A PHOTOPHYSICAL CHARACTERIZATION ON THE UNIQUE PROPERTIES OF
PERYLENE-3,4:9,10-BIS((3,4,5(TRIS(OCTYLOXY)BENZOHYDRAZIDE)-
DICARBOXIMIDE

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A PHOTOPHYSICAL CHARACTERIZATION ON THE UNIQUE PROPERTIES OF PERYLENE-3,4:9,10-BIS((3,4,5(TRIS(OCTYLOXY)BENZOHYDRAZIDE)-DICARBOXIMIDE

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Thesis

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CHAPTER I
INTRODUCTION

1.1 Perylene Dye History

Perylene dyes (PDs) were first discovered by Kardos in 1913, and have since been extensively studied for a variety of purposes, including dye pigments, laser dyes, electronic devices, and more recently solar cells. Early uses included vat dyes, primarily because of their resistance to fading when exposed to light, as well as for industrial dye pigments. It was not until much later, in 1959, that PDs were found to be extremely fluorescent. The primary reason for this late discovery was a result of their poor solubility in solution. Since this time, PDs have been found to have high (near unity) fluorescence quantum yields and photostabilities that have enabled them to serve as fluorescent standards and sensors, and laser dyes. The advantageous fluorescent properties have also enabled researchers to use these compounds as optical sensors. In this regard, PDs have been incorporated into liposomes and in antibodies, where they serve as “fluorescent immunoantibodies” that are part of analysis for locating specific binding sites. The use of PDs as laser dyes has also increased substantially over the years because of their greater photostability than one of the most used dyes, rhodamine 6G.

Over the past decade, an area of intense interest has been in the self-organization of organic compounds. Organic PDs have been particularly useful in this regard because of their ability to self-assemble into ordered aggregates, which in PDs is a function of both hydrophobic/hydrophilic interactions as well as through π-π stacking. The interactions that
lead to the self-assembly of individual chromophores into π-stacked structures are similar to those found in nature in photosynthetic light harvesting proteins and in DNA.\textsuperscript{14} 

More recently, the use of perylene diimide dyes (PDIs) in photovoltaics and solar cells\textsuperscript{3,9,10,14,16} has been shown to be one of the best of the current generation of n-type semiconductors.\textsuperscript{9,10} The intense interest in PDIs is a result of their properties such as: 1) thermal, chemical, and photochemical stability,\textsuperscript{16} 2) redox chemistry,\textsuperscript{9} 3) their ability to self-assemble,\textsuperscript{9,13,14,15} and 4) the ability for PDs to participate in both photoinduced charge and energy transfer processes. The latter is a property that has been particularly exploited in the substituted PDIs.\textsuperscript{14}

1.2 Structure

PDIs have been shown to display several distinct properties, ones that affect the solubility,\textsuperscript{3} electronic structure,\textsuperscript{17} self-aggregation,\textsuperscript{18} and solid state color.\textsuperscript{12} The molecular structure of a substituted PDI is shown in Figure 1.1. The rigid, perylene core is made up of benzene rings that act as a stabilizing feature, while the N-R single bond at each end of the molecule is known as the imide position. The bay positions are located on the edges of the benzene rings and are represented by R’. Different substitutions have been made at both the R and R’ positions, and have lead to the discoveries of the characteristic properties of PDI molecules.

![Figure 1.1](image)

Figure 1.1 The parent structure of perylene diimides (the red outline represents the perylene core).
1.2.1 Solubility

Perylene diimides that are unsubstituted at the imide nitrogens have been found to be largely insoluble. Langhals\textsuperscript{3} has contributed much work in the area of PDI solubility, and found that substituting the PDI at the imide positions with aromatic amines increases the solubility dramatically. Further substitutions on the N-amide aromatic ring with either tert-butyl groups or long chain primary and secondary alkyl groups increases the solubility of the perylene diimide even more.\textsuperscript{3,9,14,16} Substitutions at the bay positions of the PDI molecule have been shown to change the rigidity of the perlyene core to a more twisted conformation, which consequently increases the solubility as well.\textsuperscript{9,17}

1.2.2 Electronic Structure

The photochemical stability of PDI is a function of the molecule’s structure. There are nodes in the HOMO and LUMO molecular orbitals at the imide nitrogens,\textsuperscript{17} leading to a “closed chromophore,”\textsuperscript{9} or a part of a molecule where the electronic structure is largely unaffected by substitutions made at the R positions. The absorbance spectrum of an unsubstituted PDI is characterized by absorption bands with a peak occurring at 526 nm, with additional maxima at 492 and 461 nm corresponding to the 0→0, 0→1, and 0→2 vibronic overtones of the S_0→S_1 electronic transitions respectively. The fluorescence spectrum is the mirror image of the absorbance spectrum, with the most intense emission band occurring at 537 nm. Substitutions at the imide nitrogens have been shown to increase the solubility of PDIs.\textsuperscript{9} The increase in solubility leads to an observable change in both the absorbance and fluorescence spectra compared to that of the unsubstituted PDI. The absorption spectrum is characterized by band broadening with a spectral shift in wavelength that is dependent on the type and size of substituent added.\textsuperscript{9} These changes mainly occur as the N-substituents affects the rigidity of the PDI. The fluorescence emission has been shown to lose vibrational structure, as well as undergo
changes in fluorescence quantum yields, due to self-quenching caused by π-π stacking present in aggregates. However, when the rotational barriers at the N-imide positions increase, as with the case of aromatic phenyl substituents with tert-butyl groups in the ortho positions, an increase in fluorescence is observed. Similarly, secondary alkyl groups have also been shown to increase the rotational barrier, also leading to an increase in fluorescence.17

Substitutions at the bay positions result in changes in the absorbance spectra, the amount of which depends on the size and the electron donating capabilities of the substituents.9 In general, larger substituents result in larger shifts in the absorption wavelength.9 Aryl substituents also influence the fluorescent quantum yields.9,13,18 The aryl group can be an electron donating group, in which case it can potentially donate an electron into the perylene core of the PDI by electron transfer, which is a competitive process with fluorescence, and consequently leads to a decrease in the overall quantum yield of fluorescence.

1.2.3 Self-aggregation

PDIs are known to self-assemble into ordered aggregates. The aggregation is found to be a function of molecular structure and solvent, with PDIs mainly aggregating in low-polarity organic solvents.18 The driving force for self-assembly is known to occur mainly by hydrophobic effects and by π-π stacking. Wasielewski et.al investigated the self-assembly of PDIs at low concentrations and at high temperatures, finding that the driving force for aggregation was primarily a result of strong van der Waals forces arising from π-π interactions.20

PDI aggregates have tunable absorbance and fluorescence properties that appear to be based on the substituents at the imide nitrogens.9,14 Würthner has suggested that the proper substituents can also lead to supramolecular PDI assemblies, and appropriate modifications can lead to self assembly in only one or two dimensions.9 The substituents in these cases are used to direct the molecules into stacked conformations.
A number of studies have shown that PDIs generally form two types of aggregates, i.e., H- and J-type aggregates. The chromophores of H-type aggregates are found to exist in either a face-to-face or an edge-to-face configuration, while the J-type aggregates are arranged in side-by-side configurations. Both are assembled in one dimension, but the two are readily differentiated by the angles of their transition moments (Figure 1.2). In H-type aggregates, the chromophores are arranged in a slipped orientation with respect to one another, such that the transition moment of the adjacent chromophores are all parallel to one another. In J-type aggregates, the chromophores are arranged in such a way that the transition moment of the adjacent chromophores are in-line with each other.

![Figure 1.2](image)

**Figure 1.2** The two major types of aggregates are shown, H-type (a and b) and J-type (c), where each square represents a chromophore. The $\theta$ is the angle of the transition moment between the centers of the two chromophores and the arrows indicate the direction of $\theta$.

