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Molecular Control of Macromolecular Properties

by

Thomas Wesley Holcombe III

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Jean M. J. Fréchet, Chair Professor Peidong Yang Professor Rachel Segalman

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Molecular Control of Macromolecular Properties

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by

Thomas Wesley Holcombe III

Abstract

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Thomas Wesley Holcombe III

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Jean M. J. Fréchet, Chair

Molecular level control over macromolecules has been at the heart of human advancement, long before Hermann Staudinger coined the term *Makromoleküle*. From the development of primitive pharmaceuticals to the advanced materials that sent Man into outer-space, We have been tinkering with God's paint since our inception.

The work described herein primarily involves advances concerning poly-aromatic macromolecules for use in future electronic applications, particularly that of organic photovoltaics. There is a final chapter, however, that gives the reader a taste of how some molecular level changes can be directly visualized with modern microscopy techniques.

Chapter 1 provides a very brief introduction to conjugated polymers and molecular level control over macromolecular properties. Chapters 2 - 4 introduces the concept of polymer substitution as a means by which to control and improve charge generation in organic photovoltaic devices. Chapters 5 and 6 show how these polymers can take on larger, defined structures, yet are still beholden to intrinsic molecular properties – such as regioregularity, a fancy word for the regularity of the position in which two aromatic rings are joined together. Chapter 7 re-examines the role of polymer substitution on photovoltaic performance, this time with an emphasis on homo-polymer packing rather than electron transfer at the donor/acceptor interface. Finally, Chapter 8 visualizes how controlling the environment about a single metal atom can lead directly to a cyclic polyolefin. Individually, these advances do not yield any breakthroughs noticeable to a general audience; collectively, they sit atop a mountain of human knowledge, waiting to provide a stepping stone for the next generation.

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Dedications

I dedicate this to my family, although we may not see each other as much as most, you mean the world to me. Specific dedications are due to my grandparents and parents. First, my Papa, Thomas Wesley Holcombe Sr.: West Point graduate, Army Colonel, War Veteran, and true American hero; always quiet, always observant, and always there when the timing is right. Second, it would be an injustice in this modern day to overlook my Nana, who undoubtedly was a pillar of support in Papa's life, and certainly in mine. To this day I am still learning grammar from this retired English teacher, volunteer, and life-long learner – who is also still taking on modern technology as the years keep passing. Second, my father and mother: words cannot convey how important you two are to me – throughout it all.

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Without my former advisor, my undergraduate advisor, C. Grant Willson, I may never have joined Prof. Fréchet's group – or even gone to Berkeley! This Cal alum has an unbreakable tenacity for life, and it is infectious. He, too, cannot be thank enough for both his role supporting my early adventures in science, as well as his incredible (and indelible) mark on the scientific community. I wish him the best, and I look forward to a few good times together in the future!

The professors are not the only people helping to shape the lives of us young scientists, and so it is appropriate to single out two critical, non-scientists that are invaluable in every way. Chona de Mesa and Cezar Ramiro are the rising and setting sun for the Fréchet group. I looked forward to lively conversation, funny jokes, personal advice, and generally a good time every day that I went to work because of them. I don't know what I am going to do the next place I go, if I cannot take them with me!

There are a few special people that may or may not be aware of how important they were in my progress towards a Ph.D. The first is Barry Thompson (now Prof. Barry Thompson), who took me under his wing, helped me to the best of his ability (which is substantial) and managed to put up with me for two years – even though he thought I acted like I was entitled to everything I wanted. It was his patience, concise explanations, and leadership qualities that helped me to grow and really appreciate the concept of a "mentor." Dave "quicksand" Kavulak was also a true mentor. Well, that leads me to Claire H. Woo. Claire, Claire is something rare to me, a kindred spirit. For all the foundation and support that everyone listed above provided, I am not sure that the level of success I achieved during this program would have been possible without her. Not only is she an ace in the lab, sharp as a tack, and an incredibly hard working colleague, she is also an unbelievable friend and someone I hope to stay in contact with throughout my life. Finally (the best for last), Derek van der Poll and Steve Scroggins were irreplaceable helping me to learn "basic" American male traits. My upbringing, with three sisters, left a few "chasms" in the way of "bros." They were not only the best lab mates I could ask for, but are also two of the best friends I could have wished for.

Outside of the lab, I must thank my extended family: wise beyond your years (yet still fun around the holidays!), I am lucky to be related to such a supportive bunch. I am also indebted to an unbelievably vast and critically important 21st century extended family: my tribe of friends. I've known some of you since I was signing the "naughty" book in elementary school, while others I met later in life and feel as if you've known me all my life. You shape my world.

Chapter 1

A Selected Introduction to the Structure-Property Relationship

Abstract

There are many important structure-property relationships investigated under the broad field of "chemistry." The development of conjugated polymer synthesis and then the donor-acceptor concept is presented here. This text is solely meant to provide an example of how molecular structure can impact bulk material properties. Extensive reviews of conjugated polymer synthesis, donor-acceptor polymers, and the rest of the concepts presented in this dissertation can be found with only a cursory peek into the chemical literature.

1. Introduction

Everything we see is made of atoms, and more importantly, the arrangement of these atoms into molecules. Molecules and intermolecular forces are so prevalent that they hold the oceans together and can literally alter the way we think. Here, though, specific attention is paid to conjugated polymers, i.e., macromolecules comprised of a polyunsaturated backbone. These materials have become the subject of broad interest only in the last fifty years or so, and work toward the development of this field was awarded the Nobel Prize in Chemistry for the year 2000.

New chemistry and novel molecular design was necessary to advance this field, and some of that history will be covered in this section. Additionally, once synthetic methodologies for conjugated polymer synthesis were elucidated, control of these polymers' bulk properties was desired. *The desire to control color, solubility, and electron transport are just a few of the properties that motivate the development of structure property relationships in this field.*

2. Synthesis of Conjugated Polymers

Synthetic polymers were first postulated and synthesized by Staudinger and Corothers. The polymers they were interested in surround us now – polyesters, polyamides, and polyolefins. They utilized established chemistry to prove that synthetic polymers, rather than natural polymers such as rubber, could be realized. Today, as with most aspects of our technological advancements, the chemistry at the foundation of conjugated polymers was developed more recently. The development of transition metal catalyzed cross-couplings of sp²-sp² bonds was awarded the Nobel Prize just last year, in 2010. Although the award specifically mentioned palladium catalysis, the concept of homogeneous catalysis with a specific *molecular environment (ligand coordination) about any metal center*, toward a precise aryl-aryl coupling, is at the core of conjugated polymer synthesis.

Most conjugated polymers these days are prepared from Stille, Suzuki, Heck, and in special cases Kumada or Negishi cross-coupling polymerizations. Seminal work in the field of conjugated polymer synthesis relied on the production of an intermediate polymer that contained saturation along the backbone, which then proceeded to unsaturation (conjugation) through a secondary "processing" step. With the advent of the aforementioned synthetic reactions, direct access to conjugated polymers greatly accelerated progress towards functional π -conjugated systems.

2. Donor-Acceptor Polymers

The wide-spread adoption of two particular reactions, the Stille and Suzuki polymerizations, led to an explosion of data concerning donor-acceptor (D-A) polymer properties. The ability to quickly produce a plethora of AABB polymers meant that many "donor" and "acceptor" molecules could be co-polymerized and the resulting properties such as color, ionization potential, and charge carrier mobility could be examined. The fundamental physics of D-A

polymers is quite simple: at the most superficial level, the properties can be thought of as arising from the proximity that a covalent bond offers between a molecule with a low ionization potential and one with a high electron affinity. This leads to a spatial separation of the HOMO and LUMO, as well as a decreased energy barrier for electron promotion. This leads to a decreased bandgap and many other more subtle variations from a homopolymer of either the acceptor or donor component.

Additionally, this kind of polymer provides one of best examples to explain a simple structureproperty relationship. Because the nature of the two co-monomers differs dramatically, it is easy to see how replacing one of the co-monomers may have a significant impact on only some of the bulk polymer properties. The donor co-monomer possesses a lower ionization potential and the acceptor a higher ionization potential, this means that when an experimentalist would like to alter the ionization potential of the co-polymer, altering the donor co-monomer is like the most effective action.

Donor-acceptor polymers, as well as almost all the polymers that are relevant to the field of organic electronics, are thoroughly examined in the Handbook of Conducting Polymers by Reynolds and Skotheim.¹

3. Conclusions

This brief introduction excludes many important design parameters that will be discussed in this dissertation, most notably the importance polymer side-chain substitution. The importance of polymer solubilizing groups is of critical importance in each of the chapters presented, except Chapters 4 and 5. It is up to the reader to consider all the ways in which molecular structure impacts material properties throughout this work, and throughout all the chemical literature. When you start to understand how individual atoms can control the fate of entire beings (think addiction and sickle cell anemia), the structure-property relationship jumps out at you from every corner. Trying to illuminate just a few examples of how structure impacts function was the focus of this work.

4. References

(1) Skotheim, T. A., Reynolds, J. Conjugated Polymers: Theory, Synthesis, Properties, and Characterization (Handbook of Conducting Polymers, Third Edition); CRC Press, 2006

Chapter 2

All-Polymer Photovoltaic Devices of Poly(3-(4-n-octyl)phenylthiophene) from Grignard Metathesis (GRIM) Polymerization

Abstract

The synthesis of poly[3-(4-n-octyl)-phenylthiophene] (POPT) from Grignard Metathesis (GRIM) is reported. GRIM POPT is found to have favorable electronic, optical, and processing properties for organic photovoltaics (OPVs). Space-charge limited current and field effect transistor measurements for POPT yielded mobilities of 1×10^4 cm²/Vs and 0.05 cm²/V·s, respectively. Spin-casting GRIM POPT out of chlorobenzene yields a thin film with a 1.8 eV bandgap, and PC₆₁BM:POPT bulk heterojection devices yield peak performance of 3.1%. Additionally, an efficiency of 2.0% is achieved in an all-polymer, bilayer OPV device utilizing poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-(1-cyanovinylene)phenylene] (CNPPV) as an acceptor. This state-of-the-art all-polymer device is analyzed in comparison to the analogous poly(3-hexylthiophene) (P3HT)/CNPPV device. Counter to expectations, based on more favorable energy level alignment, greater active layer light absorption, and similar hole mobility, P3HT/CNPPV devices perform less well than POPT/CNPPV devices. P3HT/CNPPV devices yield a peak efficiency of 0.93%.

1. Introduction

The demand for cheap, shape-conforming and lightweight solar energy harvesting materials has motivated the development of organic polymer photovoltaics (OPVs). A well-studied system is the solution processable poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) bulk heterojunction (BHJ) OPV. With efficiencies between 4-5%, P3HT has demonstrated exceptional optoelectronic properties.^{1a} However, for OPVs to compete with commercial inorganic PVs, more of the solar spectrum must be harvested while achieving larger open-circuit voltages (V_{oc}).^{1b} For these reasons, poly[3-(4-n-octyl)-phenylthiophene] (POPT)² is an attractive alternative to P3HT. POPT has increased spectral breadth compared to P3HT (Figure 1), exhibits a lower-lying HOMO³ – correlated to increased V_{oc}⁴ and air stability⁵ – and a phenyl ring useful for tuning polythiophene optoelectronic properties.⁶ In fact, POPT has been investigated for use in OPVs by Friend *et al.* in 1998 using a laminate bilayer POPT:poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-(1-cyanovinylene)phenylene] (CNPPV) device, which yielded the highest photocurrent of its time with peak EQE of 28%.⁷ However, more thorough studies of POPT and similar derivatives have yielded only modest OPV performance ($\eta < 0.5\%$).⁸



2. Results and Discussion

Figure 1. Material structures and absorption spectra with overlaid AM1.5 photon flux. Donor materials P3HT and POPT, acceptor materials CNPPV and $PC_{61}BM$.

One barrier to high efficiency may have been the oxidative method used to synthesize poly(3phenylthiophene) semiconductors. It is known that polythiophene polymerization method^{9a}, ^{9c} and regioregularity^{9b, 9c} critically impact the optical and electronic properties of the resulting material, which in turn affects OPV performance. Grignard metathesis (GRIM), which is a redox neutral organomagnesium/aryl-halide cross-coupling polymerization, has been a particularly successful method of P3HT synthesis.¹⁰ GRIM yields high number average molecular weight (M_n), low polydispersity index (PDI), and highly regioregular (RR) P3HT.

For this study, POPT was polymerized from the 2-bromo-5-iodo-3-(4-*n*-octyl)thiophene monomer in ~50% final yield with a modified GRIM procedure. Due to the steric and electronic effects of the 3-phenyl ring, elevated metal-halogen exchange and polymerization temperatures were required to achieve a suitable polymer yield and molecular weight. POPT with M_n up to 75 kDa and PDI < 1.2 was obtained after Soxhlet purification. The purified polymer was >99% RR as determined by NMR. All subsequent electronic and device characterization reported herein was performed with 35 kDa POPT.

When spun-cast from high boiling point solvents, thin films of GRIM POPT display UV–Vis vibronic structure, unlike oxidatively synthesized POPT, which does not show such structured absorption without additional processing steps.^{2a} This difference in processing properties qualitatively illustrates the distinctive improvement to POPT afforded by the GRIM synthetic approach. We have also determined, for the first time, hole mobility values of 1×10^{-4} and 0.05 cm²/(V·s) for POPT using space-charge limited current and field effect transistor measurements, respectively. No change in mobility was observed upon thermal annealing. These mobility values are similar to those obtained for P3HT and suggest that hole extraction in OPV devices is not likely to differ much between these polythiophenes.

As a standard test for OPV material quality, POPT:PC₆₁BM (1:1) BHJ devices were fabricated. A peak efficiency of 3.1% under AM 1.5 illumination with an intensity of 100 mW cm⁻² and an average efficiency of 2% was achieved after 1 min of thermal annealing at 180 °C. These devices are ostensibly limited by the blend morphology: efficiencies decrease after longer annealing times (5–30 min), and TEM characterization of the optimized film morphology showed gross phase segregation. (See section 4, "Methods and Materials", for detailed device parameters and TEM characterization).

The relatively high solvent resistance of GRIM POPT, resulting from its high M_n and regioregularity, enables a better examination of the all-polymer system first explored by Friend.⁷ Therefore, CNPPV can be spin-coated directly on top of a POPT film using solvents such as tetrahydrofuran or ethyl acetate, which are too weak to dissolve POPT, leading to bilayer devices as opposed to the previously explored laminate design. A peak efficiency of 2.0% was achieved with this system after 2 hrs of thermal annealing at 110 °C, post-electrode deposition (average $\eta = 1.5\%$). This constitutes the highest reported efficiency to date for a solution processed all-polymer OPV.¹¹

Significantly, similar all-polymer devices optimized from GRIM P3HT yielded a max efficiency of 0.93% (Figure 2a) with an average of 0.75%. This lower efficiency of P3HT devices is due to a reduction in the short circuit current (J_{sc}). The increased J_{sc} exhibited by the POPT/CNPPV devices does not derive from increased absorption, as illustrated by the absorption spectra in Figure 2c. Under optimized conditions, the POPT/CNPPV bilayer absorbs ~75% of the light but exhibits approximately twice the photocurrent of the P3HT/CNPPV bilayers, with improved photocurrent across the entire absorption spectrum of the device (Figure 2d). Additionally, all-polymer POPT:CNPPV blend devices were fabricated but did not perform as well as the bilayer devices, making a POPT/P3HT comparison hard to evaluate in that architecture. As neither light absorption nor hole mobility can explain this striking difference in photocurrent, the electronic driving forces behind charge separation are worth investigating.

Considering that OPVs require a donor/acceptor interface to separate excitons and generate free charges, understanding charge separation is critical for advancing the field of OPVs.¹² Recent literature has attempted to relate $\Delta G_{\rm CS}^{\rm rel}$ (the relative free energy of charge separation) to the singlet excited state energy ($E_{\rm s}$) and the relative band offsets in the abbreviated Weller equation $\Delta G_{\rm CS}^{\rm rel} = E_{\rm S} - ({\rm HOMO}_{\rm donor} - {\rm LUMO}_{\rm acceptor})$.^{12a} Values for $\Delta G_{\rm CS}^{\rm rel}$ calculated from this equation correlate well with the observed short circuit currents for several polymer:PCBM devices.^{12a} However, in this study the abbreviated equation predicts a larger driving force for charge separation in the P3HT/CNPPV device, as $\Delta G^{\rm rel}$ is 0 eV for POPT/CNPPV but is 0.3 eV for P3HT/CNPPV (Figure 2b). The large difference in $J_{\rm sc}$ between these polythiophene devices, contrary to measured hole mobilities, light absorption, and predicted $\Delta G^{\rm rel}$. Notably, the abbreviated Weller equation does not include the lattice polarization energy or Coulombic attraction between bound electron–hole pairs. These neglected terms may be important in explaining the increased $J_{\rm sc}$ in POPT/CNPPV devices.



Figure 2. (a) *J-V* curves for POPT and P3HT devices under AM 1.5 100 mW/cm2 illumination. (b) Material energy band levels. (c) Absorption spectra of bilayers at optimized thicknesses for devices. (d) EQE plots of optimized devices.

3. Conclusions

In conclusion, it is clear that the more controlled GRIM method used to prepare POPT affords a polymer with desirable electronic and structural properties for applications in OPVs. The AM 1.5 efficiency of 2% achieved with POPT/CNPPV is the highest reported to date for an all-polymer based device. POPT outperformed P3HT in all-polymer devices due to a doubling of the J_{sc} . At individually optimized bilayer thicknesses, the superior performance of POPT vs P3HT in the devices with CNPPV is counter to expectations based on absorption, charge mobility, and energy level comparisons. This emphasizes the importance of understanding charge separation processes in OPV devices, particularly the effects of Coulombic attraction and lattice polarization energy. Additionally, the synthetic simplicity and tunability of the phenylthiophene class of polymers makes POPT and other 3-phenyl derivatives attractive materials for further exploration of structure–property relationships in the field of polymer-based solar cells.

4. Methods and Materials

All reagents from commercial sources were used without further purification, unless otherwise noted. All reactions were performed under dry N₂, unless otherwise noted. All dry reactions were performed with glassware that was oven dried and then flamed under high-vacuum and backfilled with N₂. All extracts were dried over powdered MgSO₄ and solvents removed by rotary evaporation under reduced pressure. Flash chromatography was performed using Merck Kieselgel 60 (230-400 mesh) silica. Methylene chloride, THF, toluene, and pyridine were purchased from Fisher Scientific and purified by passing them under N₂ pressure through two packed columns of neutral alumina (for THF, pyridine and methylene chloride) or neutral alumina and copper(II) oxide (for toluene). MEH-CN-PPV was purchased from H. W. Sands Corp. and used without further purification. The molecular weight was $M_n = 16$ kDa with a PDI of 4.5.

All compounds were characterized by ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) on a Bruker AVB 400 or AVQ 400. High-resolution mass spectra and elemental analysis (CHNS) was performed at the University of California, Berkeley Department of chemistry analytical services. Polymer ¹H NMRs (500 MHz) were obtained on Bruker DRX 500. For polymer molecular weight determination, polymer samples were dissolved in HPLC grade dichlorobenzene at a concentration of 1 mg/ml, briefly heated and then allowed to return to room temperature prior to filtering through a 0.2 m PVDF filter. SEC was performed using HPLC grade dichlorobenzene at a flow rate of 0.8 L/min on two 300 x 8 mm linear S SDV, 5 micron columns (Polymer Standards Services, USA Inc.) at 70 °C using a Waters (Milford, MA) 2690 separation module and a Waters 486 Tunable Absorption Detector monitored at 350 nm. The instrument was calibrated vs. polystyrene standards (1,050 – 135,000 g/mol) and data was analyzed using Millenium 3.2 software.

Cyclic voltammograms were collected using a Solartron 1285 potentiostat under the control of CorrWare II software. A standard three electrode cell based on a Pt button working electrode, a silver wire pseudo reference electrode (calibrated vs. Fc/Fc^+), and a Pt wire counter electrode was purged with nitrogen and maintained under a nitrogen atmosphere during all measurements. Acetonitrile was distilled over CaH₂ prior to use and tetrabutyl ammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. Polymer films were drop cast onto a Pt button working electrode from a 1% (w/w) chloroform solution and dried under nitrogen prior to measurement.

UV-Visible absorption spectra were obtained using a Carey 50 Conc UV-Visible spectrophotometer. For thin film measurements polymers were spin coated onto untreated glass slides from chlorobenzene solution (10 mg/ml). A model P6700 Spincoater was used to spin coat the films at 1200 RPM for 60 s.

TEM images were obtained using a FEI TECNAI G2 with a 200 kW accelerating voltage. Samples were prepared by spin-casting films from chlorobenzene as used for device measurement on to freshly cleaved NaCl single crystal substrates at 1500RPM for 60s. The films were floated onto water and placed onto a 600 mesh copper TEM grid (Electron Microscopy Science, Inc.).

Atomic force microscopy was performed using a Veeco (Digital Instruments) Multimode microscope with a Nanoscope V controller. Imaging was performed in semi-contact (tapping) mode using Veeco RTESP tips.

Polymer film thickness was measured by a Veeco Dektak profilometer.

