water:THF (4:1, v/v) excited with a 530 nm pump. Pump energy and probe wavelengths are listed next to each decay. The shape of the decays is a curved line with the y-axis set to a log scale, which highlights the second order nature of the kinetics.
The intrinsic lifetime does not affect the fitted annihilation constant, $\gamma$.

The intrinsic lifetime, tau, for aggregated 1 is estimated from fitting the decay in the region 700–2400 ps with the first-order fit equation, Figure A3.8. The average tau fitted for the decays collected at three different pump energies is 0.8 ns. There is significant uncertainty in that value because: (1) for the data collected, the excited species is mostly decayed by 200 ps, and (2) the delay stage of the fs-TA system is limited to 2.5 ns.
Figure A3.8 Kinetic decays of aggregated \( 1 \) in water:THF, with pump excitation at 530 nm and probe at 497 nm. Data obtained with pulse energies 0.5 \( \mu \text{J} \) (\( n \)), 1.0 \( \mu \text{J} \) (\( \Delta \)), and 3.0 \( \mu \text{J} \) (\( \cdot \)), fitted with a first order exponential fit to estimate excited state lifetime in the absence of annihilation.
Here we show the aggregate decays from 0–2400 ps fitted with Eq. 3.5. The fit parameters vary only by the value of tau: 0.8, 8.0, or 80 ns. For all values of tau, the fit to the data in the region 0–200 ps is the same, but the fits vary after 700 ps, Figure A3.9. The $\gamma$ values for all three fits are identical within error, Table A3.2.
Figure A3.9. Kinetic decays of aggregated 1 in water:THF, with pump excitation at 530 nm (1.0 µJ) and probe at 497 nm. Data fitted with second order kinetic fits, Eq. 3.5, with varying tau values. (Left) Decay in region 0–200 ps. (Right) Decay in region 500–2400 ns.
Table A3.2. Annihilation constants for data fitted with different values of tau.

<table>
<thead>
<tr>
<th>Laser Power ( mW )</th>
<th>tau ( ns )</th>
<th>Fitted k</th>
<th>%Ex</th>
<th>Gamma ( cm^3 s^{-1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.8</td>
<td>5.3</td>
<td>3.8%</td>
<td>9.3E-15</td>
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<tr>
<td></td>
<td>8.0</td>
<td>14.9</td>
<td>3.8%</td>
<td>8.2E-15</td>
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<td>80.0</td>
<td>45.0</td>
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<td>1.0</td>
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<td>7.6%</td>
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<tr>
<td></td>
<td>80.0</td>
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<td>5.8E-15</td>
</tr>
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<td>3.0</td>
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<td>21.3</td>
<td>23%</td>
<td>6.2E-15</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>63.7</td>
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<td>5.9E-15</td>
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<tr>
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<td>80.0</td>
<td>199.1</td>
<td>23%</td>
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</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>(7±2)E-15</td>
</tr>
</tbody>
</table>
Simulation of solvated 1 excited state absorption spectra. Small fractions of the ground state absorption (GSA) were added to the transient difference spectra of 1 in THF at 10 ps and 2.5 ns time delay (Figure A3.10). The addition of GSA was considered optimum when (1) the excited state absorption (ESA) in the region 400–600 nm was fully positive over the visible spectrum; and (2) local minima at ~390, 440, and 475 nm were removed. The minimum percentage of GSA addition that met these two criteria were 5% (at 10 ps time delay) and 0.8% (at 2.5 ns). Comparison of the simulated ESA spectra at 10 ps and 2.5 ns shows that the relative amplitudes of the 430 and 730 nm features vary with time. The absorption at 730 nm is nearly twice as large as the 430 nm feature at 10 ps; whereas the 430 nm band is the stronger one at 2.5 ns. This result supports the contribution of two (or more) transient species in the photophysics of solvated 1.
Figure A3.10. Excited state absorption (ESA) for 1 solvated in THF at 10 ps and 2.5 ns delay. The ESA spectra are simulated by the addition of the ground state absorption spectra (dashed lines) in the indicated proportions to the raw fs-TA spectra (red lines).