The absorbance and fluorescence spectra of the aggregates are known to have characteristic shifts in wavelength in relation to that of the monomer. The H-type aggregates typically have a more broad, blue shifted absorbance relative to the monomer, while the fluorescence emission is found to be red-shifted and mostly quenched. The fluorescence lifetimes of H-type aggregates are also known to be reduced from that of the monomer. The J-type aggregates have a more narrow, red-shifted absorbance spectrum from that of the monomer, and the fluorescence emission is usually observed as sharp and only slightly red-shifted from the
monomer fluorescence.\textsuperscript{13,21,22} The J-type aggregates have fluorescence lifetimes that are longer lived than those of the monomer, resulting in a much higher fluorescence quantum yield.\textsuperscript{13,21}

1.2.4 Solid State Color

Another property of PDIs that is related to how the molecules are packed together are the solid state properties of these molecules. The crystal structure of eleven perylene-3,4:9,10-bis(dicarboximide) pigments were first solved by Graser \textit{et al.},\textsuperscript{19} who first explained that the different colored crystals exhibit almost identical absorption spectra when in solution but have very different colors in the solid state. The dependence of the crystal color was shown to be based on the transverse and longitudinal offsets of the individual molecules (Figure 1.3). The changes in offsets were then related to red-shifted and broadened absorption bands, which was further related to the extent of the π–π contact area between the individual chromophores.\textsuperscript{9} The way the individual molecules slip relative to one another determines the color of each dye form. This distinctive characteristic has been used to optimize dye pigments.\textsuperscript{11,22}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{packing orientations.png}
\caption{The packing orientations of the various PDI crystals.}
\end{figure}

Several studies of PDI molecules and systems involving PDIs have been carefully examined throughout the years and are still being conducted today. The unique qualities mentioned earlier, such as their tunable optical properties covering a wide range in the electromagnetic spectrum, their intense fluorescence, the capabilities of PDIs to self-assemble
into ordered aggregates, the electron transfer properties, and their tunable pigment colors are all quite relevant in materials chemistry. The research presented in this thesis is a photophysical characterization of perylene-3,4:9,10-bis((3,4,5-tris(octyloxy)benzohydrazide)-dicarboximide) (1).24

![Chemical structure of Compound 1](image)

\[ \text{R} = \text{C}_8\text{H}_{17} \]

Compound 1, synthesized by Smith and Modarelli24 exhibit many of the same characteristics that have been described previously for PDIs. In this work, we have used steady state absorption, steady-state fluorescence, and time-resolved fluorescence spectroscopies to characterize the optical properties of 1. This research has examined the two morphologies of the PDI that are dependent on the method by which the molecule is purified.
CHAPTER II
PHOTOCHEMISTRY BACKGROUND

2.1 Theory

Absorption of a photon of light by a molecule produces a highly reactive electronically excited state. Electronic excitation is the result of a promotion of an electron from the highest occupied molecular orbital (HOMO) into the lowest unoccupied molecular orbital (LUMO) producing the first singlet excited state (Figure 2.1).

![Diagram of electron energy levels](image)

**Figure 2.1** The absorption of a photon producing an electronically excited state.\(^{25}\)

The energy gap from the ground state to the excited state can be represented by \(\Delta E\) in Figure 2.1, where the change in energy is equal to the energy of a photon (equation 2.1), with \(h\) being Planck’s constant and \(\nu\) is the frequency of the radiation. The frequency \(\nu\) is readily
converted to wavelength $\lambda$ as shown in equation 2.2, where $c$ is the speed of light. Most organic molecules are found to absorb light in the 200-700 nm regions, commonly known as the ultraviolet and visible regions of the electromagnetic spectrum.

$$\Delta E = h\nu$$  \hspace{1cm} 2.1

$$\nu = \frac{c}{\lambda}$$  \hspace{1cm} 2.2

2.1.1 Electronic Spin States

Every electron in a molecule has spin angular momentum with a spin quantum number of $s = \frac{1}{2}$. Spin angular momentum is described as the motion of an electron about the nucleus (Figure 2.2). The angular momentum of the electron is an intrinsic property.\(^{26}\)

![Figure 2.2](image)

Figure 2.2 An electron precessing about an axis, with the arrow representing the angular momentum of the electron.

The graphical representation of electron spin angular momentum is represented as the arrow in Figure 2.3. Two electronic states can occur when an electron is excited to a higher energy orbital upon the absorption of light, the excited singlet state and the excited triplet state (Figure 2.3).

The state that has the two spins paired, $s = + \frac{1}{2} - \frac{1}{2}$, has a spin magnetic moment that is equal to zero, and is termed the singlet excited state. The state that has the two spins parallel, $s = + \frac{1}{2} + \frac{1}{2}$, has a spin magnetic moment equal to one. The interaction between the magnetic moment and an external magnetic field results in the splitting of this electronic configuration into three quantitized states, termed the triplet state.\(^{27}\)
2.1.2 Photophysical Processes

Photophysical processes interconvert excited states with each other, and also describe the interconversion of excited states with their respective ground states. Photophysical processes can be either radiative or radiationless processes, as shown in a Jablonski diagram (Figure 2.4). All straight arrows shown in color represent radiative transitions, 1) singlet-singlet absorption, $S_0 + h\nu \rightarrow S_1$, or absorbance (purple), 2) singlet-singlet emission, $S_1 + h\nu \rightarrow S_0$, or fluorescence (green), and 3) triplet-singlet emission, $T_1 + h\nu \rightarrow S_0$, or phosphorescence (orange). The radiationless transitions are represented by the wavy grey arrows, and include 4) transitions that are between the same states of different spin, (internal conversion), and 5) transitions between excited states of different spin, (intersystem crossing). The abbreviation VR represents radiationless vibrational relaxation. The lines where the VR arrows start and end are discrete vibrational energy levels.
The Jablonski diagram can also be interpreted as the rate constants of each photophysical process (Figure 2.5). The dynamic ranges for each photophysical process are as follows: $k_f$ is $\sim 10^6$ to $10^{12}$ sec$^{-1}$, $k_{ic}$ is $\sim 10^7$ to $10^{13}$ sec$^{-1}$, and $k_p$ is $\sim 10^{-1}$ to $10^6$ sec$^{-1}$. The overall rate constant for decay is equal to the sum of all of the photophysical processes, i.e., the radiative and non-radiative decays shown in equation 2.3. The lifetime ($\tau$) for the overall decay is defined by equation 2.4.

\begin{equation}
\tau = \frac{1}{k}
\end{equation}

\begin{equation}
k = k_f + k_{ic} + k_{isc} + k_p
\end{equation}
2.2 Photophysical Instrumentation

Several different types of instrumentation are typically used in photophysical chemistry, including: absorbance spectroscopy, fluorescence spectroscopy, and time resolved fluorescence spectroscopy utilizing the time correlated single photon counting (TCSPC) technique.

2.2.1 Absorbance Spectroscopy

In absorbance spectroscopy the amount of light that is absorbed by a molecule is measured as a function of wavelength. A beam of light is attenuated by an absorbing solution of concentration $c$. The incident beam has the radiant power of $P_0$ and the transmitted light has lower radiant power $P$, with the path length of the absorbing solution is represented by $b$. To calculate absorbance, the transmittance $T$ is first calculated as shown in equation 2.3. This value is then used in equation 2.6 to obtain the absorbance.

\[
\%T = \frac{P}{P_0} \times 100\% \quad 2.5
\]

\[
A = \log \left( \frac{P_0}{P} \right) \quad 2.6
\]
For monochromatic radiation, the absorbance is directly proportional to the path length of the solution $b$ and the concentration $c$, also known as the Beer’s law relationship (equation 2.7), where $a$ is the molar absorptivity. The absorption spectrum is then dependent on the units of $b$ and $c$. When the concentration is given in mols per liter and the path length of the cell is in cm, the constant $a$ is now termed as the molar absorptivity coefficient, which is referred to as the symbol $\varepsilon$.

$$A = abc$$

2.7

A spectrophotometer is used to measure the absorbance and is represented by the block diagram below (Figure 2.6). The components that make up the instrument are represented in Figure 2.5, with the lines representing beams of light: (1) a light source that supplies a stable source of radiant energy, (2) a filter that restricts the radiation from the lamp to a limited amount of wavelengths, (3) a monochromator that scans through the exciting wavelengths, (4) a sample holder which is a transparent container for holding the sample, (5) the detector that provides an electrical response to each incident photon, and (6) a signal processor and readout that displays the transduced signal on a computer screen.

![Figure 2.6](image)

Figure 2.6       A typical schematic for an absorbance spectrometer.$^{28}$

The absorbance spectrum is measured as the intensity of light passing through the sample as a scan of excitation wavelength (Figure 2.7). Certain types of shifts in wavelength are typically associated with how the molecule absorbs light, and should be defined. A hyperchromic
or hypochromic change describes the increase or decrease in the absorbance intensity caused by changes in the sample concentration. A bathochromic shift or red-shift occurs upon either a change in substitution or solvent, and shifts the absorbance to a longer wavelength. A hypsochromic or blue-shift, shifts the absorbance to shorter wavelengths.

![Absorbance Spectrum with Shifts](image)

**Figure 2.7** A typical absorbance spectrum, with characteristic types of shifts and changes that can occur represented by the arrows.

