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The Design of Organic Polymers and Small Molecules to Improve the Efficiency of Excitonic Solar Cells

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The Design of Organic Polymers and Small Molecules to Improve the Efficiency of Excitonic Solar Cells

by

Paul Barber Armstrong

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

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University of California, Berkeley

Committee in charge:

Professor Jean M. J. Fréchet, Chair Professor K. Peter C. Vollhardt Professor Rachel Segalman

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#### Abstract

# The Design of Organic Polymers and Small Molecules to Improve the Efficiency of Excitonic Solar Cells

by

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#### Doctor of Philosophy in Chemistry

#### University of California, Berkeley

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The harvesting of solar energy using photovoltaics has the potential to provide a significant portion of the world's energy. For this to happen, the cost per watt of power produced from photovoltaics must decrease. Excitonic solar cells, including organic solar cells and dye-sensitized solar cells, have the potential to provide the necessary cost savings. However, power conversion efficiencies must be improved before these devices can become practical. This dissertation describes the implementation of several strategies to improve the efficiency of organic polymer and dye-sensitized solar cells.

Chapter 1 provides an introduction to current research on excitonic solar cells with a focus on organic polymer and dye-sensitized cells. The detailed mechanisms of photocurrent generation in each type of cell are discussed, and the factors that determine efficiencies are outlined. In addition, an overview of the progress over the last decade in research on polymer photovoltaics is given. Finally, the future prospects for achieving high efficiency devices are described.

Chapter 2 details a strategy for controlling the morphology of photovoltaic blends of conjugated polymers and small molecule perylene diimide dyes. Blends of these two materials are subject to excessive phase separation that decreases photovoltaic performance. The development of compatibilizers that alleviate this phase separation is described. A diblock copolymer of poly(3-hexylthiophene) (P3HT) and a perylene diimide (PDI) side chain polymer is an effective compatibilizer. Addition of this material to blends of P3HT and PDI suppresses the formation of micron-sized crystals and results in a 50% improvement in solar cell efficiency. The synthesis of a diblock copolymer of poly(3-(4-octylphenyl)thiophene) and the PDI side chain polymer is also described. This material functions as a compatibilizer, but does not allow for improved photovoltaic efficiency.

Chapter 3 describes the synthesis and characterization of a low bandgap conjugated polymer with thermally removable solubilizing groups. Following solutionbased deposition of thin films of this polymer, heat can induce the cleavage and evaporation of the alkyl solubilizing chains, resulting in an insoluble film. The optical properties change considerably during this process: the bandgap decreases, and the absorption coefficient increases dramatically. These properties were exploited to fabricate bilayers of the low bandgap material and a highly fluorescent commercial polymer. Fluorescence resonance energy transfer from the fluorescent material to the low bandgap polymer is efficient over 30 nm. Such a scheme could be utilized to overcome the exciton diffusion bottleneck in layered polymer solar cells.

In chapter 4, the synthesis of novel n-type polymers based on PDI monomers is described. With appropriate substitution of alkyl chains, highly rigid perylene benzimidazole ladder polymers can be made soluble in common organic solvents. These materials have exceptionally low-lying LUMOs and possess unusual fluorescence properties. Fully planar perylene ethynylene polymers are also synthesized and characterized. Despite their planarity, data from absorbance and fluorescence spectra suggest that the PDI units in these polymers are poorly coupled electronically. X-Ray diffraction shows that the  $\pi$ -stacking distance varies in these materials depending on the nature of the solubilizing groups and can be decreased through solvent annealing.

Chapter 5 describes how light harvesting can be improved in dye-sensitized solar cells by adding a second dye that transfers energy to the primary sensitizing dye. In liquid cells, incorporation of a PDI dye in the liquid electrolyte solution results in a 28% improvement in power conversion efficiency. Energy transfer is at least 50% efficient despite significant quenching of the perylene dye's fluorescence by the iodide redox couple. Efforts to employ energy transfer in solid-state dye-sensitized solar cells are also described. This is more challenging because the solid-state hole transporter is an excellent quencher of fluorescent dyes. However, it is shown that this quenching can be prevented by self-assembling dyes such as fluorescein 548 into a poly(propyleneimine) dendrimer. Unfortunately, processing conditions that allow the dendrimer/dye conjugates to penetrate the pores of the cell's titania films have not yet been found.

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## **Chapter 1 – Introduction to Excitonic Solar Cells**

#### The Current State of Photovoltaic Technology

Solar power is expected to play an important role in overcoming mankind's dependence on fossil fuels. Photovoltaics (PVs), devices that directly convert light into current, are increasingly recognized as one of the most promising and attractive methods for harvesting solar energy. Currently, however, producing electricity from a photovoltaic panel costs around \$4 per watt, which is too high to significantly influence energy markets. The US Department of Energy believes this cost must decrease to \$0.33 per watt to realize the widespread adoption of photovoltaics for electricity generation.<sup>1</sup> Achieving this cost reduction is the driving force behind most current research on PV systems.

Presently, PV modules based on crystalline silicon dominate the commercial market. Invented in 1954 at Bell Labs, they utilize a p-n junction to drive the separation of electrons and holes formed in the semiconductor upon light absorption. Typical power conversion efficiencies in commercial modules are around 15%, and these devices generally last over twenty years under continuous use without loss of performance. The high costs are related to the difficulty in producing the extremely high purity silicon needed to obtain good performance. Inevitably, prices will decrease as the scale of production rises. However, costs for power generated from crystalline silicon PVs are expected to level off around \$1-\$1.50 per watt, well above the DOE target.<sup>1</sup> As an alternative, thin film technologies based on inorganic semiconductors such as CdTe/CdS, Cu(In,G)Se<sub>2</sub> (CIGS), and amorphous silicon are currently being developed and sold by a variety of companies. But to achieve costs that are truly competitive with fossil fuel energy sources, it is generally believed that new technologies, often termed third-generation PVs,<sup>2</sup> must be developed.

Third generation solar cells include devices expected to be expensive but highly efficient as well as cells that are moderately efficient but inexpensive. The latter includes the class of PVs termed excitonic solar cells. Organic photovoltaics (OPVs), dye sensitized solar cells (DSCs), and a few inorganic nanocrystal PVs<sup>3</sup> are examples of excitonic solar cells. This overview will focus on OPVs and DSCs.

#### **Organic Polymer Photovoltaics**

Solar cells made from organic semiconductors offer the potential to provide inexpensive solar power. Cost savings are realized through the use of cheap raw materials, simple manufacturing processes (especially solution-based methods for semiconductor deposition), and savings in installation costs due to the thin and flexible nature of the modules. However, practical devices still need to be moderately efficient and have reasonable lifetimes. Generally, it is believed that power conversion efficiencies of at least 10%, and probably 15%, must be achieved to realize widespread adoption of OPVs. Furthermore, devices must last at least ten years. The current state-of-the-art laboratory efficiency is 7.4%,<sup>4</sup> and more research is needed in the area of device lifetimes.

OPVs can be divided into two general classes: devices based on organic small molecule semiconductors, and those based on polymer semiconductors. Importantly, the former are generally processed by vapor deposition under high vacuum, while the latter are deposited from solution. The potential to fabricate devices through solution-based methods, such as ink jet printing, is a major reason for the anticipated cost savings associated with OPVs. This discussion will focus exclusively on polymer OPVs. For information about small-molecule devices, the reader is referred to a recent review.<sup>5</sup>

#### Semiconducting Properties of Conjugated Polymers

Although the semiconducting properties of conjugated polymers have been known for over 60 years,<sup>6</sup> interest in the field exploded only after the discovery in 1977 that poly(acetylene) can be transformed from a weak semiconductor into a conductor by oxidation with bromine.<sup>7</sup> Initially, this prompted major research into the conducting properties of doped (oxidized or reduced) conjugated polymers with the understanding that they might replace metal wiring in electrical devices. More recently, however, interest has shifted back to the semiconducting properties of neutral conjugated polymers. Such materials are now expected to become alternatives to silicon in specialized, lowcost electronic devices.

Figure 1 shows the major classes of traditional conjugated polymers. With the exceptions of polyacetylene and polyaniline, these materials consist of linked aromatic units. The evolution of the electronic structure of such materials as the chain length is increased is shown in figure 2. The familiar Hückel  $\pi$  molecular orbitals of the aromatic units are split with each doubling of the chain length. As the length approaches infinity, the result is a band structure that nearly approximates a typical inorganic semiconductor, with a filled valence band consisting of  $\pi$ -bonding orbitals and an empty conduction band consisting of  $\pi$ -antibonding orbitals.<sup>8</sup>



Polyacetylene Polyphenylene







Polypyrrole

Polyaniline Polythiophene Figure 1: Structures of some important conjugated polymers

Simple Hückel theory actually predicts that the conduction and valence bands should merge at infinite chain length, yielding a metal. However, conjugated polymers are subject to a Peierls distortion (equivalent to a Jahn-Teller distortion) that causes bond length alternation and opens an energy gap (the bandgap, or  $E_{\alpha}$ ) between the bands.<sup>8</sup> For the structures shown in figure 1, this gap is typically around 2.0 eV or higher. Thus conjugated polymers are technically insulators or weak semiconductors. However, the structural tunability of conjugated polymers allows precise control over properties such as HOMO and LUMO energies. This advantage can outweigh the disadvantageous weak intrinsic semiconducting properties.



Figure 2: Qualitative diagram of the  $\pi$  molecular orbitals of thiophene, bithiophene, and polythiophene. As the chain length is extended, bands are formed and the electronic structure starts to resemble that of an inorganic semiconductor.

Bandgap control is critical for the design of polymers for solar applications, as Eg determines light absorption. The ideal bandgap for a light absorbing material in a single layer solar cell is around 1.5 eV,<sup>9</sup> lower than the 2.0 eV typical of the polymers in figure 1. Fortunately, much research has gone into methods for producing low bandgap polymers due to the desire, currently still unrealized, to produce a well-defined polymer with a zero bandgap. Many strategies have been explored, and for a complete discussion the reader is referred to a comprehensive review.<sup>10</sup> For solar cells, the most common approach is the donor-acceptor strategy. Polymers are designed with alternating electronrich and electron-poor aromatic units. The resulting material has a HOMO localized on the electron-rich unit and a LUMO concentrated on the electron-poor unit (figure 3). Polymers with bandgaps as low as 0.3 eV have been obtained in this manner.<sup>11</sup> The attraction of the donor-acceptor approach for solar applications relates to the ability to individually tune the HOMO and LUMO levels by altering the strength of the donor and acceptor units, respectively. This is critical for PV cell efficiency as will be discussed. A disadvantage is that donor-acceptor polymers typically have extinction coefficients up to an order of magnitude lower than their homopolymer counterparts.<sup>12</sup> This is a result of poor spatial overlap between the HOMO and LUMO orbitals due to their localization on different aromatic units.



**Figure 3**: Qualitative diagram of HOMO-LUMO interactions between an aromatic donor unit (thiophene) and an aromatic acceptor (benzothiadiazole) as the two are joined. The resulting dimer has a considerably narrowed HOMO-LUMO gap. This is meant to illustrate the principle behind the design of narrow bandgap polymers by alternating donor and acceptor units in the main chain.

#### **Charge Transport in Conjugated Polymers**

Because charge transport is crucial for the operation of solar cell, charge mobility is one of the critical factors that must be considered when designing a polymer for solar For a full treatment of the theory of charge transport in conjugated organic cells. materials, the reader is referred to a recent review.<sup>13</sup> A brief summary follows. Despite possessing an electronic band structure that resembles inorganic semiconductors, conjugated polymers typically do not exhibit band-like charge transport. This is primarily due to structural disorder in the solid state, as well as the tendency for polaron formation in conjugated organic materials. When a charge is introduced into a conjugated polymer by oxidation or reduction, a region of the chain structurally distorts, producing a low-energy state, known as a polaron state, within the bandgap. The charge is not typically delocalized over the whole chain, but instead spreads over a characteristic length, typically 8-10 aromatic units for a polymer such as polythiophene. This charge can be thought of as a mobile particle, termed a polaron. The polaron moves in the solid by "hopping" to adjacent chains through  $\pi$ -stacking interactions. Because this process involves deformation of the lattice, it has an activation energy. Thus charge transport in conjugated polymers is almost always thermally activated, and charge mobility increases with increasing temperature.

Charge mobilities in conjugated polymers can vary widely from  $10^{-6}$ -1 cm<sup>2</sup>/Vs. Several factors influence mobility. Structural disorder in solid films produces trap states that slow the movement of polarons. Therefore, achieving a high degree of crystallinity in a conjugated polymer is very important for achieving high mobility. Additionally, because charge hopping is mediated by  $\pi$ -stacking, a short  $\pi$ -stacking distance between chains (<4 Å) is necessary for high mobility. Finally, charge transport in conjugated polymers is often highly anisotropic (due again to the dependence on  $\pi$ -stacking), and mobilities can vary by several orders of magnitude depending on which direction they are measured (through a film versus along a film, for instance).

#### Solubility of Conjugated Polymers

Due to a tendency to aggregate and a low entropy of dissolution, unsubstituted conjugated polymers like those shown in figure 1 are insoluble. To render them soluble, an obvious necessity for enabling solution processing, they are typically substituted along the backbone with flexible alkyl chains. Branched chains, particularly those containing racemic chiral centers, are the best at inducing solubility but often produce amorphous materials. Straight chain alkyl groups, when judiciously placed along the backbone, can help solubility and crystallinity. In P3HT, for instance, the alkyl chains are extended in the solid state, and van der Waals interactions between alkyl groups on adjacent chains help induce crystallinity. The close spacing of chains on the backbone only allows a slight amount of interdigitation. If the chains are spaced farther apart, full interdigitation is seen in the solid state, which helps induce even greater crystallinity. This is the case for the pBTTT polymers, which possess record-setting hole mobilities due to their high crystallinity (figure 4).<sup>14</sup>



Figure 4: Representation of the solid-state packing of alkyl chains in P3HT (left) and pBTTT (right).

#### Mechanism of Charge Generation in Organic Photovoltaics

Because the dielectric constant of conjugated organic polymers is typically low ( $\epsilon = 3-4$ ), light absorption leads to the formation of a bound electron-hole pair known as an exciton. In contrast, the higher dielectric constant of most inorganic semiconductors (for silicon,  $\epsilon = 11$ ) allows for the formation of free charges immediately upon absorption of a photon. This explains why OPVs are considered excitonic solar cells and operate by a mechanism fundamentally different to that of silicon and other inorganic cells.

The coulombic force that holds the exciton together is 0.3-0.4 eV. This is much higher than the thermal energy available in the system (kT (a) 300K = 25.9 meV), ensuring that virtually no free charges will be formed in a pure polymer layer. Thus OPVs based on a single semiconductor have very low efficiencies. In a seminal paper in 1986, Tang first described the solution to this problem.<sup>15</sup> He fabricated a bilayer cell with a donor semiconductor in one layer and an acceptor in the other (both were vapor-deposited organic small molecules). Charges are split by an electron transfer reaction at

the interface. Figure 5 depicts the mechanism of current generation in such a cell. This mechanism applies to any bilayer OPV, either polymer or small molecule.

The first step is light absorption, which can occur in either the donor or acceptor phases, although it is shown in figure 5 occuring in the donor phase. Light absorption leads to formation of an exciton, which can diffuse in the cell. In organics, excitons have a lifetime in the nanoseconds, during which they typically can diffuse 10 nm on average before recombination.<sup>16</sup> If, however, an exciton reaches an interface with the acceptor, it will dissociate through an electron transfer reaction driven by the offset in LUMO energies between acceptor and donor. This offset must be at least 0.3 eV to overcome the exciton binding energy.

From this point, a charge transfer (CT) state may be formed.<sup>17</sup> In this state, analogous to an exciplex, the electron (localized on the acceptor) and the hole (localized on the donor) are still bound through a coulombic force. From here, several pathways are available: dissociation to truly free charges through thermal activation, intersystem crossing to a triplet state, or recombination. The latter two are loss mechanisms in the cell. Alternatively, the exciton might dissociate into free charges through vibrationally hot states and never reach the CT state at all.

Once the electron and hole are separated, they can migrate to the cathode and anode, respectively. This process is driven by the electric field across the device created by the different work functions of the two electrodes. A balanced and reasonable charge mobility in both phases is important in this step to avoid the buildup of charge (space charge) in either layer<sup>18</sup> and to prevent recombination.



**Figure 5**: Mechanism of charge generation in a bilayer organic solar cell. At top is a cross section view of the device. At bottom the mechanism is represented through HOMO/LUMO diagrams of the donor and acceptor materials. 1) Light absorption leads to formation of an exciton. 2) The exciton diffuses to the interface. 3) The exciton is dissociated by transfer of an electron into the LUMO of the acceptor, forming a charge separated (CT) state. 4) The CT state is dissociated, and the charges migrate to their respective electrodes.

#### Factors Controlling the Efficiency of Organic Photovoltaics

To measure the efficiency of an OPV, simulated solar light<sup>19</sup> is applied to the device, and the current density is measured as a variable bias is applied to the cell. This bias simulates the load that would be applied under real device operation. An example of the resulting current density-voltage (*J-V*) curve is shown in figure 6. The current at zero bias is termed the short circuit current, or  $J_{SC}$ . The voltage at zero current is termed the open circuit voltage, or  $V_{OC}$ . The fill factor (FF) is defined as the ratio between the maximum power output of the cell (the point on the curve where the product  $J \ge V$  is highest) and the product  $J_{SC} \ge V_{OC}$ . This is a measure of the "squareness" of the *J-V* curve. The power conversion efficiency,  $\eta$ , is the ratio of the maximum power output over the power of the light incident to the device, which can be expressed according to equation 1:

(1) 
$$\eta = (J_{\text{max}} \times V_{\text{max}}) / P_{\text{inc}} = (J_{\text{SC}} \times V_{\text{OC}} \times FF) / P_{\text{inc}}$$

where  $J_{\text{max}}$  and  $V_{\text{max}}$  are the current density and voltage at the point of maximum power output and P<sub>inc</sub> is the power incident on the cell from the simulated solar light. From this equation, it is apparent that maximizing  $\eta$  requires maximizing the  $J_{\text{SC}}$ ,  $V_{\text{OC}}$ , and FF.



**Figure 6**: An example current density-voltage (J-V) curve for a solar cell under simulated solar light. The fill factor (FF) is the ratio of the area of the inner rectangle to the area of the outer rectangle.

The  $J_{SC}$  is influenced primarily by the amount of light absorbed by the cell active layer and the relative efficiencies of internal processes such as charge separation and recombination. The  $V_{OC}$  is primarily determined by the difference in energy between the HOMO of the donor and the LUMO of the acceptor. The maximum  $V_{OC}$  at a given bandgap for the primary absorber thus occurs when the minimum energy, usually 0.3 eV, is lost in the charge separation step. The FF is influenced by a variety of factors. Obtaining a high FF requires balanced electron and hole mobilities to avoid the buildup of space charge.

#### **Development of High Efficiency Polymer Photovoltaics**

Although the Tang cell represented a major advance, bilayer OPVs are still not very efficient. They are limited by a phenomenon known as the exciton diffusion bottleneck. To absorb close to 100% of the solar radiation across the absorption band of

a polymer such as P3HT, a roughly 200 nm thick layer is required.<sup>20</sup> However, because the exciton diffusion length is limited to about 10 nm, only excitons formed within this distance of the interface are likely to dissociate and contribute to the cell photocurrent. Excitons formed away from the interface simply recombine and are lost.

The solution to this problem was first described in 1995.<sup>21</sup> Instead of using two layers, the donor and acceptor materials are dissolved together and cast into a single mixed layer. Due to the natural tendency of most materials, especially polymers, to phase separate, a biphasic, interpenetrating network of donor and acceptor is formed. If the processing conditions used to form this layer are optimized carefully, phase separation will occur on the nanometer length scale, producing a very high surface area between the phases. If the layer is made 80-200 nm thick, a large amount of light will be absorbed, but all the excitons will be near enough to an interface to be dissociated. OPVs utilizing these types of blends are known as bulk heterojunctions.

The first appealing power conversion efficiencies (close to 3%) were obtained with a bulk heterojunction OPV utilizing a poly(phenylenevinylene) polymer known as MDMO-PPV as the donor and a soluble  $C_{60}$  derivative known as PCBM as the acceptor (figure 7).<sup>22</sup> Since this discovery, blends of donor conjugated polymers with fullerene acceptors have dominated research on OPVs. Fullerenes are attractive as acceptors due their deep LUMOs, high electron mobilities, and ideal charge separation kinetics in combination with p-type polymers (fast, sub-picsecond charge separation and slow recombination).<sup>23</sup> Among fullerenes, PCBM remains the most popular, although the highest efficiencies are often now obtained through use of the C<sub>70</sub> version of PCBM due to its improved absorption coefficient in the visible.<sup>4</sup> Despite the dominance of fullerene, other materials, such as n-type small molecules<sup>24</sup>, n-type polymers,<sup>21b, 25</sup> and inorganic nanocrystals<sup>26</sup> have also been investigated as acceptors.



Figure 7: Structures of PCBM and MDMO-PPV.

A significant advance occurred with the discovery that improved efficiencies could be achieved by replacing the MDMO-PPV donor with P3HT.<sup>27</sup> Blends of P3HT and PCBM are now the best-studied bulk heterojunction pair, and are often viewed as the archetypal polymer OPV. The device architecture for an optimized P3HT/PCBM cell, which is typical for a polymer/fullerene bulk heterojunction OPV, is shown in figure 8. The anode, usually the transparent conductor indium tin oxide (ITO), is coated on a glass substrate. The ITO layer is covered with a 40-50 nm layer of the commercial hole conducting polymer poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS).

This layer acts as an electron blocker, preventing charges from leaking into the wrong electrode. The active layer is deposited on the PEDOT:PSS layer by spin coating. The device is then completed by evaporation of an aluminum cathode.

Maximum efficiencies for P3HT/PCBM cells are between 4 and 5%.<sup>27</sup> Uniquely, these bulk heterojunctions usually require a post-processing step, either thermal or solvent annealing, after deposition of the active layer by spin coating to yield high efficiencies. This step affects the morphology of the blend, producing a phase-separated network on the 10-20 nm scale (figure 8). The details of this process have been studied in depth, and interested readers are referred to a review.<sup>28</sup>



**Figure 8**: Diagram of a P3HT/PCBM bulk heterojunction solar cell. PEDOT:PSS = poly(ethylenedioxythiophene):poly(styrenesulfonate). The insets show how an initially nearly homogenous active layer is turned into a nanoscale phase separated blend through annealing (solvent or thermal).

Since the discovery of 4-5% efficiencies in P3HT/PCBM bulk heterojunction solar cells, efforts to further improve performance have mostly focused on redesigning the donor polymer. Relative to P3HT, two areas need improvement: the HOMO level needs to be lowered to maximize the  $V_{OC}$ , and the bandgap should be decreased from 1.8 eV to 1.5 eV to maximize light absorption. By utilizing the alternation of donor and acceptor monomers, many polymers have been designed and synthesized that exhibit either or both of these properties. However, several years of research initially did not yield cells with improved efficiencies. The problem lied in the difficulty in finding the right processing conditions to produce blends with phase separation in the correct size regime.

A major breakthrough occurred with the development of solvent additives used during spin coating of the active layer. While studying blends of the low bandgap polymer PCPDTBT (top left in figure 9) with PCBM, the addition of small amounts of high boiling solvents like 1,8-diiodooctane was found to significantly improve blend morphologies and efficiencies.<sup>29</sup> Successful additives have two key properties: they are higher boiling than chlorobenzene, the main solvent used for spin coating, and they

dissolve the fullerene but not the polymer. Presumably, evaporation of chlorobenzene during spin coating induces a nanoprecipitation of the polymer, which then forms a network of nanofibers. Since the additive evaporates much more slowly, the fullerene remains mobile in the solution and can slowly fill in the space between the polymer fibers. This process yields a blend morphology highly conducive to efficient exciton dissociation and charge conduction.

Since the discovery of the use of solvent additives for active layer spin coating, many polymers have been found to allow efficiencies above 5% in blends with a fullerene.<sup>4, 29, 30</sup> Figure 9 shows the structures of a selection of these polymers. All are combinations of donor and acceptor aromatic units. Likely, efficiencies will continue to rise as polymer structures are further optimized and device architectures and processing conditions are improved.



**Figure 9**: Structures of donor polymers that give power conversion efficiencies above 5% when blended with either PCBM or its C<sub>70</sub> version. <sup>1</sup>Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nat. Mater.* **2007**, *6*, 497-500. <sup>2</sup>Liang, Y.; Wu, Y.; Feng, D.; Tsai, S.; Son, H.; Li, G.; Yu, L. *J. Am. Chem. Soc.* **2009**, *131*, 56-57. <sup>3</sup>Zou, Y.; Najari, A.; Berrouard, P.; Beaupr, S.; Ach, B. R.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2010**, DOI: 10.1021/ja101888b. <sup>4</sup>Hou, J.; Chen, H.; Zhang, S.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144-16145. <sup>5</sup>(a) Chen, H.; Hou, J.; Zhang, S.; Liang, Y.; Yang, G.; Yang, Y.; Yu, L.; Wu, Y.; Li, G. *Nat. Photonics* **2009**, *3*, 649. (b) Liang, Y.; Xu, Z.; Xia, J.; Tsai, S.; Wu, Y.; Li, G.; Ray, C.; Yu, L. *Adv. Mater.* **2010**, DOI: 0.1002/adma.200903528. <sup>6</sup>Park, S. H.; Roy, A.; Beaupré, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photonics* **2009**, *3*, 297 – 302.

#### Future Prospects for High Efficiency Devices

In about a decade, efficiencies of polymer/fullerene bulk heterojunction OPVs have improved from just under 3% to 7.4%. Improvements have been made by optimizing the HOMO and LUMO levels of the donor polymer to maximize the  $V_{OC}$ , lowering the donor bandgap to around 1.5 eV to improve light absorption, and optimizing device morphology to achieve high internal quantum efficiency. However, no reported

cell has all three of these factors optimized simultaneously. When this is achieved, efficiencies approaching 11% should be possible.<sup>31</sup>

To achieve 15% efficiency, single layer cells are likely insufficient. Instead, stacked tandem architectures will have to be employed. Significant progress has been reported in developing tandem OPVs.<sup>32</sup> Currently, efficiencies lag slightly behind the best single layer devices, but 6% efficient solution-processed tandem cells have been reported.<sup>33</sup>

Since the invention of the bulk heterojunction, many researchers in the field have speculated that it might not be the ideal architecture for an OPV.<sup>20</sup> This is because the disorder inherent in the bulk heterojunction might lead to isolated domains that could trap charges, leading eventually to recombination. Also, the tortuous paths charges potentially must follow to reach the proper electrode could increase the probability of recombination. To alleviate this, an ordered bulk heterojunction (figure 10) could be developed. Fabricating such a device cheaply is challenging, however. Approaches investigated include the use of nano-structured titania<sup>34</sup> or diblock copolymers that self-assemble.<sup>35</sup> While this research is promising, high efficiencies have not yet been achieved.