**Solvated 1.** The microsecond kinetic decays for 1 dissolved in toluene were found to have two exponential components (amplitude in parentheses). At 500 nm the time constants are 160±10 µs (86%) and 10±1 µs (14%), and at 740 nm they are 140±10 µs (62%) and 10±1 µs (38%). The longer decay is assigned to the triplet-excited state. The shorter decay could be the relaxation of a small population of the charge-separated state.
Figure A3.11. Kinetic decays for solvated 1 in toluene, excited with 525 nm light, ~0.2 mJ/pulse.
**Aggregated 1.** The microsecond-scale kinetic decays for aggregated 1 are displayed below, Figure A3.12. The decays at 490 and 720 nm are normalized to highlight the absence of a power dependence. The transient signals were also monitored as a function of oxygenation. The decay at 490 nm, assigned primarily to triplet absorption, is very sensitive to oxygen quenching. The decay at 720 nm is not as sensitive to the presence of oxygen.
Figure A3.12. Normalized decay kinetics for aggregated 1 in water:THF (4:1, v/v) in nitrogen and oxygen environments with 525 nm, ~0.3 mJ/pulse excitation.
References


Chapter 4 The lowest triplet (T\textsubscript{1}) excited state of oligothiophenes probed by resonance Raman spectroscopy

4.1 Introduction

Triplet excited states (triplets) have played an important role in emerging applications of organic materials. The utilization of triplets in organic light-emitting diodes (OLEDs) was a significant development.\textsuperscript{1-4} More recently, researchers are now considering the use of triplets in organic photovoltaics (OPVs).\textsuperscript{5} Triplet excitons are anticipated to have a positive effect on device efficiency because of their long diffusion distances, up to 10 µm.\textsuperscript{5-7} Triplets have also been linked to detrimental processes in OPVs, namely charge recombination.\textsuperscript{8, 9} The successful utilization of triplet-excited states in devices depends upon a good understanding of their fundamental properties, including yield of formation, energetics, delocalization (or spatial extent), electronic structure, and lifetime.

The aromatic thiophene ring is often incorporated in organic electronic devices.\textsuperscript{10, 11, 12} Polythiophene has exceptional charge transport qualities and stability, and is readily modified.\textsuperscript{13} The triplet state of thiophene molecules has been probed in numerous studies, and a powerful approach involves the spectroscopic study of oligomers.\textsuperscript{13} \textsuperscript{14-17} For instance, transient absorption spectroscopy, combined with
excited state energy transfer, was used to determine the length-dependence of oligothiophene triplet state energies.\textsuperscript{16, 17} The spatial extent of the triplet exciton has been studied by EPR,\textsuperscript{18} optical absorption,\textsuperscript{17} and DFT calculations.\textsuperscript{19} Those studies found that the triplet state is delocalized over four or more rings. Quantification of the excited state spatial extent is important for understanding exciton dynamics, including the rate of diffusion,\textsuperscript{20} and the determination of excited state delocalization continues to be a lively topic for research.\textsuperscript{20-22}

Surprisingly, there are no reports in the literature of resolved vibrational spectra of oligothiophenes in their triplet-excited states. Here we probe the length-dependence of the resonance Raman spectra of triplet oligothiophenes, Figure 4.1. We find a convergence of the spectral band frequencies, and overall profile, for the heptamer, octamer, and nonamer. The number and placement of substituents on the molecules are also probed by comparing the spectra of three pentamer molecules with two, four, and six octyl substituents. Our experimental spectra are analyzed by comparing with calculations using density functional theory.
Figure 4.1. Oligothiophene molecules for resonance Raman experiments.
4.2 Experimental

**Synthesis and steady-state characterization.** The oligothiophene molecules in Figure 4.1, with the exception of the tetramer, were synthesized via methods described elsewhere. Molecules were purified with silica chromatography. The tetramer, 4T-dz, was purchased from Sigma-Aldrich and used as received. Tetrahydrofuran (THF) for spectroscopy was HPLC-grade and inhibitor-free (Fisher Scientific). THF was purified and dried with an alumina column immediately prior to experiments to remove peroxide impurities. Absorption spectra were measured with a UV-Vis spectrophotometer (Shimadzu, UV-3600). Samples were dissolved in THF, contained in a quartz cuvette with 1 cm pathlength, and measured with a 1 nm bandpass.