Thin-film transistors were fabricated on 300 nm SiO_2 dielectric substrates on heavily doped silicon. Bottom contact source-drain electrodes (Cr = 5 nm, Au = 100 nm) were fabricated by conventional photolithography using a transparency photomask. Channel lengths of 10 and 20 m and channel widths of 100 and 200 m were used for discrete transistors. The active semiconducting layer was applied by spin-casting 5-10 mg/mL solutions in anhydrous chlorobenzene at 2000 rpm. The films were then vacuum-dried overnight and measurements were carried out in ambient conditions using an Agilent 4156C Precision Semiconductor Parameter Analyzer.

Polymer mobility was measured using a diode configuration of ITO/ PEDOT:PSS/ Polymer/Al in the space charge limited current (SCLC) regime. At sufficient potential the conduction of charges in the device can be described by

$$J_{SCLC} = \frac{9}{8} \varepsilon \varepsilon_o \mu \frac{V^2}{L^3}, \qquad (1)$$

where ε_0 is the permittivity of free space, ε is the dielectric constant of the polymer, μ is the mobility of the majority charge carriers, V is the potential across the device (V = V_{applied} – V_{bi} - V_r), and L is the polymer layer thickness. The series and contact resistance of the device (~15 Ω) was measured using a blank device (ITO/PEDOT/Al) and the voltage drop due to this resistance (V_r) was subtracted from the applied voltage. The built-in voltage (V_{bi}), which is based on the relative work function difference of the two electrodes, was also subtracted from the applied voltage. The built-in voltage can be determined from the transition between the Ohmic region and the SCLC region and was found to be about 1 V.

Synthetic Procedures:



3-(4-nOctyl)-phenylthiophene (1) In a 250 mL 3-neck round bottom with reflux condenser, 4octyl-bromobenzene (TCI America, 15.00 g, 55.72 mmol), 3-thiophene boronic acid (Combi-Blocks, 7.85 g, 61.28 mmol, 1.1 eq), and tribasic potassium phosphate (15.40 g, 2eq of boronic acid) were dissolved in nButanol (110 mL). This mixture was degassed with N₂ for 30 minutes at which point $Pd_2(dba)_3$ (262 mg, 0.0025 eq) and 2-Dicyclohexylphosphino-2',4',6'-

triisopropylbiphenyl (X-Phos) (79 mg, 0.01 eq) was added in one portion and the reaction heated to 100 °C for 12 hours. The reaction was then rotovapped to remove nBuOH and flashed through a silica plug with hexanes and minimal chloroform (to help load the product) to remove powdered phosphates and other impurities (a clay/dirt crude product). The crude (clear & colorless) flashed product was then recrystallized from ethanol. 12.88 g, 85 % yield, white solid flakes. ¹H NMR (400 MHz, *CDCl*₃): δ ppm 7.53-7.50 (m, 2H), 7.42-7.36 (m, 3H), 7.22 (d, *J* = 8.10 Hz, 2H), 2.65-2.59 (t, 2H), 1.63 (td, *J* = 15.10, 7.54, 7.54 Hz, 2H), 1.38-1.23 (m, 10H), 0.91-0.86 (t, 3H). ¹³C (100 MHz, *Acetone-d*₆): δ ppm 142.11, 141.66, 133.19, 128.79, 126.26, 126.06, 126.03, 119.62, 35.25, 31.72, 31.41, 22.43, 13.49.

2-bromo-3-(4-octyl)-phenylthiophene (2) In a 25 mL 1 neck round bottom, 3-(4-octyl)phenylthiophene (1.26 g, 4.6 mmol) was dissolved in CHCl₃ (10 ml) and cooled to 0 °C. N-Bromosuccinimide (NBS) (825 mg, 4.6 mmol) was added in one portion to the stirring solution. The reaction was heated to 40 °C for 1 hour and then stirred at room temperature for an additional hour. Usual color change was from clear to yellow back to almost clear. The resultant pale yellow solution was diluted with Et₂O and 1M NaOH added to quench any residual NBS and Br₂. The organic layer was then separated and the aqueous layer extracted with Et₂O. The crude product was then purified by silica gel chromatography (hexanes). This reaction is neither anhydrous nor done under nitrogen. 11.5 g, 93 % yield, colorless oil. ¹H NMR (400 MHz, *Acetone-d*₆): δ ppm 7.58 (d, *J* = 5.67 Hz, 1H), 7.51 (d, *J* = 8.13 Hz, 2H), 7.30 (d, *J* = 8.00 Hz, 2H), 7.14 (d, *J* = 5.67 Hz, 1H), 2.70-2.63 (t, 2H), 1.73-1.59 (m, 2H), 1.46-1.22 (m, 10H), 0.93-0.84 (t, 3H). ¹³C (100 MHz): δ ppm 143.44, 142.88, 138.92, 130.85, 128.47, 128.29, 110.18, 72.93, 35.40, 31.76, 31.34, 22.47, 13.57. HRMS calc. *m*/z for (C₁₈H₂₃BrS) 350.0704; found 350.0701. Anal. Calcd for C₁₈H₂₄S: C, 61.53; H, 6.60; S, 9.13. Found: C, 61.76; H, 6.61; S, 9.29.

2-bromo-5-iodo-3-(4-octyl)-phenylthiophene (3) In a 1 neck flask, 2-bromo-3-(4-octyl)phenylthiophene (5.3 g, 15.04 mmol) was dissolved in CHCl₃ (1 M) and cooled to 0 °C. I₂ (2.10 g, 8.27 mmol, .55 eq) and PhI(OAc)₂ (2.90 g, 9.02 mmol, .60eq) were added while stirring. The reaction was slowly warmed to room temperature over 12 hours. The reaction was then diluted with Et₂O and saturated aqueous sodium thiosulfate was added to ensure the elimination of any residual molecular iodine. The organic layer was separated and the crude product purified by silica gel chromatography (hexanes). This reaction is neither dry nor done under nitrogen. 5.77 g, 80 % yield, colorless oil. ¹H NMR (400 MHz, *Acetone-d*₆): δ ppm 7.49 (d, *J* = 8.12 Hz, 2H), 7.38 (s, 1H), 7.31 (d, *J* = 8.09 Hz, 2H), 2.77-2.56 (t, 2H), 1.73-1.58 (m, 2H), 1.43-1.24 (m, 10H), 0.96-0.84 (t, 3H). ¹³C (100 MHz): δ ppm 143.44, 142.87, 138.92, 130.85, 128.47, 128.29, 110.19, 72.93, 35.42, 31.77, 31.36, 22.49, 13.59. HRMS calc *m*/z for (C₁₈H₂₂BrIS) 475.9670; found 475.9675. Anal. Calcd for C₁₈H₂₂BrIS: C, 45.30; H, 4.65; S, 6.72. Found: C, 45.59; H, 4.54; S, 6.86.

Poly(3-(4-octyl)-phenylthiophene) A three-necked round bottom flask with reflux condenser and stirbar was charged with monomer **3** (1.0 g, 2.1 mmol) and 50 mL dry THF. The resulting solution was cooled to -78 °C and stirred for 20 minutes. Then ^{*i*}PrMgCl (2M in THF, 1.0 ml, 0.96 eq.) was added to the reaction mixture dropwise. After stirring at -78 °C for 10 minutes, the reaction was removed from the -78 °C bath and allowed to warm to RT over a 1 hour period.

During the last 15 minutes of metal-halogen exchange, an oil bath was pre-heated to 65 °C. Then Ni(dppp)Cl₂ (4 mg, 0.35 mol%) was added in one portion and the reaction placed in the preheated oil bath and stirred for 12 hours. Following the addition, the color of the reaction mixture changed from colorless to red. The polymer was precipitated into methanol (250 mL) from the THF reaction solution and filtered through a Soxhlet thimble. The polymer was purified by Soxhlet extraction with methanol for 6 h, hexanes for 6 h, and chloroform for 6 h. The polymer was then isolated by extraction with chlorobenzene, followed by concentration under a stream of nitrogen and finally precipitation into methanol (500 mL). A typical yield of ~ 50% was obtained for these polymerizations. NMR (500 MHz, CDCl₃): δ ppm 7.19 (dd, *J* = 37.39, 8.03 Hz, 4H), 6.79 (s, 1H), 2.63-2.56 (t, 2H), 1.63-1.60 (m, 2H), 1.31-1.25 (m, 10H), 0.88-0.85 (t, 3H).

Shown below is SEC data (M&M Figure 1) and NMR data (M&M Figure 2) for POPT with M_n = 34 kDa, PDI = 1.12. The additional high molecular weight peak at exactly double the max peak in the SEC is ascribed to a polymer-polymer homo-coupling during the quench. If concentrated acid is used to quench the polymerization, the homo-coupling peak is eliminated.



M&M Figure 1. SEC trace of POPT used for electronic studies.



M&M Figure 2. NMR of POPT used for electronic studies. Note: CHCl₃ satellites are picked out at 7.47 and 7.05 ppm.

Photovoltaic Devices: All solar devices have a layered structure with the photoactive layer consisting of separate donor and acceptor layers sandwiched between the two electrodes, ITO and LiF/Al. Glass substrates coated with a 150 nm sputtered ITO pattern of 20 Ω \Box^{-1} resistivity were obtained from Thin Film Device, Inc. The ITO-coated glass substrates were ultrasonicated for 20 min each in acetone, and then 2% Helmanex soap water, followed by extensive rinsing and ultrasonication in deionized water, and then isopropyl alcohol. The substrates were then dried under a stream of air. A dispersion of PEDOT:PSS (Baytron-PH500) in water was filtered (0.45 m glass) and spin coated at 3400 RPM for 60s, affording a ~20-30 nm layer. The substrate was dried for 15 min at 140°C in air and then transferred into an Argon glove box for subsequent procedures. P3HT and POPT solutions were prepared in chlorobenzene at a concentration of 2-13mg/ml and were heated to 120°C for complete dissolution. CN-PPV solution was prepared in ethyl acetate or THF at a concentrations of 6-9 mg/ml. The solutions were stirred for 24 hrs and passed through 0.2 µm PTFE syringe filter before they were spin coated. The donor laver, consisting of P3HT or POPT, was spin coated first onto the substrate at 1200 RPM for 60s on top of the PEDOT:PSS laver. Subsequently, the CN-PPV laver was spin coated on top of the donor layer at 2000 RPM for 60s. The substrates were then placed in an evaporation chamber and pumped down in vacuum ($\sim 10^{-7}$ torr) before evaporating a 1 nm Li/F layer and subsequently a 100 nm Al layer through a shadow mask on top of the photoactive layer. The configuration of the shadow mask afforded eight independent devices on each substrate, and each device has an active layer of ~ 0.03 cm². The mechanical removal of part of the organic layer allowed contact with the ITO, and adding conductive Ag paste to the removed area to ensure electrical contact completed the device. Testing of the devices was performed under an argon atmosphere with an Oriel Xenon arc lamp with an AM 1.5G solar filter. Current-voltage behavior was measured with a Keithley 236 SMU. Eight devices were averaged for each condition.

Note: the RMS roughness (measured by AFM over a 10^2 micron area) of both the P3HT and POPT layers was between 2 and 4 nm as prepared, and these layers stayed between 2 and 4 nm after spin-casting pure THF or ethyl acetate on top of these layers, in order to simulate CNPPV deposition.

Device Optimization:

Layer thickness was the first parameter explored to optimize efficiency after determining the necessity of Li/F as a top electrode. Below is a table with performance parameters at various thicknesses (based on solution concentrations) (M&M Table 1) as well as a plot of efficiency as a function of annealing time at 110 °C, for the higher performing devices from the thickness study (M&M Figure 3).

POPT conc. in PhCI	CNPPV conc. in THF	V _{oc}	J _{sc} (mA/ cm²)	FF	η %
2 mg/ml	8 mg/ml	0.40	1.33	0.25	0.13
6 mg/ml	8 mg/ml	0.64	2.79	0.26	0.46
10 mg/ml	8 mg/ml	1.04	2.16	0.29	0.65
12 mg/ml	8 mg/ml	1.08	1.79	0.26	0.50
10 mg/ml	6 mg/ml	1.08	2.21	0.24	0.57
10 mg/ml	9 mg/ml	1.04	1.70	0.26	0.46
P3HT	CNPPV				
6 mg/ml	8 mg/ml	0.75	0.41	0.31	0.10
9 mg/ml	8 mg/ml	0.69	0.39	0.28	0.08
10 mg/ml	8 mg/ml	0.88	1.23	0.27	0.29
13 mg/ml	8 mg/ml	0.79	0.74	0.25	0.15

M&M Table 1. Thickness optimization study.



Annealing time (min) M&M Figure 3. A plot of efficiency versus annealing time for the 10 mg/ml POPT and P3HT solutions with 8 mg/ml CNPPV in the bilayer configuration.

An extensive optimization of PCBM:POPT devices is not reported here, but these *J-V* curves compare the highest performance PCBM:POPT BHJ device with one of the highest performing PCBM:P3HT devices (M&M Figure 4) at the time of the study, side-by-side. A TEM micrograph of the morphology of this device (obtained after annealing at 180 °C for 1 minute) is shown in M&M Figure 5.



Figure S4 IV curves for the highest performing POPT:PCBM based device and a control P3HT:PCBM based devices fabricated side-by-side.



M&M Figure 5. A representative TEM micrograph of POPT:PCBM morphology after 1 minute of annealing at 180 °C.

5. References

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Chapter 3

Phenyl vs. Alkyl Polythiophene: A Solar Cell Comparison using a Vinazene Derivative as Acceptor

Abstract

The solar cell performance of poly[3-(4-n-octyl)-phenylthiophene] (POPT) and poly(3hexylthiophene) (P3HT) are compared in devices using 4,7-bis(2-(1-(2-ethylhexyl)-4,5dicyanoimidazol-2-yl)vinyl)benzo[c][1,2,5]-thiadiazole (EV-BT) as the electron acceptor. Despite reduced light absorption, POPT:EH-VZ devices generate higher photocurrents in both bilayer and bulk heterojunction (BHJ) architectures than analogous P3HT:EH-VZ devices. Optimized POPT:EH-VZ BHJ devices achieve 1.4% average efficiency, whereas the analogous P3HT devices only reach 1.2%. Morphology does not account for the large difference in performance, as AFM studies of the active layer suggest a comparable level of phase separation in the two systems. Reverse bias analysis demonstrates that P3HT devices have a higher maximum potential than POPT devices but that P3HT devices appear to be more severely limited by recombination losses at standard operating conditions. A possible explanation for the superior performance in POPT devices is that the pendant phenyl ring in POPT can twist out-of-plane, which may increase the separation distance between the donor and acceptor molecule. A larger donor/acceptor separation distance would destabilize the geminate pair and leads to more efficient charge separation in POPT:EH-VZ devices. These results emphasize the importance of donor/acceptor interfacial interactions and their effects on charge separation processes in organic solar cells.

1. Introduction

Conjugated polymers offer great promise for realizing low cost, solution processable organic photovoltaics (OPVs).¹⁻³ Recent progress of OPV efficiencies over 6% for polymers and 4% for small molecules has been reported.⁴⁻⁶ In the past few years, research efforts have focused on increasing the active layer absorption to improve power conversion efficiency, either by developing low band gap polymers that have greater spectral breaths⁷⁻¹⁰ or by replacing [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) with more light-absorbing acceptors.¹¹⁻¹⁴ Recent reports have also suggested that recombination (geminate and/or bimolecular) is a major loss mechanism in OPV operation.¹⁵⁻¹⁸ Thus, the study of charge separation dynamics in polymers, especially in devices that utilize non-fullerene based acceptors, is increasingly important for understanding and ultimately overcoming current limitations in OPVs.

Poly(3-hexylthiophene) (P3HT) is a semiconducting polymer that has been studied extensively for application in OPVs, achieving ~4% power conversion efficiency (PCE) in bulk heterojunction (BHJ) devices using the fullerene derivative $PC_{61}BM$ as the acceptor.^{19, 20} Substituting the solubilizing alkyl chain with a phenyl-alkyl group significantly alters the optoelectronic properties of the polythiophene and its device performance in solar cells.²¹⁻²⁴ For example, compared to P3HT, poly[3-(4-n-octyl)-phenylthiophene] (POPT) exhibits a smaller optical band gap of 1.8 eV, while its lower lying HOMO improves its air stability.^{25, 26}

A recent report has demonstrated improved device performance of POPT over P3HT using a cyano-substituted polyphenylene-vinylene as the electron acceptor in an all-polymer bilayer solar cell.²⁴ The greater extracted photocurrent of POPT devices was not expected from considerations of absorption and energy levels, suggesting that there are other important factors affecting charge separation that have been largely ignored in the field of polymer OPVs. However, the use of acceptor polymers in combination with donor polymers are often limited by thermodynamics as two polymers tend to phase separate, affording micrometer-size domains that lead to morphologies unfavorable for BHJ devices. Thus all-polymer BHJ solar cells have only shown limited efficiencies, and most reports have focused on bilayer devices.^{12-14, 27, 28} Alternatively, small molecule acceptors offer the advantage of increased miscibility with various donor polymers, which facilitates the fabrication of BHJ devices.²⁹ In this study, a small molecule derivative of vinazene was chosen for the acceptor in solar cell devices, in order to compare the performance of POPT and P3HT. Vinazene derivatives are a new class of acceptor materials that have been shown to achieve efficiencies ranging from 0.45% to 0.94% in devices with various donor polymers.³⁰⁻³³ With easily tunable absorption, energy levels, and solubility, vinazenes provide a convenient platform to investigate polymer OPV operation with the potential to yield improved performance over fullerenes.^{34,35}

Herein, the solar cell performance of P3HT and POPT, both synthesized via Grignard metathesis (GRIM) polymerization, is reported utilizing the vinazene derivative 4,7-bis(2-(1-(2-ethylhexyl)-4,5-dicyanoimidazol-2-yl)vinyl)benzo[c][1,2,5]-thiadiazole (EV-BT) as the electron acceptor.

Additionally, a performance comparison with devices prepared from Rieke P3HT, which is considered the standard^{19, 20} for state-of-the-art P3HT:PCBM solar cells is provided.

2. Results and Discussion

The chemical structures of the materials used in this study are shown in Figure 1, and characterization data for the polymers are included in Table 1. It should be noted that both GRIM P3HT and POPT are highly regioregular (RR) and require heating to completely dissolve in chlorobenzene at higher concentrations. The limited solubility of GRIM P3HT and POPT in other organic solvents also enables the fabrication of bilayer solar cells using THF as the orthogonal solvent to spin-coat a layer of EV-BT on top of the previously spin-coated polymer layer.



Figure 1. Chemical structures of EV-BT, POPT, and P3HT.

The absorption coefficients α shown in Table 1 are measured by varying the polymer film thickness from 5–60 nm and examining the change in intensity of their absorption maximum λ_{max} . The α values are measured to be 8.1×10^4 cm⁻¹ for GRIM P3HT and 4.1×10^4 cm⁻¹ for POPT. The 50% reduction in optical density in POPT is likely due to the phenyl ring twisting out of plane from the thiophene backbone, which leads to increased spacing between the polymer backbones.³⁷ As shown in the absorption spectra of Figure 2, POPT has greater spectral breath with an absorption onset at 700 nm (1.8 eV) compared to 650 nm (1.9 eV) for P3HT. The space-charge limited hole mobility of the two polymers are similar, both on the order of 1×10^{-4} cm²/(V s). The energy levels of the polymers as measured by cyclic voltammetry (CV) are also shown in Table 1. GRIM P3HT has a HOMO level of 5.2 eV, whereas POPT has a lower HOMO of 5.5 eV. Both polymers have a similar LUMO level of 3.2 eV.

Table 1 . Characterizations of the three polymers used in this study.	
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	M _n (g/mol)	PDI	RR	Absorption coefficient α at λ_{max} (x 10 ⁴ cm ⁻¹)	(cm^2/Vs)	HOMO (eV)	LUMO (eV)
POPT	66,600	1.09	99%	4.1	1 x 10 ⁻⁴	5.5	3.2
GRIM P3HT	37,700	1.04	99%	8.1	1 x 10 ⁻⁴	5.2	3.2
Rieke P3HT	28,700	3.48	95%	6.7	1 x 10 ⁻⁴	5.2	3.2

Figure 3 shows typical *J-V* characteristics of bilayer devices fabricated from POPT and GRIM P3HT using EV-BT as the electron acceptor layer spun out of THF. The device structure is ITO/ PEDOT:PSS (30 nm)/POPT or GRIM P3HT (40 nm)/ EV-BT (40 nm)/ LiF (1 nm)/ Al (100 nm). Upon annealing at 80 °C for 20 min, the POPT devices reach an average efficiency of 0.97%, which is more than twice that of GRIM P3HT devices with an average of 0.43%. The higher efficiency of the POPT device originates from an improvement in the photocurrent as the short-circuit current (J_{sc}) is 4.0 mA cm⁻² compared to only 1.7 mA cm⁻² for the GRIM P3HT device. It is interesting to note that the POPT device has a slightly lower V_{oc} of 0.64 V compared to 0.70 V for the GRIM P3HT device, despite POPT having a lower HOMO level of 0.3 eV (-5.5 vs -5.2 eV) as determined from cyclic voltammetry.



Figure 2. Normalized solid state absorption of POPT and GRIM P3HT.