**Figure 10**: A disordered bulk heterojunction (shown at left) is created by blending a donor (blue) and acceptor (red) and relying on phase separation. At right is an ordered bulk heterojunction, depicted with the cathode lifted off for clarity. The cylinders span the active layer, allowing for easy charge transport while maintaining high surface area between donor and acceptor. Cylindrical domains are not the only possibility, a lamellar morphology is expected to be effective as well.

Recent reports, however, have called into question the notion that the bulk heterojunction is sub-optimal. Specifically, internal quantum efficiencies over 90%<sup>4</sup> and in one case approaching 100%<sup>30c</sup> have been measured. This implies that virtually no recombination occurs in at least some optimized cells, suggesting that the development of an ordered bulk heterojunction may be unnecessary.

#### **Dye-Sensitized Solar Cells**

Dye-sensitized solar cells (DSCs) are one of the major classes of excitonic solar cells, in addition to organic polymer and small molecules cells. A brief introduction to DSCs follows. For a full treatment, the reader is referred to one of a number of reviews.<sup>36</sup>

#### Architecture and Basic Operation of a Typical Dye-Sensitized Solar Cell

In DSCs, the light absorbing material is small molecule dye. Unlike in OPVs, the light absorbing material does not also transport charge. Instead, the electron transporter is mesoporous  $TiO_2$  and the hole transporter is usually  $I_3^-$  dissolved in a solvent such as acetonitrile. The cell is constructed as shown in figure 11. On a transparent fluorine-doped tin oxide (FTO) electrode is placed a layer of mesoporous titania usually 10 µm in thickness. This layer is formed by first depositing a film of  $TiO_2$  nanoparticles 20-50 nm in diameter. The particles are then sintered together with heat and chemical treatment. On this film is coated a monolayer of light absorbing dye. Dyes are functionalized with binding groups, typically carboxylic acids, to allow them to stick to the  $TiO_2$  surface. The cell is topped with a platinum counter electrode, then sealed and filled with a solution of I<sup>-</sup> and I<sub>2</sub> in acetonitrile.



**Figure 11**: Architecture of a typical dye-sensitized solar cell. On an FTO electrode (FTO = fluorine-doped tin oxide) is placed a thin layer of titania then a 10  $\mu$ m thick layer of mesoporous titania. This layer is coated with a dye (represented as red). The cell is topped with a Pt electrode and filled with an I/I<sub>3</sub> redox electrolyte solution.

The mechanism of photocurrent generation in a DSC is represented in figure 12. Light absorption by the dye is followed by rapid injection of an electron into the conduction band of TiO<sub>2</sub>. This produces a dye cation that is reduced by electron transfer from I<sup>-</sup>. After a complex series of reactions, oxidized I<sup>-</sup> is converted to I<sub>3</sub><sup>-</sup>, which can travel through the electrolyte solution to the platinum electrode, where it is re-reduced to I<sup>-</sup>. Meanwhile, the electron drifts through the disordered mesoporous titania film, eventually reaching the FTO electrode and completing the circuit.



**Figure 12**: Mechanism of photocurrent generation in a dye-sensitized solar cell. A photo-excited dye injects an electron into the  $TiO_2$  conduction band (step 1). The dye is regenerated through reduction by  $\Gamma$ . The free electron and hole (in the form of  $I_3^-$ ) can then travel to their respective electrodes.

A number of features of the cell allow for highly efficient operation. First, there is no exciton diffusion. Excited dyes are placed right on the surface of the titania, where electron injection can occur very rapidly (sub-picosecond time scale). Second, the high surface area and large thickness of the porous titania film ensures that a large fraction of solar light can be absorbed, even with only a monolayer of dye coverage. In the best cells, charge injection and dye regeneration are highly efficient and happen much faster than recombination. The result is high efficiencies: state-of-the-art DSCs currently have power conversion efficiencies exceeding 11%.<sup>37</sup>

#### Design of Dyes for Dye-Sensitized Solar Cells

Successful dyes for DSCs need posses the following attributes: they must absorb broadly across the solar spectrum, have functional groups that allow for binding to  $TiO_2$ , inject an excited electron into the  $TiO_2$  conduction band fast and efficiently, and be quickly regenerated by the iodide redox couple. The most heavily utilized dyes that posses all these characteristics are ruthenium complexes. Figure 13 shows the structure of the archetypal DSC dye, commonly called N719.<sup>37</sup> Nearly all DSCs with state-of-the-art efficiencies utilize this dye or a closely related structure.



Figure 13: The structure of N719, a champion sensitizing dye for DSCs.

The N719 dye absorbs broadly from 350-700 nm, has four acid groups that allow for tight binding to TiO<sub>2</sub>, and possesses excellent injection and regeneration kinetics. The reasons for the last attributes are subtle: the LUMO of N719 is localized heavily on the bipyridine ligands, while the HOMO is localized on the metal and the NCS ligands. Having the LUMO close to the binding groups leads to fast injection: photoexcitation essentially pushes the electron towards the TiO<sub>2</sub>.<sup>38</sup> Since the NCS groups stick out into solution away from the surface, they are highly accessible to iodide ions. Having the hole localized on the NCS ligands therefore speeds up dye regeneration. It also slows down recombination of dye cations with electrons in the TiO<sub>2</sub> conduction band.<sup>39</sup> Nearly all successful DSC dyes have a similar type of push-pull asymmetry in their excited state.

In addition to ruthenium complexes, many organic dyes have been utilized as sensitizers in DSCs. A recent review provides an excellent overview of the numerous structures investigated.<sup>40</sup> The development of organic sensitizers is expected to be important for commercialization of DSCs due to the high cost of ruthenium.

Unfortunately, efficiencies do not yet equal those obtained with cells based on ruthenium complexes. Currently the best efficiency is 9.5%.<sup>41</sup>

#### Substitutes for the Redox Electrolyte Solution

One of the largest barriers to commercialization of DSCs is their reliance on a liquid electrolyte. The volatility of this solution, which is typically acetonitrile-based, renders devices unstable without excellent encapsulation. This adds cost to the cell. The corrosive nature of iodine makes encapsulation even more difficult. Ionic liquids are appealing alternatives as they offer much reduced voltality and good thermal stability.<sup>42</sup> However, ionic liquid DSCs still utilize the  $\Gamma/I_3$  redox couple. DSCs based on solid-state hole conductors are perhaps most appealing. Such cells have been constructed utilizing copper iodide,<sup>43</sup> PEDOT,<sup>44</sup> and Spiro-OMeTAD<sup>45</sup> (figure 14) as the hole transporter. The latter is the best-studied and most successful, producing cells with efficiencies of up to 5.1%.<sup>46</sup> Efficiencies of solid-state DSCs based on Spiro-OMeTAD are much reduced relative to liquid cells for two reasons. First, the cells must be made much thinner (2-2.5 µm), limiting light absorption. This is probably because Spiro-OMeTAD does not sufficiently fill the pores of the titania film at higher thicknesses.<sup>47</sup> Second, rates of recombination are probably higher in solid-state cells than in liquid cells,<sup>48</sup> although this is not yet fully understood.



Figure 14: Structure of the solid-state organic hole transporter Spiro-OMeTAD.

Although the efficiencies of solid-state DSCs seem low relative to their liquid cell counterparts, they are close to the best efficiencies achieved by polymer OPVs. Therefore, DSCs should be considered a close competitor to OPVs. Like the latter, DSCs are made from inexpensive, nontoxic materials and can likely be fabricated cheaply. As efficiencies continue to rise, both DSCs and OPVs may begin to break into commercial photovoltaic markets. The future looks promising for both technologies.

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## Chapter 2 – The Development of Compatibilizers for Bulk Heterojunction Blends of Donor Polymers and Perylene Diimide

#### Background

As discussed in chapter 1, the bulk heterojunction is the most successful architecture for organic polymer solar cells investigated to date. The most extensively studied devices utilize blends of poly(3-hexylthiophene) (P3HT) and the C<sub>60</sub> derivative PCBM. Efficiencies between 4 and 5% are obtainable.<sup>1</sup> Significant effort has been devoted to raising these efficiencies by improving the absorption profile of the blend, usually by substituting P3HT with a low bandgap polymer that absorbs in the red and near IR.<sup>2</sup> An alternative approach is to replace the fullerene component with an electron transporting small molecule that has improved light absorption in the visible range. This is especially attractive since the fullerene content in many devices with the best efficiencies can be as high as 80% by mass.<sup>2a</sup>

Derivatives of perylene tetracarboxydiimide (PDI) are appealing candidates for substitution in place of PCBM. In addition to strongly absorbing visible light, they possess excellent photostability, allowing for applications as pigments in long-lasting car paints.<sup>3</sup> Additionally, a large number of reactions exist for modifying PDIs at both the imide nitrogens and the bay positions (figure 1).<sup>4</sup> This allows for considerable tailoring of properties such as solubility, light absorption, and HOMO/LUMO energy levels. Due to the electron withdrawing nature of the imide groups, PDIs are typically n-type semiconductors. Crucially, they are known to form crystalline domains with high electron mobilities when blended with polymers.<sup>4</sup> This suggests that they should function effectively as a replacement for PCBM in bulk heterojunction solar cells.



**Figure 1**: General structure of a PDI dye. The  $R^2$  groups at the imide positions are typically alkyl solubilizing groups, but can be almost any functionality. The R groups at the bay positions are hydrogen in the parent PDI, but can be substituted with other functionality.

However, solar cells comprised of blends of PDI and P3HT exhibit low external power conversion efficiencies, generally just below 0.2%.<sup>5</sup> This possibly is attributable to the formation of micron-sized PDI crystals upon annealing the devices. Figure 2 shows atomic force microscopy (AFM) images of the surface of 1:1 blend films of P3HT:PDI before and after annealing at 100 °C. The needle-like crystals seen after

annealing are attributable to PDI. Similar phase separation is seen after annealing at temperatures as low as 80 °C.<sup>5a</sup> The formation of such large crystals reduces the interfacial area between the donor and acceptor domains, leading to poor exciton dissociation. Furthermore, phase separation issues preclude annealing above the glass transition temperature of P3HT (approximately 120 °C), which has been shown to help crystallize P3HT in blends and improve hole mobilities.<sup>6</sup> Additionally, the low annealing temperature leaves individual PDI molecules dispersed in the polymer phase, resulting in sites for electron trapping.<sup>5a</sup> Improvements in efficiency could likely be realized by obtaining a morphology similar to that observed in P3HT/PCBM devices. One approach towards limiting phase separation is to add an ampiphilic compatibilizer, such as a diblock copolymer, to the film. Diblock copolymers have previously been used as compatibilizers for blends of immiscible polymers.<sup>7</sup> In these systems, confinement of block copolymer joints at domain interfaces reduces interfacial tension and suppresses coalescence, limiting domain sizes and improving morphological stability. The utility of this technique in stabilizing P3HT:PCBM blends towards extended thermal annealing has previously been demonstrated.<sup>8</sup>



**Figure 2**: Tapping mode atomic force microscopy (AFM) height images of P3HT/PDI thin films cast via spin coating on glass slides. a) 1:1 P3HT:PDI, no annealing. b) 1:1 P3HT:PDI, annealed at 100 °C for 30 minutes. At right: the chemical structures of P3HT and the particular soluble PDI derivitative used in this study.

#### **Results and Discussion**

#### First Generation Compatibilizer

The simplest structure that might act as a compatibilizer results from covalently linking a single PDI molecule to a P3HT chain. A target structure is shown in figure 3. Accessing this material requires the ability to selectively end-functionalize P3HT. The Grignard Methathesis (GRIM) polymerization of P3HT was chosen to accomplish this. Based on a Kumada coupling, GRIM employs a bifunctional thiophene monomer and a Ni(II) initiator. The polymerization allows for control over molecular weight, produces low polydispersity (PDI) material, and, most importantly, generates with high selectivity chains with a single bromine on one end.<sup>9</sup> That bromine can be converted into a benzyl amine, then reacted with a perylene imide/anhydride to generate the target structure. The perylene imide/anhydride is generated by partial saponification of a symmetric PDI. The synthesis is shown in scheme 1.



Figure 3: The first generation compatibilizer, in cartoon form at left, and chemical structure form at right.

The first generation compatibilizer was then evaluated by visualizing the morphology of thin films using AFM. P3HT/PDI films with varying amounts of compatibilizer 7 were cast via spin coating from chloroform. These films were then annealed at 80 - 120 °C for varying amounts of time. Unfortunately, in all cases the formation of micron-sized PDI crystals was observed upon annealing. Figure 4 shows an example image. Even replacing all the P3HT with compatibilizer does not prevent large-scale phase separation. In fact, the film morphology is indistinguishable from that observed without compatibilizer (figure 2). It is thus concluded that the first generation compatibilizer is ineffective.



Scheme 1: Synthesis of the first generation compatibilizer



Figure 4: Tapping mode AFM height image of a 1:1 blend of 7:PDI 1, annealed at 100 °C for 30 minutes.

#### Second Generation Compatibilizer

As previously mentioned, diblock copolymers have been demonstrated to function as compatibilizers. Thus, a diblock copolymer seemed an appropriate choice for the second generation compatibilizer (figure 5). The target structure includes a P3HT block connected to a block incorporating multiple PDI units. Having multiple PDI units connected to each P3HT chain should enhance compatibilizer interaction with the PDI phase in the blend, increasing the effectiveness of the compatibilizer. For the PDI block, a comb polymer first reported by the Thelakkat group was chosen.<sup>10</sup> This polymer consists of a flexible acrylate backbone with a PDI unit appended to each monomer through an 11 carbon alkyl spacer. This polymer has been shown to have a high electron mobility,<sup>10d</sup> which ensures that the presence of the compatibilizer is unlikely to harm solar cell performance by inhibiting charge transport.



Figure 5: The second generation compatibilizer, represented in cartoon form at left and in chemical structure form at right.

Well defined diblock copolymers can be synthesized by suitable end functionalization of P3HT followed by controlled radical polymerization of the pervlene acrylate component from the chain end. Reversible addition-fragmentation chain transfer (RAFT) was chosen for this purpose due to the relatively mild reaction conditions and exceptional control over molecular weight distribution.<sup>11</sup> RAFT utilizes chain transfer agents (CTAs), typically dithioesters or trithiocarbonates, in combination with standard free radical initiators such as azobisisobutyronitrile (AIBN) to mediate the controlled A benzyl dithioester CTA was chosen to allow for efficient polymerization. polymerization at mild temperatures.<sup>12</sup> This was appended to amine-functionalized P3HT 6 using standard peptide coupling protocols to yield the macro CTA 9 (Scheme 2). Polymerization of the pervlene acrylate monomer 10 (see experimental section for synthesis) was initiated with AIBN in the presence of the macro CTA 9 at 85 °C in 1,2dichlorobenzene. After 36 hours, the reaction was guenched by exposing the reaction mixture to ambient atmosphere and a diblock copolymer of fairly narrow molecular weight distribution was obtained after purification. Around the same time the synthesis of this material was reported,<sup>13</sup> several other groups reported the synthesis of closely related polymers.<sup>14</sup>

The second generation compatibilizer was then evaluated by visualizing the morphology of thin films using AFM. The compatibilizer was first evaluated in blend

films of P3HT and PDI **1**. Once again, the compatibilizer appears to have no effect on thin film morphology and phase separation of PDI **1** (figure 6, a and b). However, the PDI units on the second generation compatibilizer have longer branched solubilizing groups than PDI **1** (8-pentadecyl versus 3-pentyl). It was hypothesized that the compatibilizer might be more effective for PDI molecules with matching solubilizing chains. Towards this end, PDI **12** (figure 7) was synthesized (see experimental section). Figure 6, c and d, depicts the thin film morphology of annealed blends of PDI **12** and P3HT with and without compatibilizer. Without compatibilizer, micron sized PDI crystals are observed, although their shape is different than for PDI **1**. Addition of 10% by mass of compatibilizer **11** supresses this phase separation, yielding a film that appears homogenous by AFM. This suggests that the compatibilizer functions effectively when using PDI **12**.



**Scheme 2:** Synthesis of the second generation compatibilizer. The molecular weight and PDI were measured by size exclusion chromatography in THF calibrated to polystyrene standards.

With this information thin film solar cells in hand. (glass/ITO/PEDOT:PSS/P3HT:PDI 12: diblock 11/ LiF/Al; ITO:indium doped tin oxide, PEDOT:PSS: Poly(3.4-ethylenedioxythiophene) poly(styrenesulfonate)) were fabricated with various ratios of P3HT, PDI 12, and diblock copolymer 11. The measured power conversion efficiencies at Air Mass 1.5 Global (AM 1.5G), 100 mW/cm<sup>2</sup>, for these devices did not exceed 0.05%. However, in line with literature reports, an efficiency of 0.15% was obtained with PDI 1 and P3HT in the absence of compatibilizer.<sup>5a</sup> This clearly indicates that the longer solubilizing groups, while important for facilitating mixing in the blends, are detrimental to the overall device performance. In order to preserve the favorable device performance while preventing large-scale phase separation, the asymmetric PDI 13 was synthesized (see experimental). The longer solubilizing group at one end was retained to preserve interaction with the compatibilizer, while the shorter solubilizing group at the other end reduces the amount of insulating material in the active layer and should improve device performance. After optimization of various device parameters including annealing conditions, composition of the active layer, and the choice of solvent for spin casting (see experimental section for details), devices were

obtained with an open circuit voltage ( $V_{OC}$ ) of 0.56 V, short circuit current ( $J_{SC}$ ) of 1.85 mA cm<sup>-2</sup>, and a fill factor of 0.51. All three values are improvements over devices that have been reported earlier.<sup>5</sup> Taken together an efficiency of 0.55 ±0.03% was obtained, which represents a near threefold improvement in performance over previously reported P3HT:PDI solar cells. In the absence of the compatibilizer, and in other respects identical conditions, a maximum efficiency of 0.37 ±0.04% was observed (figure 8). These results demonstrate the beneficial effects of both the compatibilizer and the novel PDI **13** on device performance. They also represent the first instance of a polymer compatibilizer improving the efficiency of a solar cell.



**Figure 6**: Tapping-mode atomic force microscopy images of spun-cast P3HT/PDI blends. All films were annealed at 100 °C for 30 minutes. (a) 1:1 blend of P3HT and PDI **7**. (b) 1:1 blend of P3HT and PDI **7** with 10% by mass diblock copolymer added. (c) 1:1 blend of P3HT and PDI **3**. (d) 1:1 blend of P3HT and PDI **3** with 10% by mass diblock copolymer added.



Figure 7: Structures of PDI small molecules utilized in this study

To clarify the origin of the improved efficiency, the external quantum efficiencies (EQE) of the devices with and without compatibilizer were also measured (Figure 8b).

The device with compatibilizer shows a maximum EQE of 19%, compared to less than 16% for the control. The EQE is improved across a broad spectral range, but the difference is most pronounced at the short wavelength region, where the PDI component absorbs most strongly. This is not simply a result of higher light absorption at those wavelengths, as the thickness and optical absorption spectra of the films with and without compatibilizer are nearly identical (figure 9). This suggests that the improved  $J_{SC}$  results from increased dissociation of PDI excitons, perhaps due to smaller domain sizes.



**Figure 8:** a) J - V characteristics of solar cells with the configuration shown under 100 mW cm<sup>-2</sup> AM 1.5G illumination. Both devices utilized an active layer with a 4:1 ratio by mass PDI **13**: P3HT. Solar cells with compatibilizer contained 25% by mass of **11** in the active layer. b) External quantum efficiency as a functional of wavelength, measured at a 0 V bias, for the devices with and without compatibilizer.



**Figure 9:** UV-vis absorbance spectra of blend films prepared on glass slides under conditions identical to those used in solar cell preparation. The film with diblock copolymer is a 3:5:12 blend of P3HT:11:13. The film without diblock copolymer is a 1:4 blend of P3HT:13. Both films were annealed for 1 hr at 150 °C.

To demonstrate this, the polymer blends were imaged. Phase separation in these blends proved difficult to visualize by AFM, so transmission electron microscopy (TEM) was employed. Representative images of films cast under conditions identical to the best devices, followed by staining with RuO<sub>4</sub> vapor, are shown in Figure 3. The darker domains are attributable to P3HT, the more oxidatively sensitive component of the blend. Films cast without compatibilizer (Figure 10a) show large domains of P3HT and PDI, indicative of unfavorable phase separation on the micrometer length scale. In films with compatibilizer (Figure 10b) such phase separation is largely suppressed and smaller domains are observed. The nanometer scale phase separation should provide a high interfacial surface area for exciton dissociation, contributing to the improved  $J_{SC}$  and EQE.



Figure 10: TEM images of two different active layers with a 4:1 ratio by mass PDI 13: P3HT as used in photovoltaic devices. The blend with compatibilizer in Figure (b) contained 25% by mass of 11 in the active layer. Films were stained with  $RuO_4$ .

If the smaller phase separation observed by TEM is in fact leading to improved harvesting of PDI excitons, the photoluminescence (PL) spectra of the blend films should show increased quenching upon addition of compatibilizer. Figure 11 shows PL spectra of polymer films cast on glass slides under conditions identical to those used in solar cell fabrication. The emission observed is attributable to fluorescence from the PDI component. No emission from P3HT is observed, implying that the P3HT domains in both blends may contain PDI impurities, as has been previously suggested.<sup>5a</sup> Addition of the compatibilizer does result in reduced PL, consistent with the posited explanation for the improved  $J_{SC}$  and EQE in the solar cells. However, not all the PL is quenched, indicating that additional improvement should be possible with further optimization of the compatibilizer structure and device processing conditions.



**Figure 11**: Photoluminescence (PL) of blend films on glass. Both films contain a 4:1 ratio by mass PDI **13**: P3HT, with or without 25% by mass compatibilizer. Films were excited at 468 nm. The PL is normalized by dividing by the film absorbance, after subtracting the contribution to the absorbance from P3HT.

#### Solar Cells Utilizing the Diblock Copolymer as the Sole Active Layer Material

In addition to acting as a compatibilizer, diblock copolymers are of interest as materials that make up the entire active layer of a solar cell.<sup>15</sup> Classical coil-coil block copolymers are known to self-assemble into ordered patterns with domain spacings that can be as small as the exciton diffusion length.<sup>16</sup> Some of the accessible patterns, such as vertically aligned lamellae or rods, are expected to be nearly ideal for the active layer of a solar cell. However, due to the rigidity of semiconducting polymers, functional diblock copolymers with donor and acceptor blocks do not self-assemble in the same manner as classical diblock copolymers.<sup>15</sup> Therefore, achieving a solar cell with the ideal morphology and high performance through block copolymer self-assembly has proven difficult.

Nevertheless, the compatibilizer **11** has all the components necessary for a functioning solar cell: light absorbing material plus electron and hole transporters. Thus it warranted investigation as the sole active layer material. Figure 12 shows the second heating scan from a differential scanning calorimetry experiment on **11**. Separate melting transitions at 203 °C and 233 °C, attributable to the PDI and P3HT blocks, respectively, are observed. No glass transition was observed for P3HT, but this transition is often weak and difficult to observe. The presence of distinct transitions associated with each block is evidence of phase separation, a prerequisite for effective solar cell function. With this information in hand, solar cells were fabricated employing the diblock copolymer as the sole active layer material. Devices were annealed at 220 °C, above the glass transition of P3HT and the melting point of the PDI block, then cooled slowly to aid in the crystallization of both materials. Figure 13 shows the *J-V* curves before and after annealing. The performance is relatively low. Before annealing, the device had a  $V_{oc} = 0.50 \text{ V}$ ,  $J_{sc} = 0.38 \text{ mA/cm}^2$ , FF = 0.37, and  $\eta = 0.07\%$ . After annealing, the performance improves slightly due to an increased FF. This is probably attributable to better charge

transport resulting from crystallization of the polymer. For this device,  $V_{oc} = 0.51$  V,  $J_{sc} = 0.38$  mA/cm<sup>2</sup>, FF = 0.45, and  $\eta = 0.09\%$ .



Figure 12: Second heating scan from a differential scanning calorimetry experiment of diblock 11. The heating rate was 10 °C/min.



**Figure 13:** *J-V* curves of devices employing diblock copolymer **11** as the sole active layer material. The annealed device was heated for 1 hour before cooling slowly.

To understand the reason for the poor performance, films of the diblock copolymer were imaged by TEM. Figure 14 shows images of the film, both cross sectional and top views. The film morphology can be described as square-shaped domains of P3HT (dark domains) in a PDI polymer matrix. It appears that many of these domains are isolated within the film and do not contact the ITO/PEDOT anode. Thus, many holes become trapped and ultimate recombine with electrons in the other phase. This could explain the low performance.


**Figure 14**: TEM images of thin films of diblock copolymer **11**. (a) Top view, and (b) cross section. Films were annealed at 220 °C for 24 hours, and stained with RuO<sub>4</sub>. The scale bars are 100 nm.

# Poly(3-(4-octylphenyl)thiophene)/Perylene Diimide Solar Cells

Poly(3-(4-octylphenyl)thiophene) (POPT) (figure 15) is an alternative p-type polymer to P3HT. Recently, it has been discovered that it can outperform P3HT in solar cells with a variety of polymeric and small molecule acceptors, typically by improving the cell  $J_{SC}$ .<sup>17</sup> While the origin of this improved current is still under investigation, it has been suggested that the twisted phenyl ring increases the distance between donor and acceptor chromophores at domain interfaces, decreasing the coloumbic force that holds together bound electron-hole pairs that form after charge separation. This is expected to decrease geminate charge recombination, improving photocurrent.<sup>17b</sup> If this hypothesis is correct, it should be general for many different polymeric and small molecule acceptors. It was thus hypothesized that POPT might outperform P3HT when employing PDI as an acceptor.