### 2.2.2 Fluorescence Spectroscopy

Fluorescence is the process where an excited state molecule emits a photon of light as it returns to the ground state. The energy of emission is typically less than the energy of absorption\(^{29}\) and is shown in Figure 2.8. Two situations can exist for this transition, one where the first excited state surface is located directly above the ground state surface, and one where the excited state surface is displaced from the ground state surface. Excitation in the first case produces the Franck Condon state, that can then relax directly back to the ground state by fluorescence. The second case occurs when the excited state relaxes to a more stable geometry, and is therefore structurally displaced relative to the ground state. The fluorescence in either case is generally lower in energy than the absorbance, and therefore shifted to longer wavelengths.
This displacement is the Stokes Shift, and is defined as the energy separation between the 0→0 peaks for absorbance and emission. Large Stokes Shifts are indicative of large structural changes occurring in S₁.

Figure 2.8 The transitions from and to the ground state are shown in the energy level diagram, particularly from the zero point energy level to the v=1 vibrational level.²⁵

The spectra in Figure 2.9 show that the fluorescence for this compound is the mirror image of the absorbance spectrum. This feature is typically seen in compounds that are rigid and therefore have well-defined vibrational levels in both the ground and excited states. When these vibrations are too closely spaced to one another, a broad structureless emission spectrum is observed.

Figure 2.9 The absorbance and fluorescence spectrum of a rigid molecule are shown.
The basic fluorometer is shown schematically in Figure 2.10. The light from an excitation source, typically a Xenon arc lamp (1), passes through a monochromator (2) and strikes the sample (3). The incident light is absorbed by the sample, and the light emitted from the sample is termed fluorescence. The emitted light is collected through a second monochromator (4) and focused onto a detector (5), that is generally positioned at a 90° angle relative to the incident light beam, in order to minimize the risk of transmitted or reflected incident light reaching the detector.

Figure 2.10  The typical setup for a fluorescence spectrometer.28

The efficiency of fluorescence from a sample is measured as the quantum yield (\(\Phi\)), and is defined as the number of photons emitted relative to the number of photons absorbed by the sample.\(^29\) The value of the quantum yield must be between zero and one since it represents a probability. The quantum yield of fluorescence is related to the overall rate constant of fluorescence that was given earlier in equation 2.3, and is written as equation 2.8, where \(\Phi\) is the quantum yield and \(k_f\) is the emissive rate constant of the fluorophore. The denominator is the sum of all the radiative and nonradiative decay processes to the ground state. The magnitude of \(\Phi\) is close to unity when the nonradiative processes are much less than \(k_f\).\(^{29}\)

\[
\Phi = \frac{k_f}{k_f + k_{ic} + k_{isc}} \tag{2.8}
\]
2.2.3 Time-Correlated Single Photon Counting (TCSPC)

Time-correlated single photon counting (TCSPC) is a time resolved fluorescence technique used to determine fluorescence lifetimes. The principle used in the TCSPC experiment is illustrated in Figure 2.10. In this experiment, a laser pulse excites the molecule of interest, and the fluorescence is measured at a single wavelength as a series of randomly dispersed pulses, each representing the detection of a single photon. The signal is collected in a series of periods, each of which contains a single photon pulse. The laser and the detector are generally adjusted so that each period does not contain more than one photon.

![Figure 2.11](image-url)  
Figure 2.11 The figure illustrates the TCSPC detection pulses. Detection pulses are gathered for each period, and are dispersed randomly for each individual photon.\(^{30}\)

Each event is collected and stored in a memory slot that corresponds to a particular time, referenced to the excitation pulse. As more and more photons are collected, the resulting photon distribution is represented as a histogram shown in Figure 2.12 a. Fitting the histogram yields the waveform shown in Figure 2.12 b.
The memory build up in TCSPC (a) The histogram represents the storage of each photon as the memory builds up based on the individual time, (b) the optical waveform represents the actual shape that is displayed on the screen.\(^{30}\)

The TCSPC technique has been shown to record very low signals of light with excellent time resolution.\(^{29,30}\) The TCSPC instrument is composed of three main components: 1) the pulsed laser, 2) a micro-channel photomultiplier tube (PMT), and 3) the TCSPC electronics module. The electronics module is composed of several components including: a constant fraction discriminator (CFD), a time-to-amplitude converter (TAC), and a multi channel analyzer (MCA) (Figure 2.13).
Figure 2.13 The schematic represents a basic layout for a TCSPC experiment, excluding the series of optics for simplicity.\textsuperscript{29,30}

The purpose of the CFD is to eliminate the amplitude jitter associated with the build-up of pulses in the detector that arise from arbitrary amplifications. A reference signal is generated from either a photodiode or from the PMT in order to obtain a timing reference pulse from the light source, and a second CFD is typically used to remove the amplitude jitter from the reference pulse. The output pulses from each of the two CFDs are used as start and stop pulses in the TAC. The TAC produces an output signal that is proportional to the time in between the stop and start pulse. The TAC output is sent through the MCA where it is passed through an Analog-to-Digital Converter (ADC) that produces a digital detection time that is equivalent to the arrival time of a
photon. In order to characterize the resolution of a particular TCSPC experiment, an instrument response function (IRF) is detected. The IRF signal contains the pulse shape of the light source, as well as any other electronic noise resulting from the system components. The full width at half-maximum for the IRF in a TCSPC experiment should be around 25 to 80 ps, and is used for data manipulation involving fitting based on a reconvoluted exponential model. 29,30
CHAPTER III
EXPERIMENTAL

3.1 Materials

Perylene-3,4:9,10-bis((3,4,5-tris(octyloxy)benzohydrazide)-dicarboximide) (I) was synthesized by Mr. Timothy Smith\textsuperscript{24} and studied in two different morphologies: \textit{1a} and \textit{1b}, with observable differences in the solid state color, \textit{1a} was purple and \textit{1b} was red. The PDI \textit{1} was chromatographed on neutral alumina with a gradient of methylene chloride to 5% MeOH/methylene chloride as the eluant producing the PDI as a reddish solid, \textit{1b}. The solids were then split into two portions. One portion was dissolved into a minimum amount of methylene chloride. To this solution was slowly added methanol to the top of the solution. This mixed solvent system was left undisturbed for 3 days producing a purplish solid \textit{1a}.\textsuperscript{24} A standard of perylene-3,4:9,10-bis((cyclohexyl)-dicarboximide) (PDI\textit{std}) with a fluorescence quantum yield of unity was also prepared.\textsuperscript{24} All samples were dissolved in either Spectral or HPLC grade solvents (dichloromethane and toluene). The n-heptane was purified by standard methods, dissolving CaH\textsubscript{2} in n-heptane and distilling.\textsuperscript{31}

3.2 Instrumentation

The instruments used in this study involve a steady-state UV/Vis absorbance and fluorescence spectrometer, the laser, optics and detection subsystems for TCSPC, additional hardware added to instruments to induce physical change, and the calibration requirements for each instrument.
3.2.1 Steady-State UV/Vis Absorbance and Fluorescence Measurements

Steady-state absorbance measurements were run on a Shimadzu UVPC Spectrophotometer System Model UV-1601PC. Steady-state fluorescence measurements utilized an ISA Jobin Yvon-SPEX Fluorolog-3 Model 3-22 fluorometer. A 450 W xenon (Xe) arc lamp was employed as the light source in these experiments. The excitation beam was passed through a double-grating excitation monochromator, and the emission was collected at 90° (with respect to the incident excitation wavelength), focused onto another double-grating monochromator and into a photomultiplier tube detector (PMT). All components were interfaced to a computer, where the spectra were collected. Fluorescence spectra were collected by exciting at 450 nm for all samples in Sc/R mode to correct for changes in the lamp output intensity (R) and for the grating detector response (c). The temperature dependent experiments incorporated a Thermo-NESLAB RTE-101 temperature controlled cell holder which was easily inserted into both the UV/Vis and fluorescence spectrometers.