Figure 3 Typical J-V characteristics of bilayer devices made from POPT and GRIM P3HT using EV-BT as the top acceptor layer. Devices were annealed at 80 °C for 20 min. Average device parameters: $V_{oc} = 0.64$, $J_{sc} = 4.0$ mA cm⁻², FF = 0.38, PCE = 0.97% for POPT/EV-BT; $V_{oc} = 0.70$, $J_{sc} = 1.7$ mA cm⁻², FF = 0.36, PCE = 0.43% for GRIM P3HT/EV-BT.

BHJ devices have also been fabricated with varying annealing conditions, device thickness, and the weight ratio of polymer to EV-BT. The optimal device thickness is 80-100 nm for both systems, and the optimal ratio of polymer to EV-BT was 1:1 by weight with the following device ITO/PEDOT:PSS/polymer:EV-BT/LiF/Al. structure: (See section 4. "Methods and Materials", for detailed device optimization parameters). After independent optimization, POPT:EV-BT devices reach an average efficiency of 1.4% (highest 1.5%) after 40 min of annealing at 80 °C, which is superior to that of GRIM P3HT:EV-BT devices with an average efficiency of 1.1% (highest 1.2%). Rieke P3HT devices, fabricated for control purposes only, afforded a lower average PCE of 0.70%. It should be noted that Rieke P3HT bilayer devices cannot be fabricated due to the higher solubility of Rieke P3HT in THF compared to GRIM P3HT and POPT. Figure 4 shows representative J-V characteristics of BHJ devices made from the three polymers, with device parameters that change minimally up to 100 min of annealing at 80 °C. The POPT device shows a clearly improved J_{sc} over both of the P3HT devices, but the V_{oc} is lower than that of the GRIM P3HT device. The GRIM P3HT device also has a higher efficiency than the Rieke P3HT device due to a larger J_{sc} . Interestingly, the GRIM P3HT device has a lower Voc than the Rieke P3HT device, even though the two polymers have similar energy levels.



Figure 4. Typical *J-V* characteristics of BHJ solar cells comparing POPT, GRIM P3HT, and Rieke P3HT with a 1:1 weight ratio of polymer to EV-BT and annealed at 80 °C for 40 min. Average device parameters: $V_{oc} = 0.62$, $J_{sc} = 5.5$ mA cm⁻², FF = 0.40, PCE = 1.4% for POPT:EV-BT; $V_{oc} = 0.76$, $J_{sc} = 3.0$ mA cm⁻², FF = 0.48, PCE = 1.1% for GRIM P3HT:EV-BT; $V_{oc} = 0.84$, $J_{sc} = 1.9$ mA cm⁻², FF = 0.44, PCE = 0.70% for Rieke P3HT:EV-BT.



Figure 5. EQE spectra of optimized BHJ devices of POPT, GRIM P3HT, and Rieke P3HT measured at 0 V. All devices have a 1:1 weight ratio of polymer to EV-BT and were annealed at 80 °C for 40 min.

The larger photocurrent in POPT devices is confirmed by external quantum efficiency (EQE) measurements. As shown in the EQE spectra of Figure 5, the POPT:EV-BT device has greater EQE values (peak EQE = 32%) over the range 400–700 nm compared to both P3HT devices. This range covers the absorption of both POPT and EV-BT, indicating improved charge generation from both components. Additionally, the broadened absorption of POPT, with an earlier onset at 700 nm (see Figure 2), is reflected in the EQE spectrum. The comparison between the GRIM P3HT and Rieke P3HT EQE spectra also verifies the improved J_{sc} observed in GRIM P3HT devices, which show higher EQE values (peak EQE = 20%) over the entire range of the active layer absorption from 300 to 650 nm. Integration of the EQE spectrum with respect to the AM 1.5 solar spectrum confirms the J_{sc} as measured under white light illumination. The integrated EQE spectrum of the POPT:EV-BT device gives a J_{sc} of 5.7 mA cm⁻², which closely matches the measured J_{sc} of 5.5 mA cm⁻² in the actual device. Similarly, integration of the EQE spectra of GRIM P3HT and Rieke P3HT devices give 3.1 and 2.2 mA cm⁻² respectively, in agreement with measured values of 3.0 and 1.9 mA cm⁻².



Figure 6. Absorption spectra of POPT (100 nm) and GRIM P3HT (80 nm) blend films with EV-BT (1:1 ratio) at the optimized BHJ device active layer thickness for each system.

Absorption of the active layer is generally one of the major factors affecting the current generated in the device. As indicated in Table 1, the absorption coefficient of POPT is significantly lower than that of GRIM P3HT. In addition, as seen in Figure 6, the POPT:EV-BT active layer at the optimized device thickness clearly shows reduced absorption compared to the GRIM P3HT:EV-BT blend film. Absorption measurements of the pristine polymers and of the blend films both suggest that optical density most likely cannot account for the improved J_{sc} in POPT devices over GRIM P3HT devices.



Figure 7 AFM height (left) and phase images (right) of POPT (a, b) and GRIM P3HT (c, d) blends with EV-BT at 1:1 ratios annealed at 80 °C for 100 min. Scale bar is 200 nm.

Besides differences in absorption, another possible explanation for the higher photocurrent in the POPT device is improved blend morphology, which may allow for increased donor/acceptor (D/A) interfacial areas for exciton dissociation. Figure 7 shows the AFM height and phase images for films of POPT and GRIM P3HT, each blended with EV-BT at a 1:1 ratio. The samples were processed under identical conditions as the optimized BHJ devices. Notably, both samples lack any large scale phase separation, which indicates favorable mixing between the donor polymer and EV-BT. In addition, the blend films show similar domain sizes of 10-20 nm in the phase image. Since there appears to be little difference in total D/A interfacial area in both samples, morphology mostly likely does not account for the large difference in photocurrent between devices made from the two polymers.



Figure 8 Photocurrent (Jphoto) versus effective applied voltage (V0-Vapp) for optimized BHJ devices of POPT and GRIM P3HT with EV-BT.

As the higher photocurrent observed in POPT:EV-BT devices is not expected based on absorption and morphology studies, reverse bias analysis was performed to study the electric-field dependence of the charge generation process in these devices. By applying a larger electric field across the device than the field at J_{sc} , there is an increased driving force for charge separation and collection within the device.^{38, 39} At sufficiently large reverse bias, the device reaches saturation, where all the excitons that reach the D/A interfaces are separated into free charges and all separated charges are collected at their respective electrode, with minimal recombination losses. This reveals the maximum potential of each polymer:EV-BT device.^{38, 39}

In reverse bias analysis, the photocurrent is often plotted as a function of effective applied voltage. The photocurrent is defined as $J_{photo} = J_{light} - J_{dark}$, where J_{light} and J_{dark} are current densities of the device measured under illumination and in the dark. The effective applied voltage is defined as $V_{eff} = V_o - V_{app}$, where V_o is the compensation voltage defined as the voltage where $J_{photo} = 0$ and V_{app} is the applied bias. A reverse voltage sweep was applied to the polymer:EV-BT devices, and the photocurrent as a function of effective applied bias, as expected. For the POPT:EV-BT device, J_{photo} saturates relatively quickly at around $V_{eff} = 2$ V. On the other hand, in the GRIM P3HT device, J_{photo} continues to increase and does not reach saturation even at $V_{eff} = 10$ V. More importantly, the J_{photo} of the GRIM P3HT device surpasses that of POPT at $V_{eff} = 9.5$ V, indicating that GRIM P3HT:EV-BT can generate more photocurrent than POPT devices. The fact that a GRIM P3HT:EV-BT device can generate higher J_{photo} agrees with expectations based on absorption considerations (see Figure 6 and Table 1) and the

observation that the extent of D/A phase separation is similar for the two systems (Figure 7). However, at typical operating voltages, near the J_{sc} position indicated in Figure 8, POPT outperforms GRIM P3HT in terms of charge separation, as evidenced by the much higher J_{sc} in POPT:EV-BT devices. Comparing the J_{photo} at low and high fields for these two polymers, it is evident that the dissociation efficiency is much higher for the POPT device; this device is achieving more of its potential under standard operating conditions.

In both bilayer and BHJ devices with EV-BT as acceptor, POPT exhibits superior performance over P3HT with a doubling of the J_{sc} despite its reduced ability to absorb light. Surface morphology probed by AFM suggests that the amount of D/A interfacial area are comparable in the two systems and thus cannot account for the substantial differences in J_{sc} . Reverse bias analysis confirms that GRIM P3HT devices surpass POPT devices in photocurrent generation at high applied field, but charge separation is severely limited at short-circuit condition. Steadily increasing J_{photo} at higher applied bias for the GRIM P3HT system represents a highly field dependent charge separation process in these devices. A strong field dependence on photocurrent can be caused by either a high recombination rate of bound geminate pairs or the buildup of space charge in the device due to unbalanced charge transport.^{15, 40} In other words, the efficiencies of the GRIM P3HT devices are probably limited by geminate pair recombination and/or space-charge buildup; one or both of these losses are minimized in the POPT device. The electron mobility of EV-BT is lower than the hole mobilities of both POPT and P3HT,⁴¹ and this may be a limiting factor in the performance of these devices. However, the low electron mobility in the acceptor has the same effect on POPT devices and P3HT devices, and thus space-charge buildup most likely is not responsible for the large differences in the performance of the two systems investigated.

A major difference between POPT and P3HT is the pendant phenyl ring on the thiophene moieties of POPT compared to the alkyl chain in P3HT. X-ray diffraction data shows that POPT has an extra π - π stacking (010) peak at 5.1 Å in addition to the usual (010) peak at 3.8 Å observed in P3HT (see section 4, Methods and Materials). Both of the (010) peaks in POPT are also broader, indicating a wide range of configurations of the phenyl ring. Out-of-plane twisting of the phenyl ring from the thiophene backbone not only affects the packing of the polymer²² but also may affect the separation distance between the polymer backbone and an adjacent acceptor molecule. A possible explanation for the higher charge separation efficiency observed in POPT devices is that the twisted phenyl ring in POPT could sterically increase the separation distance between the polymer and EV-BT. The larger D/A separation distance would force a larger radius for the geminate pair, which sits partially on the donor and acceptor, respectively. By this mechanism, increasing the radius of the geminate pair may then lower its binding energy and facilitate its dissociation into free charges.

An interesting observation is that the V_{oc} of the EV-BT devices does not fit the trend established in previous studies of polymer/fullerene solar cells. The lower HOMO level of POPT would be expected to afford a higher V_{oc} according to the well-known empirical equation

$$V_{oc} = \frac{1}{e} \left| E_{HOMO}^{donor} - E_{LUMO}^{acceptor} \right| = 0.3 \text{ eV}$$

In which the 0.3 eV loss is believed to originate from non-idealities and field-dependent photocurrent in the device.⁴²⁻⁴⁴ Contrary to predictions arising from the use of this empirical V_{oc} equation, both bilayer and bulk-heterojunction POPT devices have a lower V_{oc} than GRIM P3HT devices, suggesting that there may be other factors affecting the V_{oc} of these devices. Here it is suggested that the V_{oc} difference may be due to a variation in charge transfer state energy⁴⁵ or the density of free charges, which can affect the internal field of the device or the energy of the free holes and electrons.⁴⁶ Another possible explanation for the lower V_{oc} of the POPT device is a larger shunt resistance in the device, which is reflected by the larger slope of the *J-V* curve near 0 V. The larger shunt resistance may also be responsible for the lower FF in the POPT device. In addition, it is observed that the V_{oc} of GRIM P3HT and Rieke P3HT devices are different even though the two polymers share the same energy levels and optical band gaps. This discrepancy further suggests that the V_{oc} in OPV devices is dependent on factors other than the energy levels of the donor and the acceptor and that the commonly used empirical equation based on donor and acceptor energy levels is not sufficient to predict the device V_{oc} .

Regardless of which polymer is blended with EV-BT, there is no large scale phase separation observed in AFM images. Using a low annealing temperature of 80 °C, POPT:EV-BT device efficiencies can be improved from an initially low efficiency of 0.7% before annealing to 1.4% after annealing for 40–100 min. The same trend of increasing efficiency with annealing is observed in devices made from GRIM P3HT (see section 4, Methods and Materials). The favorable mixing between the polymers and EV-BT allows for some control of the blend morphology through processing techniques such as thermal annealing, and this nanoscale level miscibility with the polymer is a major advantage of the small molecule vinazene derivative EV-BT over polymeric acceptors.

3. Conclusions

In both bilayer and BHJ devices using EV-BT as the acceptor, POPT outperforms GRIM P3HT with a greater J_{sc} and higher overall efficiency, despite reduced active layer absorption. Blend morphologies observed by AFM indicate similar length scales of phase separation for the two systems. Reverse bias photocurrent analysis confirms that GRIM P3HT devices have the potential to achieve higher photocurrents, but this potential is not attained under standard operating conditions. Since POPT and GRIM P3HT have similar charge mobilities, the strong field dependence of the photocurrent in GRIM P3HT devices is most likely not caused by spacecharge buildup but instead due to geminate pair recombination, which is limiting the P3HT device efficiency. In contrast, the POPT:EV-BT device has a weaker field dependence and thus manages to realize more of its potential, achieving a higher dissociation efficiency at short circuit condition and overall better performance. One distinct difference between P3HT and POPT is that the phenyl ring on POPT can twist out of plane, perpendicular to the polymer backbone, thus affecting the way that geminate pairs are separated at the D/A interface. The comparison between POPT and P3HT highlights the need for further understanding of D/A pair interactions and the effect it has on charge separation processes in polymer solar cells. Considerations based on absorption, mobility, energy levels, and morphology are not sufficient to accurately predict the device performance of a material combination.

4. Methods and Materials

The detailed synthesis of GRIM P3HT, POPT, and EV-BT have been reported elsewhere.^{24, 34-36} Rieke P3HT was purchased from Rieke Metals, Inc. and was used without further purification. Anhydrous solvents were used for the preparation of spin coating solutions.

Cyclic voltammograms were collected using a Solartron 1285 potentiostat under the control of CorrWare II software. A standard three electrode cell based on a Pt wire working electrode, a silver wire pseudo reference electrode (calibrated vs. Fc/Fc^+), and a Pt wire counter electrode was purged with nitrogen and maintained under a nitrogen atmosphere during all measurements. Dry acetonitrile purged with nitrogen prior to use and tetrabutyl ammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. Polymer films were cast onto a Pt wire working electrode from a 1% (w/w) chloroform solution and dried under nitrogen prior to measurement.

UV-Visible absorption spectra were obtained using a Cary 50 Conc UV-Visible spectrophotometer in transmission geometry. For thin film measurements polymers were spin coated from chlorobenzene solutions onto cleaned glass slides. A model P6700 Spincoater was used to spin coat the films at 2000 RPM for 60 s.

Polymer film thickness was measured by a Veeco Dektak profilometer.

Polymer mobility was measured using a diode configuration of ITO/ PEDOT:PSS/ Polymer/Al in the space charge limited current (SCLC) regime. At sufficient potential the conduction of charges in the device can be described by

$$J_{SCLC} = \frac{9}{8} \varepsilon \varepsilon_o \mu \frac{V^2}{L^3}$$
(1)

where ε_0 is the permittivity of free space, ε is the dielectric constant of the polymer, μ is the mobility of the majority charge carriers, V is the potential across the device (V = V_{applied} - V_{bi} - V_r), and L is the polymer layer thickness. The series and contact resistance of the device (~15 Ω) was measured using a blank device (ITO/PEDOT/Al) and the voltage drop due to this resistance (V_r) was subtracted from the applied voltage. The built-in voltage (V_{bi}), which is based on the relative work function difference of the two electrodes, was also subtracted from the applied voltage. The built-in voltage can be determined from the transition between the Ohmic region and the SCLC region and was found to be about 1 V.

All photovoltaic devices have a layered structure with the photoactive layer sandwiched between the two electrodes, ITO and LiF/Al. Glass substrates coated with a 150 nm sputtered ITO pattern of 20 Ω \Box^{-1} resistivity were obtained from Thin Film Device, Inc. The ITO-coated glass substrates were ultrasonicated for 20 min each in acetone, and then 2% Hellmanex soap water, followed by extensive rinsing and ultrasonication in deionized water, and then isopropyl alcohol. The substrates were then dried under a stream of dry nitrogen. A dispersion of PEDOT:PSS (Baytron PH500) in water was filtered (0.45 m glass) and spin coated at 4000 RPM for 60 s, affording a ~30 nm layer. The substrates were dried for 10 min at 140 °C in air and then

transferred into an argon glove box for subsequent procedures. Polymer solutions were prepared in chlorobenzene at a concentration of 10 mg/ml and were heated to 120 °C overnight for complete dissolution. Polymer solutions were added to pre-weighed EV-BT to yield blend solutions of different concentrations and mixing ratios. For thinner devices, the stock solutions were diluted with chlorobenzene. The active layer was spin coated at 1200 RPM for 60 s on top of the PEDOT:PSS layer. Bilayer devices were fabricated via two spin coating steps using chlorobenzene as the solvent for the bottom polymer layer and THF as the solvent for the EV-BT top layer. THF was chosen as the solvent for EV-BT because GRIM P3HT and POPT were insoluble in THF. The substrates were then placed in an evaporation chamber and pumped down to a pressure of $\sim 5 \times 10^{-6}$ Torr before evaporating a 1 nm LiF layer and subsequently a 100 nm Al layer through a shadow mask on top of the photoactive layer. Two different shadow masks were used to yield devices with active areas of 0.03 cm^2 and 0.16 cm^2 . The mechanical removal of part of the organic layer allowed contact with the ITO and adding conductive Ag paste to the removed area to ensure electrical contact completed the device. Testing of the devices was performed under an argon atmosphere with an Oriel Xenon arc lamp having an AM 1.5G solar filter to yield 100 mW cm⁻² light intensity as calibrated by an NREL certified silicon photocell. Current-voltage behavior was measured with a Keithley 236 SMU. Eight devices were averaged for each condition.

The external quantum efficiency (EQE) was determined at zero bias 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).

Atomic force microscopy (AFM) was performed to study the surface morphology of the polymer:EV-BT blends. Topographical and phase images were obtained concurrently using a Veeco Multimode V AFM in tapping mode using RTESP tips.


M&M Figure 1. SEC data for POPT with $M_n = 67$ kDa and PDI = 1.09. The additional high molecular weight peak at exactly double the max peak in the SEC is ascribed to a polymer-polymer homo-coupling during the quench. If concentrated acid is used to quench the polymerization, the homo-coupling peak is eliminated.



M&M Figure 2. SEC data for GRIM P3HT with $M_n = 38$ kDa and PDI = 1.03.

Grazing-Incidence X-ray Scattering (GIXS) experiments were conducted at the Stanford Synchrotron Radiation Laboratory on beamline 11-3. The sample was irradiated at a fixed incident angle on the order of 0.1° and the GIXS patterns were recorded with a 2-D image detector (MAR345 image plate detector). GIXS patterns were recorded with an X-ray energy of 12.72 keV ($\lambda = 0.975$ Å). To maximize the intensity from polymer sample, the incident angle (~0.1°-0.12°) was carefully chosen so that the X-ray beam penetrates the polymer sample completely but not the silicon substrate. Typical exposure times were 90-180 s. To produce identical surface condition as samples for device fabrication, a thin layer (20-30 nm) of

PEDOT:PSS was spun onto silicon substrates with a native oxide. Then the GIXS samples were prepared by spin-coating the same polymer solutions used for making devices onto silicon substrates. M&M Figure 8 shows the in-plane scattering of the polymer samples.

Device Optimization Results:

POPT:EV-BT (wt:wt)	V _{oc}	J_{sc} (mA/cm ²)	FF	η (%)
2:1	0.60	-1.51	0.42	0.39 ± 0.07
1:1	0.63	-4.20	0.40	1.06 ± 0.05
1:2	0.61	-3.45	0.38	0.80 ± 0.06
1:4	0.60	-2.72	0.34	0.56 ± 0.08

M&M Table 1. Optimization of blend ratio of POPT:EV-BT devices.

M&M Table 2. Optimization of active layer thickness of POPT:EV-BT devices.

Thickness (nm)	V_{oc}	J_{sc} (mA/cm ²)	FF	η (%)
161	0.61	-4.90	0.38	1.13 ± 0.11
107	0.62	-5.70	0.40	1.41 ± 0.11
82	0.63	-4.12	0.48	1.23 ± 0.09
53	0.62	-3.03	0.48	0.90 ± 0.10

M&M Table 4. Optimization of active layer thickness of GRIM P3HT:EV-BT devices.

Thickness (nm)	Voc	$ \begin{array}{c} J_{sc} \\ (mA/cm^2) \end{array} $	FF	η (%)
96	0.63	-2.84	0.41	0.73 ± 0.10
86	0.76	-2.92	0.50	1.11 ± 0.13
57	0.77	-2.72	0.51	1.07 ± 0.08
40	0.76	-1.71	0.49	0.64 ± 0.07



M&M Figure 3. Efficiencies of POPT, GRIM P3HT, and Rieke P3HT BHJ devices with EV-BT at different annealing times at 80 °C. All devices have a 1:1 polymer:EV-BT blend ratio.





M&M Figure 4. Solid state absorption of POPT, GRIM P3HT, and Rieke P3HT.



M&M Figure 5. The absorption spectra of POPT (100 nm), GRIM P3HT (80 nm), and Rieke P3HT (100 nm) blend films with EV-BT at a 1:1 ratio and the optimized BHJ device active layer thickness for each system.