Figure 15 shows *J-V* curves for optimized bulk heterojunction solar cells of P3HT or POPT blended with PDI. Optimized conditions are different for the two polymers. For P3HT, a 4:1 acceptor:polymer ratio is best, while for POPT the ideal ratio is 2:1. Additionally, the P3HT devices are annealed for 1 hour at 150 °C. For POPT, any amount of annealing decreases performance, even at low temperatures. The performance of the two devices is also very different. The POPT/PDI blend has a notably low  $V_{OC}$  of only 0.24 V. The origin of this reduced  $V_{OC}$  is unclear: the HOMO of POPT, measured by cyclic voltammetry, is actually slightly lower than P3HT,<sup>17a</sup> suggesting that the  $V_{OC}$  should be at least as high as the 0.57 V obtained using P3HT. On the other hand, the  $J_{SC}$  of the POPT/PDI device is much higher than the P3HT/PDI device, 5.7 mA/cm<sup>2</sup> versus 1.7 mA/cm<sup>2</sup>. This is consistent with the observations of improved  $J_{SC}$  values when using POPT in place of P3HT with other acceptors.<sup>17</sup> Due to this high  $J_{SC}$ , the overall performance of the POPT cell is improved relative to the P3HT cell, with  $\eta = 0.51\%$ .

The fact that annealing decreases performance in POPT/PDI solar cells suggests that these materials are subject to phase separation that could be alleviated through use of a compatibilizer. To further confirm this, blend films were imaged by optical microscopy. Figure 16 shows an image of POPT blended with PDI 14, an acceptor that gives similar solar cell performance to PDI 13. Large scale phase separation is clearly evident. The dark spots are most likely PDI crystals. Since phase separation occurs

without any annealing, POPT and PDI are presumably even less miscible than P3HT and PDI, suggesting that a compatilizer should help performance.



**Figure 15**: *J-V* curves for bulk heterojunction solar cells of P3HT or POPT blended with PDI. Structures of the relevant polymers and molecules are shown at right.

The compatibilizer was synthesized as shown in scheme 3. Brominefunctionalized POPT **14** is synthesized by a GRIM method very similar to that used for P3HT.<sup>17a</sup> This end group is converted to an alcohol via a Stille coupling with **15**, which is then converted to an activated bromide capable of initiating living atom transfer radical polymerization (ATRP).<sup>18</sup> Polymerization from macroinitiator **19** using a copper catalyst with PDI acrylate monomer **10** yields diblock copolymer **20**. This method provides the final diblock copolymer in fewer steps than the previously-employed RAFT method. ATRP also does not have the drawback of producing homopolymer chains derived from an externally added initiator, which happens when using RAFT.



**Figure 16**: Optical microscopy image of a 2:1 blend of PDI **14**:POPT. The blend was cast by spin coating from dichlorobenzene. No annealing was performed.

The removal of residual palladium from polymer **17** is crucial for the success of this method. In Stille couplings run at high temperature, the catalyst often degrades over time by forming Pd(0) nanoparticles. These are known to stick to conjugated polymers, and are not removed by standard purification methods including precipitation and Soxhlet extraction.<sup>19</sup> The nanoparticles can be removed by treatment of the polymer with a chelator, **16**. This compound has been shown to dissolve Pd(0) nanoparticles, producing complex **16**, which is separated from polymer by precipitation.<sup>19</sup> Complex **16** has an absorption band at 800 nm, allowing the removal of Pd to be conveniently monitored by UV/vis. Without the use of this chelator, ATRP with macroinitiator **19** fails. Most likely, residual Pd kills the polymerization by displacing the activated bromide on the end of the macroiniator.

for this hypothesis comes from the matrix-assisted Evidence laser desorption/ionization-time of flight (MALDI-TOF) mass spectrum of polymer 19 (figure 17) synthesized without the use of 16. Several sets peaks are visible. Two correspond to polymer chains with the desired end groups: one set exhibits the expected mass and the other the expected mass minus a bromine. Fragmentation during ionization is responsible for this partial loss of bromine. Another minor set of peaks corresponds to some residual 14. A final set of peaks matches the mass of the product resulting from replacement of the bromine end with Pd. The likely product is shown in figure 17. It could result from an oxidative insertion of Pd(0) into the carbon-bromine bond, producing a Pd(II) complex on the chain end. This complex could ionize by losing bromide, producing the product seen by MALDI-TOF. While the MALDI-TOF spectrum indicates only partial destruction of the active end group, it is likely that heating during ATRP results in further reaction and eventual loss of all active chain ends. Notably, when empolying the Pd chelator 16 in the synthesis of 19, the peak in the MALDI-TOF spectrum corresponding to **21** is no longer present.



**Scheme 3**: Synthesis of the POPT/PDI diblock copolymer. The molecular weight and PDI were measured by size exclusion chromatography in 1,2-dichlorobenzene calibrated to polystyrene standards.



**Figure 17**: MALDI-TOF mass spectrum of **19** synthesized without removing residual Pd from **17**. The complete mass spectrum is shown at left. The spectrum consists of sets of peaks separated by 270 mass units, the mass of a monomer unit. A zoom-in of this spectrum around the peaks corresponding to polymer chains with 37 monomer units is shown at center. Each peak corresponds to chains with different end groups; number assignments correspond to structures in scheme 3. At right is the proposed structure that gives rise to the right-most peak in the zoom-in.

Thin film solar cells (glass/ITO/PEDOT:PSS/POPT:PDI 13: diblock 20/ LiF/Al) were fabricated with various ratios of POPT, PDI 13, and diblock copolymer 20. The optimized ratio of blend components was 6:3:1 PDI:POPT:diblock, yielding an overall efficiency of  $0.29 \pm 0.03\%$ . This is only slightly higher than the efficiency obtained in the absence of compatibilier (2:1 blend of PDI:POPT),  $0.27 \pm 0.04\%$ . Notably, however, the  $J_{\rm SC}$  is improved by 25% upon addition of compatibilizer, suggesting that the diblock may be limiting phase separation as anticipated. However, devices with compatibilizer have slightly reduced FF and V<sub>OC</sub> values, which nearly negates the efficiency improvement from the increased  $J_{SC}$ . Thus the compatibilizer may limit phase separation, but likely also decrease charge mobility in one blend component, leading to decreased ff and  $V_{\rm OC}$ . This tradeoff leads to little change in efficiency. Device performance parameters and J-Vcurves are shown in figure 18. Overall, performance is lower than that shown in figure 15. This is because different batches of POPT were employed in these experiments. With POPT devices, solar cell performance appears to vary dramatically depending on the batch of polymer used. The variation could be due to small differences in  $M_n$ , which ranged from 60-80 kDa depending on the batch.



**Figure 18**: *J-V* curves for POPT/PDI blend solar cells with and without diblock **20** as a compatibilizer, together with device performance metrics. The device architecture employed was identical to that shown in figure 8. Devices with compatibilizer were 6:3:1 PDI **13**:POPT:diblock, while devices without compatibilizer were 2:1 PDI **13**:POPT.

To gain further evidence that the compatibilizer reduces phase separation, the fluorescence emission spectra of thin film blends were measured (figure 19). A film containing 20% by mass compatibilizer exhibits approximately 50% reduced PDI fluorescence, suggesting that phase separation of PDI is in fact limited by addition of the compatibilizer.



**Figure 19**: Photoluminescence (PL) of blend films on glass. Both films contain a 2:1 ratio by mass PDI **13**: POPT, with or without 20% by mass compatibilizer. Films were excited at 468 nm. The PL is normalized by dividing by the film absorbance, after subtracting the contribution to the absorbance from POPT.

# Conclusions

Amphiphilic compatibilizers were designed and synthesized to limit phase separation in polymer/PDI blends. A first generation compatibilizer consisting of a single PDI chromophore attached to the end of a P3HT chain was ineffective. However, diblock copolymers with P3HT or POPT as one block and a PDI-functionalized acrylate polymer as the second block are effective as compatibilizers. In the case of P3HT/PDI solar cells, smaller-scale phase separation achieved with the compatibilizer leads to increased  $J_{SC}$  and therefore increased efficiency. However, in the case of POPT/PDI cells, the compatibilizer decreases the ff and  $V_{OC}$  in addition to increasing the  $J_{SC}$ , resulting in little change in overall efficiency. The diblock copolymers also produce working solar cells when employed as the sole active layer material. However, the efficiencies are low.

Overall, despite achieving significantly higher solar cell efficiencies relative to literature reports on P3HT/PDI blends, the overall performance still lags far behind state of the art bulk heterojunctions based on polymer/fullerene blends. Likely, polymer/PDI devices suffer from some form of recombination. Future studies should focus on measuring rates of recombination in these devices, and correlating these rates to morphology and/or acceptor chemical structure.

# Experimental

# **Photovoltaic devices incorporating P3HT:**

ITO-coated glass substrates were purchased from Thin Film Technologies, Inc. They were cleaned by sequential sonnication for 20 min each in acetone, 2% helmanex soap in deionized (DI) water, DI water, and isopropanol. A 40 nm layer of PEDOT:PSS was subsequently deposited by spin-coating a filtered dispersion of PEDOT:PSS in water (Bayton PH500) at 3400 rpm for 45 s. The films were cured by heating on a temperaturecontrolled hot plate at 140 °C for 5 min. All subsequent steps were performed under an argon atmosphere in a glovebox. 25 mg/mL solutions of the diblock copolymer, P3HT (Rieke Metals electronic grade), and PDI in 1,2-dichlorobenzene were stirred in sealed vials on a hot plate at 100 °C for 1 hour, cooled, then filtered through 0.2 µm poly(tetrafluoroethylene) syringe filters. These solutions were then mixed in varying ratios. For the best devices, a 5:12:3 ratio of diblock copolymer: PDI-C2,7: P3HT was employed. Devices without compatibilizer used a 4:1 ratio of PDI: P3HT. Films from these solutions were deposited on the ITO/PEDOT:PSS substrates by spin-coating at 1200 rpm for 90 s. For devices involving diblock 11 as the sole active layer material, the films were prepared in an identical manner, except the stock solution of diblock copolymer was used directly for spin coating. The substrates were then annealed on a hot plate at 150 °C for 1 hour (or 220 °C for diblock only films), followed by slow cooling to 50 °C over 30 min. Electrode deposition was performed through a shadow mask in a thermal evaporator at a base pressure of 5 x  $10^{-6}$  mBar. During deposition, substrates were rotated at approximately 1 Hz to ensure even coverage. Lithium fluoride (1 nm) was deposited at a rate of 0.02 nm s<sup>-1</sup>, followed by aluminum (100 nm) deposited at 0.4  $nm s^{-1}$ . The configuration of the shadow mask ensured 8 independent devices on each substrate, each with an active area of  $3.0 \text{ mm}^2$ . To contact the ITO, a part of the film was scratched and covered with a conductive silver paste. Device testing was performed under an argon atmosphere using an oriel xenon arc lamp with an AM 1.5G solar filter. Current - voltage characteristics were measured with a Keithley 236 source-measure unit. Reported photovoltaic efficiencies are averages of all eight devices on the substrate.

### **Photovoltaic devices incorporating POPT:**

The procedures described above were employed except for the following exceptions, necessary due to the low solubility of POPT. Stock solutions of diblock copolymer **20** and PDI **13** at 25 mg/mL in 1,2-dichlorobenzene were prepared using procedures identical to those used for P3HT devices. Appropriate amounts of these solutions were added to solid samples of POPT ( $M_n = 60-80$  kDa). Additional 1,2-dichlorobenzene was added to bring the total concentration to 25 mg/mL. These solutions were stirred for 1 hour at 100 °C, then cooled to 80 °C. The hot solutions were then spun onto preheated ITO/PEDOT substrates at 1200 rpm for 75 seconds. Unless specifically noted, devices were not annealed.

# **Photoluminescence Measurements:**

Glass microscope slides were cleaned using a sonication procedure identical to that used for ITO substrates, followed by treatment with UV/ozone for ten minutes. Films were deposited on the glass slides and annealed with procedures identical to those

used for photovoltaic devices. Emission spectra were obtained using an ISA/SPEX Fluorolog 3.22 equipped with a 450W Xe lamp, double excitation and double emission monochromators, and a digital photon-counting photomultiplier. Slit widths were set to a 5 nm band-pass on both excitation and emission monochromators. Spectra were measured with front face detection, and the excitation wavelength was 468 nm. For normalization, absorbance spectra were measured using a Shimadzu UV-3600 spectrophotometer.

#### **AFM Characterization:**

Films for AFM images were cast on glass slides using procedures similar to those described for the photoluminescence experiments. Imaging was performed in semicontact (tapping) mode using Veeco RTESP tips.

## **TEM Characterization:**

The morphology of devices was determined by transmission electron microscopy (TEM) using a FEI Tecnai G2 microscope operated at 200 kV. Two different samples with and without compatibilizer were spin-coated onto sodium chloride substrates under the same conditions employed for device fabrication, followed by annealing at 150 °C for 1 h. Films were transferred onto TEM grids and then stained by exposing them to RuO<sub>4</sub> vapor for 30 mins.

# **External quantum efficiency measurement:**

The external quantum efficiency was determined at short circuit condition by illuminating the device with monochromatic light supplied by a Xenon lamp in combination with a monochromator (Spectra Pro 150, Acton Research Corporation). The number of photons incident on the sample was calculated for each wavelength by using a Si photodiode calibrated by the manufacturer (Hamamatsu).

## **Compound synthesis, general considerations:**

All glassware was dried overnight in an oven or by flame prior to use. Reactions were carried out under nitrogen or argon using standard Schlenk techniques. Unless otherwise noted, reagent solutions were added by syringe. Reactions were monitored by thin layer chromatography using Whatman<sup>®</sup> 250  $\mu$ m silica gel plates. Flash column chromatography was performed using Merck silica gel, 230-400 mesh. Solvents were removed with a rotary evaporator at aspirator pressure. Unless otherwise noted, all reagents were used as received from commercial suppliers without further purification. Tetrahydrofuran (THF), methylene chloride, and pyridine were dried prior to use by passing through two columns of neutral alumina. Acryloyl chloride was distilled to remove inhibitor prior to use. The following were synthesized by previously reported procedures: POPT,<sup>17a</sup> 11-amino-1-undecanol,<sup>20</sup> 1,<sup>21</sup> 6,<sup>8</sup> 8,<sup>12</sup> and 22.<sup>22</sup>

NMR spectra were recorded in CDCl<sub>3</sub> with a TMS standard using a Bruker AVQ-400, AVB-400, or DRX-500 spectrometer. <sup>13</sup>C NMRs were recorded at 100 MHz using <sup>1</sup>H decoupling. Mass spectrometry and elemental analysis data were recorded by staff members at the UC Berkeley mass spectrometry facility. Melting points were recorded on Electrothermal MELTEMP and are uncorrected.

#### N,N'-di(1-heptyloctyl)perylene-3,4,9,10-tetracarboxylic diimide 12:



#### Procedure:

A suspension of 3,4,9,10-perylenetetracarboxylic dianhydride (6.61 g, 17.0 mmol) and 8-aminopentadecane (9.68 g, 42.6 mmol) in acetic acid (4 mL) and N-methylpyrrolidinone (120 mL) was heated to 100 °C and stirred overnight. The resulting slurry was poured into of 1M HCl (300 mL). The precipitate was filtered and washed with water. The solid was then dissolved in chloroform (300 mL) and filtered through celite. The solvent was removed under reduced pressure to yield 10.1 g (73%) of **12** as a red solid suitable for use in the next step. Pure material for analysis and device studies was obtained through purification by column chromatography on silica gel (eluent: 8% ethyl acetate in hexanes).

#### Characterization:

mp 140 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.58-8.62 (m, 4H), 8.50 (d, J = 8.1 Hz, 4H), 5.17-5.21 (m, 2H), 2.21-2.29 (m, 4H), 1.85-1.91 (m, 4H), 1.25-1.38 (m, 40H), 0.82 (t, J = 6.8 Hz, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  134.68, 132.08, 131.32, 129.62, 126.62, 123.20, 54.97, 32.58, 32.01, 29.73, 29.44, 27.19, 22.82, 14.28; FTIR (film on NaCl): v = 2927, 2856, 1700, 1659, 1595, 1406, 1338, 1254, 851, 810, 746 cm<sup>-1</sup>; HRMS (FAB+, *m/z*): calcd for C<sub>54</sub>H<sub>70</sub>N<sub>2</sub>O<sub>4</sub>, 810.53336; found, 810.53356. Anal. calcd for C<sub>54</sub>H<sub>70</sub>N<sub>2</sub>O<sub>4</sub>: C, 79.96; H, 8.70; N, 3.45. Found: C, 79.76; H, 8.90; N, 3.43.

#### N-(1-hexylheptyl)-N'-(11-undecanol)perylene-3,4,9,10-tetracarboxylic diimide 24:



#### Procedure:

A suspension of **12** (9.40 g, 11.6 mmol) and KOH (38 g, 0.68 mol) in isopropanol (375 mL) and water (48 mL) was stirred at reflux for 70 min. After cooling the

suspension to 0 °C in an ice bath, concentrated HCl (50 mL) was slowly added. The solution was concentrated under reduced pressure and the precipitate isolated by filtration. The recovered solid was dissolved in chloroform and then poured into 1M HCl in methanol. The precipitate was recovered by filtration and dried under vacuum to yield a red solid (8.88 g) that was used in the next step without further purification.

A solution of the above solid, 11-aminoundecanol (3.26 g, 17.4 mmol), and acetic acid (2.0 mL, 35 mmol) in N-methylpyrrolidinone (60 mL) was stirred at 100 °C for 6.5 hours. The solution was poured into 1M HCl (200 mL) and the resulting precipitate was isolated by filtration and washed with water. The product was purified by column chromatography on silica gel (eluent: 15% ethyl acetate in chloroform) yielding 2.0 g of dark red solid (22% yield).

#### Characterization:

mp = 139-148 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.46-8.58 (m, 2H), 8.19-8.34 (m, 4H), 8.20 (d, J = 8.2 Hz, 2H), 5.19 (m, 1H), 4.16 (t, J = 7.6 Hz, 2H), 3.64 (t, J = 6.6 Hz, 2H), 2.24-2.30 (m, 2H), 1.85-1.90 (m, 2H), 1.72 (m, 2H), 1.57 (m, 2H), 1.22-1.53 (br m, 34H), 1.30 (t, J = 17.9 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 162.97, 134.06, 133.84, 130.89, 129.33, 128.90, 125.88, 122.90, 122.80, 122.72, 77.37, 63.14, 54.96, 40.71, 32.92, 32.47, 31.95, 31.07, 29.69, 29.66, 29.61, 29.50, 29.44, 29.37, 28.14, 27.25, 27.16, 25.84, 22.74, 14.20; FTIR (film on NaCl): v = 3478 (br), 2926, 2855, 1697, 1656, 1595, 1578, 1465, 1438, 1404, 1342, 1256, 810, 747 cm<sup>-1</sup>; HRMS (FAB+, *m/z*): calcd for C<sub>50</sub>H<sub>62</sub>N<sub>2</sub>O<sub>5</sub>, 770.46587; found 770.46656. Anal. calcd for C<sub>50</sub>H<sub>62</sub>N<sub>2</sub>O<sub>5</sub>: C, 77.89; H, 8.10; N, 3.63. Found: C, 77.73; H, 8.06; N, 4.01.

### Perylene acrylate monomer 6:



# Procedure:

To a flask charged with **24** (1.80 g, 2.33 mmol), triethylamine (0.65 mL, 4.7 mmol), and dichloromethane (50 mL) at 0 °C, was added dropwise a solution of acryloyl chloride (0.19 mL, 2.3 mmol, in 10 mL of dichloromethane). After stirring for 1 h at 0 °C, an additional solution of acryloyl chloride in dichloromethane was added in portions over the next hour until TLC showed completion of the reaction. A total of 1.25 equivalents of acryloyl chloride were added. The solution was then poured into water, the layers were separated, and the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Purification by column chromatography over silica gel (eluent: 1% ethyl acetate in chloroform) yielded 1.62 g of red solid (84% yield).

#### Characterization:

mp 135-138 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.58-8.68 (m, 8), 6.40 (dd, J = 17.3 and 1.5 Hz, 1H), 6.12 (dd, J = 17.3 and 10.4 Hz, 1H), 5.81 (dd, J = 10.4 and 1.5 Hz, 1H), 5.19 (m, 1H), 4.19 (t, J = 7.7 Hz, 2H), 4.14 (t, J = 6.7 Hz, 2H), 2.18-2.28 (m, 2H), 1.85-1.88 (m, 2H), 1.72-1.78 (m, 2H), 1.63-1.69 (m, 2H), 1.21-1.44 (br m, 34H), 0.82 (t, J = 6.9 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  166.36, 162.63, 133.64, 133.46, 130.45, 129.13, 128.72, 128.59, 125.56, 125.49, 122.70, 122.51, 122.45, 77.36, 64.77, 54.97, 40.64, 32.46, 31.94, 29.68, 29.62, 29.59, 29.57, 29.43, 29.35, 28.69, 28.11, 27.27, 27.16, 26.01, 22.72, 14.17; FTIR (film on NaCl): v = 2926, 2855, 1713, 1699, 1657, 1595, 1405, 1341 cm<sup>-1</sup>; HRMS (FAB+, *m/z*): calcd for C<sub>53</sub>H<sub>65</sub>N<sub>2</sub>O<sub>6</sub>, 831.4924; found, 831.4935. Anal. calcd for C<sub>53</sub>H<sub>64</sub>N<sub>2</sub>O<sub>6</sub>: C, 77.15; H, 7.82; N, 3.40. Found: C, 76.88; H, 8.01; N, 3.54.

N-(1-hexylheptyl)-N'-(1-ethylpropyl)perylene-3,4,9,10-tetracarboxylic diimide 9:



# Procedure:

A suspension of N,N'-di(1-ethylpropyl)perylene-3,4,9,10-tetracarboxylic diimide (5.7 g, 10.7 mmol), and KOH (35 g, 0.63 mol) in isopropanol (350 mL) and water (50 mL) was stirred at reflux for 7 h and poured into dilute HCl (500 mL). The resulting precipitate was isolated by filtration and washed with water. The solid was re-suspended in 5% KOH (100 mL) in water, stirred for 30 min, and filtered. After washing with dilute HCl, the solid was re-suspended in chloroform (50 mL) then filtered. The resulting 5.25 g of red solid was used in the next step without further purification.

To a suspension of the above product (313 mg) in N-methylpyrrolidinone (3.5 mL) was added 8-aminopentadecane (230 mg, 1.0 mmol) and acetic acid (0.17 mL, 3.0 mmol). The resulting mixture was stirred at 100 °C overnight and poured into 1M HCl (50 mL). The precipitate was isolated by filtration and washed with water. Purification by column chromatography over silica gel (eluent: 20% ethyl acetate in hexanes) gave 180 mg (40%, 2 steps) of red solid.

#### Characterization:

mp 248-250 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.59-8.67 (m, 8H), 5.15-5.23 (m, 2H), 2.21-2.33 (m, 4H), 1.84-2.00 (m, 4H), 1.21-1.37 (br m, 20H), 0.94 (t, *J* = 7.5 Hz, 6H), 0.82 (t, *J* = 6.8 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  134.68, 129.78, 126.61, 123.21, 57.90, 54.97, 32.56, 32.00, 29.72, 29.43, 27.18, 25.22, 22.82, 14.28, 11.57; FTIR (film on NaCl): v = 2927, 2856, 1702, 1659, 1595, 1405, 1336, 851, 809, 745 cm<sup>-1</sup>;

HRMS (FAB+, *m/z*): calcd for C<sub>44</sub>H<sub>50</sub>N<sub>2</sub>O<sub>4</sub>, 670.377059; found, 670.376370. Anal. calcd for C<sub>53</sub>H<sub>64</sub>N<sub>2</sub>O<sub>6</sub>: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.57; H, 7.70; N, 4.14.

## Synthesis of the first generation compatibilizer 7:



A float

A flask with attached condensor was charged with **6** (30.3 mg, 0.004 mmol), **2** (30.3 mg, 0.0657 mmol), and pyridine (1 mL). The suspension was degassed with four freeze/pump/thaw cycles, then heated to 90 °C for 6 h. The product was then purified by column chromatography over silica gel (eluent: 75% chloroform in hexanes). After concentrating the pure fractions, the polymer was precipated into methanol and isolated by filtration, yielding 25 mg (83% yield) of dark purple solid.

# Characterization:

THF-SEC (PS standard):  $M_n = 15.5 \text{ kDa}$ ,  $M_w = 16.1 \text{ kDa}$ , PDI = 1.04; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.65-8.75 (m, 8H), 6.98 (s, 49H), 5.07 (m, 1H), 2.80 (m, 98H), 2.63 (t, *J* = 7.5 Hz, 6H), 2.27 (m, 2H), 2.18 (m, 2H), 1.71 (m, 98H), 1.57 (m, 98H), 1.43 (m, 196H), 1.04 (m, 147H).

MALDI Mass Spec (Terthiophene matrix) of the First Generation Compatibilizer



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# Synthesis of P3HT with chain transfer agent as an end group (9):



## Procedure:

A 50 mL flask was charged with polymer 6 (121 mg),<sup>8</sup> chain transfer agent (CTA) 8 (83 mg), and DCC (71 mg). The flask was flushed with argon and CHCl<sub>3</sub> (10 mL), was added. The contents were stirred at room temperature and the reaction was monitored by TLC (Solvent; CHCl<sub>3</sub>;  $R_f = 0.1$  for P3HT 10 and  $R_f = 1$  for P3HT 12). After stirring overnight, the reaction mixture was precipitated into methanol. The precipitated polymer was filtered and washed thoroughly with methanol. The polymer was then dissolved in a minimum amount of CHCl<sub>3</sub> and filtered through a short pad of silica with a 3:1 mixture of CHCl<sub>3</sub> to yield 95 mg of the macro CTA 9.

#### Characterization:

THF-SEC (PS standard):  $M_n = 15.4 \text{ kDa}$ ,  $M_w = 16 \text{ kDa}$ , PDI = 1.04; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.73 (2 H, m), 7.53-7.55 (2 H, m), 7.29-7.39 (10 H, m), 7.17-7.19 (2 H, m), 6.99 (62 H, s), 4.57 (1 H, q J = 7.3 Hz), 4.28-4.5 (8 H, m), 2.82 (114 H, tJ = 7.6 Hz), 2.61-2.68 (6 H, m), 1.68-1.75 (134 H, m), 1.45(120 H, m), 1.35-1.37 (262 H, m), 0.93 (202 H, t J = 6.9 Hz).



### Synthesis of P3HT – Perylene diblock copolymer 13:



### Procedure:

To a Schlenk tube containing perylene acrylate **10** (430 mg), macroCTA **9** (20 mg), was added. The tube was evacuated and backfilled with argon. To this a standard solution of AIBN in 1,2-dichlorobenzene (285  $\mu$ L, 10<sup>-3</sup> M) was added followed by 190  $\mu$ L of 1,2-dichlorobenzene. The flask was taken through five freeze-pump-thaw cycles and immersed in an oil bath maintained at 85 °C. A vacuum was maintained in the tube was cooled to room temperature and exposed to ambient atmosphere to quench the reaction. The reaction mixture was diluted with CHCl<sub>3</sub> (4 mL) and precipitated into methanol. The precipitate was filtered and extracted with acetone in a soxhlet extractor to remove unreacted monomer. This was followed by extraction with CHCl<sub>3</sub>. The chloroform extract was concentrated and purified by chromatography to yield 69 mg of diblock copolymer.