3.2.2 Time-Resolved Fluorescence Measurements

Time resolved fluorescence measurements were carried out using the time-correlated single-photon counting (TCSPC) technique. The laser source in this system was a Quantronix 4200 Series Mode-Locked picosecond (ps) ND:YLF laser frequency doubled to an excitation wavelength ($\lambda_{ex}$) at 527 nm. The pulse width out of the laser was approximately 80 ps with a repetition rate of 76 MHz, operating at a power of 0.08 W. The fluorescence signal was dispersed by a monochromator with a 0.4 nm band-pass filter, and detected using a thermolytically cooled Hamamatsu R5108 MCP PMT connected to a Becker & Hickel TCSPC Module SPC-300 board. The instrument response function (IRF) was measured by scattering light from a cuvette containing benzonitrile. The decay curves of the samples in toluene were examined using a polarizer set to the magic angle of (54.7°) with respect to the excitation laser; the monochromator
wavelength used for detection was set to 537 nm. No polarizer was used to detect the signal of samples in n-heptane, which were measured at 650 and 537 nm. TCSPC measurements on all samples were fit using the PicoQuant FluoFit data analysis software utilizing multi-exponential decays based on the reconvolution exponential model of the Marquardt-Levenberg algorithm represented by equation 3.1. All decays were fit to have values of $\chi^2 < 1.20$. Figure 3.1 shows the optical and laser components utilized in these experiments.

$$I(t) = \int_{-\infty}^{t} I(t') \sum_{i=1}^{n} A_i e^{-\frac{t-t'}{\tau_i}} dt'$$  \hspace{1cm} (3.1)

Figure 3.1 The optical and laser components used in the TCSPC experiments. The TAC, CFD and ADC are integrated into the SPC 300 board located inside of the computer.
3.3 Procedures

The following procedures were used to characterize PDI molecules in the two morphologies of 1a-purple and 1b-red. Several different types of experiments involving absorbance and fluorescence were used, along with data analysis.

3.3.1 Absorbance Experiments

Samples of 1a and 1b were primarily studied in two different solvents, toluene and n-heptane. Samples were prepared for absorption studies utilizing two types of cuvettes dependent upon the solution concentration. Highly concentrated samples utilized a 2 mm path length quartz cuvette, and low concentration samples utilized a 10 mm path length quartz cuvette. Extinction coefficients were determined in the usual manner using serial dilutions.

The size of the solution aggregates was qualitatively studied using four highly concentrated samples of 1b, with at concentrations of 250, 200, 150, and 100 µM in n-heptane. In these experiments, the absorbance of each sample was measured before and after the sample was passed through a 0.45 µm syringe nylon filter. The area under each absorbance spectrum obtained before and after filtration was integrated using the IGOR software. The area values were used to obtain information based on the size of the aggregates formed in solution. The samples were assumed to be 100% aggregated before filtration, and the area taken after filtration was divided by the area before filtration and multiplied by 100 to obtain the percentage of aggregates left after filtration.

The absorbance spectra of PDI in different mixed solvent systems of PDI were obtained to determine the equilibrium constants for equilibria containing monomers and dimers in the aggregate solutions. A stock solution of 1b at ~97 µM was made in toluene. Eleven additional samples were made by taking 150 µl of stock and adding it to a total of 5.0 ml of solvent containing different ratios of toluene and n-heptane. The exact sample information is given in
Table 3.1. The absorption spectrum of each sample was then measured. A baseline measurement of each solvent mixture was acquired prior to each sample spectrum and subtracted from the sample measurement to eliminate any absorbance from the solvent or scattered light. Data analysis was calculated using the IGOR software program utilizing a nonlinear sigmoidal equation to fit the data, represented by equation 3.2.

\[ y(x) = \frac{(\epsilon_{\text{obs}}/\epsilon_{\text{sat}})_{\text{max}}}{1 + e^{(x-x_0)/\delta}} \]  

3.2

Table 3.1 The sample information for the mixed solvent experiment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Toluene : Heptane</th>
<th>Stock (µl)</th>
<th>Toluene (ml)</th>
<th>Heptane (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100:0</td>
<td>150</td>
<td>5.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>90:10</td>
<td>150</td>
<td>4.5</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>80:20</td>
<td>150</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>70:30</td>
<td>150</td>
<td>3.5</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>60:40</td>
<td>150</td>
<td>3.0</td>
<td>2.0</td>
</tr>
<tr>
<td>6</td>
<td>50:50</td>
<td>150</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>7</td>
<td>40:60</td>
<td>150</td>
<td>2.0</td>
<td>3.0</td>
</tr>
<tr>
<td>8</td>
<td>30:70</td>
<td>150</td>
<td>1.5</td>
<td>3.5</td>
</tr>
<tr>
<td>9</td>
<td>20:80</td>
<td>150</td>
<td>1.0</td>
<td>4.0</td>
</tr>
<tr>
<td>10</td>
<td>90:10</td>
<td>150</td>
<td>0.5</td>
<td>4.5</td>
</tr>
<tr>
<td>11</td>
<td>0:100</td>
<td>150</td>
<td>0.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

3.3.2 Fluorescence Experiments

Samples were prepared utilizing a 10 mm path length quartz cuvette. Optical densities (OD) at the excitation wavelength were kept in the absorbance range of <0.1 ± 0.05 for the steady-state fluorescence measurements to avoid reabsorption artifacts. All solutions were
saturated by bubbling with argon for approximately 5 min prior to acquisition of each spectrum. Fluorescence quantum yields were determined for 1a and 1b in solutions of toluene and in n-heptane. Fluorescence experiments indicated the fluorescence of 1a in n-heptane was essentially quenched, and so quantum yield experiments for this compound could not be accurately detected. In these experiments serial dilutions from stock solutions of 1a and 1b were used to prepare 5 samples from each stock solution. A stock solution of the PDIstd was made in dichloromethane, followed by dilution to obtain one sample to verify the quantum yields based on a one point calibration calculation using equation 3.3, where n refers to the refractive index of the solvent.

All solutions were studied using an excitation wavelength of 450 nm, and the fluorescence spectra acquired from 465 nm to 850 nm in Sc/R mode. In toluene, the slits were set to 1 mm for the entrance and exit slits, and 2 mm for the intermediate slits, with a scan rate set at 0.5 s. For the samples in n-heptane, all three of the slits were set to 2.5 mm, with a scan rate of 0.5 s. The samples used in mixed solvent experiments were the same samples represented in Table 3.1. The samples were placed into the sample holder of the fluorometer and the emission was measured for each sample.

\[
\Phi = \Phi_{\text{std}} \left( \frac{Abs_{\text{std}}}{Abs_X} \right) \left( \frac{Area_X}{Area_{\text{std}}} \right) \left( \frac{n^2}{n_{\text{std}}^2} \right)
\]

Equation 3.3

A sample concentration of ~6µM was used in the temperature dependent experiments on 1b (in n-heptane). A room temperature emission spectrum was taken of the sample prior to temperature analysis (i.e., 20 °C) by recording the fluorescence spectrum inside a temperature controlled cell holder. The cell holder was allowed to equilibrate to the set temperature prior to acquisition of the emission spectrum. Spectra were collected in 10 °C increments from 20-80 °C.
3.2.3 TCSPC Experiments

The samples in these experiments were prepared utilizing a 10 mm path length quartz cuvette. The OD’s at the excitation wavelength (527 nm) were kept between 0.1-0.15 for the time resolved measurements. All solutions were saturated with argon for ~5 min prior to analysis. Samples of 1a were studied only in toluene. The lifetime data were collected for up to a total of 2000 photon counts at 537 nm. Samples of 1b were studied in toluene under the same conditions, while solutions of 1b in n-heptane were examined using a detector wavelength of 680 nm (aggregate) and 537 nm (monomer).
4.1 Absorbance Experiments

Steady state absorbance measurements of 1a and 1b were acquired in both solutions of toluene and in n-heptane, with concentrations on the order of $10^{-6}$M (Figure 4.1). In toluene an absorbance spectrum representative of the PDI monomer is observed (green and blue), while in n-heptane an aggregated spectrum is observed (black and red). These spectra are similar to those of both monomeric and aggregated PDIs.$^{3,9,13,18}$

![Absorbance Spectra](image)

**Figure 4.1** The absorbance spectra for PDI molecules 1a and 1b in toluene and n-heptane.
For the samples in toluene, absorption maxima for 1a and 1b were observed at 461, 492, and 528 nm ($\lambda_{\text{max}}$), corresponding to the 0→2, 0→1, and 0→0 transitions, respectively. The Frank Condon principle for rigid molecules predicts the ground state vibrational eigenfunction of $v=0$ has the greatest molecular overlap, yielding the 0→0 transition seen at $\lambda_{\text{max}} = 528$ nm for 1a and 1b in toluene. The 0→1 and 0→2 transitions result from vibronic overtones.\textsuperscript{25} This absorption spectrum in toluene is representative to the structure of the monomer. In n-heptane, the most intense absorption band occurs at 497 nm, with the lowest energy band at 542 nm. These transitions correspond to the 0→1 and the 0→0 transitions, respectively. The new absorbance maximum in n-heptane is now at the 0→1 transition, which has changed relative to the monomer in toluene. This change in vibronic structure is the typical absorption pattern that has been documented previously in the literature, and is indicative of aggregation of the PDI molecules in a co-facial geometry representative of an H-type aggregate.\textsuperscript{14,15,20,23,32}

Extinction coefficients (ε) were determined for 1a and 1b in both toluene and n-heptane, and are tabulated in Table 4.1. The values of ε obtained for 1a in toluene are consistent with monomeric PDIs in the literature.\textsuperscript{9} When 1b was dissolved in toluene there was a decrease in the extinction coefficients. The decrease was found to be possibly related to the method for how 1b was prepared. Absorbance spectra from 1a and 1b aggregates were observed in n-heptane, where aggregation is known to broaden and decrease the absorption bands. This data is summarized in Table 4.1.