M&M Figure 6. AFM height (left) and phase (right) images of POPT (a, b), GRIM P3HT (c, d), and Rieke P3HT (e, f) blends with EV-BT at a 1:1 ratio and annealed at 80°C for 100 min. The scale bar is 200 nm.



M&M Figure 7. Photocurrent (J_{photo}) versus effective applied voltage (V_0 - V_{app}) for optimized BHJ devices of POPT, GRIM P3HT, and Rieke P3HT with EV-BT.



M&M Figure 8. In-plane X-ray diffraction spectra of POPT (left) and GRIM P3HT (right) films.

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Chapter 4

Steric Control of the Donor/Acceptor Interface: Implications in Organic Photovoltaic Charge Generation

Abstract

The performance of organic photovoltaic (OPV) devices are currently limited by modest shortcircuit current densities. Approaches toward improving this output parameter may provide new avenues to advance OPV technologies and the basic science of charge transfer in organic semiconductors. A two-step charge separation process is an essential component of photo-current generation. This work highlights how steric control of the charge-separation interface can be effectively tuned in OPV devices. This finding is of particular significance for non-fullerene OPVs, which have many potential advantages such as tunable energy levels and spectral breadth, but are prone to poor exciton separation efficiency – this is a result of the decreased symmetry and electron delocalization of non-fullerene electron acceptors. Computational, spectroscopic, and synthetic methods were combined to develop a structure-property relationship that correlates polymer substituents with charge-transfer state energies and, ultimately, device efficiency.

1. Introduction

State-of-the-art solution processable organic photovoltaic (OPV) devices generally rely on fullerene derivatives as both the electron acceptor and transporter.¹ Fullerene:polymer blends, termed bulk heterojunctions (BHJs), hold record efficiencies around 8%.² Although these devices have provided exceptional growth for the field of OPVs and have demonstrated rapid performance improvement over the past two decades, alternative n-type materials³ and device architectures⁴ could lead to "break-through" technological and basic science advances. Currently, the best non-fullerene OPV device efficiencies hover around 2%.⁵ To move beyond fullerene-based OPVs, a greater understanding of charge generation in organic photovoltaics is critical.

Fullerenes provide several potential advantages over polymers and non-fullerene small molecules in photovoltaic applications; they possess high molecular symmetry,⁶ are strongly polarizable, and present triply-degenerate LUMO levels.⁷ Conjugated polymers and planar small molecules are less symmetric, often have well-defined charge-transport axes,⁸ and are generally not as highly polarizable overall – conjugated polymers have a dielectric constant of ca. 3^{9a} vs. fullerenes with a dielectric constant of ca. 4.^{9b} These properties of fullerenes generally facilitate charge separation and the generation of free carriers.

Since OPVs require a donor/acceptor interface to separate the photoexcited state (Frenkel-type excitons),¹⁰ it is important to understand the thermodynamics of charge separation at this interface.^{1d, 11} The relative free energy of charge separation (ΔG_{CS}^{rel}) for several donor materials combined with a fullerene acceptor has previously been estimated by the abbreviated Weller equation $\Delta G_{CS}^{rel} = E_s - |(HOMO_{donor} - LUMO_{acceptor})|$, where the difference between the singlet excited state energy (E_s) and the relative band offsets provided good agreement with measured short-circuit current (J_{sc}).¹² Although values for ΔG_{CS}^{rel} calculated from this equation correlated with the observed J_{sc} for several devices,¹²⁻¹³ other factors such as active layer absorption breadth, optical density and morphology, as well as charge-carrier mobility and electrode choice are all known to critically affect J_{sc} in addition to ΔG_{cs} . A brief description of how morphology can specifically impact charge separation is presented in the supplementary information. Notably, the *abbreviated* Weller equation does not include the lattice polarization energy or Coulomb attraction terms, as these are not easily measured.¹⁴ Toward expanding our understanding of charge generation in OPVs, we must explore factors beyond the thermodynamics of charge separation as estimated from bulk electronic properties.

For instance, charge generation depends not only on the donor and acceptor material state energies, but also on the specific molecular environment at the donor/acceptor (D/A) interface and on the kinetics of exciton separation/recombination.^{15, 11} Akin to a chemical reaction, exciton separation to yield free charges can proceed via more than one mechanism. In some cases, no "reaction" intermediates are observed, whereas in other cases there is a spectroscopically observable "geminate pair" or charge transfer (CT) state. Probing the parameters that control the mechanism of charge generation, particularly for non-fullerene devices, is of great importance to

the field of OPVs – studies show that this electron-hole (e-h) pair is sensitive to applied electric field, and intriguingly, to hydrostatic pressure: An externally applied field during device operation is known to increase the current extracted from the device; when the bias is applied opposite ("reverse") to the voltage generated under illumination, free carriers are quickly removed from the active layer and the dipolar geminate pair is driven to separate.¹⁶ External pressure on the system is believed to have the opposite effect on the geminate pair, tightening the van der Waals interaction at the D/A interface, and leading to increased radiative recombination of the CT state with a lower energy – implying a more stable, deeply trapped intermediate.¹⁷

Our work toward understanding charge generation started from a structural point of view, and we drew inspiration from studies reported by Granstrom et al. in 1998.¹⁸ In that publication, poly[3-(4-n-octyl)-phenylthiophene] (POPT) was shown to produce the most photocurrent in any OPV device at the time, a notable achievement with the common electron acceptor material poly[2methoxy-5-(2'-ethylhexyloxy)-1,4-(1-cyanovinylene)phenylene] (CNPPV). Motivated by that research, we reported studies in which (POPT) outperformed poly(3-hexylthiophene) (P3HT) in both bilayer devices with (CNPPV)^{5b} and BHJ devices with the newer acceptor material 4,7-(EV-BT).^{5c} bis(2-(1-(2-ethylhexyl)-4,5-dicyanoimidazol-2-yl)vinyl)benzo[c][1,2,5]-thiadiazole Our first report focused on the inconsistency between expected and realized performance values for OPV devices with the acceptor CNPPV, specifically the almost double short-circuit current density (J_{sc}) for POPT devices despite reduced optical density compared to P3HT; however, very little was understood at that time about why better performance was achieved with POPT instead of P3HT. In our second report, we utilized EV-BT to make progress toward elucidating the physical properties that governed the OPV performance parameters of these non-fullerene devices - for example, reverse bias analysis suggested a tighter binding of the geminate pair at the P3HT:EV-BT interface, i.e., a lower-energy CT state provided a deeper energetic well (a trapped intermediate) for partially separated charges. We suspected that the octylphenyl content of POPT played a critical role at the D/A interface, potentially facilitating geminate pair separation.

To shed light on how using an alkylphenyl side group enhances J_{sc} compared to a simple alkyl side group, we investigated analogous material combinations with different substitution and acceptor materials. Beyond correlating structure to performance on the basis of multiple device comparisons, more direct methods to investigate the CT states were necessary to draw a fitting conclusion. Herein, we utilize a combination of computational and spectroscopic methods, as well as tailored synthesis and extensive device engineering, to understand how modifying thiophene substitution from alkyl to octylphenyl on two otherwise identical backbones, polythiophene and polyquarterthiophene, leads to a greater understanding of the effects that side group interactions at D/A interfaces have on charge generation. Structural control of the D/A interface may prove to be a powerful tool for tuning charge separation dynamics: we provide a seminal example of how steric effects can improve charge separation in organic photovoltaics.

2. Results

Both P3HT and POPT were synthesized via the GRIM polymerization method.^{5b} The structure of POPT consists of phenyl groups covalently bound to the polythiophene backbone as part of the solubilizing substituent. This functionality increases the ionization potential (deepens the HOMO level) to -5.5 eV from -5.2 eV compared to P3HT. Additionally, the optical properties are shifted toward a broader spectral response while maintaining similar charge-transport properties.^{5b} The energetic changes result in an excited state that is lower in energy (and the electron affinity is also more exothermic) in POPT compared to P3HT; thus, POPT is thermodynamically less likely to undergo exciton separation with a given acceptor, compared to P3HT (when a normal Marcus regime can be invoked). Contrary to thermodynamic expectations, though, POPT yielded more efficient charge separation as a donor material in PV cells with polymeric and small molecule acceptors, such as CNPPV and EV-BT, respectively.5b,c In particular, the considerably and recurrently higher J_{sc} prompted an in-depth investigation combining device fabrication, theoretical modeling, and advanced spectroscopy to gain insight into these systems. The following results exploit observed differences in performance caused by the presence of phenyl substituents to better understand the charge-separation process. By expanding our data set beyond the two systems already reported, we aim to probe the universality of this design strategy for improving charge generation in non-fullerene OPVs.

Four acceptors were utilized with POPT and P3HT in head-to-head comparisons: CNPPV, EV-BT, N-(1-hexylheptyl)-N'-(1-ethylpropyl)perylene-3,4,9,10-tetracarboxylic diimide (PDI),¹⁹ and poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'bithiophene) (Polyera ActiveInkTM N2200),²⁰ Figure 1a (see SI for device fabrication details). In most cases, both bilayer and bulk heterojunction devices were compared, provided that an orthogonal solvent system was found to allow the fabrication of bilayers, Here, we report the device architecture that demonstrated higher efficiencies for each acceptor material. Polymerpolymer solar cells performed better in the bilayer device architecture, whereas polymer-small molecule solar cells were better in the BHJ architecture. Based on individually optimized devices in all four comparisons, POPT consistently outperforms P3HT (Table 1 and Figure 1b). While the V_{oc} and FF of the POPT and P3HT devices are comparable in most cases, the J_{sc} of POPT devices are at least twice those of P3HT devices, leading to the higher overall efficiencies of POPT devices. It should be noted that the P3HT/N2200 device results are consistent with two recent reports that demonstrated N2200 in a BHJ device with P3HT yields ~0.2% efficiency.²¹ The effect of morphology on J_{sc} in POPT/CNPPV and P3HT/CNPPV devices is discussed in the SI.

Table 1. PV output characteristics of POPT vs. P3HT devices; maximum efficiencies for optimized device systems. Symbol '/' indicates a bilayer device while symbol ':' indicates a BHJ device. Devices were optimized first on the basis of thickness (solvent choice and solution concentration) and then on annealing conditions (various temperatures and times).

Device Active Layer	J _{sc} [mA/cm ²]	$V_{ m oc}\left[{ m V} ight]$	FF	PCE [%]
POPT/CNPPV	-5.44	1.06	0.35	2.00
P3HT/CNPPV	-2.63	1.08	0.33	0.93
POPT:EV-BT	-5.70	0.62	0.40	1.41
P3HT:EV-BT	-2.81	0.77	0.51	1.11
POPT/N2200	-2.50	0.52	0.47	0.61

P3HT/N2200	-0.80	0.46	0.46	0.17
POPT:PDI	-5.70	0.24	0.37	0.51
P3HT:PDI	-1.70	0.57	0.41	0.39



Figure 1. (a) The structures of four different acceptors (two polymers and two small molecules) that are tested in a head-to-head comparison between P3HT and POPT. (b) *J-V* curves for the devices corresponding to the acceptor components in (a).

In order to generalize the effect of interfacial steric interactions on charge generation, we expanded the scope of this study beyond POPT and P3HT to another polymer backbone, polyquarterthiophene. We synthesized poly(3,3-di(4-n-octyl)phenylquaterthiophene) PQT-OP and compared it to poly(3,3-didodecylquaterthiophene) PQT-DD (Table 2 and Figure 2). Independently optimized devices with CNPPV, EV-BT, and PDI were consistently found to perform nearly twice as well with PQT-OP than PQT-DD, due largely to an increase in J_{sc} . The V_{oc} values for PQT based devices with the same acceptor material were greater than for the polythiophene based, however there were no significant V_{oc} differences between the phenyl and alkyl PQT derivatives. This lends credence to the hypothesis that interfacial interactions could play a role that rivals the importance of the materials state energies.²²⁻²³ The CT state energy, whatever its physical structure, has already been strongly correlated with V_{oc} .²² It is worth noting that PQT-OP provides PDI-based devices with the highest performance to date. These data supported our hypothesis that the effect of this substituent could be generalized to other systems, as this is the same trend that was observed for POPT compared to P3HT.

 Table 2. PV output characteristics of PQT-OP vs. PQT-DD devices. Reported are maximum efficiencies for individually optimized device systems. A '/' indicates a bilayer device while a ':' indicates a BHJ device.

Device Active Layer	J _{sc} [mA/cm ²]	V _{oc} [V]	FF	PCE [%]
PQT-OP/CNPPV	-2.43	1.18	0.39	1.12
PQT-DD/CNPPV	-1.51	1.20	0.38	0.69
PQT-OP/EV-BT	-2.68	0.95	0.48	1.22
PQT-DD/EV-BT	-1.48	0.98	0.43	0.62
PQT-OP:PDI	-3.33	0.63	0.42	0.88
PQT-DD:PDI	-2.18	0.66	0.34	0.49



Figure 2. PQT polymer structures and a comparison of individually optimized devices. Devices were optimized first on the basis of thickness (solvent choice and solution concentration) and then on annealing conditions (various temperatures and times).

These experimental results are in contradiction with predictions based on a simple comparison of the donor polymer state energies. The larger ionization potential (lower HOMO level) of POPT compared to P3HT (-5.5 vs. -5.2 eV) in combination with a smaller bandgap should thermodynamically result in a lower J_{sc} based on the abbreviated Weller equation. However, octylphenyl devices produce significantly increased J_{sc} values compared to devices utilizing the alkyl analogs. Morphological and light absorption parameters were ruled out in previous studies as the dominant factor in this kind of comparison.^{5b,c} Analysis of the PQT polymers provided similar results. PQT-OP has a slightly larger ionization potential (IP) and a similar optical gap compared to PQT-DD; PQT-OP and PQT-DD have IPs of -5.4 vs. -5.3 eV, respectively, and optical gaps of approximately 1.9-2.0 eV (with absorption onsets of 640 and 620 nm). Again, devices using the octylphenyl-containing donor polymers consistently produce a substantially greater J_{sc} . These data clearly confirm that the material state energies and optical properties are not the only factors affecting the charge generation efficiencies in these systems. More importantly, we hypothesize that the molecular interactions at the D/A interface are a determining factor in these devices. Modeling of the D/A interface has recently predicted that the molecular configurations²³ and environment at this interface are critical in the charge-generation process, and here we aim to correlate theory with a benchmark physical test system.^{15,24}

Since the highest performing devices utilized POPT and P3HT in combination with CNPPV (Table 1, Figure 1) as the component materials, these systems were characterized in more detail to understand how their structural properties influence interfacial interactions and, ultimately, charge generation. The component materials were first analyzed using a computational description of their molecular geometries. Modeling at the Density Functional Theory (DFT)

B3LYP/6-31G(d,p) level of theory provided optimized geometries of the neutral ground states for (isolated) hexamers of the relevant species (Figure 3). Two POPT conformations were explored: the first structure allows the phenyl rings to participate in conjugation with the thiophene backbone (Figure 3b, POPT-*unconstrained*) and the second structure forces the phenyl rings to twist perpendicular to the backbone (Figure 3c, POPT-*perp*). POPT-*perp* minimizes conjugation between the pendant phenyl ring of the side group and the thiophene ring of the polymer backbone but maximizes conjugation along the backbone (see Supplementary Information (SI), Figure S1). The neutral ground-state geometries were also calculated for P3HT (Figure 3a) and CNPPV (Figure 3d), where the alkyl chains were modeled as methyl groups. The calculations show that the backbone of POPT is strictly planar only when the phenyl rings are forced out of plane with respect to the backbone, minimizing steric or electronic interactions between the thiophene and phenyl groups.



Figure 3. B3LYP/6-31G(d,p) optimized neutral ground-state structures of the hexamers of (a) P3HT, (b) POPT*unconstrained*, (c) POPT-*perp* and (d) CNPPV shown from the top-view (top) and side-view (bottom).

Vertical transition energies of the polymers can be qualitatively described from those of the oligomers by a Kuhn-type dependence on 1/N where N is the number of double bonds along the shortest path connecting the terminal carbon atoms of the molecular backbone.²⁵ The electronic structures for oligomers of increasing length were calculated and a Kuhn fit of the data was used to extrapolate the $S_0 \rightarrow S_1$ transition energies of the extended polymers. The plots for the two POPT structures, P3HT, and CNPPV are presented in Figure 4. The best agreement between theory and experiment, i.e., where the optical bandgap (E_g^{opt}) for POPT equals 1.8 eV, occurs when the polymer backbone is planar, suggesting that the phenyl groups of polymer side chains prefer to orient perpendicular to the backbone in thin films. The results for P3HT and CNPPV are also in good agreement with experiment.



1/NFigure 4.Vertical S0 \rightarrow S1 transition energies of (a) P3HT and (b) POPT-*unconstrained* and POPT-*perp* where the phenyl group is constrained to be perpendicular to the polymer backbone (c) CNPPV. N is the number of double bonds.

The presence of two dominant conformations of POPT is supported empirically by twodimensional grazing incidence X-ray scattering (2D GIXS) measurements. Figure 5a shows the 2D GIXS pattern and the in-plane line scan of the POPT sample, while Figure 5b illustrates the schematic of solid-state packing for POPT. The presence of two peaks at 3.8 and 5.1 Å suggests that there are two different π - π packing distances in the POPT thin film. Importantly, these two different π - π packing distances arise from the two major conformations for the phenyl rings relative to the POPT backbone: the π - π packing distance of 3.8 Å correlates to the phenyl ring oriented parallel with the backbone, while the π - π stacking distance of 5.1 Å correlates to a POPT-perp orientation where the phenyl ring is twisted perpendicular to the backbone and causes an increase in separation between adjacent polymers. It should also be noted that the peak broadening observed in the GIXS pattern may be an indication that the phenyl ring can adopt varying degrees of rotation between the parallel and perpendicular conformations. The packing parameters of POPT have been studied in-depth elsewhere.²⁶ GIXS data of PQT-OP also evidences two dominant conformations for the phenyl ring, resulting in π - π spacings of 5.1 and 3.9 Å (SI, Figure S2). The relative scattering intensity of the two π - π spacings in POT-OP is reversed from that of POPT. This reversal in PQT-OP can be attributed to the lack of substituents on two of the four thiophenes in the polymer repeat unit, thereby favoring the tighter π - π spacing at 3.9 Å. Detailed GIXS data for P3HT²⁷ and PQT-DD²⁸ have been analyzed previously, and backbone spacings of 3.8 and 4.2 Å were reported, respectively. CNPPV derivatives are known to be relatively amorphous; however, weak diffraction signals between 4 and 5 Å have been observed.²⁹ X-ray scattering, however, is limited to the investigation of regular periodicity in a material and is not appropriate for the study of blended interfaces. Since we are interested in the D/A interface in these material systems, we turned to computational analysis to develop a model interface for the charge separation event.

Model dimer configurations were constructed from best-fit-planes of polythiophene/CNPPV separated at distances (R) between 4 and 5 Å at 0.2 Å increments (Figure 5d). In order to construct CT states from these dimers, charges were constrained to each molecule using the constrained density functional theory (C-DFT) method implemented in NWChem Version 4.6.³⁰ A conductor polarizable continuum model (CPCM) with $\varepsilon = 4$ was used to approximate polarization effects expected in organic solid-state systems. Given the limitations of the theoretical approach, we are mainly interested in the relative CT-state energies, which are plotted in Figure 5c. The model dimer configuration of POPT-*perp* is predicted to have the highest CT state energy followed by the P3HT and then the POPT-*unconstrained* configurations. PQT-OP model calculations require many more nuclei at the interface, which is beyond the scope of the present work.



Figure 5. (a) An X-ray line scan taken parallel to the substrate surface, along the qx axis, showing peaks at *d* spacing equal to 28.6, 5.1 and 3.8 Å corresponding to the "a" distance and two different "c" distances, respectively, taken from 2D GIXS pattern of POPT on Si substrate (inset). (b) Schematic of the polymer packing relative to the substrate, with corresponding labels to the peaks indicated in (a). (c) CT State energies for the D/A systems illustrated in (d). (d) Physical representation of dimers of POPT and P3HT with a single repeat unit of CNPPV, both superimposed and side-by-side.

To verify our calculations of the CT state energies in these D/A systems, we used spectroscopic techniques to experimentally observe their CT states. Sensitive photocurrent measurement, via Fourier transform photocurrent spectroscopy (FTPS),^{22,24b} can extract the weak sub-bandgap external quantum efficiency, and photothermal deflection spectroscopy (PDS) can detect sub-bandgap absorption. These tools have previously been used to investigate charge-transfer states.³¹ A recent, and very significant FTPS study suggests that the CT state, sometimes called a CT exciton, is very efficiently split into free charge carriers at room temperature in P3HT:PCBM and MDMO-PPV:PCBM devices.³² Spectral evidence and device studies of various D/A systems

suggest that these CT states determine the V_{oc} of the PV cell and act as an intermediate in the generation *and* recombination of free charge carriers.^{22,24b} Consequently, spectroscopic techniques rooted in sub-bandgap absorption are considered a good indicator of the presence of such CT states and of the maximum V_{oc} that can be expected with a given D/A combination.