# Characterization of diblock copolymer:

THF-SEC (PS standard):  $M_n = 21$  kDa,  $M_w = 27$  kDa, PDI = 1.29; <sup>1</sup>H NMR (500 MHz, CDCl<sub>2</sub>CDCl<sub>2</sub>):  $\delta$  7.77-8.14 (m, 12H), 6.95 (s, 1H), 5.00 (s, br, 2H), 4.02 (m, 6H), 2.76-2.78 (m, 2H), 2.37 (s, br, 2H), 2.12 (s, br, 3H), 1.89 (m, 4H), 1.66-1.7 (m, 10H), 1.22-1.40 (m, 66H), 0.80-0.90 (m, 138H).

# Note on NMR integration and estimated block length:

The specific identification and integration of the end group protons was not possible from the<sup>1</sup>H NMR spectra of the block copolymers. This makes it impossible to obtain exact block lengths from <sup>1</sup>H NMR. However, approximate ratios of the two blocks can be obtained by integrating regions of the spectra that can be assigned to each monomer. The integration for the singlet at 6.95 ppm (aryl proton in the thiophene backbone of P3HT) is set to 1. The multiplet from 7.77 to 8.14 ppm represents 8 aryl protons in the perylene acrylate monomer **6**. Based on this, a ratio of 3:2 is assumed for the number of perylene and thiophene units respectively. Mass spectrometry (MALDI TOF) of the amine terminated P3HT indicates and average mass of ~ 8.5 kDa. This implies an approximate block length of about 50 units for the P3HT block. Consequently, the block length of the perylene unit is estimated to be 75 units.

# THF-SEC of polymers 9 and 11:





Procedure:

A flask with attached condensor was charged with 3-(4-bromophenyl)propanol (733 mg, 3.41 mmol), hexamethyldistannane (1.33 g, 4.06 mmol),

tetrakis(triphenylphosphine)palladium(0) (79 mg, 0.068 mmol), and toluene (5 mL). The solution was degassed with four freeze/pump/thaw cycles, then heated at reflux for 15 h. After addition of more catalyst (119 mg, 0.102 mmol), heating was continued for another 24 h. After removal of solvent, the product was purified by column chromatography over silica gel (eluent: 3:1 hexanes:ethyl acetate), yielding 176 mg (17% yield) of clear oil.

## Characterization:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.41 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 3.70 (t, J = 6.7 Hz, 2H), 2.68 (t, J = 6.8 Hz, 2H), 1.88 (m, 2H), 0.26 (s, 9H). Anal. calcd for: C, 48.20; H, 6.74. Found: C, 48.57; H, 6.80.

#### Synthesis of alcohol-functionalized POPT 17:



# Procedure:

A flask with attached condensor was charged with POPT (100 mg, 0.01 mmol,  $M_n = 20$  kDa by THF SEC, polystrene standards), **15** (15 mg, 0.05 mmol), bis(triphenylphosphine)palladium(II) dichloride (7 mg, 0.01 mmol), toluene (1 mL), and DMF (0.15 mL). After degassing with bubbling N<sub>2</sub>, the reaction was stirred at 90 °C for 15 h. After diluting with chlorobenzene (4 mL) and degassing again with bubbling N<sub>2</sub>, Pd chelator **16** (22 mg) was added. The solution was heated at 70 °C for 1 h, then poured into degassed methanol (100 mL). The polymer was isolated by filtration, then dissolved in degassed 1,2-dichlorobenzene (3 mL) with 22 mg **16**. After stirring for 2 h at 80 °C under inert atmosphere, the polymer was precipitated into degassed methanol and isolated by filtration. This treatment with the chelator was repeated a third time, after which analysis of the methanol filtrate by UV/vis showed no further formation of Pd complex. 88 mg (88% recovery) of polymer was recovered as a black solid.

### Characterization:

1,2-Dichlorobenzene-SEC (PS standard):  $M_n = 14.1 \text{ kDa}$ ,  $M_w = 17.6 \text{ kDa}$ , PDI = 1.25. NMR data were identical to that previously reported<sup>17a</sup> (peaks from end groups were not observed). Evidence of the reaction's success comes from MALDI MS.



#### Synthesis of POPT macroinitiator 19:



Procedure:

In a nitrogen glovebox, a septum-capped vial was charged with **17** (86 mg, 0.0086 mmol), 4-dimethylaminopyridine (2 mg, 0.016 mmol), and chlorobenzene (4 mL). The sealed vial was removed from the glovebox, then triethylamine (0.20 mL, 1.4 mmol) and 2-bromo-2-methylpropionyl bromide (0.10 mL, 0.81 mmol) were added sequentially by syringe. The solution was stirred at room temperature for 1 h, then 80 °C for 1 h. The reaction was quenched by addition of a small amount of degassed methanol. The solution was then precipitated into methanol. The polymer was isolated by filtration and washed with methanol, yielding 85 mg polymer (99% recovery).

Characterization:

SEC and NMR data were identical to that of 17.





#### Synthesis of POPT/PDI diblock copolymer 20:



# Procedure:

In a nitrogen glovebox, a vial was charged with **19** (20 mg, 0.002 mmol), **10** (116 mg, 0.141 mmol), copper(I) bromide (4.0 mg, 0.028 mmol), 4,4'-dinonyl-2,2'-dipyridyl (23 mg, 0.055 mmol), and 1,2-dichlorobenzene (0.29 mL). Stirred on a hot plate at 90 °C for 48 h. Diluted in 1,2-dichlorobenzene (4 mL), then precipitated into acetone. Isolated the polymer by filtration, then dissolved in 5 mL degassed 1,2-dichlorobenzene containing 60 mg **16**. This solution was stirred under N<sub>2</sub> at 60 °C for 1 h, then precipitated into methanol. The polymer was isolated by filtration, washed with methanol, then dried yielding 22 mg of product as a black solid. SEC (dichlorobenzene) appears to show that the material is a mixture of diblock and starting material **19**.

#### Characterization:

1,2-Dichlorobenzene-SEC (PS standard):  $M_n = 26.1 \text{ kDa}$ ,  $M_w = 40.2 \text{ kDa}$ , PDI = 1.54.



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# Chapter 3 – The Development of a Low Bandgap Polymer with Thermally Cleavable Solubilizing Groups and its Application in the Fabrication of Layered Structures

# Background

When designing conjugated polymers, solubility is one of the primary issues that must be addressed. Since the utilization of solution processing is the principal driving force behind the development of polymer-based electronic devices, it is of course crucial that the polymers be soluble. Unfortunately, conjugated polymers without backbone substituents are typically insoluble. There are two components to this. One is enthalpic: strong  $\pi$ - $\pi$  stacking forces tend to encourage aggregation and limit solubility. This can be addressed by substituting the backbone with bulky groups, such as dendrimers.<sup>1</sup> This approach is not typically used, however, because breaking up  $\pi$ - $\pi$  stacking is detrimental to charge transport.

The other component limiting the solubility of conjugated polymers is entropic in nature. Due to the rigidity of conjugated backbones, there is little conformational flexibility gained upon transferring from the solid to liquid states, resulting in a low entropic driving force for dissolution. This is commonly addressed by substituting the polymer with flexible alkyl chains. When linear chains are utilized, the alkyl groups can not only improve solubility but also increase polymer crystallinity through side chain interdigitation. This is the case for materials like the highly crystalline pBTTT polymers, which possess record-setting hole mobilities.<sup>2</sup> Commonly, however, branched chains, particularly those with racemic chiral centers, are necessary to achieve sufficient solubility. These groups impart solubility by making the material amorphous, thereby limiting charge mobility. Thus, there is often a trade-off between solubility and mobility that limits performance in solution-processed polymer electronic devices such as field-effect transistors (FETs) and photovoltaics (PVs).

A potential way around this tradeoff is the use of solubilizing alkyl chains that can be removed after deposition of the polymer. Removal could be accomplished by heat, if the chains are linked to the backbone with a thermally labile group. This approach is related to the solubility switch concept used in chemically amplified photoresists.<sup>3</sup> Additionally, it was utilized to fabricate organic FETs based on oligothiophenes with solubilizing chains attached via labile esters.<sup>4</sup> Removal of solubilizing groups in this case converted an amorphous film into a highly crystalline one, resulting in a high charge mobility of 0.1 cm<sup>2</sup>/Vs.

In addition to addressing the solubility/mobility trade-off, the solubility switch could be used to fabricate multi-layer devices. Bi-layers and muti-layers are of interest for PVs and organic light emitting diodes (OLEDs). For PVs, the bulk heterojunction architecture allows for higher efficiency, but the simplicity of a bi-layer often enables studies of fundamental processes at interfaces. The use of solution-based deposition techniques, such as spin coating, to fabricate these organic bi-layers is often difficult, because it requires the two polymers to have different solubility properties. This is a challenge because most conjugated polymers are soluble only in non-polar chlorinated or aromatic solvents. Polymers that can be converted with heat into an insoluble form after deposition offer a way around this problem.

Previously, a polythiophene functionalized with esters was utilized as an interface modifier in a multi-layer cell.<sup>5</sup> Thermal conversion of the esters to carboxylic acids resulted in an insoluble polymer, allowing for the deposition of an additional layer. For some applications, however, the carboxylic acid functionality may be undesirable. The thermal deprotection of carbamates to amines could also be utilized to generate a solubility switch.

The polymer chosen to demonstrate this concept, poly-N-dodecyl-2,5-bis(2'thienyl)pyrrole, 2,1,3-benzothiadiazole (PTPTB) (figure 1), is a low bandgap polymer originally designed for bulk heterojunction solar cells.<sup>6</sup> Poor solubility of this material limited the molecular weight that could be utilized in solar cells to short oligomers. This is one factor that likely limited the cell performance to 1% external power conversion efficiency, as lower molecular mass polymers often possess poor charge mobilities.<sup>7</sup> Substituting the linear alkyl chain solubilizing groups with bulky branched groups could improve solubility and allow higher molecular weights to be obtained. Thermally removing these chains after deposition might improve polymer properties as discussed above.



**Figure 1:** Structure of PTPTB, and the target version of PTPTB with a thermally cleavable solubilizing group (1). The insoluble polymer left after removal of the solubilizing chain is **2**.

PTPTB is also a good candidate for this study because it has been utilized in multi-layered cells. In the report, a thin layer of PTPTB was placed between the primary absorbing layer, poly(3-hexyl)thiophene (P3HT), and an inorganic electron acceptor layer of TiO<sub>2</sub>. In these devices, directional energy transfer from P3HT to PTPTB concentrates excitons near the donor/acceptor interface, which helps to overcome the exciton-diffusion bottleneck and results in a three fold increase in the photocurrent.<sup>8</sup> This is shown schematically in figure 2. The particular solubility properties of the high molecular weigh fraction of PTPTB, which is soluble only in hot *o*-dichlorobenzene (ODCB), exceptionally allowed for the deposition of a layer of P3HT without disturbing the PTPTB. However, a version of PTPTB with thermally cleavable solubilizing groups might simplify the process of fabricating multi-layered devices. It also might increase the efficiency of energy transfer, by increasing the density of absorbing material and thus the thin film absorption coefficient in the PTPTB layer.

The target polymer 1 is shown in figure 1. The branched alkyl group is attached to the polymer via a secondary carbamate at the pyrrole nitrogen. This functional group is known to undergo thermolysis between 150 and 300 °C, releasing volatile CO and alkenes. The resulting polymer 2 should be electronically similar to PTPTB, but insoluble.



**Figure 2:** Scheme for partially overcoming the exciton diffusion bottleneck in layered solar cells. A thin layer (5 nm) of the low bandgap polymer PTPTB is placed between the donor P3HT and acceptor  $TiO_2$  layers. Energy transfer to PTPTB helps concentrate excitons at the interface.

# **Results and Discussion**

# Synthesis and Thermal Conversion of 1

Polymer 1 was obtained via a Stille coupling polymerization in THF at reflux using a Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> precatalyst from monomeric precursors synthesized according to standard procedures (scheme 1 and experimental section). An excess of the stannylated monomer (1.2 equivalents) versus the brominated monomer was necessary to obtain longer polymer chains. This is likely because some stannyl groups are consumed converting the Pd(II) catalyst precursor to an active Pd(0) species. Degradation of stannyl groups during polymerization may also play a role. The crude polymerization product was fractionated via Soxhlet extraction using MeOH, hexanes, and acetone to first remove impurities and short oligomers, followed by THF to isolate the pure polymer. Size exclusion chromatography (SEC) in THF using polystyrene as a standard indicates that the polymer has a relatively high molecular mass ( $M_n = 11,400 \text{ g mol}^{-1}$ , PDI = 1.96). By comparison, the soluble fraction of PTPTB had an  $M_n$  of only 1,780 g mol<sup>-1</sup>.<sup>6a</sup> The improvement results from better solubility brought by the branched alkyl chains. <sup>1</sup>H NMR in CDCl<sub>3</sub> confirms the expected ratios of the different monomer units.



Scheme 1: Synthesis of polymer 1. (i) 1. NaH, THF. 2. 4-nitrophenyl(2-hexadecyl)carbonate (yield 81%). (ii) NBS, THF, -78°C (94%). (iii) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 2-(tributylstannyl)thiophene, THF, 60°C (71%). (iv) 1. LDA, THF, -78°C. 2. Me<sub>3</sub>SnCl (91%). (v) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, THF, 60°C.

Thermogravimetric analysis (TGA) of polymer 1 confirms the occurrence of the thermolysis reaction, as well as the good thermal stability of the deprotected polymer (figure 3). Infrared spectroscopy before and after thermal treatment at 280 °C of a thin film of 1 confirms the loss of the carbamate protecting group via the disappearance of the

C=O stretching vibration of the carboester group at 1753 cm<sup>-1</sup> and the appearance of the N-H vibration at 3448 cm<sup>-1</sup>. The evaporation of the alkyl groups is confirmed by the loss of the great majority of the peaks corresponding to C-H stretching vibrations (figure 4).



Figure 3: Thermogravimetric analysis of 1, heating at 5°C/min under inert atmosphere.



**Figure 4:** Infrared spectrum of thin film of 1 on NaCl plate a) before, and b) after thermal treatment at 280 °C.

# **Optical Characterization of Polymers 1 and 2**

Having demonstrated the thermal removal of the solubilizing group, the effect of this removal on the electronic properties of the polymer was examined. The bulky solubilizing groups probably affect the planarity of the polymeric backbone, and also modify the energies of the  $\pi$  orbitals due to the electron-withdrawing nature of the carbamate. This results in a bandgap higher than that of PTPTB, as observed by the blue shift of the absorption band of 1 in ODCB ( $\lambda_{max} = 590$  nm for PTPTB,  $\lambda_{max} = 540$  nm for 1), and in thin films ( $\lambda_{max} = 655$  nm for PTPTB,  $\lambda_{max} = 580$  nm for 1).

Cleavage of the solubilizing groups considerably modifies the optical properties of the polymer. This can be first visually confirmed by the strong color change, from purple to green, observed while annealing the polymeric film. Thermal treatment of a thin film of **1** deposited onto a glass substrate by drop casting from a chloroform solution was followed by UV-Vis spectrometry (Fig. 5). Important shifts in the absorption bands toward lower energies were observed after annealing the film at 280 °C for 30 min ( $\Delta\lambda_{max}$  = 90 nm). The optical bandgap of a thin film of **1** was determined to be 1.74 eV before annealing and 1.47 eV after thermal treatment, based on the onset of the absorption band.

This large shift is due at least in part to an electronic effect. PTPTB possesses a low bandgap due to the alternation of an electron rich thiophene-pyrrole-thiophene segment with an electron poor benzothiadiazole unit in the backbone. Alternating donor and acceptor units in the main chain of conjugated polymers is known to produce low bandgap materials.<sup>9</sup> By weakening the donor strength of the pyrrole unit with an electron-withdrawing carbamate, the donor/acceptor effect is attenuated. Removing the carbamate protecting group restores the donor character of the pyrrole, and likely also increases polymer planarity, resulting in a much reduced bandgap.



**Figure 5:** At left, absorption spectra of thin films of **1** drop-cast on glass from chloroform solution, before (i) and after (ii) thermal treatment for 1h at 280 °C. At right, photographs of the films showing the color change from purple to green.

In addition to reducing the bandgap, removal of the solubilizing groups should increase the absorption coefficient of the polymer film, which is advantageous for a number of applications. To measure this, uniform thin films of 1 were spin coated on glass from a chloroform solution. The thermal deprotection process was monitored by atomic force microscopy (AFM). After annealing at 280 °C, the film thickness decreased from 32 nm to 15 nm, a change of 53%. No significant distortion of the film shape accompanied this change: both films were highly smooth, possessing RMS roughnesses of 0.48 nm and 0.64 nm before and after annealing, respectively. The thin film absorption coefficient is often expressed as absorbance units/film thickness. For polymers 1 and 2, this value is  $0.0072 \pm 0.0002$  nm<sup>-1</sup> and  $0.0172 \pm 0.0008$  nm<sup>-1</sup>, respectively. For PTPTB, this value is  $0.0073 \pm 0.0001$  nm<sup>-1</sup> and for P3HT, a polymer typically considered to have an exceptionally high absorption coefficient, it is 0.011 nm<sup>-</sup> Another figure of merit for quantifying the total amount of light absorbed by a polymer is the integral absorbance area, calculated by integrating the area under the main absorbance peak and dividing by film thickness.<sup>10</sup> This probably provides a better measure of total light absorbing capacity than the single wavelength absorption coefficient. The integral absorbance areas for polymers 1, 2, PTPTB, and P3HT are 1.15  $\pm$  0.03, 3.50  $\pm$  0.17, 1.36  $\pm$  0.03, and 1.76 nm<sup>-1</sup>, respectively. These values are summarized in table 1. Thus, by either measure, but especially by the integral absorbance area, the deprotected polymer 2 is an exceptionally strong absorber. This illustrates a benefit of the use of thermally cleavable solubilizing groups. Upon deprotection, the polymer is mobile enough at high temperature to fill in any void space left behind by evaporation of the alkyl chains, resulting in a film very dense in absorbing material. Notably, polymer **2** absorbs strongly at its peak and has a very broad absorbance spectrum, making it ideal for applications in solar energy collection.

Overall, the changes in the optical properties of **1** upon thermal treatment are advantageous for electronic device applications. Shifting the absorption properties of conjugated organic molecules to lower energy often gives rise to oxidative stability problems. However, the present polymer displays a low bandgap only after post-processing treatment. Polymer **1** can be seen as a soluble precursor to a low bandgap polymer, making its manipulation during deposition easier due to its good solubility and stability. In contrast, the poor solubility of the high molecular weight fraction of PTPTB has limited its application in electronic devices.<sup>6b</sup>

Polymer	$\lambda_{max}$ (nm)/absorption coefficient (nm <sup>-1</sup> ) <sup>a</sup>	Integral Absorbance Area (nm <sup>-1</sup> ) <sup>b</sup>
1	$585/0.0072 \pm 0.0002$	$1.15 \pm 0.03$
2	$694/0.0172\pm0.0008$	$3.50 \pm 0.17$
PTPTB	$683/0.0073 \pm 0.0001$	$1.36 \pm 0.03$
P3HT <sup>c</sup>	567/0.011	1.76

**Table 1**: Optical Data for Select Polymers. <sup>*a*</sup>This value was obtained by dividing the absorbance at the  $\lambda_{max}$  by the film thickness. <sup>*b*</sup>This value was obtained by dividing the integral area under the main absorbance peak by the film thickness. <sup>*c*</sup>Values for P3HT are from reference 10.

### Use of 1 for Fabricating Multi-Layer Structures

Due to the exciton diffusion bottleneck, bilayer organic solar cells are normally inefficient. The problem is the low exciton diffusion length in polymers, which is typically less than 10 nm.<sup>11</sup> However, layered architectures do have some advantages. In particular, charge mobilities tend to be superior in pure layers relative to bulk heterojunction blends, beause charges do not have to follow tortuous paths to reach electrodes. High charge mobilities prevent the build-up of space charge<sup>12</sup> and also increase the probability of separating the geminate pair formed after initial exciton dissociation.<sup>13</sup> Thus, it would be advantageous to develop a scheme for increasing the exciton diffusion length of conjugating polymers to allow high efficiencies from layered cells. Materials that form triplet excitons are known to have large diffusion lengths due to their long excited-state lifetimes.<sup>14</sup> However, intersystem crossing to form a triplet state is usually accompanied by a loss of 0.4-0.8 eV in energy, which severely limits the  $V_{OC}$  that can be obtained from a device utilizing triplet excitons. A method to increase the diffusion length of singlet excitons is therefore desired.

One such method is the use of fluorescence resonance energy transfer (FRET) to concentrate excitons near an interface, as described in figure 2. For FRET between two chromophores, the characteristic  $R_o$ , or distance over which transfer is 50% efficient, is typically 2-4 nm. This might suggest that FRET could offer little, if any, advantage over random exciton diffusion, since typical diffusion lengths in conjugated polymers are 5-10 nm. However, single chromophore to chromophore (point to point) transfer does not accurately describe the situation for the device configuration in figure 2. An excited chromophore in the donor phase can transfer to any chromophore in the acceptor phase. Thus, the transfer can be described as point to slab (figure 6). For point to point transfer, the rate is proportional to  $1/r^6$ , where r is the distance between points. For point to slab, this rate equation must be integrated over all possible transfers. The rate then becomes

proportional to  $1/x^3$ , where x is the distance to the closest point on the slab. This situation is described schematically in figure 6. Such a relaxed distance dependence has been previously recognized for its importance in describing FRET to metal films,<sup>15</sup> between dyes in layered Langmuir-Blodgett structure,<sup>16</sup> and in heterostructure organic light emitting diodes (OLEDs).<sup>17</sup> It implies that FRET in a layered solar cell can be efficient over distances much longer than 2-4 nm.



**Figure 6**: Schematic showing three different geometries for energy transfer. At left is point to point transfer, at center is point to plane, and at right is point to slab. Only a single excited donor chromophore is shown, although it is in actuality embedded in a matrix of unexcited chromophores. The arrows represent possible energy transfer pathways.

In the previous report, energy transfer from P3HT to PTPTB improved the effective diffusion length from roughly 3 nm to 8 nm.<sup>8</sup> While this resulted in a tripling of the  $J_{SC}$  from 0.44 to 1.3 mA/cm<sup>2</sup>, this is still about one tenth the current obtained from the best bulk heterojunction cells. Clearly, more efficient FRET must be achieved to make this approach viable for obtaining high efficiency solar cells. According to Förster theory, the factors that influence the rate of energy transfer are the radiative rate of the donor (or its fluorescence quantum yield), the extinction coefficient of the acceptor integrated across the absorption band, and the spectral overlap of the donor emission and acceptor absorbance.<sup>18</sup> In the P3HT/PTPTB system, only the spectral overlap is optimal. The fluorescence quantum yield of P3HT is very low (<2%),<sup>19</sup> and the integrated extinction coefficient of PTPTB is less than half that of polymer **2**.

To try to test the limits of exciton transfer via FRET, model bilayers consisting of DOW Red (FRET donor) and polymer 2 (FRET acceptor, cast using 1 as a precursor) or TiO<sub>2</sub> (electron acceptor) were constructed. DOW Red is a propriety polymer designed for use in OLEDs. It has a fluorescence quantum yield of 70%, among the highest for any conjugated polymer. Additionally, the integrated extinction coefficient of 2 is among the highest known for a polymer. Figure 7a shows the overlap between the emission of DOW Red and the absorption of 2. Clearly, the spectral overlap is optimal as well. Thus, FRET in this system should be about as efficient as can reasonably be expected.

To test the effectiveness of exciton transfer via FRET, films of varying thickness of DOW Red were cast on a thin layer of a quencher, either 2 (8 nm) or  $TiO_2$  (<5 nm) on glass. The insolubility of 2 allowed the easy fabrication of ideal bilayers with no layer interpenetration. Fluorescence intensity was then measured as a function of DOW Red thickness. The data is then plotted as the fraction of excitons harvested, which is determined by comparing the fluorescence intensity with a quencher to the intensity observed for DOW Red on glass with no quencher. When  $TiO_2$  is used as the quencher,

exciton harvesting should reflect only random diffusion, as the wide bandgap of  $TiO_2$  prevents FRET. When **2** is used, however, FRET should allow for improved exciton harvesting. Figure 7b shows the results. The black squares indicate the results for DOW Red on TiO<sub>2</sub>. This data is fit (black line) using a previously described model for exciton diffusion<sup>14a, 20</sup> with a diffusion length of 3 nm. DOW Red was likely intentionally designed to have a low exciton diffusion length because migration of excitons is undesirable in OLEDs.

When polymer 2 is used in place of  $TiO_2$ , fluorescence quenching becomes much more pronounced due to FRET. Interestingly, the quenching data (black triangles) can still be fit to the same diffusion model (red line), but this time with a diffusion length of 27 nm. Thus, FRET allows polymers to obtain effective diffusion lengths approaching 30 nm. This is a large improvement over typical diffusion lengths of 5-10 nm, and should allow for significantly improved efficiency in layered solar cells.



**Figure 7**: a) Emission spectra of DOW Red (red line) and absorbance spectra of **2** (purple line). b) Fraction of excitons harvested versus DOW Red film thickness on energy acceptor **2** (black triangles) and on the quenching surface  $TiO_2$  (black squares). The lower black curve is a model corresponding to a diffusion length of 3 nm. The upper red curve is a model assuming a diffusion length of 27 nm.

Because DOW Red was designed for use in OLEDs, it has a very low charge mobility. Thus, solar cells utilizing DOW Red function poorly. The system investigated here is therefore a model designed to test the limits of exciton transfer via FRET. Future implementation of this concept in a working solar cell will require the development of a highly luminescent polymer that also transports charge. However, it is apparent that diffusion lengths approaching 30 nm are feasible. This is still short of the 100 nm length required for full light absorption. However, it is possible to pattern a TiO<sub>2</sub> surface with highly ordered nanostructures on the 30-50 nm length scale.<sup>21</sup> The use of such patterned TiO<sub>2</sub> in combination with a FRET scheme could completely overcome the exciton diffusion bottleneck without the use of a disordered bulk heterojunction.

# Conclusions

A version of the low bandgap polymer PTPTB with thermally cleavable solubilizing groups has been developed. The use of branched solubilizing chains allowed high molecular weight polymer to be synthesized. These chains are attached to the polymer via a carbamate linkage that degrades above 220 °C, releasing volatile

byproducts and leaving behind an unsubstituted pyrrole in the main conjugated chain. This reaction alters the optical properties of the polymer, significantly lowering the bandgap, as well as rendering the material insoluble. The volume of the polymer decreases significantly upon deprotection, resulting in a material with a very high absorption coefficient.