**Microscope Raman Spectroscopy.** THF solutions of thiophene (0.3–2.0 mM) were prepared in an argon-filled glovebox. For transient resonance Raman spectroscopy of the octamer and nonamer, anthracene (~6 mM) was added as a triplet sensitizer. Samples were loaded in a glass vial and placed in an atmosphere-controlled brass vessel with an attached quartz capillary (Polymicro, TSP050150). Nitrogen gas (50-350 psi) drove the sample through the capillary.

Resonance Raman spectra of the lowest triplet state were acquired with an upright optical microscope (Zeiss, Axio Imager) that was modified for transient spectroscopy of samples flowing through a capillary. The samples were pumped with a quasi-continuous wave beam (78.8 MHz) which was the second-harmonic of the tunable 750 –800 nm output from a Ti:Sapphire oscillator (Spectra-Physics, Mai Tai). Pump wavelengths were selected to excite thiophene (3T, 375 nm; 4T, 400 nm; 5T, 400 or 415 nm; 6T–7T, 400
nm) or the anthracene sensitizer (8T−9T, 377 nm). An argon/krypton ion laser (Laser Innovations Innova−70C) produced the probe beam. Probe wavelengths were chosen to be near-resonant with the thiophene triplet state (3T, 488.0 nm; 4T, 568.2 nm, 5T−9T 647.1 nm).\(^{14}\)

A dichroic beamsplitter (Thorlabs, DMLP425) external to the microscope was used to send the pump and probe beams into the epi-illumination path. A second dichroic beamsplitter (Chroma, Q430lp) inside the microscope directed the two beams downward through an objective (Seiwa, UV PlanAPO 20×; NA = 0.5, focal length 10 mm). The choice of this apochromatic objective was important for matching the depths of the focal points within the sample capillary, for both the near-UV pump and visible probe wavelengths. The angle of the first beamsplitter was adjusted so that the pump and probe beams entered the objective at slightly different angles, which resulted in a ~25 µm separation of the focused spots, parallel to the direction of the sample flow.

The focused pump and probe beams had diameters of ~2 and ~1 µm, respectively. The pump power was 1-2 mW, and probe power was ~5 mW at the sample. The high probe irradiance likely caused multiple excitations to higher-lying triplet excited states (T\(_1\)→T\(_n\)) during the transit of a molecule through the focus of the probe beam. However, fast T\(_n\)→T\(_1\) relaxation counteracted the excitations. Spectra of 6T-\(\alpha_4\) acquired at 10–100 times lower irradiance matched the spectrum of 6T-\(\alpha_4\) reported here.

The average time delay between pump and probe was calculated to be ~4 µs, based upon the flow rate and pump/probe separation. In some runs, more than half of the large triplet state population could have decayed via triplet-triplet annihilation (TTA) within that time. The time delay was a compromise between the need to reject pump
fluorescence (improved by greater pump/probe separation) and to enhance the triplet population (improved with closer spacing). However, the benefits of high triplet concentration were mitigated significantly by the enhanced delayed fluorescence caused by TTA. Relatively long time delays tended to give the best outcome.

The back-scattered light was directed out of the microscope and into a spatial filter that focused the Raman scattering through a 10 µm pinhole to exclude a significant portion of pump-induced sample fluorescence. The spatial filter decreased the fluorescence background by 20-fold. An edge filter (Semrock) blocked the Rayleigh scattering from the probe. The Raman signal was focused into a spectrograph (Horiba Jobin-Yvon, iHR-320) and dispersed with a 1200 groove/mm holographic grating. Spectrograph slits were 0.024–0.030 mm, which yielded a bandpass of 3 cm$^{-1}$ or less. Spectra were calibrated with a standard solution of acetonitrile and toluene. Cosmic signals were removed manually. Additional experimental details were described previously.$^{25}$