Here, PDS spectra were obtained by detecting the mirage effect in a transparent, inert medium (Fluorinert[®]) with a probe HeNe laser beam. Non-radiative heating associated with absorption of a monochromatic pump beam causes the mirage effect to occur. PDS was used in this investigation to support our hypothesis that molecular orientation of the phenyl groups affects the CT state energy. PDS measurements were performed on drop cast and spun cast films of POPT and P3HT blended with CNPPV. We underline that bilayer films do not provide enough interfacial surface area to produce good signal-to-noise ratios; in addition, the *molecular level interface* is not expected to change upon going from the bilayer to BHJ morphology, *vide infra*. Figure 6 shows the PDS spectra of the homopolymers and the polymer blends under investigation; spectra are scaled to absolute values of absorption coefficient by matching the signal near the absorption edge to that from UV-vis spectra of the same films.

Blends of both P3HT and POPT with CNPPV produce non-additive absorptions that are attributed to the presence of CT states at the D/A interfaces. For P3HT:CNPPV (1:1 wt/wt), a CT state absorption is present at 1.26 eV. For POPT, however, there are two sub-bandgap peaks attributed to CT states, one at 1.17 eV and one at 1.50 eV - indicating two distinct interfacial configurations. These peak maxima are extracted by fitting an exponential for the band edge and Gaussian curves for the CT peaks in the sub-bandgap regions. The results of the calculations presented in Figure 5c are qualitatively fully consistent with the observed PDS absorption peaks, in that the P3HT:CNPPV blend has a CT state energy that resides between the two POPT:CNPPV CT state energies. (We note that, in addition to the intrinsic limitations of the methodologies, the difference in energy between theory and experiment may due in part to the fact that the physical size of the CT state (e.g. the extent that the CT exciton is delocalized) could be larger than what was considered in the calculations). To verify that the energies of these CT states remain unchanged with film morphology and film thickness, POPT:CNPPV (1:1) films were compared as both drop cast and spun cast from 1,2-dichlorobenzene (SI, Figure S3). While the CT state peak positions do not change, the relative intensity of the sub-bandgap absorption to the UV-vis absorption is enhanced in the spun cast film, likely a result of finer scale phase segregation that leads to greater D/A interfacial surface area and increased relative sub-bandgap absorption.



Figure 6. Absorption spectra of P3HT, POPT and blends with CN-PPV. Thick solid lines are UV-vis absorption spectra of the homo-polymers, symbols are the PDS absorption spectra of drop cast films. The arrows indicate the sub-bandgap features attributed to CT states in the blend systems. P3HT:CNPPV peak maximum at 1.26 eV, while POPT:CNPPV possesses two peaks at 1.17 and 1.50 eV.

PDS measurements were also performed to probe the CT state energies of the PQT-based polymers blended with CNPPV. The PQT-DD:CNPPV (1:1 wt/wt) shows little non-additive sub-bandgap absorption, while PQT-OP presents two sub-bandgap absorption peaks at 1.25 eV and 1.56 eV. The higher energy CT state peak is significantly less intense for PQT-OP compared with POPT (SI, Figure S4); the reason for this is discussed below. It should be noted that our first attempts to obtain a clean PDS signal from PQT polymers were difficult until we discovered that residual palladium from the cross-coupling polymerization led to an erroneous mirage effect and dramatically increased background signal (Figure S5).

3. Discussion

A thermodynamic driving force for charge generation, i.e., exciton dissociation leading to charge separation, is present at the interface between the donor/acceptor (D/A) materials in an OPV active layer. Photon absorption by either the donor or acceptor materials produces the opportunity for charge-carrier generation: in the case of "donor" excitation, the system decreases in potential energy from the singlet excited state (E_s) by transferring an electron from donor to acceptor; in the case of "acceptor" excitation, by transferring a hole from acceptor to donor. For simplicity, the process is generally discussed from the viewpoint of an excited donor material. A general diagram depicting charge separation is presented in Figure 7.

Although a thermodynamic driving force helps to generate free charge, the immediate physical separation of the electron and hole does not necessarily lead *directly* to free charges. The low dielectric constant of the active layer can produce a Coulomb trap for a partially separated exciton at the D/A interface. This state is usually referred to as a charge-transfer (CT) state. The CT state may either recombine to the initial ground states of the donor and acceptor materials, or it may undergo further separation into free charges. It is broadly debated whether an intermediate CT state is requisite to charge separation^{11,32} and it is more recently debated whether this separation/generation can occur from lowest-lying CT₁ states.³² It was also recently reported that a modest thermodynamic driving force of 0.1 eV leads to reasonable quantum yields of photocurrent with fullerene-based devices, based on commonly measured material properties, which supports our previous finding with POPT/CNPPV.³⁴ The contention surrounding the lowest-lying CT states is that they can be bound (vs. the charge-separated states) by more energy than thermally available from $k_{\rm B}T$ (where $k_{\rm B}$ is the Boltzmann constant); thus, it is postulated that excess energy released during partial exciton dissociation could create higher-lying (excited) CT states (CT*), which are more likely to escape the Coulomb trap.^{33c} Strictly discussing the thermodynamics of charge separation ignores the important kinetic considerations of this process.

The efficiency of the charge separation (CS) process indeed depends on kinetic factors. Given that there is greater potential energy stored in the singlet exciton than a charge transfer exciton, and the possibility that sub-bandgap absorption produces excited CT* states that may relax down to CT₁, two rates are of critical importance: the rate of charge separation (k_{CS}) and the rate of vibrational relaxation of an excited CT state down to CT₁ (k_{VR}), see Figure 7. If $k_{CS} > k_{VR}$, then the electron is expected to readily escape the Coulomb potential and proceed to the CS state. If $k_{VR} > k_{CS}$, then relaxation to the CT₁ state leads to a more tightly bound (lower energy) intermediate. The electron can still escape from this state;³² however, other processes start to compete with charge separation: if either the donor or acceptor material possesses a triplet level (T₁) below the CT₁ state, intersystem crossing leads to long-lived metastable triplets. Also, the CT₁ state for some systems can radiatively or vibrationally decay to the ground state S₀.^{16c,35} For these reasons, the kinetics of CS must be considered when parsing the charge-generation process.



Figure 7. A diagram of possible electron flow pathways at the D/A interface, relative to potential energy. CT state energies (ground state solid black, excited state dashed black) are shown in relation to the D/A singlet excited state (S_1) , triplet state (T_1) and ground state (S_0) . Competing energetic pathways and rates are also depicted: vibrational relaxation of the CT state (k_{VR}) , intersystem crossing of the CT state to the donor triplet state (k_{IC}) , recombination of the CT state to the ground state (k_{Rec}) , and finally charge separation (k_{CS}) . In addition to thermodynamics considerations, the kinetics of these processes will determine the charge separation behavior for each photovoltaic system.

In this work, OPV devices comparing POPT to P3HT and PQT-OP to PQT-DD were fabricated and analyzed. POPT and PQT-OP possess phenyl groups covalently bound to the polymer backbone as part of the solubilizing substituents. This functionality decreases the thermodynamic driving force for charge separation (*vide supra*), but both POPT and PQT-OP produced remarkably higher J_{sc} relative to their alkyl analogs. All relevant PV characteristics are summarized in Tables 1 and 2. Further, X-ray scattering data evidenced that both POPT and PQT-OP can adopt planar-with- and perpendicular-to-the-backbone conformations for the pendant phenyl rings. CT state energies for model dimer configurations were calculated and are plotted in Figure 5c: POPT-*perp* is predicted to have the highest CT state energy, while the CT state energy for P3HT lies between those of the POPT-*perp* and POPT-*unconstrained* conformations. Finally, experimental spectroscopic evidence of charge-transfer states at the interface with the acceptor CNPPV, gathered via PDS for all four donor polymers, is consistent with the relative values predicted by the model dimer calculations.

Due to the out-of-plane twist of the phenyl rings, the separation distance between POPT and the acceptor molecule likely increases as steric repulsion from the phenyl rings hinders backbonebackbone interaction. PDS data confirm the presence of two distinct features in the sub-bandgap regime, which is likely a direct result of these two dominant conformations at the D/A interface, as has been explained in the previous section. Since these conformationally dependent states are both involved as intermediates in the charge-generation process, the corresponding geminate pairs must overcome different energetic barriers to split into free charges. We postulate that the twisted phenyl ring conformation of POPT (POPT-*perp*) is beneficial for charge generation, as an intermediate with increased potential energy is more likely to fully separate into free charges (Figure 8). FTPS measurements could lead to a quantitative description of the quantum yields for these two states, and this is the focus of future work. This study also generated two additional significant and supportive findings. PDI-based acceptors have garnered much attention as alternative n-type materials to replace fullerenes;^{3a} here, we produce the highest efficiency devices with this acceptor to date, despite tremendous efforts with alternative approaches towards higher efficiency.^{3a,13a,19} This is just another indication that control over the interfacial geometry at the molecular level can lead to much improved device performance, as a complementary tool to morphology and state energy control. Additionally, the photovoltaic performance with the high mobility n-type polymer ActiveInkTM N2200 demonstrates that POPT outperforms P3HT both in our labs and compared to two very recent reports.²¹

Combining all the data, analysis, and literature context, we have synthesized and proposed a general design principle for improved charge separation in non-fullerene OPVs: tuning the D/A interfacial interaction through steric control can facilitate photocurrent generation. Regardless of whether charge separation happens from a relaxed CT_1 state or an excited CT state, increasing the steric bulk at the D/A interface decreases the Coulomb binding strength exerted on the geminate pair. We postulate that the phenyl ring pendant to POPT and PQT-OP provides an almost ideal interaction distance between the charge carrying components of the D/A interface, and this leads to two of the best non-fullerene devices to date. The higher energy of the intermediate CT state, with a lower activation barrier to free carrier generation, improves photocurrent generation and provides the key to the observed phenomenon (Figure 8). This effect was not limited to one donor polymer or one acceptor material, but rather it was general for two donors and four acceptors – four polymers and two small molecules, for a total of seven materials combinations. All of these material combinations yielded optimized devices, with the phenyl containing polymeric substituent producing substantially greater photocurrent, and overall power conversion efficiency, than the alkyl analogs.



Figure 8. (a) Cartoon of how steric interactions can lead to an increase in backbone spacing, a decrease in the Coulomb binding force and destabilization of the geminate pair. (b) Schematic of how the change depicted in cartoon (a) leads to a different energy landscape with increased charge separation probability in POPT, as the CT state is considered an intermediate trapped in an energetic well.

4. Conclusions

In conclusion, we have utilized computational modeling, PDS spectroscopy, and tailored synthetic design in order to probe the importance of steric interactions at the donor/acceptor interface in non-fullerene OPV devices. By introducing the octylphenyl substituent onto the investigated polymer backbones, the thermally relaxed charge-transfer state, and potentially excited charge-transfer states, can be raised in energy. This decreases the barrier to charge separation and results in increased photocurrent generation. The design principle was shown to be general across two polythiophene backbones and with four different acceptors – two polymeric and two small molecules. The lower energy PDS onset for POPT based devices with CNPPV (1.17 eV) vs the onset for PQT-OP with CNPPV (1.26 eV) is reflected in the V_{oc} of these devices. The combined data from POPT and PQT-OP devices and their materials analyses suggest that controlling the steric interaction at the D/A interface could be a general design principle toward improving charge generation in non-fullerene OPVs.

5. Supporting Information

All commercially available reagents obtained from suppliers were used without further purification. Unless otherwise noted, all reactions were carried out under nitrogen with standard Schlenk techniques, and all glassware used in dry reactions were flame dried under high-vacuum prior to use. All organic extracts were dried over magnesium sulfate (MgSO₄) powder, and solvents were removed under reduced pressure with a rotary evaporator. Toluene and tetrahydrofuran (THF) were purified and dried by passing through two columns of neutral alumina under nitrogen prior to use. All solvents used in Pd-catalyzed cross-coupling reactions were degassed prior to use. Flash chromatography was performed using Silicycle SiliaFlash ® P60 (particle size 40-63 m, 230-400 mesh) silica gel.

All ¹H and ¹³C NMR spectra were obtained in chloroform-*d*, unless otherwise noted, with a Bruker AVQ-400, AVB-400, DRX-500, AV-500 or AV-600 instrument. ¹³C spectra were measured with a proton-decoupling pulse program.

Polymer molecular weight determination: Polymer solutions (1 mg/mL) were prepared using HPLC grade tethrahydrofuran (THF). Samples were briefly heated and then allowed to return to room temperature prior to filtering through a 0.45 μ m PVDF filter. Size exclusion chromatography (SEC) was performed with HPLC grade THF eluent at 1.0 mL/min by using three PLgel columns (7.5 x 300 mm) with pore sizes of 10⁵, 10³, and 500 Å, respectively. The particle size in columns was 5 μ m and the columns were thermostated at 35 °C. The SEC system consisted of a Waters 510 pump, a Waters 717 autosampler, a Waters 486 UV-Vis detector, and a Wyatt Optilab DSP differential refractive index detector. The apparent molecular weights and polydispersities (M_w/M_n) were determined with a calibration based on linear polystyrene standards using Empower software from Waters.

UV-Vis spectral data were measured with Varian Cary 50 spectrophotometer. Thin film measurements were collected by spin-coating the sample solution in chloroform onto untreated quartz slides.

Cyclic voltammograms were collected using a Solartron 1285 potentiostat under the control of CorrWare II software. A standard three electrode cell based on a Pt wire working electrode, a silver wire pseudo reference electrode (calibrated vs. Fc/Fc^+ at -5.12 eV), and a Pt wire counter electrode was purged with nitrogen and maintained under a nitrogen atmosphere during all measurements. Acetonitrile was purchased anhydrous from Aldrich and tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. Small molecule films were drop cast onto a Pt wire working electrode from a 1% (w/w) chloroform solution and dried under nitrogen prior to measurement.

Grazing-incidence x-ray scattering (GIXS) experiments were conducted at the Stanford Synchotron Radiation Laboratory on beamline 7-2. Samples were irradiated at a fixed incident angle on the order of 0.1° and their GIXS patterns were recorded with a 2-D image detector (MAR345 image plate detector). GIXS patterns were recorded with an X-ray energy of 12.71 keV ($\lambda = 0.975$ Å). To maximize the intensity from the sample, the incident angle (~ 0.1° –

 0.12°) was carefully chosen such that the X-ray beam penetrated the sample completely but did not interact with the silicon substrate. Typical exposure times were 30-600 s.

Synthesis



2-bromo-5-(5-bromo-4-(4-n-octylphenyl)thiophen-2-yl)-3-(4-n-octylphenyl)thiophene (1): In a 100 mL round bottom, 2-bromo-3-(4-octyl)-phenylthiophene (1.45 g, 4.16 mmol), Pd(PhCN)₂Cl₂ (16 mg, 1 mol. %), AgNO₃ (1.42 g, 8.32 mmol), and potassium fluoride (0.48 g, 8.32 mmol) and 20 mL of anhydrous DMSO were combined. This reaction was heated to 60 °C for 3 hours, and then another two equivalents of AgNO₃ and KF were added. The reaction continued overnight. In the morning, the reaction was filtered through celite with diethyl ether, and the filtrate was washed with 1M HCl and excessive amounts of water. The diethyl ether was removed by roto-evaporation and the crude product purified by column chromatography (100% hexanes). 800 mg of a pure white solid were obtained (28% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.68 (d, *J* = 8.10 Hz, 4H), 7.47 (s, 2H) 7.46 (d, *J* = 8.03 Hz, 4H), 2.90-2.81 (m, 4H), 1.93-1.79 (m, 4H), 1.64-1.40 (m, 20H), 1.10 (t, *J* = 6.75, 6.75 Hz, 3H). ¹³C (100 MHz, CDCl₃): δ = 142.89, 142.09, 136.13, 131.82, 128.48, 128.36, 125.52, 107.37, 35.77, 31.89, 31.37, 29.48, 29.39, 29.26, 22.67, 14.11

poly(3,3-di(4-n-octyl)phenylquaterthiophene):

50 mL 3-neck round bottom flask, 2-(trimethylstannyl)-5-(5-In а (1) and (trimethylstannyl)thiophen-2-yl)thiophene were combined and dissolved in 15 mL of PhCl. This solution was degassed by bubbling with nitrogen for 10 minutes, and then Pd₂(dba)3 (11.53 mg, 3 mol. %) and P(o-tol)₃ (15.33 mg, 12 mol. %) were added in one shot (together). The mixture was stirred for 36 hours, at which point a strongly complexing ligand (N,N-Diethylphenylazothioformamide, CAS# 39484-81-6) was then stirred with the polymer to remove any residual catalyst before being precipitated into methanol (200 mL). The precipitate was filtered through a Soxhlet thimble and purified via Soxhlet extraction for 12 h with methanol, 1 h with hexanes, chloroform until the eluent went clear, and finally extracted with PhCl. The PhCl solution was then passed through a plug of silica, neutral alumina, and celite (1:1:1), with excess CHCl₃ and then concentrated by evaporation and precipitated into methanol (200 mL). A significant quantity of polymer was lost in the chromatography step because of poor solubility. Pure PQT-OP was filtered off as a dark solid (90 mg). SEC analysis: $M_n = 29.3$ kDa, PDI = 1.54

The synthesis of **poly(3,3-didodecylquaterthiophene) PQT-DD** has been reported by our group previously – *Macromolecules*, **2007**, *40* (21), pp 7425–7428

Device Fabrication

A11 devices were fabricated on ITO-coated glass substrates (pre-patterned, $R = 20 \Omega^{-1}$, Thin Film Devices, Inc.). The substrates were sonicated for 20 minutes in 2% Helmanex soap water and rinsed extensively with deionized (DI) water. They were then sonicated for 20 minutes in DI water, 20 minutes in acetone, and 20 minutes in isopropyl alcohol, followed by drying under a stream of air. The substrates were then UV-ozone cleaned for 5 minutes. A thin layer (30-40 nm) of PEDOT:PSS (Clevios PH) was spin-coated onto each substrate at 4000 RPM for 40 s, followed by 10 minutes of drying at 140 °C in air. The samples were then transferred to a glovebox under N₂, where the active layers were spin-coated at 1200 RPM for 40 s followed by 2000 RPM for 1 s. The cathode was thermally evaporated under vacuum ($\sim 10^{-7}$ torr) through a shadow mask that defines an active area of ~ 0.03 cm². Some of the samples were then thermally annealed by placing them substrate-side down (active layer facing up) on a hot plate. Current-voltage (J-V) curves were measured using a Keithley 2400 sourcemeasure unit under AM 1.5 G solar illumination at 100 mW cm⁻² (1 sun) using a Thermal-Oriel 150 @ solar simulator. During optimization of devices, different solution concentrations, donoracceptor ratios and annealing conditions were tested in order to obtain the optimized process conditions, and the experiments were repeated multiple times to ensure data reproducibility. Eight distinct devices on each substrate were tested.

The reader is referred to our previous work for detailed device fabrication procedures regarding $CNPPV^1$ and $EV-BT^2$ work.

POPT/N2200	$PCE_{max} = 0.61\%$
Bilayer device	
POPT	7.5 mg/ml chlorobenzene
N2200	7.5 mg/ml THF
Annealing	No improvement with
Cathode	Al
P3HT/N2200	$PCE_{max} = 0.17\%$
Bilayer device	
P3HT	7.5 mg/ml chlorobenzene
N2200	7.5 mg/ml THF
Annealing	110°C 1hr
Cathode	Al
POPT:PDI	$PCE_{max} = 0.51\%$
BHJ device	
POPT:PDI	1:2
Blend concentration	25 mg/ml in dichlorobenzene
Annealing	NO (no improvement with)
Cathode	Al

BHJ deviceSee Rajaram, Armstrong, and Frechet ³ for detailed fabrication procedurePQT-OP/CNPPVPCEmax = 1.12%Bilayer devicePQT-DDPQT-DD5 mg/mL in chlorobenzeneCNPPV8 mg/mL in ethyl acetateAnnealing10 minutes at 110 °CCathodeLiF (1 nm) / Al (100 nm)PQT-DD/CNPPVPCEmax = 0.62%Bilayer devicePQT-DDPQT-DD7 mg/mL in chlorobenzeneCNPPV8 mg/mL in ethyl acetateAnnealingNO (no improvement with)CathodeLiF (1 nm) / Al (100 nm)PQT-OP/EV-BTPQT-OP/EV-BTPCEmax = 1.22%Bilayer devicePQT-OPPQT-OP5 mg/mL in chlorobenzeneEV-BT7 mg/mL in THFAnnealing140 minutes at 80 °CCathodeLiF (1 nm) / Al (100 nm)PQT-DD12 mg/mL in chlorobenzeneEV-BT4 mg/mL in thFAnnealing10 minutes at 110 °CCathodeLiF (1 nm) / Al (100 nm)PQT-OP:PDIPQT-OP:PDI1:2Blend concentration24 mg/mL in chlorobenzeneAnnealing10 minutes at 110 °CCathodeLiF (1 nm) / Al (100 nm)PQT-OP:PDIPQT-OP:PDI1:2Blend concentration24 mg/mL in chlorobenzeneAnnealing10 minutes at 110 °CCathodeLiF (1 nm) / Al (100 nm)PCEmax = 0.49%BHI devicePCEmax = 0.49%	P3HT:PDI	$PCE_{max} = 0.39\%$	
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PQT-DD:PDI PCE _{max} = 0.49% BHI device	Cathode	LiF (1 nm) / Al (100 nm)	
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BHI device	POT-DD:PDI	$PCE_{max} = 0.49\%$	
	BHJ device		

PQT-OP:PDI	1:2
Blend concentration	20 mg/mL in chlorobenzene
Annealing	NO (no improvement with)
Cathode	LiF (1 nm) / Al (100 nm)

Supporting Figures



Figure S1. P3HT and POPT molecular orbitals.