This polymer was utilized in bilayers to improve the effective exciton diffusion length of DOW Red from 3 to 27 nm. Two properties made this possible. First, the ability to thermally convert the polymer into an insoluble form allowed for the easy fabrication of well-defined bilayers. Second, the high absorption coefficient of the material helped maximize the efficiency of FRET, allowing for long-range transfer of excitons. This long-range transfer could potentially be utilized to fabricate efficient multi-layer solar cells if a highly emissive donor polymer with good charge transport properties could be developed.

# Experimental

#### **Thin Film Fabrication**

Dow Red polymer films of various thicknesses were deposited by spin coating in a nitrogen-filled glove box at 2000 rpm from chlorobenzene solutions. By using solutions with a range of polymer concentrations, films with thicknesses spanning 5 -110 nm were deposited. The polymer thickness was measured using a combination of Xray reflectivity, atomic force microscopy (AFM), and absorption spectroscopy. Polymer films were spin coated on glass substrates, glass substrates with <5 nm thick titania films (for measuring exciton quenching by intrinsic migration to the titania/polymer interface and subsequent electron transfer), and glass with  $\sim 8$  nm thick films of 2 (for measuring exciton quenching by long range energy transfer). Thin titania films were fabricated via Titanium(IV)-ethoxide was mixed with a solution of 40:1 a sol-gel route. ethanol:HCl(concentrated). Thin films of the titania precursor were spin coated on glass substrates at 2000 rpm and thermally treated at 150 °C in an oven for >8 hours to allow condensation and densification of the thin films. Finally these films were calcined at 450 °C to crystallize the titania films. Films of 1 were spin cast from a chloroform solution and subsequently converted to 2 by heating at 250 °C for 30 minutes in a nitrogen environment. The RMS roughness of all interfaces was found to be less than 1 nm.

#### **Photoluminescence Data**

532 nm s-polarized light was used for excitation. Photoluminescence spectra were collected using a cooled-CCD camera. Samples were held in a sealed chamber in nitrogen to protect the organic films from photodegradation when they were removed from the glove box.

#### Materials.

DOW Red was obtained from the DOW Chemical Company and used as received. All other reagents were purchased from Aldrich and used without further purification unless otherwise noted. 4,7-Dibromobenzo[1,2,5]thiadiazole 7 was prepared using a method described by Edelman and  $al.^{22}$  All solvents (reagent grade) were purchased from Fisher or EM Science. Tetrahydrofuran (THF) was distilled over

sodium/benzophenone. Methylene chloride, and pyridine were dried prior to use by passing through two columns of neutral alumina. Diisopropylamine was distilled over CaH<sub>2</sub>. *N*,*N*-Dimethylformamide (DMF) was stored over molecular sieves. *N*-bromosuccinimide (NBS) was recrystallized from acetic acid prior to use. All reactions of air- and water-sensitive materials were performed under nitrogen in flame-dried glassware and degassed solutions. 'Degassed' refers to solutions that have been subjected to three successive freeze-thaw cycles on a nitrogen/high-vacuum line. All solvents were removed with a rotary evaporator at aspirator pressure. Reactions were monitored by thin layer chromatography using Whatman<sup>®</sup> 250 µm silica gel plates. Flash column chromatography was performed using Merck Kieselgel 60 silica, 230-400 mesh.

# Characterization.

<sup>1</sup>H NMR and <sup>13</sup>C NMR (using <sup>1</sup>H decoupling) were recorded in CDCl<sub>3</sub> with TMS as standard on Bruker AM-400 and AMX-400. Low and high resolution fast atom bombardment (FAB) and electronic impact (EI) mass spectrometry was performed at the UC Berkeley MS Facility. High resolution mass spectrometry measurements are valid to  $\pm$  5 ppm. Thermogravimetric Analysis (TGA) was performed using a Seiko instruments SSC 5200 TG/DTA 220, at a speed of 5°C/min. THF GPC was carried out at 1.0 mL/min. Three Plgel columns (7.5 x 300 mm) with pore sizes of 10<sup>5</sup>, 10<sup>3</sup>, and 500 Å were used. The particle size was 5 µm. The GPC system consisted of a Waters 510 pump, a Waters 717 autosampler, a Waters 486 UV-vis detector, a Wyatt DAWN-EOS light scattering detector, and a Wyatt Optilab differential refractive index detector. The columns were thermostatted at 35 °C. Absorption spectra were recorded on a Cary 50 UV-Vis spectrometer. FT-IR spectra were obtained on NaCl plates with an ATI Mattson Gemini spectrometer. MALDI-TOF MS was performed on a PerSeptive Biosystems Voyager-DE, using *trans*-3-indoleacrylic acid as the matrix.

# 4-Nitrophenyl(2-hexadecyl)carbonate:



Procedure:

A solution of 2-hexadecanol (2.38 g, 0.830 mmol) and pyridine (0.81 mL, 10 mmol) in  $CH_2Cl_2$  (25 mL) was cooled to 0 °C. To this solution was added dropwise a solution of 4-nitrophenylchloroformate (2.00 g, 9.93 mmol) in  $CH_2Cl_2$  (5 mL). The resulting solution was allowed to stir overnight while slowly warming to room temperature. The solution was then poured into water (40 mL). After separating the layers, the aqueous layer was extracted with  $CH_2Cl_2$  (40 mL). The combined organic layers were then dried over  $Na_2SO_4$  and concentrated under reduced pressure. The resulting oil was purified by flash column chromatography ( $CH_2Cl_2$ :hexanes 1:3) to yield 3.60 g (90%) of 1 as a white solid.

#### Characterization:

m.p. = 46.3-47.0 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.28 (d, J = 9.2, Hz, 2H), 7.39 (d, J = 9.2 Hz, 2H), 4.88 (m, 1H), 1.73 (m, 1H), 1.60 (m, 1H), 1.38 (d, J = 6.3 Hz, 3H), 1.26 (br s, 24H), 0.88 (t, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  155.91,

152.31, 145.46, 125.46, 122.00, 77.89, 35.93, 32.13, 29.90, 29.87, 29.84, 29.77, 29.70, 29.58, 25.46, 22.90, 19.96, 14.33. HRMS (FAB+) m/z calcd for (C<sub>23</sub>H<sub>38</sub>NO<sub>5</sub>) 408.2750; found 408.2749. Anal. calcd for (C<sub>23</sub>H<sub>37</sub>NO<sub>5</sub>) C, 67.78; H, 9.15; N, 3.44; found: C, 68.02; H, 9.47; N, 3.45.

### 1-(2-Hexadecoxy)carbonylpyrrole (3):



Procedure:

A suspension of sodium hydride (0.21 g, 8.0 mmol) in THF (20 mL) was cooled to 0°C, and pyrrole (0.69 mL, 9.9 mmol) was added dropwise. After stirring for 5 min, the evolution of gas was observed. After an additional 25 min of stirring, a solution of 4nitrophenyl(2-hexadecyl)carbonate (3.36 g, 8.25 mmol) in THF (5 mL) was added dropwise, resulting in the formation of copious amounts of an orange precipitate. The solution was then stirred overnight as it slowly warmed to room temperature. After removing the solvent under reduced pressure, the resulting solid was suspended in ethyl acetate (100 mL), then extracted with dilute NaHCO<sub>3</sub> (100 mL) followed by water (2 x 100 mL) and brine (100 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, then concentrated under reduced pressure. The resulting oil was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:hexanes 1:3) to yield 2.23 g (81%) of **3** as a clear oil.

Characterization:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.27 (t, *J* = 2.2 Hz, 2H), 6.23 (t, *J* = 2.3 Hz, 2H), 5.06 (m, 1H), 1.73 (m, 1H), 1.60 (m, 1H), 1.35 (d, *J* = 6.3 Hz, 3H), 1.26 (br s, 24H), 0.88 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  150.24, 120.13, 112.30, 75.19, 36.05, 32.13, 31.05, 29.88, 29.86, 29.83, 29.75, 29.69, 29.60, 29.57, 25.49, 22.89, 20.13, 14.31. MS (FAB+): *m*/*z* = 336 (M + H). Anal. calcd for (C<sub>21</sub>H<sub>37</sub>NO<sub>2</sub>) C, 75.17; H, 11.11; N, 4.40; found: C, 75.19; H, 11.51; N, 4.40.

# 1-(2-Hexadecoxy)-2,5-dibromocarbonylpyrrole (4):



# Procedure:

A solution of **3** (640 mg, 1.90 mmol) in THF (20 ml) was cooled to -78 °C. The flask was covered to exclude light, and *N*-bromosuccinimide (680 mg, 3.80 mmol) was added in portions over 5 minutes. The resulting suspension was allowed to stir overnight

while slowly warming to room temperature. The solution was then concentrated under reduced pressure without using any heat. The resulting crude product was dissolved in hexanes (10 mL), filtered, and then concentrated to yield 884 mg of 3 (94%) as a yellow oil which was used immediately in the next step without further purification.

Characterization:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.27 (s, 2H), 5.14 (m, 1H), 1.82 (m, 1H), 1.66 (m, 1H), 1.43 (d, *J* = 6.3 Hz, 3H), 1.25 (br s, 24H), 0.88 (t, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.92, 116.82, 100.78, 77.73, 35.83, 32.14, 29.90, 29.87, 29.83, 29.75, 29.68, 29.58, 25.48, 22.91, 19.89, 14.34.

### 1-(2-Hexadecoxy)-2,5-bis(2-thienyl)carbonylpyrrole (5):



Procedure:

To a solution of 2-(tributylstannyl)thiophene (1.6 mL, 5.1 mmol) in THF (10 mL) was added 4 (850. mg, 1.70 mmol). The solution was degassed using three freeze/pump/thaw cycles. Under high nitrogen pressure, dichlorobis-(triphenylphosphine)palladium(II) (60 mg, 0.09 mmol) was added quickly. The resulting solution was stirred at 60 °C overnight. The solution was then concentrated under reduced pressure, and the crude product was purified by flash column chromatography (2:1 hexanes/CH<sub>2</sub>Cl<sub>2</sub>) to yield 611 mg (71%) of 5 as a yellow oil which crystallized after extensive drying under high vacuum.

#### Characterization:

m.p. = 37-41 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.31 (d, *J* = 5.1 Hz, 2H), 7.09 (d, *J* = 3.4 Hz, 2H), 7.03 (t, *J* = 4.3 Hz, 2H), 6.35 (s, 2H), 4.79 (m, 1H), 1.63 (m, 1H), 1.26 (br s, 25H), 1.01 (d, *J* = 6.2 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  134.54, 129.06, 127.46, 126.97, 125.91, 114.24, 76.31, 35.44, 32.15, 29.92, 29.88, 29.77, 29.66, 29.59, 28.49, 22.92, 19.13, 14.35, 13.82. HRMS (FAB+) *m/z* calcd for (C<sub>29</sub>H<sub>41</sub>NO<sub>2</sub>S<sub>2</sub>) 499.2579; found 499.2588.

# <u>1-(2-Hexadecoxy)-2,5-bis(5-trimethylstannyl-2-thienyl)carbonylpyrrole (6):</u>



### Procedure:

A solution of diisopropylamine (0.35 mL, 2.5 mmol) in THF (10 mL) was cooled to -78  $^{\circ}$ C and butyllithium (2.1 N in hexanes, 0.93 mL,1.9 mmol) was added dropwise.

After stirring for 5 min at -78 °C, the solution was allowed to warm slowly to room temperature over 30 min. The solution was then cooled to -78 °C in a dry ice/isopropanol bath, and **5** (480 mg, 0.96 mmol) dissolved in THF (10 mL) was added dropwise. After stirring the solution for 30 min at -78 °C, the dry ice was removed from the bath and the temperature was allowed to warm to -40 °C over 30 min. The solution was then cooled again to -78 °C, and trimethyltin chloride (1.0 M in THF, 1.9 mL, 1.9 mmol) was added dropwise. The resulting solution was then allowed to warm slowly to room temperature. After stirring overnight, the solution was poured into water (75 mL), then extracted with diethyl ether (2 x 75 mL). The combined organic fractions were washed with brine (75 mL), dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (alumina, CH<sub>2</sub>Cl<sub>2</sub>:hexanes 1:4) to yield 640 mg (80%) of **6** as a yellow oil.

#### Characterization:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.19 (d, J = 3.2 Hz, 2H), 7.10 (d, J = 3.4 Hz, 2H), 6.32 (s, 2H), 4.76 (m, 1H), 1.25 (br s, 26H), 1.00 (d, J = 6.2 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H), 0.38 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  151.32, 140.28, 138.39, 135.06, 129.26, 128.40, 113.82, 76.10, 35.42, 32.15, 29.92, 29.88, 29.83, 29.71, 29.58, 25.11, 22.92, 19.04, 14.35, -8.00. HRMS (FAB+) *m/z* calcd for (C<sub>35</sub>H<sub>57</sub>NO<sub>2</sub>S<sub>2</sub><sup>118</sup>Sn<sup>120</sup>Sn) 823.1893, found 823.1906.

# <u>Poly[2-(5-(2,1,3-benzothiadiazol-4-yl)-2-thienyl)-1-(2-hexadecoxy)-5-(2-thienyl)-</u> carbonylpyrrole] (1):



A solution containing **6** (184 mg, 0.230 mmol) and 4,7-dibromo-2,1,3benzothiadiazole (55.0 mg, 0.190 mmol) in THF (4 mL) was degassed using 3 freeze/pump/thaw cycles. Under high nitrogen pressure, dichlorobis(triphenylphospine)palladium(II) (4 mg, 0.06 mmol) was added quickly. The solution was heated at 60 °C for 18 h, during which time the color changed from light yellow to dark purple. The solution was then poured into methanol (150 mL), producing a dark precipitate that was collected by filtration through an extraction thimble. The solid was washed in a Soxhlet extractor for at least twelve hours with each of the following solvents: hexanes, methanol, and acetone. Soxhlet extraction with THF followed by precipitation from methanol afforded 62 mg of **5** as a brown powder.

#### Characterization:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.10 (m, 2H), 7.89 (br s, 2H), 7.25 (d, J = 3.7 Hz, 2H), 6.54 (br s, 2H), 4.94 (m, 1H), 1.0-1.4 (br m, 29H), 0.87 (t, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  128.01, 127.73, 125.51, 114.64, 35.62, 32.16, 29.89, 29.80, 29.61, 25.18, 22.92, 19.39, 14.36. FTIR (film on NaCl, cm<sup>-1</sup>): 2921, 2851, 1753, 1482, 1445, 1274, 787. MALDI-TOF: 2402 (H-(TPTB)<sub>3</sub>-TPT-H), 3035 (H-(TPTB)<sub>4</sub>-TPT-H),

3668 (H-(TPTB)<sub>5</sub>-TPT-H). UV-Vis: (CHCl<sub>3</sub>, nm): 370, 540; (dropcast on glass from CH<sub>3</sub>Cl solution, nm): 390, 580. Anal. calcd for  $(C_{35}H_{41}N_3O_2S_3)_n$  C, 66.52; H, 6.54; N, 6.65; S, 15.22.; found: C, 66.35; H, 6.81; N, 6.34; S, 14.82.

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# Chapter 4 – Synthesis and Characterization of N-type Polymers Based on Perylene Diimide

# Background

Among bulk heterojunction organic solar cells, blends of a p-type conjugated polymer and a fullerene n-type small molecule have been by far the most successful. The fullerene is almost always either [6,6]-phenyl-C<sub>61</sub> butyric acid methyl ester (PCBM) or the  $C_{70}$  version  $PC_{71}BM$ . A variety of p-type polymers exist that when blended with one of these fullerenes give power conversion efficiencies between 4-6.7%.<sup>1</sup> In many of these cells, most of the processes involved in device operation are very efficient, including splitting of excitons into free charges and collection of these charges at electrodes. In fact, an internal quantum efficiency approaching 100% has been observed in at least one case.<sup>1e</sup> However, in most cases light absorption is not optimal, either because the devices must be made too thin (external quantum efficiencies are typically 40-70%, lower than internal quantum efficiencies), or because the polymer/fullerene combination does not absorb broadly across the solar spectrum. Open circuit voltages  $(V_{\rm OC})$  are also typically not optimal. This is because more energy is lost in the transfer of an electron from polymer to fullerene than is believed to be necessary. Improving the efficiency of bulk heterojunction solar cells will thus require optimizing the HOMO and LUMO energy levels of both the donor and acceptor components to maximize light absorption and the device  $V_{\rm OC}$ .

Unfortunately, in polymer/fullerene blends, only the donor polymer can be easily altered to tune HOMO/LUMO levels, as the energy levels of fullerenes do not typically change much upon chemical functionalization. Furthermore,  $C_{60}$  has a very low absorption coefficient in the visible due to the symmetry forbidden nature of the  $\pi$ - $\pi$ \* transition. The use of  $C_{70}$  mitigates this problem considerably, but the absorption is still not tunable. As a result, it would be advantageous to replace PCBM with a highly absorbing n-type conjugated polymer. While a number of reports have investigated polymer-polymer blends in solar cells,<sup>2</sup> the efficiencies of these devices have not yet exceeded 2%. This may be due in part to the fact that the development of high mobility n-type conjugated polymers that could replace PCBM has lagged behind that of p-type polymers.

Despite the relative lack of n-type polymers exhibiting high performance in transistors or solar cells, the field of n-type transistors based on vapor deposited small molecules is quite robust and well developed. Among the classes of molecules studied for this purpose, perylene diimides (PDI) (figure 1) are some of best and most commonly employed, exhibiting mobilities over 2 cm<sup>2</sup>/Vs.<sup>3</sup> In addition to high charge mobility, PDIs also have a number of advantageous properties, including excellent ambient stability and well-developed methods for chemical functionalization.<sup>4</sup> This suggests that PDI derivatives might be good monomers upon which to base construction of conjugated n-type polymers. Despite this, however, only a few reports describe polymers containing PDI as part of the conjugated backbone.<sup>5</sup> This study describes two new families of such polymers, including methods to synthesize them and their basic properties.

The first family of polymers is inspired by one of the best currently available ntype polymers, poly(benzimidazobenzophenanthroline ladder) (BBL) (figure 2). BBL has reported field-effect transistor mobilities as high as  $0.1 \text{ cm}^2/\text{Vs.}^6$  Furthermore, BBL has performed well in layered donor/acceptor solar cells: efficiencies ( $\eta_e$ ) of up to 1.4% were reported.<sup>7</sup> This remarkably high efficiency for a solar cell with a layered architecture could perhaps be improved by incorporating BBL into a blend with a p-type polymer. Unfortunately, BBL cannot be blended with most p-type polymers due to its insolubility in aprotic organic solvents. Thus new derivatives of BBL that exhibit solubility in common organic solvents are needed. In this study, the synthesis and characterization of several such polymers is reported.



**Figure 1**: General structure of a PDI dye. The  $R^2$  groups at the imide positions are typically alkyl solubilizing groups, but can be almost any functionality. The R groups at the bay positions are hydrogen in the parent PDI, but can be substituted with other functionality.

Rendering BBL soluble in organic solvents requires the attachment of flexible and bulky groups to the polymer backbone. However, the monomers used in the 1,2,4,5-tetraaminobenzene polymerization of BBL. and 1.4.5.8naphthalenetetracarboxylic dianhydride, are both difficult to functionalize. This problem can be avoided by substituting the naphthalene dianhydride for a perylene dianhydride, which can be functionalized through a number of well-known routes. Condensation of a perylene bisanhydride with 1,2,4,5-tetraaminobenzene gives a novel ladder polymer, poly(benzimidazoperylenebisimide ladder) (BPL) (figure 2). The synthesis and characterization of derivatives of BPL soluble in organic solvents is reported herein.



**Figure 2:** a) The structure of BBL. b) General structure of PBL, where R is a solubilizing group. c) General structure of ethynyl-linked PDI polymers, where  $R^1$  and  $R^2$  are solubilizing groups.

Another way to generate n-type polymers incorporating PDI units is to build conjugation through the bay positions of PDI monomers. Polymers of this type have
been reported twice.<sup>5</sup> However, in both reports phenyl<sup>5a</sup> or fused thiophene<sup>5b</sup> units were used to link the PDI monomers together. Such structures likely cannot realize a planar, fully conjugated conformation due to steric hinderance between phenyl and bay position hydrogens. Structures linked through ethynyl linkages (figure 2), however, likely can be planar, and thus might exhibit favorable properties. The synthesis and characterization of these polymers is also reported herein.

# **Results and Discussion**

#### Synthesis and Characterization of Ladder Polymers

PDIs functionalized in the bay positions are typically accessed by dibrominating perylene dianhydride, then converting to the diimide. This procedure produces a mixture of 1,7-dibromo and 1,6-dibromo isomers. In the past, the major 1,7-disubstituted isomer was isolated in pure form only after repetitive recrystallization and in a yield of only 22%.<sup>8</sup> However, the procedure reported here, involving imidization of the crude brominated dianhydride with 2-ethylhexylamine followed by recrystallization via the slow vapor diffusion of hexanes into toluene produces pure 1,7-dibromo PDI **1** in yields that varied from 29-50% (scheme 1). Notably, this procedure takes only one week while the literature procedure requires six.



**Scheme 1**: Synthesis of dibromo PDI **1**. The minor isomer (4:1 major:minor after column chromatography) is eliminated after recrystallization via the slow diffusion of hexanes vapor into toluene.

The dibrominated PDI can easily be functionalized via nucleophilic aromatic substitution with amines<sup>8</sup> or phenols,<sup>9</sup> or by metal-catalyzed cross coupling. In this study, PDI **1** was functionalized with phenyl rings using a Suzuki coupling. Substitution of alkyl chains in different patterns around these phenyl rings should allow for tuning the solubility and degree of  $\pi$ -stacking of the final ladder polymers. Since phenyl boronic esters functionalized with alkyl chains are easily accessible, this procedure provides a simple route to soluble polymers.

Scheme 2 shows the route employed to synthesize the phenyl boronic ester with alkyl solubilizing groups in the 3 and 5 positions. Selective dilithiation of 1,3,5-tribromobenzene is accomplished with *t*-BuLi in diethyl ether. Quenching with 1-decanal followed by acid workup yields **2**. The benzyl alcohols are then reduced with boron

trifluoride diethyl etherate and triethylsilane. A moderate amount of elimination biproduct containing a single styrenic double bond is observed under these conditions. While this biproduct could not be separated from the desired product 3, the double bond can be reduced at a later stage of the synthesis. The aryl bromide is then converted to the pinacolate boronic ester 5 using lithium/halogen exchange followed by quenching with boronate 4.



Scheme 2: Synthesis of a phenyl boronic ester with alkyl solubilizing groups in the 3 and 5 positions.

Scheme 3 shows the synthesis of a phenyl boronic ester with a single solubilizing chain in the 4 position. This group may be less effective as a solubilizing group, but potentially could allow for closer  $\pi$ - $\pi$  stacking distances. Synthesis is accomplished by alkylating 4-bromophenol with decyl bromide, then converting to the boronate ester via lithium/halogen exchange and quenching with 4.



Scheme 3: Synthesis of a phenyl boronic ester with a single solubilizing chain in the 4 position.

With the boronate ester solubilizing groups in hand, polymers P1 and P2 are synthesized as shown in scheme 4. Solubilizing groups are added to PDI 1 using a Suzuki coupling facilitated by microwave radiation. The resulting PDIs 8 and 9 are converted to dianhydrides 10 and 11 by saponification. These monomers are polymerized with 1,2,4,5-tetraaminobenzene in quinoline with  $Zn(OAc)_2$  as a Lewis acid catalyst, yielding ladder polymers P1 and P2.

Polymers **P1** and **P2** are both isolated as dark bluish black solids. **P1** has excellent solubility in a variety of organic solvents, including THF, chloroform, and chlorobenzene. By size exclusion chromatography (THF, polystyrene standards) **P1** has  $M_n = 10$  kDa and  $M_w = 30$  kDa, demonstrating that perylene-based ladder polymers can be made soluble even at moderately large molecular weights. In contrast to **P1**, **P2** is not soluble in organic solvents unless acid is added. A mixture of 5% trifluoroacetic acid (TFA) in chloroform is a good solvent for **P2**. This limited solubility prevented analytical determination of the molecular mass of **P2**. Attempts to characterize both **P1** and **P2** by matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) were unsuccessful. <sup>1</sup>H NMR spectroscopy also yields no useful information, as no peaks are visible even at temperatures as high as 100 °C, presumably due to the exceptional rigidity of these polymer backbones. Both polymers show no thermal transitions by differential scanning calorimetry (DSC) up to 400 °C.



Scheme 4: Synthesis of polymers P1 and P2.

IR spectroscopy, on the other hand, yields useful structural information about P1 and P2. Figure 3 shows IR spectra of both polymers. In both cases, there are no peaks corresponding to carboxylic acids or amides, which would appear around 1720 and 1650 cm<sup>-1</sup>, respectively.<sup>10</sup> This demonstrates that there are little, if any, defects in the polymer chains due to branching or incomplete cyclization. In polymer P1, there are also no anhydride C-O stretching peaks or aniline N-H stretching peaks, which would appear at 1750 cm<sup>-1</sup> and above 3000 cm<sup>-1</sup>, respectively. This suggests a very low concentration of chain ends, implying that a high molecular weight has been achieved. In fact, excluding the presence of alkyl C-H stretching peaks, the IR spectrum of P1 closely resembles the spectrum of high molecular weight BBL.<sup>11</sup> On the other hand, the spectrum of **P2** shows moderate intensity peaks at 3518 cm<sup>-1</sup> and 1748 cm<sup>-1</sup>, which correspond to end groups. This is not surprising, as the reduced solubility of **P2** probably results in the precipitation of polymer before high molecular weights are achieved. Notably, there is no evidence in the IR spectrum of residual TFA in thin films of P2, even though no special treatments were performed on the dropcast films to eliminate any remaining acid.

Polymers P1 and P2 can also be characterized by UV/vis absorbance Both possess a single, broad absorbance peak from spectroscopy (figure 4). approximately 500-800 nm. The pronounced vibrational structure characteristic of PDI absorbance spectra disappears upon polymerization. This may because the polymer absorbances are broadened due to polydispersity effects as well as the presence of syn and anti isomers (referring to the relationship of the two carbonyls across each pervlene unit) within each chain.<sup>12</sup> The bandgaps, calculated from the onset of the thin film absorbance, are 1.50 eV for both polymers, close to the ideal value for a single layer solar cell.<sup>13</sup> This fact, along with the broadness of the absorbance, make these polymers highly attractive as absorbing materials for solar cells.