Table 4.1 The absorbance results for 1a and 1b in toluene and n-heptane.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Type</th>
<th>Abs. Range (nm)</th>
<th>$\lambda^a$ (ε)\textsuperscript{b}</th>
<th>$\lambda^b$ (ε)\textsuperscript{b}</th>
<th>$\lambda^c$ (ε)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Toluene</td>
<td>Monomer</td>
<td>420-550</td>
<td>528 (7.03)\textsuperscript{c}</td>
<td>492 (4.86)</td>
<td>461 (2.02)</td>
</tr>
<tr>
<td>1a</td>
<td>Heptane</td>
<td>Aggregate</td>
<td>410-630</td>
<td>542 (1.43)</td>
<td>497 (2.15)\textsuperscript{c}</td>
<td>-</td>
</tr>
<tr>
<td>1b</td>
<td>Toluene</td>
<td>Monomer</td>
<td>420-550</td>
<td>528 (3.23)\textsuperscript{c}</td>
<td>492 (2.11)</td>
<td>461 (0.78)</td>
</tr>
<tr>
<td>1b</td>
<td>Heptane</td>
<td>Aggregate</td>
<td>410-630</td>
<td>539 (0.72)</td>
<td>495 (1.30)\textsuperscript{c}</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a}$\lambda$ in nm \textsuperscript{b}Absorbance $\times 10^4$cm$^{-1}$ M$^{-1}$, and \textsuperscript{c}most intense band
For self-aggregation experiments in n-heptane, absorbance spectra were acquired before and after samples of 1a were passed through a syringe filter with a pore size of 0.45µm (Figure 4.2). The inset in Figure 4.2 shows the absorbance spectra after filtration. The shape of the absorbance spectra indicates the presence of aggregates or even higher ordered structures, and therefore we assume the data before filtration has 100% aggregation for all solutions, with the area under the absorbance curve decreasing as the concentration of the solution decreases. After the samples were passed through the filter, the intensity of the absorption decreased dramatically indicating the percentage of aggregates in solution has decreased. The distance between two PDI molecules stacked one on top of the other is known to be ~3.5 Å.\textsuperscript{33} Using this distance, along with the pore size of the filters, the size of the aggregate not passing through the filter can be estimated as having a maximum of \( \geq 2,572 \) PDIs stacked on top of the other in a co-facial orientation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area</th>
<th>% Aggregation</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 µM</td>
<td>130.6520</td>
<td>100</td>
</tr>
<tr>
<td>200 µM</td>
<td>96.0131</td>
<td>100</td>
</tr>
<tr>
<td>150 µM</td>
<td>73.0891</td>
<td>100</td>
</tr>
<tr>
<td>100 µM</td>
<td>56.7211</td>
<td>100</td>
</tr>
<tr>
<td>250 µM\textsuperscript{a}</td>
<td>2.8163</td>
<td>2.16</td>
</tr>
<tr>
<td>200 µM\textsuperscript{a}</td>
<td>3.1668</td>
<td>3.30</td>
</tr>
<tr>
<td>150 µM\textsuperscript{a}</td>
<td>3.1258</td>
<td>4.28</td>
</tr>
<tr>
<td>100 µM\textsuperscript{a}</td>
<td>4.1258</td>
<td>7.27</td>
</tr>
</tbody>
</table>

\(\textsuperscript{a}\text{after filtration}\)
From Table 4.2 it is clear that most of the aggregates in solution have been removed by filtration. The highest percentage left in solution is ~7 % for the lowest concentrated solution (100 µM). It is unlikely the loss in absorbance is due to scattering, because the solutions are less concentrated after filtration. These results suggest that the size of the aggregates in solution at high concentrations is large, with aggregate formation possibly forming larger clusters or even a highly ordered structure that is greater than the size of the filter pore.

Figure 4.2 The absorbance spectra of PDI molecules of 1a in n-heptane at various concentrations are shown. Absorption spectra after filtration are illustrated in the inset.

Scanning electron microscopy (SEM) data of 1a and 1b suggest that 1a forms highly ordered self-assembled nanoribbons. The nanoribbons were formed by dissolving 1a from a mixed solvent system (methanol/methylene chloride) and evaporating off the solvent onto a glass slide, thereby forming a thin film. The width of the nanoribbons was found to be ~15 µm on average with lengths on the order of 50 µm (Figure 4.3). Several studies have already reported the formation of PDI aggregates in solution. From the filtration experiment the results show that the aggregate size of 1a is fairly large, especially at high concentrations. The
solid state data verifies that upon evaporation of the solvent an even more ordered structure is formed. Additional experiments, including fluorescence anisotropy experiments are necessary to determine how ordered the aggregated structure might be in solution. The results from this present work yields theoretical size based on the distance between two PDI molecules and the pore size of the 0.45 µm syringe filter. The amount of aggregates left behind is an extremely small percentage compared to how much there is initially, and is representative of aggregates still maintained in solution that have not formed into the higher ordered structures. The results also show that sample concentration affects the aggregation results. At the highest concentration of 250 µM, a smaller percentage of aggregates were left in the solute after filtering, implying again the formation of highly ordered structures at higher concentrations (Table 4.2).

Figure 4.3 An SEM micrograph of 1a formed from a mixed solvent system (methanol/methylene). The yellow arrow shows the width of a nanoribbon, which is calculated as ~15 µm.

For the mixed solvent experiments, the absorbance of 1b in 100% toluene (Figure 4.4) is the same as the absorbance of 1b in toluene shown earlier in Figure 4.1, with λmax at 528 nm. As
the proportion of n-heptane is increased in the solution, the absorbance spectrum undergoes a substantial change, with the 0→0 transition decreasing in intensity with increasing heptane. This band, together with the 0→1 and 0→2 transitions have nearly completely disappeared by the time the ratio is 40:60 toluene: heptane. The 40:60 sample (grey) is consistent with the typical aggregation absorbance spectrum for 1b (Figure 4.1). The intensity of the 0→1 transition is now larger than the 0→0 transition, which is known for the covalently bound perylene dimer\textsuperscript{14} and is typical for PDI molecules aggregated in a co-facial geometry representative of H-type aggregates.\textsuperscript{3,9,14,15,20,23,32}

![Figure 4.4](image.png)

**Figure 4.4** The absorbance spectra of PDI 1b dissolved in various ratios of toluene and n-heptane solvents. The arrows indicate directions of change upon addition of n-heptane.

The presence of isosbestic points in this series of spectra at ~480, 500, 520, and 543 nm (Figure 4.4) suggests that there are two absorbing components in equilibrium. The previous filtration results clearly indicate higher ordered structures in solution, but for simplicity, this data...
will be approached as if dimer formation were the predominant form of the aggregate to illustrate the changes in the absorption spectra. A more complicated approach is presented in Appendix A. The results were treated as a single monomer (M) to dimer (D) equilibrium, following a method used by Bergmann.\textsuperscript{35} The equilibrium between M and D can be described by the equilibrium constant $K$, shown in equation 4.1. The total molar concentration of 1b in solution ($C_T$) is given by equation 4.2, relating the concentrations of the monomer and dimer with the total concentration of the solution. Using equations 4.1 and 4.2, the fraction of the monomer ($f_m$) can be related to the concentration of the monomer with respect to the total concentration (equation 4.3).

$$M + M \leftrightarrow D, \quad \text{where } K = \frac{[D]}{[M]^2} \quad 4.1$$

$$C_T = [M] + 2[D] \quad 4.2$$

$$f_m = \frac{[M]}{C_T} \quad 4.3$$

Using these equations it is possible to calculate the equilibrium constant at each solvent ratio. Values for $f_m$ can be obtained by two methods. In the first approach, the molar extinction coefficient ($\varepsilon$) at the wavelength of maximum absorption ($\lambda_{\text{max}} = 528 \text{ nm}$) for each sample (this maxima has the largest change in $\varepsilon$ from monomer to dimer) is divided by $\varepsilon_{547}$, which is the extinction coefficient at the isosbestic point. This step eliminates any nonsystematic errors in the value of $C_T$ for the samples.\textsuperscript{32} These values are plotted against the change in concentration, represented by the percent of n-heptane (Figure 4.5).
Figure 4.5 The values of $\varepsilon_{528/547}$ plotted versus the % heptane added. A sigmoidal fit of the data was obtained using equation 3.2 from section 3.3.1.