Figure S2. 2D GIXS data and 1D line-scan, along the qx axis, from this data for a film of PQT-OP on Si. The reader is referred to *Macromolecules*, **2007**, *40* (21), pp 7425–7428 for GIXS details concerning PQT-DD.



Figure S3. Absorption spectra of POPT:CN-PPV (1:1) blends. The thick solid line is the UV-Vis absorption spectra of the blend film used to calibrate the PDS spectra. Symbols are the PDS absorption spectra. PDS spectra of a drop cast film (hollow triangles) is compared with that of a thinner spun cast film (solid triangles).



Figure S4. Absorption spectra of PQT, and POPOP and blends with CN-PPV.



Figure S5. Absorption spectra of PQT-DD and PQT-OP and blends with CN-PPV. This plot demonstrates that removal of Pd contamination after cross-coupling polymerization is necessary to eliminate background signal in the PDS measurement, as Pd metal absorbs in the IR and causes an erroneous mirage effect.

Supporting Discussion

Effects of morphology on charge separation: Another factor that must be discussed in relation to J_{sc} is morphology. Here, we discuss morphology from the viewpoint of the charge separation, rather than the more traditional viewpoints of exciton diffusion to the D/A interface and migration of free carriers to the electrodes.⁴ The idea that donor and acceptor domains larger than the exciton diffusion length may provide enhanced geminate pair separation was put forth by Peumans and Forrest based on an extension of the Onsager model for charge separation utilizing Monte Carlo simulations,⁵ and McNeill and Marsh have confirmed this experimentally with detailed device studies.⁶ Here, we support these findings with the bilayer POPT/ and P3HT/CNPPV devices, which are sensitive to annealing and top-layer deposition solvent in a manner that is consistent with improved performance upon coarsening of the D/A interface – see our previous SI with performance vs. annealing time.¹ There is, of course, debate concerning the effect of device annealing: one related hypothesis is that annealing P3HT devices increases the donor HOMO level, in addition to increasing the hole mobility and crystallinity, and thus a greater ΔG_{cs} is expected; this would facilitate an increase in J_{sc} .⁷

<u>Further discussion of PQT PDS measurements</u>: When considering the differences between POPT and PQT-OP PDS signals, it is important to realize that the octylphenyl content of the PQT-OP

polymer is half that of POPT, i.e., two out of the four thiophenes comprising the POT-OP repeat unit do not possess a solubilizing substituent. Therefore, less contribution from the higher energy sub-bandgap transition is expected, and this is well correlated with reduced scattering intensity from the 5.1 Å spacing in the GIXS spectra (SI, Figure S2). The substituent-free bithiophene comonomer of PQT-OP offers no steric repulsion between the conjugated parts of the molecules at the D/A interface, and thus more of the octylphenyl groups are expected to adopt a planar configuration instead of the perpendicular configuration. This configuration means that fewer high energy CT states are expected to be populated. The relative population of the low and high energy CT states does not control the absolute energies of these states, however, and the relatively lower energy CT state for the PQT-OP polymer is actually higher in energy than the low-energy CT state for POPT. This may explain why an increased V_{oc} and decreased J_{sc} is observed for PQT based devices. The blend PQT-DD:CNPPV provides very modest CT state signal, and this observation has previously been correlated with poor device photocurrent and may indicate that the CT exciton of PQT-DD/CNPPV rapidly decays to a triplet state via intersystem crossing, which is not beneficial for efficient charge generation and is unobservable by PDS measurement.⁸ Additionally, the overall intensity of the PQT polymers blends' PDS spectra was low. This could be due to poor mixing of these the PQT polymers with CNPPV, leading to larger pure-polymer domains of these blends compared to POPT and P3HT. Larger domains of homopolymer would reduce the interfacial surface area between the donor and acceptor polymers, reducing the relative signal from CT absorption compared to that in the visible (this kind of phenomenon has already been illustrated in this manuscript by observing the difference in PDS signal between drop cast and spun cast blends of POPT and CNPPV, Figure S3).

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Chapter 5

Synthesis, Properties, and Electronic Applications of Size-Controlled Poly(3-hexylthiophene) Nanoparticles

Abstract

Semiconducting polymer nanoparticles have attracted increasing interest for the use in the fabrication of organic electronic devices. These nanoparticles could provide the ability to control thin film morphology independently of optical and electronic properties. Using poly(3-hexylthiophene), surfactant-free synthesis and characterization of size-controlled, semicrystalline polymer nanoparticles is demonstrated. A method that produces discrete nanoparticles, which can be suspended in solution, is explored and thin films were produce by stand fabrication methods. By controlling the molecular weight, polydispersity, and regioregularity of the polymer, as well as varying its initial solution concentration, both the size and crystallinity of the resulting nanoparticles were tuned. Organic field effect transistors (OFETs) using nanoparticles made from this method produce good semiconducting devices, with hole mobilities on the order of 10^{-3} cm²/(V·s). This approach to forming polymer nanoparticles is attractive for the introduction of solution-processable, well-characterized nanoscale crystalline domains of a variety of conjugated polymers and may prove useful for the fabrication and optimization of organic electronic devices.

1. Introduction

Solution-processed, π -conjugated polymers and small molecules have garnered significant interest as alternative semiconductors, primarily for use in lightweight, inexpensive thin film electronic devices.^{1, 2} The performance of these devices is highly sensitive to the packing of the molecular thin film because the solid-state morphology influences critical semiconductor parameters such as the bandgap and charge carrier transport.^{3, 4} For example, in thin film transistors, certain polymer chain orientations and crystal packing structures are often necessary to achieve effective charge transport.⁵ For efficient photovoltaic cells, mixing between p-type and n-type molecules must be achieved on the nanometer scale while preserving distinct bicontinuous conduction pathways.^{6, 7}

Recently, there has been increasing interest in the synthesis of semiconducting polymer nanoparticles (PNPs) for use in organic photovoltaics, light-emitting diodes, and field effect transistors⁸⁻¹¹ because preformed, nanostructured conjugated polymers may provide direct access to a desired film morphology. Current methods for generating ideal morphologies require extensive optimization of the solvent choice,^{12, 13} small-molecule additives,⁶ deposition techniques,^{14, 15} and post-fabrication annealing.^{7, 16} Furthermore, recent work indicates that thin films made from solution mixtures of pre-aggregated and fully solvated polymers perform better than "as-cast" thin films made from dissolved polymers alone.¹⁰ The use of high-performance polymer nanoparticles would also aid in the formulation of printable electroactive inks and solutions, which would be useful in roll-to-roll processing.

However, to realize the inherent potential of these new materials, it is necessary to both understand and control the structural, optical, and electronic properties of the resulting nanoparticles. Because most organic electronic devices are ≤ 200 nm thick and because of the localized excitonic nature of organic semiconductors,¹⁷ it would be advantageous to develop a general solution-phase strategy for forming discrete, nanoscale polymer domains with controlled size and packing structure prior to forming the associated thin films. Here, we report a new method for the synthesis of surfactant-free, size-controlled semiconducting polymer nanoparticles using poly(3-hexylthiophene) (P3HT), a well-studied standard for high-performance conjugated polymers. Furthermore, we correlate the primary structure of P3HT (i.e., molecular weight distribution and regioregularity) with PNP size, shape, crystallinity, and performance in organic field effect transistors (OFETs).

2. Results and Discussion

Three conditions were set for the successful synthesis of semiconducting polymer nanoparticles: (i) the method of preparation needs to provide control over nanoparticle size, preferably affording nanoparticles with a diameter of less than 30 nm; (ii) the process should be surfactantfree in order to minimize barriers to charge conduction in the final particle film; and (iii) the nanoparticles must retain the optical and electronic properties of the original polymer. To demonstrate the ability of this synthetic method to control the PNP size, particles were prepared from commercially available P3HT at three different concentrations (**R1**, **R2**, and **R3** formed from initial 0.5, 0.05, and 0.005 wt.% solutions, respectively) and compared to particles formed from 35 kDa GRIM-synthesized polymer (**G1**, **G2**, and **G3** prepared from 0.5, 0.05, and 0.005 wt.% solutions, respectively). These polymer samples were chosen because they have similar molecular weights but different polydispersity (PDI) and regioregularity (Table 1). Therefore, if either PDI or regioregularity (RR) significantly influences the final nanoparticle size, then there will be large discrepancies between the average sizes of the nanoparticles formed from the two polymer samples.

РЗНТ	M _n (kDa)	Regioregularity (RR)	Polydispersity Index (PDI)
Rieke	29.4	92	2.14
GRIM	35	>98	1.08
96RR	28.6	96	1.50
92RR	19.5	92	1.29
80RR	14.3	80	1.29

Table 1. Physical Properties of Polymers Used to Synthesize PNPs.

The size and uniformity of the resulting PNPs were analyzed using transmission electron microscopy (TEM) and dynamic light scattering (DLS). A comparison of the polymer samples shows that the diameter of the resulting nanoparticles is significantly influenced by the initial concentration of the chloroform solution of polymer (Figure 1), with lower concentrations affording smaller nanoparticles. Interestingly, PNPs formed from three additional P3HT samples at final concentrations of 0.5 wt % (Table 1) also have particle sizes very similar to those of **R1** and **G1**. Because each polymer listed has a different PDI and RR, these results suggest that the average particle size is largely unaffected by either of these parameters.



Figure 1. (a) Bar graph indicating that the PNP size trends as a function of initial polymer solution concentration and polymer physical properties. The PNP average diameter decreases as the initial polymer concentration

decreases; however, a small trend correlating the polymer primary structure with the PNP diameter is observed. Diameters reported here are measured from TEM imaging. The plotted values and standard deviations represent the average diameter and average standard deviation for three independent experiments, with N = 100 PNPs for each experiment. (b) Bar graph indicating PNP size trends as a function of initial polymer solution concentration and polymer physical properties. Diameters are measured by DLS analysis, and are 15-17% higher than the values measured by TEM.

TEM and DLS analyses of the nanoparticle colloids confirm the discrete nature of the PNPs: no large aggregates or solubilized polymer chains are observed (Figure 1b and Figure 2). Although TEM images indicate that the **R1** and **G1** particles do not differ significantly in overall size, they clearly exhibit different morphologies. The samples of **R**-PNPs are composed of more spherical nanoparticles, whereas the **G**-PNPs have more anisotropic shapes. The differences observed in PNP shape may be due to differences in polymer chain packing within the various nanoparticles as well as differences in the arrangement of polymer crystalline domains within each nanoparticle, where both chain packing and crystalline domain structure are known to be closely related to the original polymer PDI and regioregularity.^{18, 21} These results are also consistent with the preferred packing structure of highly regioregular P3HT in thin films, which forms anisotropic, crystalline nanofibrils with the π - π stacking direction along the long axis of the fiber.^{22, 23}



Figure 2. TEM images of (a) R1-PNPs, (b) G1-PNPs; the scale bar is 100 nm. (c) An individual R1-PNP, and (d) an individual G1-PNP, illustrating dispersity and morphology. The scale bar is 20 nm.

To correlate these differences in particle morphology with crystal structure as well as elucidate how the condensation of polymer into nanoparticles influences its ability to form crystalline domains, PNPs were investigated by both UV–Vis spectroscopy and GIXS. UV–vis spectroscopy can be a powerful tool for characterizing the bulk structural features of colloidal nanocrystals;²⁴ additionally, the method has proven particularly useful in characterizing the solid-state packing of P3HT.²⁵ Therefore, spectra of PNP dispersions of **R1-R3** and **G1-G3** were compared to samples of the same P3HTs that were fully dissolved in chloroform (Figure 3). All PNP dispersions are significantly red-shifted compared to the comparable polymer solution. This 70 evidence is consistent with the existence of unsolvated P3HT chains, which exhibit a longer effective conjugation length.^{25, 26} The large red shift and pronounced phonon shouldering of **G1-G3** indicate highly ordered polymer chains as well as an extended intermolecular π – π stacking interaction.²⁷ The 0–0 and 0–1 vibrational peaks in **R1-R3** are blue-shifted and less resolved than those obtained from the **G** series of PNPs. These blue-shifted absorption features, which are attributed to the intrachain uniformity in the solid state, indicate a reduction in the average conjugation length resulting from shorter or less-planar polymer backbones. This blue shift may result from either or both of the following factors: (1) an overall decrease in the size of the crystalline regions within the PNP and (2) a higher density of crystal defects within the PNP because of steric twisting caused by more head-to-head couplings (not requiring a steric twist, but promoting less long-range order) within the polymer backbone. The reduced shoulder at longer wavelengths also suggests that the degree of intermolecular π – π stacking is lower in the **R**-PNPs. These apparent differences in crystallinity between **R** and **G** particles is consistent across all three of the PNP size regimes investigated (Figure 3).



Figure 3. UV–Vis spectra comparing the optical features of colloidal suspensions composed of PNPs made from highly regioregular, low PDI **G**-P3HT (bottom) and commercial **R**-P3HT (top) in ethanol. The black traces correspond to spectra of the respective P3HT samples solubilized in CHCl₃. The solid black bar at 0.99 a.u. illustrates the bathochromic shift in absorption for the **G** series.

To isolate the influence of polymer regioregularity on nanoparticle formation and crystallinity, PNPs were synthesized from polymer samples exhibiting a range of well-defined regioregularities and similar PDIs (Table 1, RR series). Here, as the regioregularity of the starting polymer increases, the spectra of the resulting PNPs systematically red shift and the shoulder at ~605 nm increases in intensity (Figure 4), indicating an increase in PNP crystallinity. These results highlight an interesting trend in nanoparticle formation: although the RR does not play a significant role in controlling the diameter of PNPs, it is directly correlated to their optical features and crystallinity.



Figure 4. Spectra of PNPs made from P3HT samples with a range of regioregularities (96%, 92%, and 80%). Arrow shows direction of increasing regioregularity.

Together, these results demonstrate active control of PNP size through the initial polymer concentration and PNP crystallinity by careful choice of regioregularity. To understand the influence of PDI on the nanoparticle size and optical features, it is useful to consider experiments using the lowest initial concentration of polymer in solution (0.05 mg/mL). During PNP formation at this concentration, the average distance between polymer chains is approximately 130 nm and there is no evidence of intermolecular interactions by solution-phase UV–Vis, which has no shouldering beyond 550 nm (full calculation in section 4, Methods and Materials). Therefore, it is postulated that the resulting PNPs are likely composed of only a few polymer chains. If the PDI had an influence on nanoparticle formation, then there should be a marked difference between the optical features of the largest PNPs and the smallest within a single batch of polymer (i.e., **R1** and **R3** spectra should show different degrees of phonon shouldering, for example), and there should also be an increase in the polydispersity of PNP diameters as the initial polymer concentration decreases. However, an examination of absorption spectra across particle sizes shows little change in the optical features and no marked increase in PNP diameter

dispersity, which suggests that there is little influence of PDI on the PNP formation, size, and crystallinity.

Because the optical properties of P3HT arise from its crystalline structure, the different absorption spectra suggest that certain P3HT-PNPs have different internal structures. To investigate these differences, 2D GIXS spectra were taken of both **R** and **G** PNPs and compared to thin films of P3HT spun from chloroform. Interestingly, line scans taken parallel to the substrate plane show that both PNP samples contain crystalline regions with identical diffraction peak positions and that these positions are the same as those observed for thin films of P3HT (plane spacings: d(100) = 16.6 Å, d(010) = 3.8 Å) (Figure 5).^{3, 28, 5} Notably, whereas the UV–Vis spectra indicate that the nanoparticle crystal defects and crystallite sizes vary between PNP samples, the P3HT crystal plane spacings are unchanged even after being kinetically confined as a nanoparticle. This indicates that while the long range order within the PNPs varies, the packing parameters do not.



Figure 5. GIXS scans of (A) R1-PNPs, (B) G1-PNPs, and the corresponding (C) P3HT thin film. (D) Onedimensional line scans taken in the qx direction from each spectrum showing that each sample produces the same packing geometry.

Further GIXS analysis sheds light on the morphology of thin films composed of P3HT nanoparticles in comparison to films fabricated from a solution of fully solublized polymer. As expected, 2D GIXS spectra depict a difference in the crystalline orientation for the samples relative to the substrate. The thin film spun from chloroform (Figure 5c) exhibits an anisotropic crystalline orientation. There is a mixed texture or preferred orientation with roughly equal fractions of crystallites favoring either the (100) or (010) direction perpendicular to the substrate. The (100) orientation is the most commonly observed orientation for annealed, highly regioregular P3HT on SiO₂ surfaces because of energetic interactions between the polymer sidechains and the substrate surface.^{3, 29} However, thin films formed from PNPs show a slightly more isotropic orientation for the G1 particles and an almost completely isotropic orientation for the R1 particles. These results qualitatively match the PNP structure as observed by TEM. A film of irregularly shaped particles whose crystal lattice has an anisotropic orientation (as could be the case with G1-PNPs) should give a more oriented 2D thin film when compared with a film composed of spherical nanoparticles (R1-PNPs), which should exhibit no preferential orientation of the crystal lattice with respect to the substrate. Thus, for PNP samples the orientation of the polymer crystal lattice relative to the substrate is likely a product of their shape and is largely independent of the substrate surface chemistry, contrasting with what is typically observed for P3HT spun from solution.

The charge carrier mobility in traditional solution-processed P3HT OFETs is very dependent on the solid-state polymer packing and orientation as well as on the molecular weight and regioregularity of the polymer (ranging from 10^{-4} up to 10^{-1} cm²/(V·s) for highly ordered samples of P3HT).^{28, 30, 31, 32} To investigate the performance of PNPs for electronic device applications, bottom-contact OFETs were fabricated from **R1** and **G1** PNP films similar to those analyzed by GIXS. Octadecyltrichlorosilane-functionalized substrates were spin-coated with P3HT either fully dissolved in chloroform or as PNPs from ethanol. To the best of our knowledge, these experiments represent one of the first tests for films composed of only surfactant-free polymer nanoparticles with no interstitial solubilized polymer.

A comparison of the transistor performance, tested inside an argon glovebox, can be seen in Figure 6 along with SEM images of representative channels filled by either PNP or solubilized P3HT thin films. Both **R1-** and **G1-**PNP films exhibited hole mobilities on the order of $10^{-3} \text{ cm}^2/(\text{V} \cdot \text{s})$ (1.2×10^{-3} and $1.4 \times 10^{-3} \text{ cm}^2/(\text{V} \text{ s})$, respectively). It has been shown previously that increased charge carrier mobility is observed from thin films with higher degrees of crystallinity, so it is interesting that the two nanoparticles exhibit similar mobilities despite their differences in crystallinity. We hypothesize that this similarity is due to the random orientation of nanoparticles in the OFET channel and that this leads to a regime in which mobility is limited by the interface between two adjacent particles. This model is analogous to limitations observed in OFETs made from thin films of semicrystalline polymers, where amorphous regions are a limiting factor in charge transport.³¹ The thin film of commercial P3HT gave $_{h} = 1.2 \times 10^{-3}$, and

the more crystalline P3HT gave $_{h} = 1.6 \times 10^{-2} \text{ cm}^{2}/(\text{V}\cdot\text{s})$. Here, the mobilities obtained from films of PNPs are the same or higher than for thin films cast from solubilized commercial P3HT, and these values are comparable to those for previously reported OFETs fabricated in a similar manner with similar polymers.¹² The mobilities obtained from the PNPs demonstrate that the electronic character of the semiconducting polymer is not degraded during nanoparticle formation or device fabrication and that there is sufficient electronic communication between particles after deposition without any need for postdeposition annealing processes. Although these mobilities are lower than the values measured from the highly oriented film of GRIM-synthesized P3HT, these deviations are consistent with the high directional dependency of OFET measurements and the substrate-independent film formation of the nanoparticles (*vide supra*). The similarity in performance between the PNPs and the commercial polymer thin film fabrication procedures.



Figure 6. Field effect transistor characteristics (a, b) **G1**-PNP and (d, e) **G**-P3HT thin film. (c) SEM of the FET channel with **G1**-PNPs spun from ethanol and (f) a **G**-P3HT thin film spun from CHCl₃.

3. Conclusions

Taken together, these results demonstrate the surfactant-free formation and characterization of discrete, semicrystalline all-polymer nanoparticles for use in thin film electronics which yields a series of design parameters for the fabrication of semiconducting polymer nanoparticles. By controlling the basic physical properties of the polymer and varying the initial polymer concentrations, both the size and crystallinity of the resulting PNPs is tunable. Additionally, size and crystallinity are depend largely on initial polymer concentrations and polymer regioregularity, respectively, without a significant influence of polymer sample PDI. OFETs

using P3HT PNPs made from this method produce good semiconducting devices with hole mobilities on the order of 10^{-3} cm²/(V·s). This approach to forming PNPs is very suitable to the introduction of solution-processable, well-characterized nanoscale crystalline domains of a variety of conjugated polymers and should be broadly applicable in further efforts toward the fabrication and optimization of organic electronic devices.