Figure 3: FTIR spectra of polymers P1 (a) and P2 (b). Spectra were recorded from drop-cast thin films on NaCl disks.

Notably, the thin film and solution absorbance of **P1** are almost identical. In conjugated polymers, including poly(thiophene)s, contrast. most poly(phenylenevinylene)s, and poly(phenylene)s, exhibit significant red shifts in their main UV/vis absorbance peaks when going from solution to the solid-state. However, other ladder polymers, such as ladder-type poly(phenylene), exhibit no red shift.<sup>14</sup> Likely, the red shifts observed for the non-ladder polymers result from planarization of flexible bonds that can twist in solution, yielding improved conjugation in the solid-state. Ladder polymers like **P1**, however, are fully rigid and extended both in solution and in the solid-state, and are thus fully conjugated in both states. Polymer P2 shows a red shift in the main absorbance peak upon dissolution in 5% TFA in chloroform. This is due to protonation of the benzimidazole nitrogen upon dissolution.



Figure 4: UV/vis absorbance spectra of polymers P1 (a) and P2 (b) in solution (red) and in spin-coated thin films (black). For P1, the solvent for the solution spectrum was chloroform, while for P2 it was 5% trifluoroacetic acid in chloroform.

Polymer **P1** has unusual fluorescence properties (figure 5). In solution in chloroform, **P1** has essentially no Stokes shift. Likely, the highly rigid nature of the conjugated chain prevents geometric relaxation upon excitation. Other conjugated ladder

polymers also exhibit small stokes shifts, such as 9 nm for ladder-type poly(phenylene).<sup>15</sup> However, a Stokes shift of zero is particularly notable. Most interestingly, however, thin films spun from chloroform show an exceptionally large Stokes shift of 94 nm. This dramatic difference between the solution and solid-state emission spectra is unique and not currently understood. However, it is possible that in the films, emission occurs from an interchain-delocalized state that forms only after absorption and initial exciton formation.



Figure 5: UV/vis absorbance (blue) and fluorescence emission (black squares) spectra of P1 in a chloroform solution (a) and a thin film spin-coated from chloroform (b).

To determine if **P1** and **P2** can function effectively as n-type materials, their reduction potentials (thin film) were measure by cyclic voltammetry (figure 4). Both polymers show broad, reversible reduction peaks. Reversible oxidation peaks, on the other hand, were not observed. For the polymers, the electron affinity (LUMO level), calculated from the onset of the reduction peak, is determined to be 4.2 eV for both **P1** and **P2**. This implies that both polymers have very deep LUMOs, lower than fullerene (electron affinity of 3.9-4.1 eV) and comparable to BBL (electron affinity of 4.0-4.4 eV).<sup>7</sup> This demonstrates that the new ladder polymers are promising as acceptor materials in solar cells or as n-type semiconductors in field effect transistors.



**Figure 6:** Cyclic voltammetry curves for polymers **P1** (a) and **P2** (b). Potentials were measured on polymer thin films deposited by dip coating the Pt working electrode in chloroform or chloroform/trifluoroacetic acid solutions of the polymers. The scan rate was 50 mV/s.

Initial attempts to fabricate blend solar cells utilizing polymer **P1** as the acceptor and several common p-type polymers, including poly(3-hexylthiophene) and the poly(phenylenevinylene) derivative MDMO-PPV, as donors yielded cells with very low efficiencies. However, improvements may ultimately be achieved through improved processing conditions or through the use of alternative p-type polymers. Polymer **P2** cannot easily be incorporated into blend solar cells, as the TFA necessary to dissolve the polymer damages most p-type materials. However, it may be useful for the fabrication of multi-layer devices, as its lack of solubility in pure organic solvents can allow for the deposition of subsequent layers. In this manner, it serves as a good complement to **P1**.

# Ethynyl Linked Perylene Polymers

Polymers conjugated through the bay positions of the PDI unit can easily be synthesized from monomer **1**. The ability to eliminate the 1,6-dibromo regioisomer of **1** from the desired 1,7-dibromo isomer is important for these materials, as the 1,6-isomer would introduce kinks into the polymer chain, leading to disorder and likely hampering charge transport. For this study, ethynyl linked polymers were synthesized by a Sonagashira coupling. Diethynyl dialkoxy phenyl monomers were synthesized according to literature procedures.<sup>16</sup> These monomers allow for incorporation of additional solubilizing alkyl chains into the backbone of the structure. These solubilizing groups also allow for tuning of the polymer structure to optimize solubility and crystallinity. Two different ethynyl monomers were used: **12**, which features two 3,7-dimethyloctyl solubilizing groups, and **13**, which has two straight-chain octyl groups. The former should maximize solubility, while the later might facilitate better crystallinity.

Scheme 5 shows the synthesis of the two polymers, accomplished via Sonogashira coupling using Pd and Cu co-catalysts. To achieve soluble material, it is necessary to limit the molecular weight of the polymers by using a small excess (1.03 equivalents) of 1 relative to 12 or 13. Use of an excess of diethynyl monomer results in insoluble polymer, probably because side reactions resulting in oxidative coupling of ethynyl groups allow for chain growth even after all aryl bromides are consumed. The polymers produced are dark greenish-blue. Polymer P3, containing all branched alkyl chains, is soluble in THF, chloroform, and chlorinated aromatic solvents such as 1,2-dichlorobenzene. Polymer P4, containing straight chain octyl groups, is less soluble as expected and does not dissolve in THF.

By SEC (THF or 1,2-dichlorobenzene), both polymers show broad peaks that change with the solution concentration. This is indicative of aggregation of polymer chains, and implies that meaningful molecular weight data cannot be obtained via SEC. NMR also yields no useful information, presumably due to chain aggregation as well. Some structural data can be obtained using MALDI-TOF mass spectroscopy. Figure 7 shows the MALDI-TOF mass spectrum of **P3**. The spectrum for **P4** is similar. As expected, all the chains are terminated on either end with PDI monomers, due to the excess used in the polymerization. End groups are a mixture of bromines, hydrogens, and a small number of methoxy groups that originate from the methanol used to precipitate the polymer. The hydrogens probably arise from dehalogenation side reactions that can occur in Pd-catalyzed cross coupling polymerizations.<sup>17</sup> The molecular

weight of **P3** appears low, but higher mass chains are often difficult to observe by MALDI. Thus, the ions observed are probably a sampling of chains with a low degree of polymerization, and do not represent the true molecular weight of the overall sample.



Scheme 5: Synthesis of P3 and P4 by Sonogashira polymerization.



**Figure 7**: MALDI-TOF mass spectrum of polymer **P3**. The full spectrum is shown at left. The spectrum at middle shows only peaks corresponding to chains with a degree of polymerization of 4.5. At right, the full structure of the peak labeled "Br-(polymer)-Br" is shown for clarity.

To determine if polymers **P3** and **P4** are n-type transporters, reduction potentials were measured by CV (figure 8). Both polymers show similar, reversible reduction peaks. Neither possess a reversible oxidation. The LUMO level, calculated from the onset of the reduction peak, is 4.1 eV for both polymers. Thus both **P3** and **P4** are n-type polymers with high electron affinity.

The UV/vis absorption spectra of polymers P3 and P4 in solution and in thin films are shown in figure 9. Both are characterized by several transitions, with

absorption extending across the entire visible range. For polymer **P3**, the longest wavelength transition and its shoulder appear to increase in intensity going from 1,2-dichlorobenzene (a poor solvent) to chloroform (a better solvent), and finally to a thin film. Meanwhile, the transition just below 500 nm decreases in intensity. A similar phenomenon is observed for **P4**, but the increase in intensity of the long wavelength transitions is even more pronounced. Furthermore, solvent annealing with chloroform vapor can induce additional changes in the absorbance spectrum. This does not happen for **P3**, however. Likely, the long wavelength absorptions are associated with aggregation of the polymer. The straight chain alkyl groups present in **P4** encourage this aggregation, resulting in higher intensity of the long wavelength absorptions. The peak at just below 500 nm may arise from transitions on isolated PDI units, which decrease in intensity upon increasing aggregation.



**Figure 8**: Cyclic voltammetry curves for polymer **P4**. Potentials were measured on polymer thin films deposited by dip coating the Pt working electrode in a chloroform solution of the polymer. The scan rate was 50 mV/s.



Figure 9: UV/vis absorbance spectra for P3 (a) and P4 (b). All spectra are normalized to the highest energy peak.

Further evidence for this phenomenon can be seen in fluorescence spectra of **P4** in chloroform solution (figure 10). **P4** has two emissive states: one emitting at 540 nm and another at 720 nm. The former bears strong resemblance to the fluorescence of isolated PDI units, while the later is probably emission from an aggregated state. In dilute solution (0.0216 mg/mL) excitation at 495 nm (the peak of the shorter wavelength absorption) gives rise primarily to emission at 540 nm, with some emission at 720 nm. When the solution is made more concentrated (0.108 mg/mL), however, excitation at 495 nm gives rise primarily to long wavelength emission. This is likely because the polymer is more highly aggregated at higher concentration. This increases the probability of energy transfer from isolated PDI units to aggregated PDIs, resulting in more emission at 720 nm, presumably due to highly efficient energy transfer to the low energy aggregated states. This provides additional evidence for the assignment of the absorption peaks as isolated PDI units at 495 nm, and as aggregated PDIs at 671 nm.



**Figure 10**: UV/vis absorbance spectra of polymer **P4** in chloroform at left. At right are fluorescence spectra in dilute chloroform solution (0.0216 mg/mL) or concentrated chloroform solution (0.108 mg/mL), exciting at either 495 nm or 671 nm.

The fact that PDI units in these polymer chains absorb and emit as isolated units suggests that conjugation through the ethynyl bonds linking the polymer together is not very strong. This may have negative consequences for charge transport in these materials. Nevertheless, a highly crystalline polymer should transport charge well, even if conjugation along the chain is interrupted. To examine the crystallinity of polymers P3 and P4, films were examined by X-Ray diffraction (figure 11). The polymers show two diffraction peaks, one corresponding to a spacing of 2.14 nm. This is about the length of a perylene monomer with fully extended alkyl chains, suggesting that this peak corresponds to the interlamellar spacing between adjacent polymer chains. The other peak, much weaker and broader, corresponds to the  $\pi$ - $\pi$  stacking between chains. Polymer P3 has a  $\pi$ - $\pi$  stacking distance of 4.0 Å, while P4 has a shorter stacking distance of 3.8 Å, which decreases further to 3.7 Å upon solvent annealing. This matches what is seen in the UV/vis of thin films, which suggest increased aggregation going from P3 to P4 to solvent-annealed P4. Presumably, the straight chain alkyl groups facilitate planarization of the polymer chains, resulting in closer  $\pi$ - $\pi$  stacking and increased aggregation.

Despite the improved  $\pi$ - $\pi$  stacking between chains in polymer P4 after solvent annealing, the XRD shows a polymer that is still largely amorphous. Thus, these materials are not expected to be excellent charge transporters. Preliminary data from field effect transistors (FETs) show an n-type mobility of only 2.8 x 10<sup>-5</sup> cm<sup>2</sup>/Vs. Nevertheless, polymers P3 and P4 have some desirable properties that may eventually make them useful as acceptors in polymer solar cells, including broad light absorption across the visible range and high electron affinity.



Figure 11: XRD spectra of polymer P3 and P4.

# Conclusions

Two classes of novel n-type polymers based on PDI have been synthesized. Ladder benzimidazole polymers (BPL) can be made soluble by functionalizing the backbone with alkyl-subsituted phenyl rings. Depending on the substitution pattern of alkyl groups on the phenyl rings, the polymers can be made highly soluble in organic solvents (P1) or only soluble in organic/acid solvent mixtures (P2). BPL polymers have high electron affinity, broad absorption in the visible and near IR, and exhibit unusual fluorescence properties. The ladder polymer with 3,5-disubstituted phenyl solubilizing groups (P1) has a near zero Stokes shift in chloroform, but a large Stokes shift of almost 100 nm in a thin film.

Ethynyl-linked PDI polymers bridged with dialkoxy phenyl groups were also synthesized. These materials also have high electron affinity and broad absorption. Although delocalization through the ethynyl bonds appears poor, the polymers have broad absorption due to aggregation of PDI units, both in solution and in thin films. Although solvent annealing can increase this aggregation and decrease the  $\pi$ - $\pi$  stacking distance between chains, the polymers are mostly amorphous and appear to exhibit low electron mobility.

# Experimental

#### General

All glassware was dried overnight in an oven or by flame prior to use. Reactions were carried out under nitrogen or argon using standard Schlenk techniques. Unless otherwise noted, reagent solutions were added by syringe. Reactions were monitored by thin layer chromatography using Whatman<sup>®</sup> 250 µm silica gel plates. Flash column chromatography was performed using Merck silica gel, 230-400 mesh. Solvents were removed with a rotary evaporator at aspirator pressure. Unless otherwise noted, all reagents were used as received from commercial suppliers without further purification. Tetrahydrofuran (THF), methylene chloride, and DMF were dried prior to use by passing through two columns of neutral alumina. The following were synthesized by previously reported procedures: **6**,<sup>18</sup> and **12-13**.<sup>16</sup> 1,2,4,5-tetraaminobenzene was purchased as the tetrahydrochloride salt and converted to the free base and purified using a published procedure.<sup>19</sup>

NMR spectra were recorded in CDCl<sub>3</sub> with a TMS standard using a Bruker AVQ-400, AVB-400, or DRX-500 spectrometer. <sup>13</sup>C NMRs were recorded at 100 MHz using <sup>1</sup>H decoupling. Mass spectrometry and elemental analysis data were recorded by staff members at the UC Berkeley mass spectrometry facility. Melting points were recorded on Electrothermal MELTEMP and are uncorrected. XRD spectra were recorded on a Bruker AXS D8 Discover GADDS XRD Diffractometer system. Emission spectra were obtained using an ISA/SPEX Fluorolog 3.22 equipped with a 450W Xe lamp, double excitation and double emission monochromators, and a digital photon-counting photomultiplier. Slit widths were set to a 5 nm band-pass on both excitation and emission monochromators. Spectra were measured with front face detection for thin films, and with right angle detection for solutions.

Cyclic voltammetry (CV) was performed using a Solartron 1285 potentiostat. Polymer thin films were deposited onto a Pt wire working electrode by dip-coating from a chloroform solution of the polymer. Electrodes were submerged in CH<sub>3</sub>CN freshly distilled from CaH<sub>2</sub>. All measurements were performed using a silver wire pseudoreference electrode, a platinum auxiliary electrode, and were referenced to the ferrocene/ferrocenium couple, which was taken to be -5.1 eV relative to vacuum. Tetrabutylammonium tetrafluoroborate (NBu<sub>4</sub>BF<sub>4</sub>) was the supporting electrolyte for all measurements. UV/vis absorbance spectra were measured using a Shimadzu UV-3600 spectrophotometer.

### **FET Measurements**

Heavily doped n-type silicon wafer substrates were used with the substrate acting as a back-gate in a bottom contact device configuration. A layer of silicon dioxide 1000 Å thick was grown at 900°C from steam. Gold electrodes were pre-patterned on the SiO<sub>2</sub> using a baseline photolithographic process before deposition of the active layer. The patterned silicon wafers were cut and then cleaned for 10 minutes in oxygen plasma to yield substrates with a contact angle below 20°. The polymer was then spun cast onto the substrates from 10 mg/mL solutions in chloroform at 2000 rpm. The resulting films were tested without further processing.

The electrical measurements were performed in a nitrogen atmosphere using an

Agilent 4156C Precision Semiconductor Parameter Analyzer. All devices were tested as p-type OFETs in the accumulation regime and saturation mobilities were calculated using the equation,  $\mu = g_m^2 / 2I_DC_{ox}(W/L)$ , where  $g_m =$  transconductance,  $I_D =$  current measured at the drain electrode,  $C_{ox} =$  capacitance of the insulator, W = width of the electrodes, and L = channel length.

# <u>N,N'-Di(2-ethylhexyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic Acid Bisimide</u> 1:



Procedure:

A flask was charged with 2,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisanhydride (6.13 g, 11.1 mmol), 2-ethylhexylamine (4.5 mL, 30 mmol), 1-methyl-2-pyrrolidinone (50 mL) and acetic acid (3.5 mL). The suspension was heated at 100 °C for 2 days then poured into 1 M HCl (200 mL). The red precipitate was isolated by filtration then washed with water and methanol. The product was purified by column chromatography on silica gel (eluent: 70-80% dichloromethane in hexanes). The red solid was then dissolved in 50 mL of toluene. This solution was exposed to the vapor of hexanes over 7 days, resulting in the crystallization of the product as a red powder. Isolation by filtration yielded 2.46 g product (29% yield) that contains only the 1,7-dibrominated regioisomer by 500 MHz NMR.

### Characterization:

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.45 (d, J = 8.0 Hz, 2H), 8.90 (s, 2H), 8.67 (d, J = 8.0 Hz, 2H), 4.14 (m, 4H), 1.95 (m, 2H), 1.2-1.5 (m, 16H), 0.95 (t, J = 7.5 Hz, 6H), 0.90 (t, J = 7.0 Hz, 6H). Anal. calcd for C<sub>40</sub>H<sub>40</sub>N<sub>2</sub>O<sub>4</sub>Br<sub>2</sub>: C, 62.19; H, 5.20; N, 3.63. Found: C, 62.43; H, 5.08; N, 3.73.

### 1-Bromo-3,5-di(1-hydroxydecyl)benzene (2):



#### Procedure:

A flask containing 1,3,5-tribromobenzene (4.61 g, 14.6 mmol) and diethyl ether (150 mL) was cooled to -78 °C. To this was added a solution of *tert*-butyllithium in pentane (35.2 mL, 1.7 M) dropwise by syringe over 15 min. The solution changed from clear to orange. After stirring at -78 °C for 30 min, 1-decanal (6.03 mL, 32.1 mmol) was added dropwise by syringe over 10 min. After warming to room temperature, dilute aqueous ammonium chloride (150 mL) was added. The layers were separated, and the aqueous layer was extracted with diethyl ether (100 mL) and ethyl acetate (100 mL). The combined organics were washed with brine (100 mL) and dried over sodium sulfate. The

solvent was removed at reduced pressure yielding a white solid. This product was purified by column chromatography on silica gel (eluent: 15-25% ethyl acetate in hexanes) yielding 5.1 g of white solid (74% yield).

Characterization:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.32 (d, J = 1.3 Hz, 2H), 7.19 (s, 1H), 5.22 (d, J = 4.5 Hz, 2H), 4.48 (m, 2H), 1.54 (m, 4H), 1.21 (m, 28H), 0.84 (t, J = 6.6 Hz, 6H); HRMS (EI+, m/z): calcd for C<sub>26</sub>H<sub>45</sub>O<sub>2</sub><sup>81</sup>Br, 470.25825; found, 470.25892. Anal. calcd for (C<sub>26</sub>H<sub>45</sub>O<sub>2</sub>Br): C, 66.51; H, 9.66. Found: C, 66.58; H, 9.67.

#### 1-bromo-3,5-didecylbenzene (3):



# Procedure:

A flask was charged with 2 (1.50 g, 3.19 mmol), triethylsilane (3.6 mL, 22 mmol), and dichloromethane (14 mL). The solution was cooled to 0 °C, then boron trifluoride diethyl etherate (2.8 mL, 22 mmol) was added dropwise by syringe. The solution was allowed to slowly warm to room temperature while stirring for 1 day. Potassium bicarbonate (1 M) was then added with vigorous stirring until the solution turned basic. This solution was extracted with dichloromethane (2 x 200 mL). The organics were dried with sodium sulfate then concentrated and dried to yield 1.28 g of light orange oil (92% yield). This material contained 15% by mole the product resulting from elimination of one alcohol and reduction of the other.

## Characterization:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.13 (s, 2H), 6.89 (s, 1H), 2.52 (t, *J* = 7.6 Hz, 4H), 1.57 (m, 4H), 1.26 (m, 28H), 0.88 (t, *J* = 6.7 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  145.20, 128.82, 127.57, 122.31, 35.86, 32.14, 31.54, 29.84, 29.80, 29.69, 29.56, 29.49, 22.92, 14.35; FTIR (film on NaCl): v = 2929 (br), 2854, 1602, 1569, 1466, 1378 cm<sup>-1</sup>; HRMS (EI+, *m/z*): calcd for C<sub>26</sub>H<sub>45</sub><sup>81</sup>Br, 438.26842; found, 438.26831. Anal. calcd for (C<sub>26</sub>H<sub>45</sub>Br): C, 71.37; H, 10.37. Found: C, 71.64; H, 10.35.

**Pinacol Boronate 5:** 



#### Procedure:

A flask containing **3** (1.07 g, 2.45 mmol) and THF (15 mL) was cooled to -78 °C. To this solution was added *tert*-butyllithium in pentane (3.2 mL, 1.7 M) dropwise by syringe over 10 min. After stirring for 20 min at -78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,2,3-dioxaborane (0.65 mL, 3.2 mmol) was added by syringe over 3 min. After stirring for 25 min, the solution was warmed to room temperature and quenched by addition of dilute aqueous ammonium chloride (50 mL). This solution was extracted with ethyl acetate (3 x 60 mL). The organics were dried over sodium sulfate and concentrated under reduced pressure. Drying under vacuum yielded 1.20 g of clear oil (100% yield).

#### Characterization:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.45 (s, 2H), 7.09 (s, 1H), 2.57 (t, *J* = 7.7 Hz, 4H), 1.60 (m, 4H), 1.35 (s, 12H), 1.26 (m, 28H), 0.88 (t, *J* = 6.8 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  145.19, 128.82, 127.57, 122.32, 35.86, 32.14, 31.99, 31.54, 29.85, 29.80, 29.69, 29.57, 29.49, 25.08, 22.92, 14.35; FTIR (film on NaCl): v = 2917, 2849, 1465 cm<sup>-1</sup>; HRMS (EI+, *m/z*): calcd for C<sub>32</sub>H<sub>57</sub><sup>-11</sup>BO<sub>2</sub>, 484.44516; found, 484.44561.

#### Boronate ester monomer 7:



Procedure:

A flask containing **6** (1.21 g, 3.86 mmol) and THF (30 mL) was cooled to -78 °C. A 1.62 M solution of *tert*-butyllithium in pentane (4.89 mL, 7.92 mmol) was added dropwise by syringe over 10 min, resulting in a faint yellow color. After stirring at -78 °C for 30 min, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.95 mL, 4.6 mmol) was added dropwise by syringe over 5 min, resulting in the disappearance of the yellow color. The solution was warmed to room temperature, then poured into 75 mL of dilute ammonium chloride solution. This solution was extracted with ethyl acetate (2 x 50 mL). The combined organic layers were dried over sodium sulfate then concentrated at reduced pressure. After drying under vacuum, obtained 1.39 g of white solid (100% yield).

## Characterization:

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.74 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 1.78 (m, 2H), 1.2-1.5 (m, br, 14H), 1.33 (s, 12H), 0.88 (t, *J* = 6.3 Hz, 3H); Anal. calcd for (C<sub>22</sub>H<sub>37</sub>O<sub>3</sub>B): C, 73.33; H, 10.35. Found: C, 73.51; H, 10.44.

#### **Perylene Diimide Monomer 8:**



# Procedure:

A 20 mL microwave vial was charged with 1 (0.70 g, 0.91 mmol), 5 (1.05 g, 2.18 mmol)mmol), potassium carbonate (1.25 g, 9.1 mmol), THF (14 mL), and water (2 mL). This solution was degassed with bubbling  $N_2$  for ten minutes. PdCl<sub>2</sub>(Ph<sub>3</sub>)<sub>2</sub> (127 mg, 0.181 mmol) was added and the vial was sealed. The solution was then heated with microwave radiation to 130 °C and stirred for 12 minutes, during which time the color changed from orange/red to dark purple. The solution was poured into water (50 mL) and extracted with dichloromethane (2 x 50 mL). The organic extracts were dried over sodium sulfate and concentrated at reduced pressure. This product was purified twice by column chromatography on silica gel (eluent: 15-35% dichloromethane in hexanes for the first column and 5% ethyl acetate in hexanes for the second column) yielding 816 mg of dark purple solid. A diimide reduction was then performed to reduce the alkenes present in the solubilizing groups. The solid was dissolved in chloroform (6.5 mL) and isopropanol (16 mL). To this solution was added copper sulfate (98 mg, 0.61 mmol) and hydrazine hydrate (2.7 mL, 55 mmol). The solution was stirred vigorously in open air for two days, then poured into water (100 mL). This was extracted with dichloromethane (100 mL). The organic extracts were dried over sodium sulfate and concentrated at reduced pressure. The solid was dried under vacuum vielding 813 mg of  $\mathbf{8}$  as a purple solid (68%) yield).

#### Characterization:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.63 (s, 2H), 8.11 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.16 (s, 4H), 7.10 (s, 2H), 4.12 (m, 4H), 2.61 (t, J = 7.3 Hz, 8H), 1.94 (m, 2H), 1.94 (s, br, 8H), 1.24-1.39 (m, br, 72H), 0.84-0.95 (m, br, 24H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  164.22, 163.98, 145.26, 142.15, 141.86, 135.60, 135.32, 132.82, 130.38, 129.54, 129.43, 129.20, 127.82, 126.40, 122.26, 121.93, 77.43, 44.42, 38.19, 36.12, 32.14, 31.79, 30.99, 29.87, 29.84, 29.67, 29.56, 29.50, 28.95, 24.27, 23.30, 22.91, 14.34, 10.87; FTIR (film on NaCl): v = 2925, 2855, 1698, 1656, 1597, 1463, 1405, 1328, 1244 cm<sup>-1</sup>; HRMS (FAB+, *m/z*): calcd for C<sub>92</sub>H<sub>130</sub>O<sub>4</sub>N<sub>2</sub>, 1327.00306; found, 1327.00288. Anal. calcd for (C<sub>92</sub>H<sub>130</sub>O<sub>4</sub>N<sub>2</sub>): C, 83.20; H, 9.87; N, 2.11. Found: C, 83.10; H, 10.22; N, 2.10.

#### Perylene Bisimide 9:



#### Procedure:

A 20 mL microwave vial was charged with 1 (318 mg, 0.412 mmol), 7 (356 mg, 0.988 mmol), potassium carbonate (0.6 g, 4 mmol), THF (8 mL), and water (2 mL). This solution was degassed with bubbling N<sub>2</sub> for ten minutes.  $PdCl_2(Ph_3)_2$  (35 mg, 0.049 mmol) was added and the vial was sealed. The solution was then heated with microwave radiation to 130 °C and stirred for 12 min, during which time the color changed from orange/red to dark purple. The solution was poured into water (50 mL) and extracted with dichloromethane (2 x 50 mL). The organic extracts were dried over sodium sulfate and concentrated at reduced pressure. This product was purified twice by column chromatography on silica gel (eluent: 5-10% ethyl acetate in hexanes for the first column and 50%-100% dichloromethane in hexanes for the second column) yielding 322 mg of dark purple solid (72% yield).