**Ultraviolet Resonance Raman Spectroscopy.** The ultraviolet resonance Raman (UVRR) set-up was reported previously,$^{26}$ but it is briefly summarized here. The excitation beam was generated by a Ti:Sapphire laser (Photonics Industries) and frequency doubled with a lithium triborate (LBO) crystal. Wavelengths were 355, 400, and 435 nm. A backscattering geometry was employed for excitation and collection of the Raman signal. The power at the sample was 1–2 mW. Two cylindrical lenses (focal lengths = 200 and 75 mm) focused the beam at the sample, and the spot size varied with excitation wavelength: ~50x360 µm (355 nm), ~40x210 µm (400 nm), ~30x130 µm (435 nm). Samples were held in a 1 cm pathlength quartz cuvette, and stirred during the
Back-scattered light was collected with a UV compound lens, focused into the entrance slit of a prism prefilter, and dispersed in a spectrograph (JY Horiba, Spex 500 M with 1200 gr/mm holographic grating). The Raman signal was detected with a CCD detector (Roper Scientific, Pixis 400 B). Spectra were calibrated with an ethanol standard, and the spectral response was measured with a mercury lamp. The spectral resolution was ~8 cm\(^{-1}\). Artifacts from cosmic rays were identified by comparing several spectra, and were removed point-by-point.

**Computations.** Normal modes of vibration, and Raman spectra were computed with density functional theory (DFT) using Gaussian 09W software.\(^{27}\) To reduce computation time, calculations were carried out on oligothiophenes with ethyl substituents instead of octyl and dodecyl substituents. The B3LYP functional and 6-31G(d) basis set were used for all ground state computations. The same basis set and functional were used for \(T_1\) calculations, but the spin was unrestricted. The calculated normal mode frequencies were scaled by a factor of 0.9614 that was previously optimized for ground-state calculations,\(^{28}\) and used here for triplet calculations as well.

4.3 Results

**CW absorption spectroscopy.** The oligomer absorption spectra shown in Figure 4.2 are broad and lack vibrational features. The spectra red-shift steadily with an increase in oligomer length. The longer oligomers have a shoulder at ~345 nm (5T-\(O_2\), 8T-\(O_4\), and 9T-\(O_6\)) or ~337 nm (7T-\(O_2\)). Similar features have been previously reported for oligothiophenes.\(^{14}\) The absorption spectra narrow slightly with an increase in oligomer length. The full width at half maximum (FWHM) of the trimer is 6800 cm\(^{-1}\) and for the
nonamer is 6000 cm$^{-1}$. The spectra of the three pentamers are shown in Figure 4.2. The pentamer with substituents only on its outermost rings, 5T-o$_4$, has an absorption maximum at 410 nm. The pentamer 5T-o$_2$ with octyl substituents on its central ring, and 5T-o$_6$ with octyl substituents on both central and outer rings, have blue-shifted maxima at 390 and 386 nm, respectively.
Figure 4.2. UV-Vis absorption spectra of thiophene oligomers in THF. (Upper) Spectra of a series of thiophene oligomers with different numbers of rings. (Lower) Spectra of three pentamers with different numbers of octyl substituents.
Ground state Raman spectroscopy. The off-resonance Raman spectra of the ground-state oligothiophenes are shown in Figure 4.3. The strongest bands are in the ~1385-1530 cm\(^{-1}\) region, and the most intense of them is centered at ~1470 cm\(^{-1}\). This region is attributed to C=C and C−C stretches.\textsuperscript{25,29-31} All of the oligomers have a small feature at about 1050 cm\(^{-1}\) assigned to C–H in-plane bends.\textsuperscript{25,29,31} Bands in the 600-1000 cm\(^{-1}\) frequency region have very low intensity. These modes consist of C–S stretches and ring deformations.\textsuperscript{25,29-32}

The ground state Raman spectra are nearly identical for all seven oligomers, consistent with earlier reports.\textsuperscript{29,33} However, small changes in the high frequency region are observed. The Raman shift for the highest energy band, ~1510–1530, decreases with oligomer length. Additionally, the relative intensity of the two highest frequency bands is less than 2:1 for the trimer and increases to at least 3:1 for the nonamer.
Figure 4.3. Raman spectra of thiophene oligomers dissolved in THF. (Left panel) Ground state. (Right panel) Triplet excited state. The probe excitation wavelengths were 488 nm (3T), 568 nm (4T), and 647 nm (5T–9T). The pump wavelengths for the triplet spectra were 375 nm (3T), 400 nm (4T, 6T, 7T), and 415 nm (5T). The 8T and 9T triplet excited states were generated through sensitization from triplet-excited anthracene generated with 377 nm light.
Figure 4.4 displays resonance Raman spectra of the trimer, hexamer, and nonamer in the ground state. The band positions and relative intensities for these spectra are very similar to those acquired off-resonance. The lower resolution of the resonance Raman experiment is the primary source of the small differences.