4. Methods and Materials

Commercial P3HT was obtained from Rieke Metals, Inc. and used as received. All other P3HT samples were synthesized either by Grignard metathesis (GRIM) and/or the McCullough method and were then purified and characterized according to published procedures.^{18, 19} All other materials were obtained from Aldrich and used as received unless otherwise noted. Sample preparation, including nanoparticle synthesis, was routinely conducted in a glovebox under a nitrogen atmosphere at room temperature. All glassware was rinsed with Nanopure water (18.2 $M\Omega$) and dried under a stream of nitrogen prior to use. All compounds were characterized by 1H NMR (400 MHz) on a Bruker AVB 400 or AVQ 400. Regioregularity (RR) values were calculated by comparing the integrated 1H NMR peaks corresponding to the a-methylene protons on the hexyl chains in head-to-tail (HT) versus head-to-head (HH) linkages²⁰ at δ 2.78 and δ 2.54, respectively. For molecular weight determination, polymer samples were dissolved in tetrahydrofuran at a concentration of 1 mg/mL and filtered through a 0.2 m PVDF filter. These samples were then analyzed by size exclusion chromotography using HPLC-grade tetrahydrofuran at a flow rate of 0.8 mL/min on two $300 \times 8 \text{ mm}^2$ linear S SDV 5 m columns (Polymer Standards Services) at 40 °C using a Waters (Milford, MA) 2690 separation module and a Waters 486 tunable absorption detector monitored at 350 nm. The instrument was calibrated using polystyrene standards (1050-135000 g/mol), and the data was analyzed using Millenium 3.2 software. These results are summarized in Table 1.

In a typical experiment, 5 mg of a given polymer was dissolved in 1 mL of chloroform (CHCl₃, anhydrous, 99%) and stirred overnight at room temperature. After complete dissolution, aliquots of this solution were diluted with CHCl₃ to produce 0.5 and 0.05 mg/mL concentrations; all three concentrations were then used for synthesis. At the same time, ethanol (EtOH, 200 proof, molecular biology grade) was bubbled with nitrogen for 30 min and immediately transferred to a glovebox. Next, 500 L of the polymer solution was loaded into a syringe and subsequently introduced dropwise (rate 10 L/s) into 5 mL of the stirring EtOH.

This approach produced stable, surfactant-free colloidal suspensions of P3HT nanoparticles at final concentrations of 0.5, 0.05, and 0.005 wt %, which could be used without the need for further purification. Particle formation was carried out in a nitrogen glovebox to avoid potential photo-oxidation of P3HT during particle formation. The resulting PNPs are stable for more than 2 months when handled in or out of a glovebox with minimal agitation. However, because the nanoparticle suspension contains no surfactants or stabilizing ligands there is no screening or charge–charge repulsion from a ligand shell to resist particle coalescence; therefore, particles must be handled with care and minimal agitation. These nanoparticles are related to many organic nanostructures of interest, including highly crystalline 1D nanowires¹¹ and surfactant-

stabilized nanoparticles prepared either by *in-situ* metal-catalyzed reactions^{9a, 9b} or by miniemulsion processes.^{9c} However, in the case of highly crystalline nanowires, synthesis conditions can be difficult to reproduce batch to batch,^{11a} and mini-emulsion procedures require high-energy shear forces, surfactants, and immiscible solvents, often complicating post-fabrication processing.^{9c} The synthesis presented here offers an alternative route to semiconducting polymer nanostructures that is both surfactant- and byproduct-free and does not require modification to produce nanoparticles (with diameters < 100 nm) from several P3HT derivatives (*vide infra*).

Organic field effect transistors (OFETs) were fabricated using n-doped silicon wafers as the gate and thermally oxidizing the surface to form a 100 nm silicon dioxide dielectric layer. Substrates were cleaned successively in acetone and isopropanol while sonicating and were dried under nitrogen. After UV/ozone treatment for 15 min, each substrate was introduced into a solution of octadecyltrichlorosilane (OTS, 90%, 40 mM in hexadecane) for 2 h. The substrates were then briefly sonicated in toluene (<30 s), further dip-rinsed in toluene, and dried under a stream of nitrogen. Functionalized substrates were transferred to a nitrogen-filled glovebox, and the semiconducting material was deposited on the functionalized substrates by spin-coating (30 s at 1500 rpm for dissolved polymer solutions and 30 s at 300 rpm (x 10) for PNP solutions). The channels tested with this preparation had widths ranging from 200 to 400 m and lengths of 10 m. Current–voltage (I–V) characteristics were measured in a nitrogen glovebox using a Keithley 236 SMU at room temperature.

Transmission electron microscopy (TEM) was carried out using an FEI Technai G2 S-Twin electron microscope operating at 200 kV. Samples were prepared by drop casting 10 L of the as-synthesized nanoparticle colloid onto a 400 mesh Cu TEM grid coated with a Formvar film (Ted Pella, Inc.).

Scanning electron microscopy (SEM) was performed using a Zeiss Gemini Ultra-55 analytical scanning electron microscope operating at a 5 kV accelerating voltage and an average working distance of 4.2 mm. Samples were prepared on either HOPG (Ted Pella, Inc.) or were taken from field effect transistor channels directly on highly doped silicon.

Dynamic light scattering (DLS) was performed using a Zetasizer Nano ZS (Malvern Instruments). Nanoparticle samples were measured at an optical density of 0.1 in EtOH and measured in a 1-cm-path-length quartz cuvette.

UV-Vis spectra of nanoparticle colloids were taken using a Shimadzu 3600 spectrophotometer.

Grazing incidence X-ray scattering (GIXS) spectra were obtained at the Stanford Synchrotron Radiation Lightsource on beamline 11-3. The sample was irradiated at a fixed incident angle (angle = 0.10°), and the GIXS patterns were recorded with a 2D detector (MAR345 image plate). The X-ray energy was 12.72 keV ($\lambda = 0.975$ Å). Samples were prepared by spin-casting multiple layers of the as-synthesized nanoparticles onto silicon substrates coated with a native oxide.

Additional Information on Nanoparticle Synthesis:

Polymer nanoparticles were synthesized using a modified nanoprecipitation methodology. Unlike mini-emulsion procedures which require high-energy shear forces, surfactants and immiscible solvents, nanoprecipitation methods require only two fundamental components: dilute polymer solutions and miscibility of solvents.^{33, 34} Dilute polymer solutions are necessary to ensure that the solvent displacement interactions dominate nanoparticle formation, and that there are no pre-defined polymer aggregates when the solution is introduced into the polymer non-solvent. Solvent miscibilities are crucial in order to obtain a homogeneous colloid (as opposed to an emulsion or phase-separated state) upon introduction of the polymer solution into the polymer non-solvent. Although alternative approaches to nanoprecipitation are possible, we have used a method where the polymeric solution is introduced dropwise into a stirring non-solvent phase. This approach avoids the time and product costs associated with other nanoprecipitation techniques such as dialysis, and also has been empirically shown to produce smaller diameter nanoparticles.³⁵

Additional Information on Nanoparticle Size:

Here, electron microscopy (EM) and DLS are used as complementary characterization techniques for polymer nanoparticle size. Because EM requires ultra-high vacuum conditions, dried polymer nanoparticle samples may experience shrinkage and/or deformation as compared to their structures in the solution phase. On the other hand, DLS measures diameter as the hydrodynamic radius, meaning the fully solvated nanoparticle plus associated solvent molecules.³⁶ More importantly, DLS relies upon Rayleigh scattering for measurement, and Rayleigh scattering intensity is highly dependent on particle diameter (*d*) where intensity scales as $d^{6.36}$. This dependency can skew the measured diameter in the presence of even a small population of larger diameter particles. Therefore, when one uses DLS data obtained from a sample that may contain even a small population of large aggregates, one expects an average diameter measurement that is skewed higher than the actual average nanoparticle diameter. Given these advantages and limitations, EM and DLS are used to establish the lower-bound and upper-bound average PNP diameters.

Calculation of Polymer Concentration in Solution:

Under conditions for the smallest PNP formation, the polymer solution has a concentration of 0.05 mg/mL and taking the average polymer molecular weight to be $M_n = 35$ kDa, the initial polymer concentration in chloroform can then be represented as:

Average number of P3HT chains in solution: $0.025 \text{ mg P3HT} / 0.5 \text{ cm}^3 \text{CHCl}_3$

$$\frac{0.025 \text{ mg P3HT}}{35 \text{ kg}_{\text{mole}}} \times N_{A} = 4.30 \times 10^{14} \text{ P3HT chains.}$$

Number of P3HT chains in a cubic micrometer:

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\frac{4.30E14 \text{ P3HT chains}}{0.5 \text{ cm}^3 \text{ CHC} \iota_g} = 860 \text{ P3HT chains} / \mu \text{m}^3 = 1 \text{ P3HT chain} / 116 \times 10^6 \text{ nm}^3
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This calculation estimates the volume occupied by a single P3HT chain at this concentration, and we model this as a cube with dimensions of 105 nm x 105 nm x 105 nm of solvent that contains one P3HT of $M_n = 35$ kDa.

Now, calculating the length of a 35 kDa P3HT chain assuming a fully extended chain: $35 \text{ kDa P3HT chain}/_{165.267 \text{ Da monomer}} = 212 \text{ monomers per P3HT chain}$

Physical length of P3HT chain: 212 monomers $\times \frac{0.38 \text{ nm}}{\text{monomer}} = 80.56 \text{ nm long}$

Therefore, even under the unlikely condition where the P3HT chain was completely and linearly extended in solution, each P3HT chain is shorter from end-to-end than the length of the cubic space that it may occupy based on solution concentration. Thus each polymer chain is unlikely to be in close proximity to any neighboring chain in the initial chloroform solution. This calculation described the closest possible distance between two polymer chains at any time during the nano-precipitation process at 0.025 mg/0.5 mL. Upon addition of the chloroform polymer solution to the stirring ethanol, the solvents mix and the P3HT is further diluted. To take the other extreme, assuming full mixing of the solvents before crystallization occurs, where the P3HT is completely diluted in ethanol before condensation into nanoparticle form:

Concentration of P3HT in chloroform/ethanol mixture:

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\frac{0.025 \text{ mg P3HT}}{5 \text{ cm}^3 \text{ ethanol}}
\frac{0.025 \text{ mg P3HT}}{35 \text{ kg}/_{\text{mole}}} \times N_A = 4.30 \times 10^{14} \text{ P3HT chains}
\frac{4.30\text{E14 P3HT chains}}{5 \text{ cm}^3 \text{ Ethanol}} = \frac{86 \text{ P3HT chains}}{\mu \text{m}^3} = \frac{1 \text{ P3HT chain}}{116 \times 10^7 \text{ nm}^3}
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Now, there is likely only 1 P3HT chain per cube of solvent that is 227 nm x 227 nm; demonstrating that it is even less likely that neighboring chains will interact during nanoparticle formation. Taken together, it is clear that at no time during the nanoprecipitation synthesis are multiple P3HT chains required to occupy the same volume of space. Furthermore, there is no indication from the solution UV-Vis of any aggregated polymer chains at concentrations used in the nanoparticle synthesis. Therefore, under the lowest concentration conditions, there is only a

slight probability for multiple polymer chains interacting before condensation in particles during the nanoprecipitation process.

5. References

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Chapter 6

Oligo- and Polythiophene/ZnO Hybrid Nanowire Solar Cells

Abstract

The basic operation of an organic/inorganic hybrid single nanowire solar cell is demonstrated. End-functionalized oligo- and polythiophenes were grafted onto ZnO nanowires to produce p–n heterojunction nanowires. The hybrid nanostructures were characterized via absorption and electron microscopy to determine the optoelectronic properties and to probe the morphology at the organic/inorganic interface. Individual nanowire solar cell devices exhibited well-resolved characteristics with efficiencies as high as 0.036%, $J_{sc} = 0.32 \text{ mA/cm}^2$, $V_{oc} = 0.4 \text{ V}$, and a FF = 0.28 under AM 1.5 illumination with 100 mW/cm² light intensity. These individual test structures may enable detailed analysis to be carried out in areas that have been difficult to study in bulk heterojunction devices.

1. Introduction

Hybrid solar cells composed of organic semiconductors¹ and inorganic nanostructures² are an area of immense study as they are alternatives to organic bilayer³ and bulk heterojunction device structures.^{4, 5} The organic/inorganic hybrid system⁶⁻⁹ has opened new opportunities for the development of future generation solar cells, new device technologies, and a platform to study three-dimensional morphology.¹⁰ A multitude of concepts have been demonstrated by combining p-type donor polymers with n-type acceptor inorganic nanostructures such as CdSe,^{6, 7, 11} TiO₂,^{8-10, 12-15} and ZnO.^{8-10, 14} One-dimensional (1-D) inorganic semiconductor nanostructures are among some of the most attractive nanomaterials for solar cell devices because they provide a direct path for charge transport.² Other advantages include high carrier mobilities, solution processability, thermal and ambient stability, and a high electron affinity necessary for charge injection from the complementary organic donor material. ZnO nanowires are an example of this class of materials that have been used for hybrid solar cells.^{8-10, 14, 16} Poly(3-hexylthiophene) (P3HT)/ZnO nanowire composite solar cells are benchmark systems that have attained power conversion efficiencies ranging from 0.02 to 2%.^{9, 16-17} Despite the vast efforts in this area of research, solar cells based on hybrid composites have yielded efficiencies only close to those of organic bilayer devices and significantly less than organic bulk heterojunction solar cells. Knowledge regarding interfacial charge separation and/or transport in hybrid nanowire devices is only partly understood.^{10, 17} If this class of materials is to play a part in the future of next generation solar cells, then there must be an improved fundamental understanding of the organic/inorganic interface in order to increase power conversion efficiencies. While nanowire array and bulk inorganic/organic blend devices are technologically relevant, their electrical properties depend on nanostructure size, uniformity, crystallinity, phase segregation, interfacial interactions, mobility, trap density, and many other factors. For macroscopic devices, these parameters can vary significantly over the active area, making it difficult to attribute any change in performance to a particular phenomenon. Single nanowire devices allow for more precise control over and characterization of the properties listed above, greatly reducing the uncertainty in data interpretation.

In this study, end-functionalized p-type oligo- and polythiophene are utilized to chemically graft an organic component to an n-type ZnO nanowire, producing a p-n core-shell nanowire from which a single nanowire solar cell is subsequently fabricated. P3HT and quaterthiophene was functionalized with a phosphonic ester and acid, respectively, and self-assembled onto the ZnO surface in the solution phase. Organic shells with thicknesses of about 5–20 nm were obtained. The synthesis and characterization of the organic/ZnO composites, high-resolution transmission electron microscopy (TEM) of the organic/ZnO interface, and results on the photovoltaic characteristics of individual nanowire devices are reported. The nanowire devices yield low efficiencies of about 0.03% but provide an effective platform for isolating and studying the many phenomena that affect bulk hybrid solar cell performance.

2. Results and Discussion

ZnO nanowires were prepared via solution and vapor-phase synthesis as previously reported.¹⁸⁻²⁰ Both methods can produce high-quality, single crystalline nanowires with lengths of several micrometers and diameters ranging from 30 to 100 nm. Regioregular P3HT was prepared from 2-bromo-3-hexyl-5-iodothiophene through the Grignard metathesis (GRIM) polymerization reaction²¹ to afford a bromine-terminated polymer with a molecular weight of ~7000 Da, as determined by MALDI-TOF spectroscopy. End-functionalization was carried out by reacting P3HT-Br with butyllithium and then diethylchlorophosphate to yield a phosphonic ester. Didodecylquaterthiophene (QT) was end-functionalized via a similar pathway; however, the ester was subsequently hydrolyzed to afford a phosphonic acid. Note: the P3HT–phosphonic ester was not hydrolyzed to the phosphonic acid because the reaction conditions using trimethylsilyl bromide degrade the properties of P3HT. Figure 1 outlines the synthetic steps toward functionalization of the two organic materials. Core–shell nanowires were obtained by stirring a suspension of ZnO nanowires in a 2 mg/mL chlorobenzene solution of the respective functionalized organic components overnight.



Figure 1. Synthetic pathway for end-functionalizing (a) poly(3-hexylthiophene) (P3HT) and (b) didodecylquaterthiophene (QT) with a phosphonic ester and acid, respectively. The oligothiophenes are self-assembled onto ZnO nanowires overnight in 2 mM chlorobenzene solutions.

The composite materials were purified by centrifugation followed by removal of the supernatant containing excess organic component. THF was added to the precipitated nanowires, and the purification step was repeated an additional three times. No efforts were made to vary the concentration of the oligothiophene in organic solvent. However, THF and chloroform were substituted for chlorobenzene, and similar results were obtained. Large-scale quantities (~20 mg) of functionalized nanowires were prepared from both organic components. Dry powders were stored in a nitrogen box to prevent oxidation. ZnO/P3HT composites are light purple in color while the ZnO/QT composites are yellow (Figure 2b). The hybrid nanowires can be easily redispersed by sonicating in methanol for 5-10 s.



Figure 2. (a) Schematic structure of the oligothiophene-modified ZnO nanowire substrate utilized for UV-vis absorption measurements. (b) Digital photograph of the as-prepared solution-phase ZnO nanowires, ZnO/QT, and ZnO/P3HT in their dry powder form.

UV absorption spectroscopy was used to verify the grafting of oligothiophenes onto ZnO nanowires. Arrays of ZnO nanowires on quartz substrates were employed in this experiment because light scattering prevented solutions of the hybrid nanowires from yielding quality spectra. Figure 2a shows the schematic structure of the hybrid ZnO nanowire arrays and the solid-state absorption spectra of ZnO/P3HT and ZnO/QT. Grafting of the organic component onto ZnO arrays was carried out under similar conditions as described for solution-phase

nanowires. Figure 3a shows an overlay of the pristine end-functionalized P3HT spin-coated on a quartz substrate and the P3HT-modified ZnO nanowires. The peak centered at 370 nm corresponds to the ZnO absorption, while the three low-energy bands are attributed to the vibronic transitions of P3HT. Figure 3b shows the spectra of the pristine phosphonic acid-terminated quaterthiophene and an overlay of the ZnO/QT nanowire array. The ZnO absorption is again observed at 370 nm while a broad shoulder centered at 400 nm correlates well with the absorption band of the free QT oligomer.



Figure 3. (a) A UV-vis absorption spectra of the P3HT-modified ZnO nanowires, and (b) QT-modified ZnO nanowires. An overlay of the pristine polymer and oligomer is also included in the respective spectra.

High-resolution TEM was used to determine the thickness of the grafted organic components onto ZnO nanowires. Figure 4a-c show TEM micrographs of ZnO/P3HT hybrid structures with P3HT thicknesses ranging from about 7 to 20 nm. The grafting of P3HT onto ZnO results in a somewhat uneven morphology, yet complete coverage throughout the surface of the nanowires is reproducibly observed. Figure 4d-f show TEM micrographs of ZnO/QT hybrid nanowires with shell thicknesses ranging from 6 to 13 nm. It is worth pointing out that small-molecule grafting shows significantly smoother shells compared to P3HT grafts. The reason is unclear, but it may be possible that nanoscale disorder predominates in self-assembled polymer thin films compared to small-molecule thin films. This does not imply that P3HT is unable to self-assemble into highly ordered domains. In fact, highly organized domains were repeatedly observed when ZnO/P3HT nanowires were imaged with HR-TEM, as shown in Figure 4c. This organization is known as lamellar chain packing and is documented in literature for thin films using HR-TEM bearing similar molecular weights to that of the P3HT used in this study.²³ From the

known unit cell parameters of P3HT,^{22, 23} the averaged molecular weight, and the chemical repeat unit of P3HT, one can estimate the length of a P3HT chain and explain the shell thickness based on the lamellar repeat folding (along the *c*-axis of the chain). For instance, the estimated unit cell parameters for P3HT from literature are a = 16.2, b = 3.8, and c = 7.8 Å,²¹⁻²³ and from an ~7 kDa polymer (by MALDI-TOF), a shell thickness of about 6–11 nm is estimated. This is assuming the lamellar fold length is on the order of 5–10 nm based on observed TEM images (Figure 4c) and from measurements in literature reports.²²⁻²³ A diagrammatic illustration of the chain packing at the ZnO interface as shown in Figure 5a. Note: this illustration is not to scale, and the intent is to show a plausible scheme of lamellar chain packing on the surface of ZnO.



Figure 4. Transmission electron microscopy (TEM) images of (a-c) ZnO/P3HT core-shell nanowires and (d-f) ZnO/QT core-shell nanowires.