#### Characterization:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.56 (s, 2H), 8.13 (d, J = 10.8 Hz, 2H), 7.84 (d, J = 11.2 Hz, 2H), 7.44 (d, J = 11.6 Hz, 2H), 6.99 (d, J = 11.6 Hz, 2H), 4.13 (m, 4H), 4.05 (t, J = 8.4 Hz, 4H), 1.8-2.0 (m, 6H), 1.2-1.6 (m, br, 44H), 0.8-1.0 (m, 18H).





#### Procedure:

A flask was charged with **8** (813 mg, 0.612 mmol), potassium hydroxide (3.44 g, 61.2 mmol), and isopropanol (19 mL). The resulting suspension was heated at reflux for 2 hr. The suspension was then poured into a mixture of acetic acid (75 mL) and water (250 mL), then extracted with hexanes (3 x 150 mL). The combined organic fractions were dried over sodium sulfate and concentrated at reduced pressure. The product was purified by column chromatography on silica gel (eluent: 5-10% ethyl acetate and 0.5% acetic acid in hexanes) yielding 459 mg of dark purple solid (70% yield).

### Characterization:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.67 (s, 2H), 8.14 (d, *J* = 8.2 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.15 (s, 6H), 2.62 (t, *J* = 7.6 Hz, 8H), 1.58 (m, 8H), 1.25-1.30 (m, br, 56H), 0.86 (t, *J* = 6.7 Hz, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.21, 159.83, 145.74, 142.91, 141.13, 137.60, 136.37, 133.64, 131.45, 130.88, 130.03, 129.88, 129.86, 126.14, 118.70, 118.30; FTIR (film on NaCl): v = 2925, 2854, 1778, 1740, 1597, 1291, 1040 cm<sup>-1</sup>; HRMS (FAB+, *m/z*): calcd for C<sub>76</sub>H<sub>96</sub>O<sub>6</sub>, 1105.72852; found, 1105.72678. Anal. calcd for (C<sub>76</sub>H<sub>96</sub>O<sub>6</sub>): C, 82.57; H, 8.75; found: C, 82.26; H, 8.91.

#### Perylene dianhydride 11:



#### Procedure:

A flask was charged with 9 (322 mg, 0.298 mmol), potassium hydroxide (1.67 g, 29.8 mmol), and isopropanol (10 mL). The resulting suspension was heated at reflux for 2 hrs, then poured into a mixture of water (50 mL) and acetic acid (10 mL). The resulting suspension was extracted with dichloromethane (50 mL). The organic extracts were dried with sodium sulfate, then concentrated at reduced pressure. The product was purified by column chromatography on silica gel. Initially an eluent of 25% ethyl acetate and 0.5% acetic acid in hexanes was used to eliminate impurities. This was followed by 75% dichloromethane and 0.5% acetic acid in hexanes to elute product. Purification yielded 213 mg of 11 as a dark purplish blue solid (83% yield).

#### Characterization:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.65 (s, 2H), 8.19 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 4H), 7.02 (d, *J* = 8.8 Hz, 4H), 4.06 (t, *J* = 6.4 Hz, 4H), 1.86 (m, 4H), 1.52 (m, 4H), 1.2-1.4 (m, br, 24H), 0.89 (t, *J* = 6.8 Hz, 6H); Anal. calcd for (C<sub>56</sub>H<sub>56</sub>O<sub>8</sub>): C, 78.48; H, 6.59. Found: C, 78.61; H, 6.98.



Procedure:

A flask was charged with **10** (354 mg, 0.320 mmol), 1,2,4,5-tetraaminobenzene (44.2 mg, 0.320 mmol), and zinc acetate (29 mg, 0.16 mmol). In a separate flask, quinoline (4 mL) was degassed with bubbling  $N_2$  gas for 10 min. This was then transferred via cannula to the first flask. The resulting solution was then degassed further with 3 freeze/pump/thaw cycles. The solution was then heated to 200 °C and stirred for 2 days. The color changed from purple to dark bluish green. The solution was diluted in chloroform, then precipitated into methanol. The polymer was filtered into a Soxhlet thimble, then washed via Soxhlet extraction with methanol for 12 h. The product was then taken up into THF via washing in a Soxhlet apparatus until the washings appeared clear. The THF extracts were concentrated to less than 5 mL under reduced pressure and then poured into a methanol/triethylamine mixture. The resulting precipitate was isolated via filtration and dried under vacuum, yielding 305 mg of black solid (81% yield).

#### Characterization:

No peaks could be detected in a 500 MHz <sup>1</sup>H NMR, even at temperatures up to 100 °C. SEC (THF, polystyrene standards):  $M_n = 9.7$  kDa,  $M_w = 29.5$  kDa. FTIR (film on NaCl): v = 2926, 2852, 1695, 1596, 1557, 1497, 1466, 1368, 1322, 1028, 859 cm<sup>-1</sup>. UV/vis (chloroform solution):  $\lambda_{max} = 694$  nm.



#### Procedure:

A flask was charged with **11** (32.9 mg, 0.0384 mmol), 1,2,4,5-tetraaminobenzene (5.30 mg, 0.0384 mmol), zinc(II) acetate (3.5 mg, 0.019 mmol), and quinoline (0.5 mL, degassed with bubbling  $N_2$ ). The solution was degassed with three freeze/pump/thaw

cycles, then heated to 200 °C and stirred for 52 h. After cooling, the solution was diluted in 10% TFA in chloroform (5 mL). This solution was poured into 10% triethylamine in methanol (100 mL). The precipitate was isolated by filtration. The product was washed in a Soxhlet apparatus with methanol and THF for 12 h each. The remaining solid polymer was dried under vacuum yielding 24 mg of black product (68% yield).

#### Characterization:

FTIR (film on NaCl): v = 3518, 2925, 2855, 1747, 1697, 1594, 1494, 1425, 1324, 1248, 834 cm<sup>-1</sup>. Anal. calcd for (C<sub>62</sub>H<sub>58</sub>N<sub>4</sub>O<sub>2</sub>): C, 80.67; H 6.33, N 6.07; found: C 80.23, H 6.14, N 6.29.

# Perylene Ethynylene Polymer P3:



#### Procedure:

A flask was charged with 1 (354.6 mg, 0.459 mmol), 12 (195.5 mg, 0.446 mmol), toluene (14 mL), and diisopropylamine (1.4 mL). The solution was degassed with 3 freeze/pump/thaw cycles. The co-catalysts  $PdCl_2(PPh_3)_2$  (16 mg, 0.023 mmol), and copper iodide (5.0 mg, 0.026 mmol) were then added. After stirring at 65 °C for 22 h, the color changed from orange to black and the solution turned to a gel. Chloroform was added until the gel dissolved. This solution was then poured into methanol to precipitate the polymer. The precipitate was isolated by filtration, then washed in a Soxhlet apparatus with methanol, THF, and toluene for 12 hrs each. The polymer was then taken up in chloroform via Soxhlet extraction, concentrated, and precipitated into methanol. Isolation by filtration and drying under vacuum yielded 316 mg of black solid (66% yield).

### Characterization:

MS (MALDI-, terthiophene matrix, m/z): calcd for H-(repeat unit)<sub>4</sub>-PDI-H, 4809.2; found, 4802.5; calcd for H-(repeat unit)<sub>4</sub>-PDI-OMe, 4839.2; found, 4832.5; calcd for H-(repeat unit)<sub>4</sub>-PDI-<sup>79</sup>Br, 4888.2; found, 4881.5; calcd for <sup>79</sup>Br -(repeat unit)<sub>4</sub>-PDI-<sup>79</sup>Br, 4967.2; found, 4959.9; calcd for H-(repeat unit)<sub>5</sub>-PDI-H, 5857.8; found, 5848.6;

calcd for H-(repeat unit)<sub>5</sub>-PDI-H. Anal. calcd for (C<sub>706</sub>H<sub>84</sub>N<sub>2</sub>O<sub>6</sub>): C, 80.12; H, 8.07; N, 2.67. Found: C, 80.21; H, 8.03; N, 2.86.

## Perylene Ethynylene Polymer P4:



Procedure:

The procedure was identical for that used for **P3**. The following amounts of reagents were used: **1** (158.1 mg, 0.205 mmol), **13** (76 mg, 0.199 mmol),  $PdCl_2(PPh_3)_2$  (7.0 mg, 0.0099 mmol), copper(I) iodide (3.3 mg, 0.017 mmol), toluene (6 mL), and diisopropylamine (0.6 mL). **P4** was isolated as a black solid (156 mg, 79% yield).

# References

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# Chapter 5 – Improving Light Harvesting in Dye-Sensitized Solar Cells Through the Use of Energy Relay Dyes

# Background

Dye-sensitized solar cells (DSCs) are currently the subject of intense investigation due to their potential to provide inexpensive solar power. Light harvesting in these cells is accomplished by a sensitizing dye (SD) attached to a wide bandgap semiconductor oxide, typically mesoporous TiO<sub>2</sub>.<sup>1</sup> External power conversion efficiencies over 11% can be obtained with cells employing a liquid electrolyte solution containing  $I/I_3$  as a redox couple.<sup>2</sup> These state-of-art devices absorb light from 350-700 nm. Extending this absorption beyond 700 nm into the near infrared could improve efficiencies. A device utilizing the  $I/I_3$  redox couple and absorbing 80% of the solar spectrum from 350-900 nm would reach an efficiency of 15%.<sup>3</sup> To achieve this improved absorption, one might try to design SDs with broader spectral coverage. However, the SD has traditionally been made from ruthenium based complexes (e.g. N719 and Z907)<sup>1</sup> that already have a fairly broad absorption spectrum ( $\Delta\lambda \sim 350$ nm), but low molar extinction coefficients (5,000-20,000 M<sup>-1</sup> cm<sup>-1</sup>). Organic SDs have recently been developed with substantially higher molar extinction coefficients (50,000-200,000 M<sup>-1</sup> cm<sup>-1</sup>) but narrow spectral bandwidths  $(\Delta\lambda \sim 250 \text{ nm})$ <sup>4</sup> As a general rule, dyes that absorb strongly do not typically exhibit broad absorption.

Co-sensitization of titania by multiple SDs with complimentary absorption spectra could potentially enhance light absorption and broaden the spectral response of organic However, the limited number of sites on the titania surface to attach dye DSCs.<sup>5</sup> molecules places a constraint on the light absorption achievable by co-sensitization. Furthermore, co-sensitization requires that each dye adsorb strongly on the surface with a similar binding constant, or it becomes difficult to achieve equal levels of coverage. Finally, few dyes exist that are both excellent absorbers and possess the requisite energy levels and chemical anchoring groups to be good sensitizing dyes. An alternative to cosensitization is to utilize Förster resonant energy transfer (FRET) to transfer excitations from a high energy dye to a lower energy SD. One recent study has demonstrated the use of FRET between covalently linked energy donor molecules to the SD attached on the titania surface.<sup>5</sup> Siegers et al. were able to demonstrate a high excitation transfer efficiency (>89%) between attached dye molecules and an improvement in the device external quantum efficiency of 5-10% between 400-500nm. However, the overall power conversion efficiency enhancement of the DSC was low (< 9%) and linked more to an increase in the open circuit voltage rather than an increase in the short-circuit photocurrent density.

Herein it is demonstrated that unattached, highly luminescent chromophores inside the liquid electrolyte can absorb high energy photons and efficiently transfer excitations via FRET to an anchored near-IR SD, increasing the absorption bandwidth of the DSC. Figure 1 shows two routes for charge generation incorporated in this system. In typical DSCs, light is absorbed by the SD (1), which transfers an electron into the titania and hole into the electrolyte. In the new design, the unattached energy relay dye (ERD) is excited by higher energy (blue) photons and then undergoes FRET (2) to the

SD. Using energy relay dyes has several important advantages. First, since the attached dye only has to absorb light over a smaller spectral region, it can be chosen to have a stronger and narrower absorption spectrum. Second, the SD can be red shifted compared to the commonly used dyes since the energy relay dye can absorb higher energy photons. Furthermore, it is possible to place multiple ERDs with complimentary absorption spectra to tailor light absorption inside the device. Finally, the ERD does not need to be attached to the titania surface and with no additional processing steps can be mixed in very large concentrations inside the electrolyte. In summary, the addition of energy relay dyes into the electrolyte makes the overall absorption spectrum wider and stronger for the same film thickness. It is important to note that the ERDs do not participate in the charge transfer or collection process and thus do not require precise energy levels or specialized attachment groups.



**Figure 1:** DSC schematic representation of a dye-sensitized solar cell with energy relay dyes. The right side of the figure shows the typical absorption process for lower energy (red) photons in DSCs: light is absorbed by the sensitizing dye (1) which then transfers an electron into the titania and a hole is transported to the back contact through the electrolyte. The energy relay dye process is similar except that higher energy (blue) photons are first absorbed by the energy relay dye that undergoes Förster energy transfer (2) to the sensitizing dye.

The energy relay dye concept is particularly applicable to DSCs that do not utilize the traditional liquid electrolyte solution. The volatility of this solution, typically iodide in acetonitrile, is a barrier to commercialization of DSCs. As a result, non-volatile replacements for the liquid electrolyte, including ionic liquids, polymer gels, and solidstate hole transporters, have been developed. Unfortunately, these replacements generally result in lower cell efficiencies. For instance, the best solid-state devices, employing the organic hole transporter Spiro-OMeTAD (figure 2) as the redox couple, achieve efficiencies up to 5.1%.<sup>6</sup> The decrease in efficiency is due to a higher rate of recombination, which necessitates the use of thin devices (usually 2 µm instead of 10 µm), thereby limiting light absorption. In such a thin cell, the ability to incorporate an additional dye could increase light absorption and improve efficiency.



Förster resonant energy transfer involves dipole-dipole coupling of two chromophores known as the donor and acceptor through an electric field.<sup>7</sup> An excitation of the donor, in this case the ERD, can be transferred nonradiatively through the field to the acceptor, or SD, if there is overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor. Efficient energy transfer over 3-8nm can be achieved with strong spectral overlap and high donor emission efficiencies, for an isotropic alignment between individual chromophores in solution. Given that pore sizes are typically 20-50 nm in a DSC, one might expect significant losses due to the potentially large separation between ERD and SD. If, however, the single acceptor chromophore is replaced by a dense 2D array (i.e. sensitizing dyes tightly packed on the titania surface) FRET can become efficient well over 25 nm from the interface.<sup>8</sup>

High FRET transfer rates ( $k_{FRET}$ ) are essential to quickly transfer the energy before the excited ERD nonradiatively decays. The FRET rate is dependent upon the Förster radius ( $R_0$ ) between the energy relay dye and the sensitizing dye, the separation distance between the ERD and the SD/TiO<sub>2</sub> interface, and the natural fluorescence decay rate of the ERD,  $k_0=1/\tau_0$ . The FRET radius ( $R_0$ ), or the distance in which Förster energy transfer is 50% probable between individual chromophores, can be calculated using equation (1).

<sup>(1)</sup> 
$$R_o^6 = \frac{9000 \cdot \ln(10)\kappa^2 Q_D}{128 \cdot \pi^5 n^4 N_A} \int F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda$$

Where n is the index of refraction of the host medium (1.4-1.5 for the DSC electrolyte),  $\kappa^2$  is the orientational factor (2/3 for random orientation), N<sub>A</sub> is Avogadro's number, Q<sub>D</sub> is the photoluminescence efficiency, F<sub>D</sub> is the emission profile of the donor, and  $\epsilon(\lambda)$  is the molar extinction coefficient.

For either solid-state or liquid electrolyte DSCs, the biggest challenge in implementing FRET as described is quenching of ERD fluorescence by iodide (in the case of liquid cells) or Spiro-OMeTAD (in the case of solid-state cells). This quenching lowers  $Q_D$ , thereby lowering  $R_o$  and decreasing the efficiency of FRET. Herein, however, it is demonstrated that this quenching can be limited in either one of two ways: through the use of ERDs with very short fluorescence lifetimes, or by physical encapsulation of ERDs in structures such as dendrimers. For liquid cells, improved efficiency through the use of an ERD is demonstrated. For solid-state cells, progress towards improving efficiency is shown.

# **Results and Discussion**

# Energy Transfer in Dye-Sensitized Solar Cells with Liquid Electrolytes

A family of tetraphenoxy perylene diimide dyes were synthesized to act as ERDs for the liquid-based cells (figure 3). Perylene diimides (PDIs) are ideal energy relay dye candidates because of their extremely high photoluminescence efficiency (>90%), fast fluorescence lifetime (4.8ns), excellent photo and air stability, and relatively strong absorption coefficient (50,000 M<sup>-1</sup> cm<sup>-1</sup> at 580nm).<sup>9</sup> Each dye has bulky groups designed to isolate the dye core from it's chemical environment. This should prevent fluorescence quenching, which can occur either by aggregation of dyes at high concentration (concentration quenching) or by collisions between iodide and excited dye. Three dyes were designed: the first, PDI 1, has bulky phenyl groups that sit above and below the conjugated plane of the dye due to sterics. The second, PDI 2, is functionalized with third generation Fréchet-type benzyl ether dendrimers.<sup>10</sup> Fréchet-type dendrimers have been successfully used to site-isolate luminescent lanthanide ions,<sup>11</sup> and should provide even better chemical insulation than the phenyl groups on PDI 1. Finally, PDI 3 is functionalized with linear poly(ethyleneglycol) (PEG) chains of 3 kDa each. These chains might provide insulation by wrapping around the dye. PEG chains are known to protect drug carriers by wrapping around them in aqueous environments when attached to dendritic drug delivery systems.<sup>12</sup> However, it is not known if this wrapping phenomenon will be as pronounced in organic solvents such as acetonitrile as in water.



Figure 3: Tetraphenoxy PDI dyes utilized in this study.

These dyes were synthesized as shown in scheme 1. PDI **1** is synthesized by imidization of tetrachloroperylene dianhydride, followed by nucleophilic aromatic substitution of the chlorides with 4-*tert*-butylphenoxide. Dyes **2** and **3** are made by imidization with  $\alpha$ -methylbenzylamine, phenoxide substitution, then cleavage of the methylbenzyl groups with boron tribromide. The bromide-functionalized dendrimer or polymer is then attached by an S<sub>N</sub>2 reaction.

With the dyes in hand, it was then necessary to evaluate how they might function as ERDs in a liquid DSC. First, it was determined that all three dyes do not concentration quench up to their solubility limit in  $\gamma$ -butyrolactone. This solvent was chosen because it functions equally well as the solvent for the redox couple in DSCs as acetonitrile, but better dissolves the PDI dyes. Next, it was necessary to determine the extent of quenching by I<sup>-</sup> in the redox couple. Dynamic, collisional quenching is described by the Stern-Volmer equation (2),<sup>13</sup>

(2) 
$$\frac{PL_0}{PL} = \frac{\tau_0}{\tau} = 1 + k_q \tau_o[Q]$$

where  $PL_0$  is the photoluminescence in the absence of a quencher, PL is the photoluminescence for given quencher concentration [Q],  $\tau_0$  is the natural fluorescence lifetime,  $\tau$  is the fluorescence lifetime for a given [Q], and  $k_q$  is the bimolecular quenching constant typically around  $10^9-10^{10}$  M<sup>-1</sup> s<sup>-1</sup>. Because the bimolecular constant and the electrolyte concentrations are relatively fixed, a short  $\tau_0$  is important for minimizing the fluorescence quenching. To measure  $k_q$ , PL<sub>0</sub>/PL values (determined from steady-state photoluminescence measurements) are determined at several concentrations of quencher, and a Stern-Volmer plot is constructed.



Scheme 1: Synthesis of PDI dyes 1-3.

Stern-Volmer plots for each dye are shown in figure 4b. Plots were constructed using both 1-methyl-3-propyl imidazolium iodide (PMII) and iodine, the two components of the redox electrolyte used in DSCs. Both quench the dyes to some degree. To verify that the quenching is dynamic, fluorescence lifetime measurements were performed to directly measure  $\tau_0/\tau$  and confirm that these values match PL<sub>0</sub>/PL. Figure 4a shows fluorescence decay curves for PDI **1** with varying PMII concentrations. In the absense of quencher, a lifetime of 10.7 ns is determined. PMII reduces  $\tau$  such that measured  $\tau_0/\tau$  values match PL<sub>0</sub>/PL values determined from steady-state photoluminescence, confirming that the quenching is dynamic. Similar results are obtained for **2** and **3**.



**Figure 4**: a) Stern-Volmer plots of quenching of PDI dyes 1-3 with  $I_2$  or PMII (I). b) Time-resolved photoluminescence decay of PDI 1 with increasing concentrations of PMII.

Table 1 summarizes data from both time-resolved and steady-state photoluminescence experiments on dyes 1-3. Using the  $\tau_0$  and  $k_q$  values with equation (2), it is possible to estimate the quantum yield of the dyes in a device, assuming [PMII]=0.1M, [I<sub>2</sub>]=0.01M, and the quantum yield in the absence of quencher is 100%. This data is shown in the right-most column of table 1. The best performing dye is 2, likely due to the steric bulk of the third-generation benzyl ether dendrons. However, dye 1 is nearly as good, with a quantum yield only 2% lower than 1. This suggests that steric bulk in the immediate vicinity of the dye core has the most effect on shielding the dye from collisional quenching. Likely, the dendrons are not large enough to completely wrap around the dye, and the extra mass on the outer part of the dendrimer has little effect. Dye 3 has the lowest quantum yield of the three, suggesting that linear PEG chains do not provide good encapsulation in  $\gamma$ -butyrolactone.

	$\tau_0(ns)$	$k_q I_2$	k <sub>q</sub> PMII	Estimated PLQE in a device
PDI 1	10.7	1.42E+10	3.09E+09	17.2%
PDI <b>2</b>	13.0	1.18E+10	1.98E+09	19.6%
PDI 3	13.6	1.51E+10	4.08E+09	11.6%

**Table 1**: Data from time-resolved and steady-state photoluminescence experiments on PDI dyes 1-3. PLQE = photoluminescence quantum efficiency (quantum yield).

Because PDI 1 performs nearly as well as 2 but has a much lower molar mass (meaning better light absorption) and is easier to synthesize, it was used in all subsequent studies. For the sensitizing dye, a previously reported zinc phthalocyanine (figure 5)<sup>14</sup> was chosen for its high molar extinction coefficient of 191,500 M<sup>-1</sup> cm<sup>-1</sup> as well as good overlap of its absorbance spectrum with the emission of 1 (figure 5). The FRET radius (R<sub>o</sub>) for the PDI 1/TT1 pair, calculated using equation (1), is 8.0 nm. When the quantum yield of 1 is reduced to 17%, as it should be in a DSC, R<sub>o</sub> decreases to 6.0 nm.



Figure 5: Absorbance and emission spectrum of 1 and absorbance spectrum of TT1 (at left). At right is the structure of TT1.

To determine if the FRET scheme will work in a DSC, it is necessary to model the excitation transfer efficiency (ETE), or the probability that an excited ERD will transfer its energy to an SD. The ETE for a single relay dye molecule is dependent upon the rate of FRET,  $k_{FRET}$ , relative to the combined rate of all decay mechanisms including the natural decay rate and quenching rate, equation (3).

(3) 
$$ETE(\vec{x}) = \frac{k_{FRET}(\vec{x})}{k_0 + k_{QUENCH} + k_{FRET}(\vec{x})}$$

The FRET rate is a function of the separation distance between the ERD molecule to nearby acceptor molecules. The rate of FRET between isolated chromophores, known as point-to-point transfer, is given by  $k_{FRET} = k_0 (R_0)^6/r^6$ , where r is the separation distance. When multiple acceptor molecules are present, the FRET rate is equal to the sum of the transfer rates to each of the acceptors. ERDs within the FRET  $R_0$  of the SD array will transfer their excitation with high efficiency, while ERDs in the middle of a large pore may be quenched before energy transfer occurs. Hoke *et. al.* have developed a model to quantify FRET efficiency in a DSC by approximating the nanopores as either cylinders or spheres.<sup>15</sup> Using this model and equation (3), excitation transfer efficiency profiles,  $ETE(\vec{x})$ , are calculated for the two idealized pore geometries. The morphology of the pores has important implications on ERD/SD array separation distance. Figure 6 shows how the average excitation transfer efficiency, ETE, depends upon the pore diameter for

cylindrical and spherical pores using the parameters calculated for the PDI 1/TT1 DSC system. Despite the quenching due to  $\Gamma$  and  $I_2$ , the expected  $\overline{ETE}$  is still between 76-87% in a 15nm pore.

With this encouraging result in hand, devices were fabricated to try to verify the model. The titania film was comprised of 20 nm particles to ensure close proximity of the energy relay dye to the sensitizing dye. The 20 nm  $TiO_2$  particles produce pore diameters between 22-38nm. Chloroform was chosen as the electrolyte solvent because PDI 1 is significantly more soluble in it (>50mM) compared to commonly used solvents such as acetonitrile (0 mM) and  $\gamma$ -butyrolactone (<2 mM). However, chloroform based electrolytes displayed lower internal quantum efficiency (70% vs. 80%) and lower power conversion efficiencies than previously reported.<sup>14</sup> This is caused by a reduced  $I_3$ concentration, lower solubility of useful additives such as LiI and guanidinium rhodanide, and the lower dielectric constant of chloroform ( $\varepsilon$ =5) compared to acetonitrile  $(\varepsilon=36)$ .<sup>16</sup> Devices without the ERD were also made with acetonitrile-based electrolytes and had similar device performance compared to literature.<sup>14</sup> It should be noted that chloroform has a low boiling and during electrolyte filling the concentration of 1 inside the DSC invariably changed. Higher molar concentrations of 1 in the electrolyte did not increase dye loading, but did result in clogging of the hole as the electrolyte gelled quickly. A precise determination of the true concentration 1 was therefore not possible.



**Figure 6**: Modeled excitation transfer efficiency as a function of pore diameter for spherical and cylindrical pores. Here a Förster radius of 6.0 nm and a dye coverage of  $0.2 \text{ nm}^{-2}$  were used.