The ground state spectra for the three pentamer molecules are shown in Figure 4.5. The spectra are almost identical except for two small differences. The strongest band for 5T-o₂, 1467 cm⁻¹, up-shifts to 1481 cm⁻¹ for 5T-o₄ and 5T-o₆. The band at 1390 cm⁻¹ loses nearly all of its intensity for the pentamer with four ethyl groups, 5T-o₄, and this molecule also has the greatest intensity in the C-H in-plane bend region, at ~1050 cm⁻¹.
Figure 4.4. Resonance Raman spectra of three ground-state thiophene oligomers dissolved in THF. The blue spectra were collected with the probe wavelengths 355 nm (3T-o$_2$), 400 nm (6T-o$_4$), and 435 nm (9T-o$_6$). The off-resonance spectra (red) were acquired with 488.0 nm (3T) and 647.1 nm (6T, 9T).
Figure 4.5. Resonance Raman spectra of three pentamers with different numbers of octyl substituents in the triplet excited state (black) compared with the ground state off-resonance spectra (red), collected with 647.09 nm probe.
**Triplet state resonance Raman spectroscopy.** The resonance Raman spectra of the oligomers (3T–9T) in their excited triplet states are shown in Figure 4.3. In general, the triplet spectra have a much stronger dependence on length than the corresponding ground state spectra. The most intense band of the trimer is the highest frequency C=C stretch with maximum at 1515 cm\(^{-1}\). Similarly, the highest frequency C=C stretching band of the tetramer is also the strongest in amplitude, however this band is downshifted by 40 cm\(^{-1}\) compared to the trimer. Shifts of this magnitude are much greater than any seen for the ground-state spectra. For 5T-o\(_2\), 6T-o\(_4\), 7T-o\(_2\) spectra, the highest frequency band is a small shoulder, centered at approximately 1490 cm\(^{-1}\), 1510 cm\(^{-1}\), and 1519 cm\(^{-1}\), respectively. The C=C band that is lower in frequency but more prominent, tends to downshift with length: 4T (1482 cm\(^{-1}\)) \(\rightarrow\) 5T,6T (1432, 1431 cm\(^{-1}\)) \(\rightarrow\) 7T (1402 cm\(^{-1}\)).

There are also large changes in the frequencies and intensities for bands <1200 cm\(^{-1}\). For example, the bands in the region \~1100–1200 cm\(^{-1}\) are strongest for 6T-o\(_4\). Both 6T-o\(_4\) and 5T-o\(_2\) have relatively strong bands in the 500- 800 cm\(^{-1}\) region, compared with longer and shorter oligomers.

Despite the changes highlighted above, an important finding is that the spectra of 7T, 8T and 9T are generally similar. The overall profiles in the spectral region with the most scattering intensity (1300–1600 cm\(^{-1}\)) resemble one another. One difference among the spectra in this region is the relatively large magnitude of the \~1510–1520 cm\(^{-1}\) band for 8T and 9T, relative to 7T. All three spectra have four relatively weak bands in the 1000 – 1300 cm\(^{-1}\) region (1030-1040 cm\(^{-1}\); 1090 cm\(^{-1}\); 1150-1160 cm\(^{-1}\); 1210 cm\(^{-1}\)). There are no distinct bands <1000 cm\(^{-1}\), with one exception (610 cm\(^{-1}\) band 8T).
Figure 4.5 shows the $T_1$ spectra for the pentamers with different numbers of octyl substituents. All three spectra have the distinct profile of the pentamer: a shoulder at ~1490 cm$^{-1}$, intense bands in the range ~1340–1460 cm$^{-1}$, and strong low frequency bands. However, there are several subtle differences between the spectra. Most notably, 5T-o$_2$ has the greatest band resolution in the high frequency region, and there is significant variation in relative band intensity for the ~1100-1200 cm$^{-1}$ region for the three pentamers.