The value of $f_m$ at each solvent ratio was found by using a sigmoidal fit of this data (Figure 4.5) to obtain the upper and lower limits of the fit, with an upper limit seen at $(\varepsilon_{528/547})_{\text{max}} \sim 4.6$ and a lower limit at $(\varepsilon_{528/547})_{\text{min}} \sim 0.6$. The values of these limits were then used in equation 4.4 to calculate $f_m$, the values of which are listed in Table 4.3.

$$1 - f_m = \frac{(\varepsilon_{528/547})_{\text{max}} - (\varepsilon_{528/547})_{\text{min}}}{(\varepsilon_{528/547})_{\text{max}} - (\varepsilon_{528/547})_{\text{min}}}$$  \hspace{1cm} 4.4

In the second approach, the extinction coefficients at $\lambda = 528$ nm of the pure monomer ($\varepsilon_M$) and dimer ($\varepsilon_D$) at 528 nm, obtained in separate solutions of toluene and n-heptane respectively (where $\varepsilon_M = 3.2 \times 10^{-4}$ and $\varepsilon_D = 0.903 \times 10^{-4}$), were used to calculate $f_m$ using equation 4.5.36 These values of $f_m$ are also listed in table 4.3 (under method 2), as are both the calculated monomer and dimer concentrations, and the calculated equilibrium constants for each sample. The calculated equilibrium constants show that the equilibrium lies to the right of equation 4.1, consistent with an increase in dimer/aggregate formation with increasing ratios of heptanes.

$$\varepsilon_{528} = f_m \varepsilon_M + \frac{(1-f_m)\varepsilon_D}{2}$$  \hspace{1cm} 4.5
Table 4.3 The results for the isosbestic calculations of 1b calculated using Methods 1 and 2 as described in the text.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Heptane</th>
<th>fm Method 1</th>
<th>fm Method 2</th>
<th>( a_b[M])</th>
<th>( a_b[D])</th>
<th>( a_c[K])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.9568</td>
<td>0.9998</td>
<td>(2.79 \times 10^{-6})</td>
<td>(1.26 \times 10^{-7})</td>
<td>(1.62 \times 10^{-14})</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.9294</td>
<td>0.9712</td>
<td>(2.71 \times 10^{-6})</td>
<td>(2.06 \times 10^{-7})</td>
<td>(2.81 \times 10^{-14})</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>0.7808</td>
<td>0.8152</td>
<td>(2.28 \times 10^{-6})</td>
<td>(6.39 \times 10^{-7})</td>
<td>(1.23 \times 10^{-15})</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>0.6753</td>
<td>0.7043</td>
<td>(1.97 \times 10^{-6})</td>
<td>(9.46 \times 10^{-7})</td>
<td>(2.44 \times 10^{-15})</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>0.4563</td>
<td>0.4743</td>
<td>(1.33 \times 10^{-6})</td>
<td>(1.58 \times 10^{-6})</td>
<td>(8.96 \times 10^{-15})</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>0.2491</td>
<td>0.2566</td>
<td>(7.26 \times 10^{-7})</td>
<td>(2.19 \times 10^{-6})</td>
<td>(4.15 \times 10^{-16})</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>0.1184</td>
<td>0.1192</td>
<td>(3.45 \times 10^{-7})</td>
<td>(2.57 \times 10^{-6})</td>
<td>(2.16 \times 10^{-17})</td>
</tr>
<tr>
<td>8</td>
<td>70</td>
<td>0.1026</td>
<td>0.1027</td>
<td>(2.99 \times 10^{-7})</td>
<td>(2.62 \times 10^{-6})</td>
<td>(2.92 \times 10^{-17})</td>
</tr>
<tr>
<td>9</td>
<td>80</td>
<td>0.0901</td>
<td>0.0895</td>
<td>(2.63 \times 10^{-7})</td>
<td>(2.65 \times 10^{-6})</td>
<td>(3.84 \times 10^{-17})</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>0.0901</td>
<td>0.0895</td>
<td>(2.63 \times 10^{-7})</td>
<td>(2.65 \times 10^{-6})</td>
<td>(3.84 \times 10^{-17})</td>
</tr>
<tr>
<td>11</td>
<td>100</td>
<td>0.0715</td>
<td>0.0699</td>
<td>(2.08 \times 10^{-7})</td>
<td>(2.71 \times 10^{-6})</td>
<td>(6.23 \times 10^{-17})</td>
</tr>
</tbody>
</table>

*Calculated using fm values from method 1, *b The units are in molar concentration, *c The units are in M⁻¹.

4.2 Fluorescence Experiments

Steady state fluorescence measurements of 1a and 1b were acquired in both toluene and n-heptane, (Figure 4.6). In toluene, fluorescence spectra consistent with that of a monomeric PDI are observed (green and blue traces, Figure 4.6), while in n-heptane, the spectra from aggregates are observed (black and red). The shapes of the monomer fluorescence spectra is consistent with the literature. The inset in Figure 4.6 represents the scaled up fluorescence spectra of 1a and 1b in n-heptane. The spectrum for 1b is different from that of 1a because it retains a small amount of monomer fluorescence. In general, aggregation is known to result in self-quenching in PDIs. The fact that 1b has two pronounced peaks at 518 and 559 nm indicates either residual
monomers are present and fluoresce, or indicate a “slipped” H-type conformation of the π-stacked PDIs. There is a broad and structureless emission maximum in both 1a and 1b at 680 nm that is red shifted from the emission of the monomer. Such a result is consistent with excimer formation in solution and likely results from aggregation.25

![Fluorescence spectra](image)

**Figure 4.6** The fluorescence spectra of PDI’s 1a and 1b in different solvents. The inset refers to the fluorescence of 1a and 1b in n-heptane.

The results from emission in dimers and aggregates can be described in three ways: (1) monomer emission, (2) excimer formation, and (3) excitonic coupling. In order to be considered an excimer a molecule in the ground state forms a complex with another molecule upon electronic excitation. The excimer generally has a short lifetime, and exhibits a structureless and red-shifted spectrum relative to that of the monomer. The lack of structure in the emission spectrum results from too many overlapping vibrational levels. Identifying which level the energy from the excimer originated from is generally impossible to interpret.25 Pi-stacking is known to result in excimer formation.25 The lack of substitution at the bay positions of PDI 1a leads to π-stacking between the chromophores and aggregation. The mostly structureless
emission band centered at 680 nm may therefore be characteristic of an excimer. Similar structureless bands have also been observed in H-type aggregates having co-facial orientations. Aggregation described in this way is expected to lead to an enhanced amount of electronic communication between the co-facially stacked PDI chromophores, that would then enable efficient energy or charge transfer.

Co-facially stacked H-type aggregates have been shown to have parallel transition moments. Based on the shapes of both the absorbance and fluorescence spectra of 1a, the transition from the ground state to the excited state can also be explained using the exciton model (Figure 4.7). The energy diagram in Figure 4.7 illustrates the potential transitions in a dimer having parallel transition moments according to the exciton model. For ease of explanation, the model will be used to describe dimer transitions. The exciton model involves the resonance splitting of degenerate excited state energies on two (or more) closely spaced molecules, represented in the monomer by $E^1$. In a dimer, this transition splits into two new transitions, $E^1$ and $E^2$, for which $E^1$ is a lower energy and forbidden transition, and $E^2$ is a higher energy allowed transition. The absorbance spectrum of 1a in toluene has a transition at 492 nm. That transition becomes more intense in the aggregate absorbance spectrum when in n-heptane, relative to the low energy band of the monomer at 528 nm, which in toluene is the most intense transition. The
The entire spectrum in n-heptane also becomes broader. The fluorescence spectrum in n-heptane is a broad and somewhat structureless, emission with a small shoulder on the blue edge at ~640 nm and a more intense emission band at 680 nm. This spectrum mirrors the vibronic structure of the absorption spectrum in n-heptane, where the shoulder at 527 nm most likely results from the lower energy forbidden excitonic state. Previous interpretations for PDI aggregates indicate that bulky imide substituents force the molecules into excited state geometries that do not have parallel transition moments, and therefore the previously forbidden low energy excitonic coupling transition becomes allowed.\textsuperscript{14} In other words the change in structure yields orientations where the transition from the lower exciton state E\textsuperscript{2} to the ground state E\textsubscript{0} becomes partially allowed.