Figure 7 shows the photocurrent density-voltage (*J-V*) characteristics of DSCs with and without the energy relay dye measured under AM 1.5G (100 mW cm<sup>-2</sup>) conditions. Devices containing no ERD (0 mM 1) had power conversion efficiencies (PCE) of 2.55% while devices with 13 mM of 1 had a PCE of 3.21%. The 26% increase in device performance is attributed to the increase in short-circuit photocurrent density ( $J_{SC}$ ) caused by an increase in the EQE from 400-600nm as shown in Figure 8a, while the

Fill Factor and  $V_{OC}$  remained relatively unchanged (see table 2). Devices made with 1 but without the sensitizing dye were found to have very low photocurrent ( $J_{SC} = <42 \mu A/cm^2$  and PCE~0.01%), demonstrating that energy transfer to the SD is necessary for photocurrent generation by the ERD.



Figure 7: Photocurrent density-voltage (J-V) characteristics of devices with (13 mM 1) and without (0 mM 1) energy relay dye under AMA 1.5 (100 mWcm<sup>-2</sup>). Dash-dot lines represent the dark current for ERD containing DSC (blue) and the control device without any SD (green).



**Figure 8**: a) External quantum efficiency versus wavelength of DSC with energy relay dye (PTCDI) and a control device (0mM PTCDI). b) EQE addition (black line) caused by FRET from the energy relay dye to sensitizing dye. Peak  $EQE_{ERD}$  generated by 1 was 29.5% at 530nm. PDI 1 absorption (blue line) does not perfectly match  $EQE_{ERD}$  due to light scattering caused by TiO<sub>2</sub> nanoparticles and competitive light absorption with the sensitizing dye (TT1).

	13mM PDI 1	0mM PDI 1	Change
$J_{\rm SC} ({\rm mA \ cm}^{-2})$	8.78	6.88	28%
$V_{\rm OC}({\rm mV})$	553	562	-1.60%
FF	0.66	0.65	-1.50%
η (%)	3.21%	2.55%	26%

Table 2: Performance data from photovoltaic cells fabricated with and without 1 as an ERD.

A lower bound for external quantum efficiency of the energy relay dye (EQE<sub>ERD</sub>) can be calculated from the difference between the EQE of the device containing the ERD and the EQE of the control,  $\Delta$ EQE, shown in Figure 8b. The EQE enhancement has a peak of 29.5% at 530 nm, which is 8x greater than the control (0 mM 1). The  $\Delta$ EQE spectrum does not perfectly match the absorption of PTCDI because light scattering is greater at lower wavelengths increasing the optical pathway and at longer wavelengths (>550nm) the ERD and SD compete for light absorption. The external quantum efficiency of the energy relay dye is equivalent to the product of the absorption efficiency of the dye, the average excitation transfer efficiency,  $\overline{ETE}$ , and the internal quantum efficiency (IQE) of the control device, equation (4).

(4) 
$$EQE_{ERD} = \eta_{abs,ERD} \bullet \overline{ETE} \bullet IQE$$

A minimum bound for the average excitation transfer efficiency can be calculated by assuming that there is complete light absorption at the  $\Delta$ EQE peak. Using the dye absorption profiles, this corresponds to  $\eta_{abs,ERD} = 89.7\%$  from 1 and 10.3% by TT1. If the IQE is assumed to be equal to the peak EQE (70%), a minimum average ETE of 47% is calculated.

Using the distribution of pore sizes in the DSC measured by the Brunauer, Emmett, and Teller (BET) method in combination with the model shown in figure 6, an average excitation transfer efficiency of 49% for the cylindrical pores and 63% for the spherical pores is predicted. This is consistent with the minimum possible excitation transfer efficiency observed from the EQE data.

It should be possible to increase the average excitation transfer efficiency by reducing the average pore size inside of the titania film. The excitation transfer efficiency can be greater than 80% when using smaller nanoparticles (e.g. 14nm) assuming a sensitizing dye surface concentration of 0.5 dye/nm<sup>2</sup> and a spherical pore geometry, as shown in figure 6. Incorporating PDI dyes that are soluble in acetonitrile or  $\gamma$ -butyrolactone into films that contain smaller pores should allow power conversion efficiencies exceeding 5.5% for the PTCDI/TT1 system. If multiple relay dyes are incorporated into the system which have complimentary absorption spectra, a power conversion efficiency >7% is possible.

### Energy Transfer in Solid-State Dye-Sensitized Solar Cells

Like iodide, the Spiro-OMeTAD hole transporter used in solid-state DSCs is an excellent fluorescence quencher for most organic dyes. However, the quenching problem in solid-state devices is worse than in liquid cells, likely because the hole transporting material is 100% quencher, rather than a solution of quencher. PDI dyes 1-3 are all completely quenched when blended in a Spiro-OMeTAD matrix (figure 9). Evidently, even the bulky benzyl ether dendrons around PDI 2 do not prevent close contact between the hole transporter and the dye core. Thus, extending the concept of energy harvesting through FRET to solid-state DSCs is challenging.

Yum *et. al.* was recently able to overcome the quenching problem to some extent by using a phosphorescent Ru complex as the ERD in a solid-state DSC.<sup>17</sup> However, the

complex was still quenched by a factor of 69 when dispersed in Spiro-OMeTAD. While FRET was observed, the efficiency was low, as evidenced by an external quantum efficiency of only 8% at 460 nm, the peak absorption wavelength of the ERD. Clearly, a method to prevent quenching of the ERD is needed to fully realize the potential of FRET in solid-state DSCs.

Since quenching occurs via electron transfer and requires close physical contact between the hole transporter and ERD, chemical encapsulation of the ERD could prevent quenching. Dendrimers have found extensive use in encapsulating small molecule guests via self-assembly.<sup>18</sup> In one notable report, Jansen *et. al.* encapsulated small molecules with acidic groups, such as carboxylic acids, in a fifth generation poly(propyleneimine) (PPI) dendrimer functionalized on the periphery with protected amino acids.<sup>19</sup> The tightly packed shell of the dendrimer, rigidified by intramolecular hydrogen bonds between exterior amides, prevented encapsulated guests from escaping. It was hypothesized that this "dendritic box" could encapsulate fluorescent ERDs and prevent fluorescence quenching by Spiro-OMeTAD. A schematic of this concept is shown in figure 10.



Figure 9: Photoluminescence (P.L.) of PDI **3** in polystrene and Spiro-OMeTAD. Virtually complete quenching of the P.L. is observed when blending **3** in with Spiro-OMeTAD. Identical results are seen for PDIs **1** and **2**.

A potential problem with this approach is the mass taken up in the cell by the dendrimer. Spiro-OMeTAD occupies 65% of the pore space in a solid-state DSSC, leaving less than 35% of the pore volume for additional material.<sup>20</sup> To allow for incorporation of enough dye to absorb a large fraction of incident solar radiation, it is necessary to minimize the mass of the dendrimer. A fourth generation PPI dendrimer was chosen for this purpose, as this is the smallest generation for which intramolecular hydrogen bonding is observed upon amidation of the peripheral amines.<sup>19</sup> The dendrimer exterior was functionalized with ethyl hexyl amides (figure 11), as these were the

smallest functional groups found to impart sufficient solubility to the dendrimer in chlorobenzene, the solvent used for infiltrating Spiro-OMeTAD into the mesoporous titania.

PDI derivatives cannot be employed as the ERD in this case because their emission is quenched by amines. Instead, a highly fluorescent commercial dye, fluorescein 548 (figure 11), was used. A disadvantage of fluorescein 548 is its narrow absorption and small Stokes shift, the later of which might somewhat lower the FRET efficiency. However, the combination of fluorescein 548's commercial availability and two acidic protons that should bind to the amines in the dendrimer interior makes it attractive for initial studies.



**Figure 10**: Schematic representation of a solid-state dye sensitized solar cell incorporating dendrimerprotected energy relay dyes. The dendrimer prevents fluorescence quenching of the energy relay dyes, allowing for excitation transfer via FRET to the sensitizing dye.

To test if the dendrimer is effective at preventing quenching of encapsulated dyes, steady-state fluorescence spectra of thin films were measured (figure 12). Spectra were recorded using front-face detection of the emission, and are normalized by the absorbance of the film at the excitation wavelength. The emission spectra of fluorescein 548 dispersed in an inert polymer matrix, poly(methylmethacrylate) (PMMA) were first examined. The fluorescence intensity of a single dye in the dendrimer is equal to the intensity of the deprotonated dye in PMMA, demonstrating that the dendrimer itself does not quench the dye. Loading multiple dyes in the dendrimer results in some quenching, likely due to dye aggregation in the confined interior of the dendrimer. The quenching is only a factor of two for three dyes per dendrimer, however. Next, the fluorescence spectra in a Spiro-OMeTAD matrix were examined. Without dendrimer, the deprotonated dye is nearly completely quenched. However, the dye:dendrimer conjugates appear highly fluorescent in Spiro-OMeTAD. Concentration quenching is again observed when multiple dyes are loaded in the dendrimer, but this quenching is about the same magnitude as observed in PMMA films, suggesting that all three dyes are encapsulated equally well.



Dendrimer **10** Figure 11: Structure of the dendrimer and dye used in solid-state DSC studies.



**Figure 12**: Fluorescence spectra of fluorescein 548 in an inert matrix poly(methylmethacrylate) (a) and in a Spiro-OMeTAD matrix (b). The dendrimer and dye together made up 10% by mass of each film. The y axis is arbitrary intensity units for both (a) and (b). Spectra are normalized to the absorbance of the film at the excitation wavelength. Quantitative comparisons between the two graphs are not possible due to diffraction effects.

Due to diffraction issues caused by the different refractive indexes of Spiro-OMeTAD and PMMA, quantitative comparisons between emission spectra recorded using front-face detection are not possible. To obtain a quantitative comparison, spectra must be recorded in an integrating sphere. Figure 13 shows such spectra taken for 3:1 dye:dendrimer conjugates in PMMA and Spiro-OMeTAD. The fluorescein is quenched only by about 20% by Spiro-OMeTAD, demonstrating that the dendrimer is highly effective at insulating the fluorescein dye. Thus, FRET should be efficient between dendrimer-bound dyes and SDs in a solid-state DSC.



**Figure 13**: Fluorescence spectra of thin films of fluorescein 548/dendrimer **10** conjugates in PMMA or Spiro-OMeTAD. The dendrimer and dye together made up 10% by mass of each film. Spectra are normalized to the absorbance of the film at the excitation wavelength. Spectra were recorded in an integrating sphere to eliminate effects due to the varying refractive indexes of the different films.

Having established the effectiveness of dendrimer **10** in insulating dyes like fluorescein 548, it was then determined whether enough dendrimer could be incorporated into a cell to absorb a significant fraction of solar light. Figure 14 shows a simulation of light absorption in a solid-state DSC containing varying amounts of dendrimer. The percent of solar light absorbed was calculated using Beer's law with the following assumptions: a 2.5  $\mu$ m thick cell, a titania film with 60% porosity, 63% pore filling, a density of 1.87 g/mL for spiro and dendrimer, and an average dye extinction coefficient of 20,000 M<sup>-1</sup> cm<sup>-1</sup>. The last number is roughly the extinction coefficient of PDI averaged across the wavelength range 450-600 nm. Thus, this simulation represents an idealized system with a well-designed but realistic dye. As can be seen in figure 14, with three dyes loaded in each dendrimer and 25% of the hole-transporting film made up of dendrimer, 80% of the light from 450-600 nm is absorbed. Thus, dendrimer encapsulation appears to be a reasonable route to achieve high efficiency solid-state DSCs that harvest light by FRET.

With this information in hand, DSCs were fabricated incorporating 25% by mass 3:1 dendrimer:dye conjugates. Dendrimer was infiltrated into the pores by spin coating from a chlorobenzene solution either before, simultaneous to, or after Spiro deposition. Unfortunately, in all cases cells showed essentially zero photocurrent. To examine why this might be the case, the infiltration of the dendrimer into the porous titania was studied

using depth profiling by X-Ray photoelectron spectroscopy (XPS). This technique has been previously utilized to measure the vertical composition gradient of Spiro-OMeTAD is DSCs.<sup>20</sup> Because the pure dendrimer is difficult to detect by XPS in a film containing other carbon and nitrogen-containing materials (i.e. Spiro-OMeTAD), CuCl<sub>2</sub> was selfassembled into dendrimer 10 before infiltrating into the titania film. The dendrimer could then be tracked by monitoring the copper signal by XPS. Figure 15 shows an XPS depth profile of a DSC containing 25% dendrimer added simultaneously to Spiro-OMeTAD. Carbon, copper, titanium, and tin signals were measured. The rise of the Ti signal pinpoints the beginning of the porous titania, while the rise of the Sn signal signifies the end of the porous titania and the start of the fluorine tin oxide (FTO) electrode. The copper signal is very strong right at the surface of the titania, then quickly decreases going deeper into the film. This indicates that the dendrimer is penetrating the titania poorly, and likely forms an overlayer above the porous film. Such an overlayer would interfere with the electrical contact between Spiro-OMeTAD and the top electrode, leading to a very high series resistance in the cell. This likely explains the very low photocurrent.



**Figure 14**: Simulation of light absorption in a DSC containing varying amounts of dendrimer **10** mixed with Spiro-OMeTAD. Light absorption was calculated from Beer's Law using the following assumptions: a 2.5  $\mu$ m thick cell, a titania film with 60% porosity, 63% pore filling, a density of 1.87 g/mL for spiro and dendrimer, and an average dye extinction coefficient of 20,000 M<sup>-1</sup> cm<sup>-1</sup>.


Figure 15: XPS Depth Profile of a DSC prepared by spinning a chlorobenzene solution containing dendrimer 10 plus  $CuCl_2$  (50 mg/mL) and spiro-OMeTAD (130 mg/mL) into a 2.5 µm thick porous titania film.

# Conclusions

Incorporation of multiple dyes into DSCs may be necessary to absorb the entire solar emission from 350-1000 nm and thereby achieve the highest possible efficiencies. One way to do this is to utilize FRET to transfer excitations from energy relay dye(s) dissolved in the redox electrolyte to the sensitizing dye on the titania surface. Using PDI 1 as the ERD and TT1 as the SD, a device photocurrent enhancement of 28% relative to a device without any ERD was observed. The energy transfer efficiency was at least 50%, in accordance with a theoretical model. This result demonstrates that high energy transfer efficiencies are possible in DSCs even when employing ERDs subject to quenching by iodide-based electrolyte solutions, provided the ERD is a fast emitter and is substituted with bulky groups.

Given that energy transfer efficiencies above 80% are feasible, the development of DSCs with power conversion efficiencies greater than 15% should be possible by using a series of ERDs that absorb light from 350-800 nm and an SD that absorbs from 800-1000 nm. Such an SD does not yet exist, however, and will have to be developed.

Incorporation of ERDs into solid-state DSCs seems promising, but has so far remained difficult. The main challenge, photoluminescence quenching of ERDs by the Spiro-OMeTAD hole transporter, can be overcome by encapsulating the ERD in a PPI dendrimer. However, the dendrimer-encapsulated dyes do not easily infiltrate the pores of the Spiro-OMeTAD/titania film. Nevertheless, more than enough free space exists in the porous film to theoretically accommodate enough encapsulated dye to absorb a high percentage of the solar emission. So far, only spin coating has been tried as an infiltration method. Other methods, such as melt infiltration, are promising and will be explored in the future. The strategy of encapsulating ERDs by self-assembly into PPI

dendrimers remains attractive, as it should work for a variety of dyes. The dyes only need be of reasonable size and possess an acidic proton to facilitate self-assembly.

# Experimental

## **Liquid DSC Fabrication**

A 10-µm-thick layer of 20nm particles and a 5-µm-thick layer of 400nm scattering particles (CCIC, HPW-400) were formed via screen printing, sintered at 450°C, and subsequently treated in TiCl<sub>4</sub>.<sup>21</sup> The films were then dipped in a 1x10<sup>-5</sup>M solution of TT1 with 10mM chenodeoxycholic acid for four hours and rinsed in acetonitrile.<sup>22</sup> The chloroform electrolyte contained 0.6 M PMII, 0.05 M I<sub>2</sub>, <0.04 M tertbutyl pyridine, < 0.01 M LiI, and <0.02 M guanidinium thiocyanate in chloroform. 13 mM of **1** was subsequently added before electrolyte filling of the DSC. The preparation of the platinum counter electrode on FTO glass (TEC 15  $\Omega$ /, 2.2 mm thick, Pilkington) is described in a previous report.<sup>23</sup> Electrodes were sealed using a 25-µm-thick hot-melt film (Surlyn 1702, Dupont). A small hole was drilled in the counter electrode and electrolyte was filled using a vacuum pump.

## Solid-State Cell Fabrication and XPS Depth Profiling

Procedures for the standard preparation of solid-state dye sensitized cells have previously been published.<sup>24</sup> The sensitizing dye utilized was a squaraine derivitive; published procedures for fabricating solid-state DSCs with this SD were followed.<sup>17</sup> For the procedure utilized for fabricating films for XPS depth profiling and for recording the measurements themselves, see Ding *et. al.*<sup>20</sup> The solution used for infiltrating Spiro-OMeTAD and the dendrimer into the films contained 130 mg/mL Spiro and 50 mg/mL dendrimer **10**/CuCl<sub>2</sub> conjugate in chlorobenzene.

#### **Electrical Characterization**

The power of the AM 1.5 solar simulator (100 mW cm<sup>-2</sup>) was calibrated using a reference silicon photodiode equipped with an infrared cutoff filter (KG-3, Schott) in order to reduce the mismatch between the simulated light and solar spectrum from 350-700 nm to less than 2%.<sup>25</sup> The *J-V* curves were obtained by externally biasing the DSC and measuring the photocurrent using a Keithley 2400 digital source meter. All measurements were performed using a metal mask with an aperture of 0.159 cm<sup>2</sup> to reduce light scattering.

The EQE measurement light source was a 300W xenon lamp (ILC Technology, USA), which was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd). EQE measurements were performed at 1% sun using a metal mask with an aperture area of 0.159 cm<sup>2</sup>. Integrating the EQE spectra of the ERD containing and control DSC result in slightly higher (~10%) estimated  $J_{SC}$  at full sun than those measured in the devices. This is a result of charge transport limitations caused by the electrolyte at higher light intensities. Extrapolating device results from measurements taken at 10% sun to full sun are consistent with the estimated  $J_{SC}$  from the EQE results. The difference in the integrated EQE spectrum between the ERD containing and control devices is the same ratio as the differences in  $J_{SC}$  at full sun.

### **Photoluminescence Lifetime Measurements**

Time resolved PL measurements were performed using a Time-Correlated Single Photon Counting (TCSPC) system from PicoQuant. Solutions were excited with a pulsed laser diode, (model LDH 485: 481nm, 70ps FWHM, 5MHz) detected with a single photon avalanche diode (PDM 100CT SPAD) attached to a monochromator and processed by a PicoHarp 300 correlating system.

## **Dendrimer Self-Assembly**

To self-assemble the dye or  $CuCl_2$  in the dendrimer, the two were mixed together in appropriate ratios (16 equivalents of  $CuCl_2$  per dendrimer, and 1, 2, or 3 equivalents dye per dendrimer) in THF at 5 mg/mL, then stirred for 1 hr. The solvent was evaporated slowly with a stream of nitrogen, then the solid dendrimer conjugates were dried under vacuum. They were then dissolved in chlorobenzene with appropriate additives, such as Spiro-OMeTAD or PMMA.

## **Steady-State Photoluminescence Measurements**

Quartz slides were cleaned using by sonication in acetone and isopropanol, followed by treatment with UV/ozone for ten minutes. Solutions were prepared containing 60 mg/mL PMMA or Spiro-OMeTAD plus 6 mg/mL dendrimer/dye conjugate in chlorobenzene. These were spin-coated onto the quartz slides at 800 rpm. Emission spectra were obtained using an ISA/SPEX Fluorolog 3.22 equipped with a 450W Xe lamp, double excitation and double emission monochromators, and a digital photon-counting photomultiplier. Spectra were measured with front face detection (except where an integrating sphere was used), and the excitation wavelength was 490 nm. For normalization, absorbance spectra were measured using a Shimadzu UV-3600 spectrophotometer. When using an integrating sphere, the emission was measured first with direct excitation of the film (film directly in the path of the excitation beam), then with diffuse excitation (film outside the path of the excitation beam). The later spectrum was substracted from the former before normalization.

### **Materials Synthesis**

All glassware was dried overnight in an oven or by flame prior to use. Reactions were carried out under nitrogen using standard Schlenk techniques. Reactions were monitored by thin layer chromatography using Whatman<sup>®</sup> 250  $\mu$ m silica gel plates. Flash column chromatography was performed using Merck silica gel, 230-400 mesh. Solvents were removed with a rotary evaporator at aspirator pressure. All reagents were used as received from commercial suppliers without further purification. Tetrahydrofuran (THF), methylene chloride, DMF, and triethylamine were dried prior to use by passing through two columns of neutral alumina. The following compounds were made by previously reported procedures: 4,<sup>26</sup> 5-7,<sup>27</sup> 8,<sup>10</sup> and TT1.<sup>14</sup>

NMR spectra were recorded in CDCl<sub>3</sub> with a TMS standard using a Bruker AVB-400 spectrometer. <sup>13</sup>C NMR was recorded at 100 MHz using <sup>1</sup>H decoupling. Mass spectrometry and elemental analysis data were recorded by staff members at the UC Berkeley mass spectrometry facility.

### <u>*N*,*N*'-di(2,5-diisopropylphenyl)-1,6,7,12-tetra(4-*tert*-butylphenyoxy)- perylene-3,4,9,10-tetracarboxylic diimide 1:</u>



Procedure:

A solution of **5** (3.00 g, 3.54 mmol), 4-*tert*-butylphenol (2.66 g, 17.7 mmol), and potassium carbonate (2.92 g, 17.7 mmol) in anhydrous *N*-methylpyrrolidinone (50 mL) was stirred at 130 °C for 16 h. The solution was rapidly poured into 1M HCl (200 mL) and the resulting precipitate was isolated by vacuum filtration and washed repeatedly with water. The precipitate was dissolved in chloroform and extracted twice with water. The chloroform layer was then dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Purification by flash column chromatography (eluent: 40-55% dichloromethane in hexanes) yielded 1.55 g of red solid (34% yield). A portion of this product was further purified by recrystallization: 1.00 g of product was dissolved in dichloromethane (100 mL) and placed in a 1000 mL graduated cylinder. Methanol (200 mL) was carefully layered on top of the dichloromethane, and the two layers were allowed to mix slowly over 1 week. The resulting red crystals were isolated by filtration and dried under vacuum, yielding 740 mg of red product.

#### Characterization:

m.p. > 300 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.29 (s, 4H), 7.42 (t, J = 7.8 Hz, 2H), 7.22-7.28 (m, 12H), 6.87 (dt, J = 8.8 and 2.5 Hz, 8H), 2.71 (m, 4H), 1.28 (s, 36H), 1.13 (d, J = 6.8 Hz, 24H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  163.55, 156.12, 152.99, 147.55, 145.82, 133.44, 130.88, 129.60, 126.88, 124.09, 122.89, 120.97, 120.45, 120.39, 119.41, 34.58 31.66, 29.28, 24.24. FTIR (film on NaCl): v = 2963, 2870, 1709, 1675, 1588, 1505, 1406, 1340, 1285, 1209, 1175 cm<sup>-1</sup>. HRMS (FAB+, *m/z*): calcd for C<sub>88</sub>H<sub>91</sub>N<sub>2</sub>O<sub>8</sub>, 1303.6775; found, 1303.6786. Anal. calcd for C<sub>88</sub>H<sub>90</sub>N<sub>2</sub>O: C, 81.07; H, 6.96; N, 2.15. Found: C, 80.08; H, 6.97; N, 2.09.

## (G3 benzyl ether dendrimer)2-PDI 2:



Procedure:

A flask was charged with 7 (19.4 mg, 0.020 mmol), 8 (66 mg, 0.040 mmol), potassium carbonate (17 mg, 0.10 mmol), and DMF (0.3 mL). This solution was stirred at 100 °C for 14 h. The reaction was then diluted in chloroform and poured into methanol to precipitate the product. The precipitate was isolated by filtration then purified by flash column chromatography over silica gel (eluent: 5% ethyl acetate in toluene). The product was dissolved in chloroform, then poured into diethyl ether. The precipitate was isolated by filtration, yielding 37 mg of blue solid (45% yield).

Characterization:



#### **PEGylated PDI 3:**



#### Procedure:

3000 kDa PEG with methyl and hydroxide end groups (1.0 g, 0.33 mmol) and carbon tetrabromide (0.55 g, 1.67 mmol) were dissolved in dichloromethane (8 mL). Solid triphenylphosphine (0.44 g, 1.67 mmol) was added in a single portion. The resulting solution was stirred overnight then concentrated. Water (15 mL) was added, and the suspension filtered to eliminate triphenylphosphine oxide. The water was removed by lyophilization, yielding 1.00 g polymer product. Some residual triphenylphosphine oxide remained (roughly 3% by mass), but the product was suitable for use in the next step.

A flask was charged with 7 (20 mg, 0.020 mmol), the above polymer product (150 mg, 0.045 mmol), potassium carbonate (13 mg, 0.080 mmol), potassium iodide (7 mg, 0.04 mmol), 18-Crown-6 (2 mg, 0.008 mmol), and DMF (1 mL). The solution was stirred at 70 °C overnight, then poured into water (20 mL). This solution was extracted with dichloromethane (2 x 20 mL), then the combined organics were dried over Na<sub>2</sub>SO<sub>4</sub>. After concentrating, the solid was purified by column chromatography over silica gel (eluent: 6-20% methanol in dichloromethane), yielding 20 mg of **3** as a purple solid (14% yield).





### (2-ethylhexylamide)<sub>32</sub>-PPI dendrimer 10:



#### Procedure:

Amine-terminated G4 PPI dendrimer (758 mg, 0.216 mmol) was dried by azeotropic distillation of water with toluene. The dry dendrimer was dissolved in THF (15 mL) and triethylamine (1.17 mL). 2-ethylhexanoyl chloride (1.32 mL, 7.6 mmol) was added dropwise by syringe over 5 min, resulting in the formation of precipitate. The suspension was stirred for 2 days. After removing the solvent at reduced pressure, diethyl ether (25 mL) was added and the suspension was refluxed for 1 hr. The ether was decanted off, and the product dissolved in a minimal amount of methanol. This solution was poured into sodium carbonate (1.5 g) in water (100 mL), resulting in formation of a waxy precipitate. This solution was extracted with dichloromethane (2 x 50 mL). The organics were dried over sodium sulfate and concentrated, yielding 1.49 g of product as a light yellow viscous oil (91% yield).

#### Characterization:

Anal. calcd for C<sub>440</sub>H<sub>880</sub>N<sub>62</sub>O<sub>32</sub>: C, 70.00; H, 11.74; N, 11.12. Found: C, 69.90; H, 12.10; N, 11.12.

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