4.4 Discussion

In the following sections we will discuss the changes observed for the $T_1$ Raman spectra as a function of substituents, length, and conformation. We will also attempt to correlate vibrational normal modes to the most prominent bands.

$T_1$ Raman spectra length-dependence. The triplet Raman spectra are highly dependent on the length of the thiophene oligomer. One illustration of this dependence is that there is a $>$30 cm$^{-1}$ downshift in the highest frequency $T_1$ band for the tetramer compared to the trimer. This shift is exceptionally significant when compared to the much smaller (4 cm$^{-1}$) difference in the highest frequency ground state band for 4T-d$_2$ compared to 3T-o$_2$. Further, compared to the ground state, where the relative intensities and bandwidths change very little with length, the $T_1$ spectra have very significant changes. Even between the four shortest oligomers studied, 3T-o$_2$, 4T-d$_2$, 5T-o$_2$, and 6T-o$_4$, the relative intensities and band resolutions change dramatically.

At a chain length of seven rings, the $T_1$ spectra start to converge. The $T_1$ spectra for 7T-o$_2$, 8T-o$_4$, and 9T-o$_6$ all have a strong, broad intensity from ~1300 cm$^{-1}$ to ~1520
cm$^{-1}$, and all three spectra have little or no intensity below $\sim$1300 cm$^{-1}$. The two most significant changes for 9T-o$_6$ compared to 7T-o$_2$ are the decrease in relative intensity of the $\sim$1320 cm$^{-1}$ band and increase in relative intensity of the 1508 cm$^{-1}$ band. From this data, we conclude that the T$_1$ excitation includes 7 rings, similar to findings from optical absorption$^{17}$ and theoretical studies.$^{34}$ Our results strongly suggest that the 9T-o$_6$ spectrum represents the polymeric thiophene triplet Raman spectrum, specifically for poly(3-octylthiophene) and poly(3-methyl-4-octylthiophene).$^{17}$

**Ring distortion in pentamer variants.** The ground state absorbance spectra clearly show that 5T-o$_4$ has the longest effective conjugation because it has the most red-shifted absorption. For 5T-o$_2$ and 5T-o$_6$ the substituents on the central ring disturb the conjugation, likely by twisting the ring out-of-plane. This twisted structure results in blue-shifted absorption maxima for 5T-o$_2$ and 5T-o$_6$. Despite the loss of planarity, the low frequency region of the triplet Raman spectra is similar for all three pentamers. Bands in the low frequency region are often assigned to hydrogen out-of-plane modes that are fully symmetric, and therefore resonantly enhanced, upon loss of planarity. If these bands reflected out-of-plane motion, we would expect a significant increase in relative intensity for the region $<$800 cm$^{-1}$ for the twisted pentamers. Other possible assignments are C–S stretches and ring distortions.$^{25, 29-32}$ The fact that all three pentamers have strong bands in the 550-750 cm$^{-1}$ range suggests that ring distortions and C–S stretches are the primary vibrations.
**DFT mode analysis of the triplet excited state.** We compare the DFT calculated triplet spectra of the nonamer, hexamer, and trimer to elucidate the differences between their experimental spectra, Figure 4.6. A cursory look at the number of modes for each oligomer gives a clue into the broadened spectral features observed for the longest oligomers. The number of modes with non-zero intensity, as calculated by DFT, in the region 1300-1600 cm$^{-1}$ are: 16 (3T-e$_2$), 36 (6T-e$_4$), and 54 (9T-e$_6$). The increase in the number of modes is consistent with the loss in band resolution with increasing chain length. A similar increase in the number of modes is observed for the ground state. However, the additional ground state modes observed for the nonamer are within ~5 cm$^{-1}$ of the modes observed for the trimer. Therefore the extra modes do not contribute to spectral broadening.