More studies are needed to further explain the emission structure. It is possible that both excimer and excitonic interactions occur. Experiments using TCSPC that scan along the entire emission band should yield different lifetimes if both excimer and exciton coupling is present in the emission. Recent studies involving different size cofacially bound PDIs have indicated that the lifetime of a PDI excimer is on the order of ~9 ns whereas the excitonic portion of the band had lifetimes on the order of ~50 ps.\textsuperscript{14} A summary for the results from the fluorescence experiments are shown in Table 4.4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Type</th>
<th>Fl. Range (nm)</th>
<th>λ(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Toluene</td>
<td>Monomer</td>
<td>510-670</td>
<td>537\textsuperscript{a} 578 680 -</td>
</tr>
<tr>
<td>1a</td>
<td>Heptane</td>
<td>Aggregate</td>
<td>490-800</td>
<td>- - 640 680\textsuperscript{a}</td>
</tr>
<tr>
<td>1b</td>
<td>Toluene</td>
<td>Monomer</td>
<td>510-670</td>
<td>537\textsuperscript{a} 578 680 -</td>
</tr>
<tr>
<td>1b</td>
<td>Heptane</td>
<td>Aggregate</td>
<td>490-800</td>
<td>518 559 640 680\textsuperscript{a}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Indicates the most intense peak in the fluorescence spectrum.
Quantum yield experiments were completed for 1a in toluene while measurements for 1b were taken in both toluene and n-heptane. For 1a in toluene the quantum yield was found to be $\Phi = 0.761 \pm 0.008$. The quantum yield for 1b in toluene was similar to 1a with $\Phi = 0.714 \pm 0.003$. These results are similar to the literature for perylene diimides having phenyl substituents.$^9$ The decrease in quantum yield is due to the competitive process of electron transfer, the energy must be conserved leading to radiationless transitions, which is known to decrease the value of the quantum yield. For 1b in n-heptane the quantum yield is $\Phi = 0.00083 \pm 6.35 \times 10^{-5}$, consistent with $\pi-\pi$ stacking.

For the mixed solvent experiments, the fluorescence measurements for 1b acquired in the solvent mixtures (toluene and n-heptane) described in the absorbance section were measured. The results show (Figure 4.8) that there is an initial increase in fluorescence upon the addition of n-heptane to the toluene solution, such that the 90:10 and the 80:20 toluene/heptane solutions have more intense fluorescence spectra than the all-toluene spectrum. Starting with the 70:30 sample however, the fluorescence decreases with each addition of heptane.

Figure 4.8 The fluorescence spectra of PDI 1b dissolved in various ratios of toluene and n-heptane. The arrows indicate the overall direction of change in the fluorescence.
The absorbance spectra of these samples in the same solvent mixtures indicated that aggregation formation increases with increasing heptanes concentration, most likely as the result of self-assembly due to π-π stacking into aggregates. The fluorescence data supports the absorbance results with nearly complete quenched fluorescence for the 100% heptane sample, which is characteristic of aggregated PDIs.

For the temperature analysis experiment, a sample of 1b was prepared in n-heptane and studied at various temperatures by fluorescence spectroscopy. The fluorescence spectra of the sample at different temperatures is shown in Figure 4.9. The temperature range for these experiments was 20-80 °C. The fluorescence of the sample at 20 °C (black) is nearly quenched and is structured similar to a spectrum of an aggregated PDI. In addition to the monomer emission at 518 and 560 nm, a broad emission band centered at 680 nm is also observed. With increasing temperature, an increase in the monomeric portion of the emission at 518 and 560 nm is observed. An additional emission band at 610 nm is observed at temperatures >60 °C, characteristic of the 0→2 transition of the monomer emission. These results indicate that at low temperatures in n-heptane the emission is excimer-like, and that formation of higher ordered aggregates are dominant in this temperature range. As the temperature is increased, the aggregates appear to dissociate and form monomers. The data from this experiment was further used to determine the ratio of monomers to aggregated molecules. Each emission spectrum was fit to five gaussian peaks, and the area of each peak was used to determine the amounts of monomer and aggregate, shown in Tables 4.5 and 4.6. The results in Table 4.6 show the overall results for the ratio of monomer to aggregates. At low temperatures a higher percentage of aggregates are observed, whereas at higher temperatures a larger portion of monomers is observed.
Figure 4.9 The fluorescence of 1b in n-heptane at temperatures ranging from 20-80 °C (the arrows indicate the direction of change).

Table 4.5 The five calculated fluorescence peak areas of 1b from the temperature analysis experiments, where M and A are the areas of the total monomer or aggregate portions of the emission spectra.

<table>
<thead>
<tr>
<th>Temp.(°C)</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
<th>Peak 5</th>
<th>M</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.61E+06</td>
<td>8.89 E+05</td>
<td>2.72E+06</td>
<td>6.50E+07</td>
<td>1.61E+07</td>
<td>2.50E+06</td>
<td>8.38E+07</td>
</tr>
<tr>
<td>30</td>
<td>1.67E+06</td>
<td>2.92E+06</td>
<td>2.86E+06</td>
<td>5.97E+07</td>
<td>1.08E+07</td>
<td>4.58E+06</td>
<td>7.33E+07</td>
</tr>
<tr>
<td>40</td>
<td>6.38E+06</td>
<td>4.34E+06</td>
<td>9.92E+06</td>
<td>3.00E+07</td>
<td>2.63E+07</td>
<td>1.07E+07</td>
<td>6.62E+07</td>
</tr>
<tr>
<td>50</td>
<td>1.29E+07</td>
<td>7.69E+06</td>
<td>8.48E+06</td>
<td>4.33E+07</td>
<td>5.83E+06</td>
<td>2.06E+07</td>
<td>5.76E+07</td>
</tr>
<tr>
<td>60</td>
<td>2.94E+07</td>
<td>1.94E+07</td>
<td>1.27E+07</td>
<td>4.22E+07</td>
<td>1.47E+07</td>
<td>6.16E+07</td>
<td>5.69E+07</td>
</tr>
<tr>
<td>70</td>
<td>5.80E+07</td>
<td>3.76E+07</td>
<td>1.38E+07</td>
<td>1.51E+07</td>
<td>7.20E+07</td>
<td>1.09E+08</td>
<td>8.71E+07</td>
</tr>
<tr>
<td>80</td>
<td>1.15E+08</td>
<td>8.02E+07</td>
<td>2.75E+07</td>
<td>6.57E+07</td>
<td>2.95E+07</td>
<td>2.22E+08</td>
<td>9.52E+07</td>
</tr>
</tbody>
</table>

*Peaks 1-5 are in order from left to right shown in the emission spectra (Figure 4.9)*
Table 4.6  The ratio of monomers to aggregates, where M and A are the areas of the total monomer or aggregate portions of the emission.

<table>
<thead>
<tr>
<th>Temp.(°C)</th>
<th>Total Area</th>
<th>M/total area</th>
<th>A/total area</th>
<th>Monomer to Aggregate (M:A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>8.63E+07</td>
<td>2.89E-02</td>
<td>9.71E-01</td>
<td>1:33</td>
</tr>
<tr>
<td>30</td>
<td>7.79E+07</td>
<td>5.88E-02</td>
<td>9.41E-01</td>
<td>2:32</td>
</tr>
<tr>
<td>40</td>
<td>7.69E+07</td>
<td>1.39E-01</td>
<td>8.61E-01</td>
<td>5:29</td>
</tr>
<tr>
<td>50</td>
<td>7.82E+07</td>
<td>2.63E-01</td>
<td>7.37E-01</td>
<td>9:25</td>
</tr>
<tr>
<td>60</td>
<td>1.18E+08</td>
<td>5.20E-01</td>
<td>4.80E-01</td>
<td>18:16</td>
</tr>
<tr>
<td>70</td>
<td>1.97E+08</td>
<td>5.57E-01</td>
<td>4.43E-01</td>
<td>19:15</td>
</tr>
<tr>
<td>80</td>
<td>3.17E+08</td>
<td>7.00E-01</td>
<td>3.00E-01</td>
<td>24:10</td>
</tr>
</tbody>
</table>

4.3  Time Correlated Single Photon Counting (TCSPC) Experiments

Time Correlated Single Photon Counting (TCSPC) measurements were completed for 1a in toluene, while TCSPC measurements for 1b were acquired in both toluene and n-heptane. A typical decay curve for 1a in toluene is shown in Figure 4.10. The decay curves were all fit to bi-exponential decays and are tabulated in table 4.7.

Figure 4.10  The decay curve for PDI 1a in toluene (monomer).
Table 4.7 Monomer fluorescence lifetimes in toluene.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>( \tau_1 ) (ns) (%cont.)</th>
<th>( \tau_2 ) (ns) (%cont.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a(^a)</td>
<td>Toluene</td>
<td>2.27 ± 0.04 (93)</td>
<td>0.594 ± 0.09 (7)</td>
</tr>
<tr>
<td>1b(^a)</td>
<td>Toluene</td>
<td>2.41 ± 0.07 (90)</td>
<td>0.791 ± 0.08 (10)</td>
</tr>
</tbody>
</table>

\(^a\) \( \lambda_{\text{excitation}} = 527 \text{ nm, } \lambda_{\text{detection}} = 580 \text{ nm} \)

The fluorescence lifetimes calculated for monomer forms of 1a and 1b in toluene are comparable to other PDIs, for which lifetimes of ~3.8 ns have been reported.\(^{14}\) The slight decrease in the lifetimes of PDIs 1a and 1b can be attributed to the bulky substituents, which increase the nonradiative decay rate constant, thereby decreasing the fluorescence lifetimes. The TCSPC measurements for 1b in n-heptane were detected at two different wavelengths, 650 and 537 nm, in order to determine both excimer and monomer lifetimes. The decay curve for 1b in n-heptane detected at 650 nm is shown in Figure 4.11, and the decay curve for 1b in n-heptane detected at 537 nm is shown in Figure 4.12. Both curves were fit using multi-exponential decays, with the results listed in Table 4.8.

Figure 4.11 The decay curve for 1b in n-heptane detected at 650 nm (excimer).
Figure 4.12    The decay curve for 1b in n-heptane detected at 537 nm (monomer).

Two types of emission were observed upon excitation of 1b in n-heptane. Emission from the monomer is observed at 518 and 559 nm, and an aggregate or excimer-like emission is observed at 680 nm. The decay curve shown in Figure 4.11 was obtained upon excitation at 527 nm with a 100 ps laser pulse and detection at 650 nm. The decay was fit to three exponentials, with lifetimes of 82 ps (43% of the decay), 304 ps (36% of the decay) and 1.17 (21% of the decay) for the aggregate. The monomer was fit to two exponentials with lifetimes of 27 ps (64% of the decay) and 2.103 ns (36% of the decay). J-type aggregate lifetimes are usually observed to be much longer than monomer fluorescence lifetimes because of the way they are stacked. The lifetimes observed for the PDI aggregates are shorter on the whole than the monomer emission

Table 4.8    Aggregate fluorescence lifetimes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>( \tau_1 ) (ns) (%cont.)</th>
<th>( \tau_2 ) (ns) (%cont.)</th>
<th>( \tau_3 ) (ns) (%cont.)</th>
<th>( \tau_{\text{avg}} ) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b(^a)</td>
<td>n-heptane</td>
<td>0.082 ± 0.02 (43)</td>
<td>0.304 ± 0.03 (36)</td>
<td>1.17 ± 0.05 (21)</td>
<td>1.55 ± 0.03</td>
</tr>
<tr>
<td>1b(^b)</td>
<td>n-heptane</td>
<td>0.027 ± 0.01 (64)</td>
<td>2.103 ± 0.06 (36)</td>
<td>-</td>
<td>2.13 ± 0.035</td>
</tr>
</tbody>
</table>

\(^a\) \( \lambda_{\text{det}} = 650 \text{ nm} \), \(^b\) \( \lambda_{\text{det}} = 537 \text{ nm} \), \(^c\) The time resolution of this instrument is estimated at ~50 ps with this excitation \( \lambda \)
lifetime, providing further evidence for H-type aggregation, and are similar to what has already been observed in the literature.\textsuperscript{14} The very low quantum yields of the PDI in its aggregated state (i.e., 1b in n-heptane), are consistent with the short long-lived component ($\tau = 1.17 \pm 0.05$ ns).

The shorter fluorescent lifetimes are indicative of H-type aggregates which are known to have lifetimes shorter to that of the corresponding monomer.\textsuperscript{21}

Additional TCSPC experiments are needed to better characterize the aggregate emission bands. The results from these experiments seem to be wavelength dependent, and studying the emission at several wavelengths will more confirm a wavelength dependent system. Also, fluorescence anisotropy experiments will provide information about PDI aggregate size, and can be compared to the filtration work described in section 4.1.
CHAPTER V
SUMMARY

The photophysical characterization of perylene-3,4;9,10-bis((3,4,5-
tris(octyloxy)benzohydrazide)-dicarboximide) (1) has been completed in order to better understand the photophysical characteristics of the two different morphologies of this PDI in two different solvents. When 1a or 1b is dissolved in toluene, the absorbance spectrum for the monomeric PDI was observed. In n-heptane, the absorbance spectrum consistent with an aggregate is observed. PDI 1, regardless of morphology, exhibits similar steady state absorbance characteristics (i.e., vibronic structure and transition energies) that have already been reported in the literature for PDIs. The steady state fluorescence experiments reveal the two morphologies exhibit different fluorescence properties. The fluorescence spectrum and the quantum yields of the monomer in toluene indicates little difference between 1a and 1b, (Φ₁ₐ = 0.761 ± 0.008 and Φ₁₉ = 0.714 ± 0.003). The aggregate fluorescence of 1a and 1b, however, display significant differences. The fluorescence spectra of aggregated PDI 1 was essentially quenched and consistent with an H-type aggregate. The fluorescence of 1b in n-heptane showed that in addition to the excimer-like emission there were two distinct monomer emission peaks that were also observed, suggesting the individual PDIs may exist in a “slipped” conformation.

These results inspired additional absorbance and fluorescence experiments. Absorbance experiments in mixed solvent conditions (varying ratios of toluene/heptane) indicate a change from monomer to dimer/aggregate with increasing heptane, consistent with the presence of isosbestic points that are consistent with an equilibrium process. Equilibrium constants were
obtained under these conditions, and the results revealed increasing dimer/aggregate formation as more n-heptane is added, further supporting self-assembly into ordered aggregates. The fluorescence spectra indicated a decrease in the monomer emission leading to fluorescence quenching, probably resulting from π-stacking. At high concentrations, a larger, more ordered nanoribbon arrangement of the aggregates is observed (from SEM data as well as the filter experiments). The width of these nanoribbons are estimated at ~15 µm. The temperature dependent fluorescence studies determined that the number of monomer to dimer/aggregate molecules in solution increases with increasing temperature. Thus at low temperatures more dimer/aggregate molecules exist than monomer molecules and the emission is therefore mostly dimer-like.

The TCSPC results for the monomer gave similar lifetimes for 1a and 1b, with $\tau_{1a} = 2.27 \pm 0.04$ and $\tau_{1b} = 2.41 \pm 0.07$. The aggregate emission of PDI 1b was also examined in order to reveal information about the excimer-like and monomeric fluorescence. The fluorescence lifetimes were found to be wavelength dependent, with the short processes on the order of picoseconds contributing to most of the fluorescence decays. These shorter-lived processes at the aggregate emission wavelength are consistent with H-type aggregate lifetimes. More TCSPC studies of these aggregate systems are needed, but are difficult due to the low quantum efficiency of this particular PDI molecule that results from self-quenching.

In conclusion, the experiments performed in this thesis indicate PDI 1 is likely to be a co-facially stacked H-type aggregate that highly aggregates with dimer-like characteristics. Both the fluorescence and the TCSPC results reveal both excimer and excitonic information. This data suggests that the stacking that occurs between adjacent molecules is uniform and close together, further supporting these short-lived processes are due to aggregation, along with the other experiments suggesting the possibility of higher ordered structures. These results are
characteristic to what has already been reported, and are suitable for similar applications, most importantly for photovoltaics and organic solar cells.
REFERENCES

1. Kardos, M., *Ber.*, 1913, 46, 2068
26. Levine, I.N.; *Quantum Chemistry*; Prentice Hall, 2009

A modified approach of the Bergmann method\textsuperscript{35} presented earlier is given, provided, where A (represented in the equations below) refers to any size aggregate, and the value of two, from equation 4.1 found in section 4.1, has been replaced by $n$ to represent any integer. The equilibrium can then be written as:

$$M + M \leftrightarrow A \text{, where } K = \frac{[A]}{[M]^n}$$

$$C_T = [M] + n [A]$$

$$fm = \frac{[M]}{C_T}$$

Solving for $n$ using the equilibrium constant $K$ yields an equation useful for any size aggregate:

$$n = \log \left( \frac{[M]}{K} - [A] \right)$$

This approach has not been used for this set of data.