The DFT spectra do not take into account the contribution of resonance effects or Franck-Condon displacements on the band intensities. Furthermore, the use of DFT for the calculations of triplet excited state properties, including normal modes of vibrations, is questionable. Given the limitations of the calculated spectra, any attempt we make to correlate a calculated mode with an experimental band is tentative.
Figure 4.6. DFT calculated Raman spectra of ethyl-substituted thiophene oligomers (9T-e_6, 6T-e_4, 3T-e_2) in the triplet-excited state. Experimental spectra are shown in black. The 9T-e_6 and 6T-e_4 calculated spectra are scaled along their y-axis as indicated. Calculated frequencies are scaled by 0.9614.
Several of the calculated vibrational modes overlap well with the experimental spectra. Further, some 3T-e$_2$, 6T-e$_4$, and 9T-e$_6$ modes can be grouped together based on similar vibrational movements and frequencies. The mode diagrams in Figure 4.7 highlight several triplet modes for 3T-e$_2$, 6T-e$_4$, and 9T-e$_6$, and they are split into five sections. (A) This first set of calculated modes include the 1515, 1510, and 1508 cm$^{-1}$ bands of the 3T-o$_2$, 6T-o$_4$, and 9T-o$_6$ experimental spectra, respectively. The active C=C stretches are largely localized in the central ring for the trimer; between the two-centermost rings for the hexamer; and in every ring for the nonamer. Significant relative intensity is observed for this mode in the 9T-o$_6$ and 3T-o$_2$ experimental spectra, but it is small in the 6T-o$_4$ spectrum. (B) This next mode might represent the 1470, 1431, and 1410 cm$^{-1}$ modes of the 3T-o$_2$, 6T-o$_4$, and 9T-o$_6$ experimental spectra, respectively. The mode is characterized by a combination of intra-ring C=C and C−C stretches, and inter-ring C=C stretches. It has significant experimental intensity for all three oligomers, with the relative intensity increasing with oligomer length. (C) The third set of calculated modes likely correspond to the 1386, 1356, and 1380 cm$^{-1}$ modes of the 3T-o$_2$, 6T-o$_4$, and 9T-o$_6$ experimental spectra, respectively. The mode consists mostly of CC stretches and C-H in-plane bends. The CC stretches in the trimer are localized to the outermost rings, the hexamer has movement throughout the chain, and the outermost rings of the nonamer are silent. This mode appears to have significant intensity in the experimental spectra for all three oligomers. (D) The next lowest energy mode depicted is not present in the trimer, and it is tentatively associated with the 6T-o$_4$ and 9T-o$_6$ experimental bands 1340 and 1345 cm$^{-1}$, respectively. This mode is mostly C-C stretches on the outermost, aromatic rings for the hexamer and nonamer. Experimental spectra for both have
significant intensity in the region of this mode. (E) Similar to the mode above, the lowest frequency vibration presented does not have any significant experimental or calculated intensity for the trimer. The DFT modes depicted likely correspond to the 1183 and 1163 cm\(^{-1}\) bands of 6T-o\(_4\) and 9T-o\(_6\). The mode is predominately a C–C stretch in the center of the molecule. For the even-numbered hexamer, the stretching is in the two central rings, and in the odd-numbered nonamer, the stretching is only in the central ring. This mode is prominent in the experimental hexamer spectrum, and is much less significant in the nonamer spectrum. To summarize the findings of the DFT simulations, the experimental nonamer spectrum, i.e. the converged spectrum, exhibits the diversity of the intense hexamer C=C and C–C bands in the region ~1330–1430 cm\(^{-1}\), as well as the strong trimer C=C mode at ~1500 cm\(^{-1}\). It is interesting that the ~1500 cm\(^{-1}\) band has little relative intensity in the hexamer spectrum. One possible explanation is symmetry effects. Unlike the trimer and nonamer, the hexamer is an even numbered oligomer, and therefore has an inversion center. However, there is not enough evidence to make any conclusions about the role of symmetry in the intensity of the ~1500 cm\(^{-1}\) band.
Figure 4.7. Mode diagrams for ethyl substituted 9T-e₆, 6T-e₄, and 3T-e₂ in the excited \( T_1 \) state calculated with DFT. Calculated frequencies scaled by 0.9614.
Effect of Conformations on T<sub>1</sub> Raman Spectra. Multiple conformations of oligothiophene commonly exist in solution in the ground state.\textsuperscript{35-39} We wondered how the presence of different conformations in the triplet state might affect the Raman spectra. More specifically, we were interested in whether those changes contribute to the loss of spectral resolution in the longest conformers. Figure 4.8 shows the DFT calculated spectra for four energetically accessible conformations of 3T-e<sub>2</sub>, 6T-e<sub>4</sub>, and 9T-e<sub>6</sub>. Surprisingly, no significant changes in mode frequencies are observed in the region 1300–1600 cm<sup>-1</sup>. Some variation in mode frequencies are observed in the region 1000–1200 cm<sup>-1</sup>, but no more variation for 9T-e<sub>6</sub> than for 6T-e<sub>4</sub> and 3T-e<sub>2</sub>. In the Appendix we include spectra of the all-cis conformers, which do show significant changes in the calculated T<sub>1</sub> Raman spectra. However, the existence of more than a trace population of energetically-unfavorable all-cis nonamer in solution is unlikely. From the off-resonance DFT calculations there is no reason to conclude that the presence of multiple conformations has a significant effect on the T<sub>1</sub> Raman spectra of the longest oligomers studied here.
Figure 4.8. DFT calculated T₁ Raman spectra of three thiophene oligomers with different conformations. Experimental spectra are shown in gray.
Experimental data is also incongruent with attributing the loss of band resolution in the triplet Raman spectra to the presence of multiple conformers. In the particular series of oligomers studied here, the ground state absorption spectra narrow with increasing oligomer length. This result suggests that, rather than increasing, the population of conformations other than all-trans decreases with an increase in chain length.\textsuperscript{40}

4.5 Conclusions

We probed the effect of length on the triplet Raman spectrum of a series of thiophene oligomers. Despite the similar Raman spectra of the ground-state molecules, the spectra of the triplet state were very different for oligomers with three to seven rings in length. The spectral band frequencies and intensities for the heptamer, octamer, and nonamer were similar to one another. We suggest that the heptamer may represent the fully extended triplet excited state of polythiophene at room temperature in solution.
References


Appendix of Chapter 4

**Density functional theory calculated Raman spectra.** Figure A4.1 shows that different conformations of the same oligomers produce the same ground state Raman spectra. Calculated triplet Raman spectra of the all-trans and all-cis conformers are displayed in Figure A4.2. The all-cis trimer is accessible at room temperature where kT=0.026 eV; however, the all-cis hexamer and nonamer are energetically unfavorable (Table A4.1). The energy differences are measured in the ground state because conformational changes are unlikely to occur in the triplet state where there is a quinoidal structure. The high-energy regions of the two conformations of the trimer are almost identical. The high-energy region varies some for the hexamer, and the largest changes in band frequencies and intensities are observed for the two nonamer conformations.
Figure A4.1. DFT calculated ground state Raman spectra of three thiophene oligomers with different conformations. Experimental spectra are shown in gray.
Figure A4.2. DFT calculated triplet state Raman spectra of the all-trans and all-cis conformations of three thiophene oligomers. Experimental spectra are shown in gray.
Table A4.1. DFT calculated energies for \textit{cis} conformations.

<table>
<thead>
<tr>
<th>Oligothiophene</th>
<th>Middle Bond \textit{cis} \textit{(eV)}</th>
<th>One \textit{cis} End \textit{(eV)}</th>
<th>Two \textit{cis} Ends \textit{(eV)}</th>
<th>All-\textit{cis} \textit{(eV)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>9T</td>
<td>0.012</td>
<td>0.003</td>
<td>0.004</td>
<td>0.127</td>
</tr>
<tr>
<td>6T</td>
<td>0.005</td>
<td>0.001</td>
<td>0.009</td>
<td>0.094</td>
</tr>
<tr>
<td>3T</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
<td>0.013</td>
</tr>
</tbody>
</table>

DFT calculated ground state energy difference between the all-\textit{trans} conformation and the conformation listed in the column header.