The molecular packing of QT on ZnO is highly uniform, as evidenced by the smooth shell on ZnO from Figure 4e. The length of a QT molecule is about 1.9 nm; however, shell thicknesses of 6-13 nm are measured by TEM. This can be explained by the QT bilayers which are strongly interacting via three molecular forces. A schematic illustration of the proposed solid-state structure is shown in Figure 5b. The planar backbone of QT forms $\pi - \pi$ interactions with nextnearest neighbor molecules along the plane of the ZnO nanowire. H-bonding between endfunctionalized phosphonic acid groups from QT bilayers can also interact strongly with one another to stabilize the molecular framework. Phosphonic acids are capable of forming strong P-O-H···O=P hydrogen interactions with a bond strength of approximately 10-20kcal/mol.²⁴ Jen and co-workers previously reported similar interactions with pyrene phosphonic acid molecules that form polycrystalline films through π -interactions and H-bonding.²⁵ In addition to the two forces already discussed, QT frameworks are also assisted by van der Waals interactions between dodecyl side-chains. Therefore, if three bilayers of OT stack vertically, a thickness of about 9 nm can be estimated. Well-ordered architectures composed of alternating oligothiophene/ZnO lamellar nanostructures were recently reported by Stupp and coworkers.²⁶ In their study, the hybrid nanocomposite was employed as a photoconductor device that generated extremely large spectral responsivities. It has also been shown that endfunctionalized oligothiophenes can self-assemble onto ZnO nanorods as highly crystalline monolayers.²⁷ The molecules were found to pack in a herringbone pattern, and the packing density correlated well with a core-shell thickness of ~3 nm. The hybrid nanostructures were subsequently fabricated into transistors, and ambipolar behavior was observed.²⁷



Figure 5. (a) Diagrammatic representation of the ZnO/P3HT interface. The illustration is not to scale and is intended to estimate the lamellar organization of P3HT on ZnO. The self-assembled polymer thin film is believed to contain ordered domains and regions of azimuthal disorder. (b) Speculated molecular packing at the ZnO/QT nanowire interface. Also shown are the three molecular forces that assist in interfacial self-assembly.

The p-n heterojunction nanowires were further characterized by measuring their photovoltaic characteristics. The organic/ZnO nanowires were dispersed in methanol and drop cast onto oxidized silicon substrates. The nanowire devices were fabricated by a top contact approach using electron beam lithography (EBL). Part of the organic shells were etched away from ZnO nanowires using oxygen plasma through defined EBL patterns. Next aluminum electrodes (100 nm) were deposited to make Ohmic contacts directly onto ZnO. EBL was utilized again to define and deposit gold electrodes (100 nm) directly onto oligothiophene shells. Figure 6a shows a schematic configuration of a completed nanowire device. All photovoltaic measurements were carried out in vacuum probe station (10^{-6} Torr) equipped with a solar simulator (Oriel). Figure 5b-c show current density – voltage (J-V) characteristics for the two types of photovoltaic cells investigated in this work. The plot of a typical ZnO/P3HT nanowire device yielded a J_{SC} of ~0.32 mA/cm², V_{OC} of ~0.40 V, FF of ~0.28, and an efficiency of ~0.036% under AM 1.5 illumination with 100 mW/cm² light intensity (Figure 6b). These results are consistent with literature values of ZnO/P3HT bulk nanowire solar cells, where the average characteristics yielded a J_{sc} of 0.74 mA/cm², V_{OC} of 0.17 V, FF of 0.34, and an efficiency of 0.04%.⁹ This suggests that increasing the P3HT thickness will not significantly improve the performance of the nanowire device (assuming the exciton diffusion length of P3HT is similar or less than the core-shell thickness of 10 nm). Since P3HT defines the relevant optical absorption in our nanowire device, the maximum current density can be calculated by integrating the absorption coefficient of end-functionalized P3HT over the solar spectrum (AM 1.5)²⁸ and this yields an estimated current density of ~0.75 mA/cm². This difference in experimental versus theoretical current density is similar to that in bulk heterojunction solar cells where a maximum current is calculated at ~19 mA/cm² and experimental results yield about 10–12 mA/cm².²⁸



Figure 6. (a) Schematic configuration of a discrete ZnO/oligothiophene nanowire solar cell. (b) SEM image of a discrete ZnO/P3HT nanowire device fabricated by EBL and the corresponding current–voltage characteristics. (c) SEM image of a discrete ZnO/QT nanowire device and the current–voltage characteristics. The devices were measured under AM 1.5 irradiation (100 mW/cm2).

Similar photovoltaic results were found for a ZnO/QT nanowire device (Figure 6c) yielding a J_{sc} of 0.29 mA/cm², V_{OC} of 0.35 V, FF of 0.32, and an efficiency of 0.033%. An important finding in this work is that the open circuit voltages these devices are larger than those reported in literature from ZnO/P3HT bulk nanowire array devices.^{9, 29} This may suggest that the ZnO/P3HT interface for the grafted polymer is superior to the bulk spin-coated method. It is also possible that single-nanowire devices increase the shunt resistance by eliminating shorting paths present in the bulk ZnO array devices. There remains significant room for improvement of these devices by modifying the device fabrication procedure and electrode deposition technique. Nevertheless, ideal characteristics and reproducible measurements were observed in these devices. Although one could argue that device performance will be limited by the thickness of the grafted oligothiophene (since more material will absorb more sunlight), the reality is that only the excitons that are photogenerated within a diffusion length of the respective material will be effectively dissociated at the interface, transported, and collected into the external circuit. Smaller band gap semiconductor nanowires and organic semiconductors with larger absorption coefficients, longer diffusion lengths, and higher mobilities will be best suited for improving the performance in single nanowire devices. These devices will play a critical role in understanding fundamental device physics at interfaces and in the development of new device concepts and technologies.

3. Conclusions

In summary, the basic operation of individual organic/inorganic hybrid nanowire solar cells was demonstrated. End-functionalized oligo- and polythiophenes were grafted onto ZnO nanowires to produce p-n heterojunction nanowires. The hybrid nanostructures were characterized via absorption and electron microscopy to determine the optoelectronic properties and to probe the morphology at the organic/inorganic interface. Hybrid p-n heterojunction nanowire solar cell devices exhibited ideal characteristics. These individual test structures will enable detailed analysis to be carried out in areas that have been difficult to study in nanostructured array and heterojunction devices.

4. Methods and Materials

Structural Characterization: Scanning electron microscopy was done on a JEOL JSM-6340F operating at 5 kV. Transmission electron microscopy was performed on a Philips CM200 FEG operating at 200 kV.

End-Functionalization of P3HT: In a 100 mL 3-neck round-bottom flask, 41 mg of P3HT was dissolved in 50 mL of anhydrous toluene. This required heating at 90 °C for 2 hours. The solution was then cooled to room-temperature and then further cooled to 0 °C. The bright orange solution turns dark orange and opaque at this point. 0.2 mL of 2.5M nBuLi was then added dropwise and stirred at 0 °C for 5 minutes and at room temperature for 1 hour before the reaction was cooled back down to 0 °C and 0.3 mL of diethylchlorophosphate was added dropwise. After

2 hours, the reaction was precipitated into methanol (200 mL) and filtered, with extensive methanol and acetone washing.

QT-ester: In a 100 mL 3-neck round bottom flask, 5,5'-bis(3-dodecyl-2-thienyl)-2,2'bithiophene (Aldrich, 0.50 g, 0.749 mmol) was dissolved in 40 mL of anhydrous THF. The reaction was cooled to -78 °C (solution became a slurry) and n-butyllithium (Aldrich, 0.315 mL 2.5M in hexanes, 1.15 eq) was added dropwise. The reaction was stirred at at -78 °C for 2.5 hours and then diethylchlorophosphate was added dropwise (Aldrich, 0.155 g, 0.898 mmol, 1.2 eq). The reaction becomes an orange color at -78 °C and then turns red over the course of 6 hours as the reactions warms to room-temperature. The crude reaction was quenched with a few drops of water and then diluted with diethylether and washed with 1M HCl. The ether was evaporated to yield crude product that was purified by column chromatography (40% EtOAc in Hexanes). 130 mg, 22% yield. 1H NMR (400 MHz, Acetone-d₆ δ ppm 7.49 (d, J = 8.53 Hz, 1H), 7.38 (d, J = 5.21 Hz, 1H), 7.32 (dd, J = 3.77, 1.46 Hz, 2H), 7.25 (d, J = 3.83 Hz, 1H), 7.12 (d, J = 3.80 Hz, 1H), 7.03 (d, J = 5.21 Hz, 1H), 4.15-4.06 (m, 4H), 2.86-2.78 (m, 6H), 1.71-1.61 (m, 4H), 1.40-1.15 (m, 44H), 0.84 (t, J = 6.76, 6.76 Hz, 6H) 31P (9.86)

End Functionalization of QT-Acid: In a 1-neck 25 mL round-bottom flask 130 mg of

DD-QTPO-Ester was dissolved in 7 mL of dichloromethane. 0.2 mL of bromotrimethylsilane (8 eqs) and 0.21 mL of triethylamine (8 eqs) were stirred overnight. 1 mL of water was added and stirred for an hour as an emulsion with dichloromethane. ~50 mL of dichloromethane was added and the organic phase washed with 1M HCl. The 2dichloromethane was removed under reduced pressure to yield a yellow solid (90 mg, 75% yield). 1H NMR (400 MHz, CD₂Cl₂ δ ppm 7.70-7.30 (m, 2H), 7.21-6.81 (m, 7H), 2.78-2.65 (m, 4H), 1.69-1.52 (m, 4H), 1.38-1.13 (m, 38H), 0.88-0.76 (m, 6H).

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Chapter 7

Synthetic Control of Structural Order in *N*-Alkylthieno[3,4c]pyrrole-4,6-dione-Based Polymers for Efficient Solar Cells

Abstract

The correlation between different alkyl substituents on thieno[3,4-c]pyrrole-4,6-dione (TPD)based polymers and solar cell device performance was investigated. After a thorough optimization of device parameters, these TPD-based polymers provided photovoltaic power conversion efficiencies ranging from 4.0% to 6.8%, depending on the size and shape of the alkyl solubilizing groups. Further, the impact of the alkyl groups on the structural order and orientation of the polymer backbone, using extensive grazing incidence X-ray scattering (GIXS) analysis, was correlated to this variation in performance. Fine tuning of these parameters delineated the critical role that solubilizing groups play towards developing polymers with improved power conversion efficiency.

1. Introduction

Intense interdisciplinary research in the field of organic photovoltaics (OPVs) has led to a significant increase in their power conversion efficiencies (PCEs) over the past decade.¹ One of the most important advances in OPVs has been the introduction of the bulk heterojunction (BHJ) architecture,² in which the photoactive thin film consists of an interpenetrating blend of electron donor and electron acceptor components. Extensive research efforts have focused on improving the polymeric electron donor component of the BHJ while retaining fullerene derivatives as the electron acceptor.³ Key developments have involved narrowing the polymer bandgap, in order to better match the optical absorption with the solar spectrum, and optimizing the energy level offsets with fullerene to achieve maximum open-circuit voltage (V_{oc}).⁴ For the design of new polymers, non-energetic parameters such as those that influence the physical interaction between the bulk polymer and fullerene are also important.⁵ In particular, the choice of solubilizing groups is a critical factor, yet reports that directly correlate solubilizing patterns with device performance have been limited.⁶ Herein, we investigate the correlation between different alkyl substituents on *N*-alkylthieno[3,4-*c*]pyrrole-4,6-dione (TPD)-based polymers and BHJ device performance, reaching PCEs over 6.5%.

2. Results and Discussion

Leclerc *et al.* recently reported on a linear alkyl-substituted TPD-based polymer showing PCEs on the order of 5.5%.⁷ Polymers (**P1–P3**, see Figure 1a and Table 1) were synthesized independently and concurrenly. Device configurations yielding PCEs between 4% and 6.8% were identified. By preserving the π -conjugated backbone structure while modulating the size and branching of the alkyl substituent appended to TPD, we were able to maintain consistent electronic properties among the polymers. This allowed us to focus on the specific influence of solubilizing groups on OPV performance.

Table 1. Number-Average Molecular	Weight (M_n) , Polydispersity Ind	dex (PDI) and optical properties for	r P1-P3
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Polymer	M _n (kDa)	PDI	$\lambda_{max}(nm)$	$\lambda_{onset}(nm)$	Eg ^{opt} (eV)
P1	42	2.5	608	707	1.75
P2	39	3.0	616	728	1.70
P3	35	2.7	627	716	1.73

The thin-film optical absorption spectra of the polymers display three maxima in the 400–700 nm range (Figure 1b). By replacing the shorter but bulkier ethylhexyl chains in **P1** with the longer but less bulky octyl side chains in **P2** and **P3**, broader and red-shifted absorption spectra with more defined vibronic structure were obtained. This is indicative of a planarization of the conjugated backbone and more efficient packing of the polymer.⁸ From the onset of the absorption spectra, an optical bandgap value of about 1.7 eV was estimated for all three polymers. Cyclic voltammetry (CV) was carried out to determine the electrochemical highest

occupied molecular orbital levels of P1–P3. Similar values (P1, 5.48 eV; P2, 5.57 eV; and P3, 5.4 eV; all values relative to Fc/Fc^+ at -4.8 eV) were found for all three materials.



Figure 1. (a) Molecular structure of the TPD-based polymers P1-P3. (b) Normalized absorption spectra of the polymer films.

properties of P1-P3 were investigated in structure The photovoltaic the device ITO/PEDOT:PSS/polymer:[6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM)/Ca/Al. The active layers were spin-coated from chlorobenzene (CB), and in some cases a small amount of the high boiling-point additive 1,8-diiodooctane (DIO)⁹ was used in order to optimize the morphology. The solubility of all three polymers in CB was high enough to allow for extensive characterization. The best J-V curves are reported in Figure 2, and the average device parameters are listed in Table 2. When comparing P1 and P2, it is clear that decreasing the branch length from two carbons to one and moving the branching point from the 2-position to the 3-position leads to an improvement in device performance. In optimized devices, the PCE increases from 3.9% for P1, which possesses an ethylhexyl side chain, to 5.4% for P2, which possesses a dimethyloctyl side chain. The elimination of branching on the TPD side chain in P3 further enhances performance. We obtained a maximum PCE value of 6.8% in our best device with a short-circuit current $J_{sc} = 11.5 \text{ mA/cm}^2$, an open-circuit voltage $V_{oc} = 0.85 \text{ V}$, and a fill factor FF = 69.8%. The high FF values obtained in the best-performing devices suggest that an optimized morphology was achieved. (See section 4, "Methods and Materials", for detailed device parameters and AFM images). The external quantum efficiency spectra of the optimized

devices are shown in Figure 2b, and the maximum values are among the highest reported for solar cells based on polymer: $PC_{61}BM$ blends, to date.



Figure 2. (a) Characteristic J-V curves of bulk-heterojunction solar cells fabricated from P1, P2 and P3 under illumination of AM 1.5G, 100mW/cm². (b) External quantum efficiency spectra of P1, P2 and P3 based devices.

In the cases of **P1** and **P2**, the addition of DIO to the blend solution dramatically improved the performances of the devices. The use of high-boiling-point additives has been shown to promote the packing of the polymer by avoiding excessive crystallization of the fullerene.¹⁰ This is a possible cause for the large enhancement in the device performances of **P1** and **P2** with DIO. In contrast, for devices realized using **P3**, the addition of DIO led to only slight improvements. These results suggest that **P3** has already reached a high level of order in the blend without DIO.

PX:PC ₆₁ BM (wt:wt)	J _{sc} [mA/cm ²]	V _{oc} [V]	FF [%]	PCE (PCE _{max}) [%]
P1 1:2	-5.5	0.89	55	2.7 (2.8)
P1 1:2 DIO ^a	-8.1	0.87	56	3.9 (4.0)
P2 1:1.5	-7.3	0.82	62	3.7 (3.9)
P2 1:1.5 DIO ^b	-9.7	0.81	67	5.4 (5.7)
P3 1:1.5	-10.6	0.86	68	6.3 (6.4)
P3 1:1.5 DIO ^b	-11.5	0.85	68	6.6 (6.8)

Table 2 Comparison of photovoltaic parameters of P1, P2, P3 in the blend with PC₆₁BM

^aDevices prepared from mixed solvents chlorobenzene/1,8-diiodooctane (98/2, v/v). ^bChlorobenzene/1,8-diiodooctane (99/1, v/v).

To confirm these hypotheses, we investigated the influence of the different alkyl substituents on the molecular organization in the polymer thin films using grazing incidence X-ray scattering (GIXS). Polymer blends with $PC_{61}BM$ were also examined to directly correlate microstructural order in the blends with device performance. As shown by the GIXS patterns of **P1**, **P2**, and **P3** (Figure 3a), the (010) peak corresponding to π -stacking is more prominent in the out-of-plane

direction, which suggests that most of the polymer backbones are oriented parallel to the substrates (inset, Figure 3b). This face-on orientation is beneficial for charge transport in the device, and the effect is enhanced by reducing the distance d_2 (inset, Figure 3b) between the backbones. As extracted from the out-of-plane GIXS profile (Figure 3b), the value of d_2 is equal to 3.8 Å for P1 and 3.6 Å for both P2 and P3. Therefore, by replacing the ethylhexyl substituent on P1 with the dimethyloctyl and *n*-octyl analogues on P2 and P3, respectively, the π -stacking distances are reduced, which correlates well with increased device performance. The stronger intensity of the reflection coming from P3 compared to P2 (Figure 3a) indicates that a higher fraction of polymer backbones are oriented in the direction parallel to the substrate in the case of the P3 film. An additional intense peak, corresponding to the reflection from the (100) crystal plane, is present in all pristine polymer films. This peak represents the distance d_1 (inset, Figure 3b), which corresponds to the lamellar spacing in the plane. Since this distance is likely to be related to the length of the side chain, it is smaller for the hexyl derivative P1 ($d_1 = 18.9$ Å) than for the octyl derivatives P2 ($d_1 = 21.6$ Å) and P3 ($d_1 = 21.2$ Å).



Figure 3. (a) 2D Grazing Incidence X-ray Scattering (GIXS) patterns of films of P1, P2 and P3. (b) Out of plane linecuts of GIXS. Inset: Schematic illustration of the face-on orientation of the polymers with the backbone parallel to the substrate. The lamellar spacing and the π -stacking distance are labeled d_1 and d_2 respectively.

Interestingly, the same diffraction peaks of the pristine polymers are still visible in the 2D patterns of the blends with $PC_{61}BM$ together with the characteristic reflection of fullerene. Figure 4 shows the 2D GIXS patterns of the polymer: $PC_{61}BM$ films, obtained from the same CB and CB/DIO solutions used for device fabrication. Except for the pattern of the **P1**: $PC_{61}BM$ film without DIO (Figure 4a), the π -stacking peak is visible in all samples, indicating that the polymers are able to retain the same face-on orientation when blended with fullerene. Compared to the samples without DIO (Figure 4a–c), GIXS images of the films cast from the mixed solution CB/DIO (Figure 4d–f) show increased intensity of the π -stacking peak. This enhancement could be attributed to the additive, which likely promotes ordering of the polymer domains. The **P3**: $PC_{61}BM$ blend from the CB/DIO solution clearly shows the highest intensity peak, indicating more extended π -stacking with respect to the other samples. The increased ordering in **P3** films is probably due to the reduction of the side-chain bulkiness, which allows the polymer to crystallize more easily, even in the presence of $PC_{61}BM$. This increased order could contribute to the higher device efficiency observed for **P3**.

By extracting the π -stacking distance from the GIXS pattern, it is observed that blend films containing **P2** and **P3** exhibit the same d_2 value as the pristine films (3.6 Å). From the GIXS analysis, it is concluded that these TPD-based polymers are able to maintain the face-on orientation of the backbone and preserve a small π -stacking distance in the blends with fullerene.



Figure 4. 2D GIXS patterns of blend of PX with $PC_{61}BM$ (a) P1, (b) P2 and (c) P3 in the optimized condition, spincoated from chlorobenzene, and P1 (d), P2 (e) and P3 (f) blends prepared from mixed solvent chlorobenzene/1,8diiodooctane.

These structures provide one of the first reports of face-on oriented polymer for solar cell applications.¹¹ The unique molecular packing structure is likely one of the main reasons why the TPD-based polymers are able to out-perform regioregular poly(3-hexylthiophene), which has edge-on orientation with respect to the substrate.¹² In addition to the face-on orientation of the polymer backbone, the extended microstructural order observed in the blend film of **P3** also contributes to the high performance of this polymer.

The crystallinity of the polymer affects the blend morphology, which in turn influences charge separation and charge transport in the active layer. The focus of this study was on how the shape and size of the substituents dictate the degree and the extent of the molecular packing, and it was shown that these parameters have a strong influence on device performance.

3. Conclusions

In conclusion, the synthesis and device performance of a series of alkyl-substituted TPD-based polymers with photovoltaic responses ranging from 4.0% to 6.8% was presented and analyzed. Depending on the choice of the alkyl solubilizing pattern, the performance and solid-state structure varied substantially. GIXS analysis demonstrates how variations in the solubilizing groups impact structural order and orientation in polymer backbones, critically affecting device performance. These results provide important insights for the design of new polymeric and molecular systems to be used in efficient solar cells.

4. Methods and Materials

All reagents from commercial sources were used without further purification, unless otherwise noted. All reactions were performed under dry N_2 , unless otherwise noted. All dry reactions were performed with glassware that was oven dried and then flamed under high-vacuum and backfilled with N_2 . All extracts were dried over powdered MgSO₄ and solvents removed by rotary evaporation under reduced pressure. Flash chromatography was performed using Merck Kieselgel 60 (230-400 mesh) silica. Methylene chloride, THF, toluene, and pyridine were purchased from Fisher Scientific and purified by passing them under N_2 pressure through two packed columns of neutral alumina (for THF, pyridine and methylene chloride) or neutral alumina and copper(II) oxide (for toluene).

Synthetic Procedures:


A representative procedure is listed below for the synthesis of TPD-based monomers. NMR and GC-MS characterization is reported for all the monomers used. This synthetic method was adapted from *Org. Lett.*, **2004**, 6, 3381–3384.

(i) **1H,3H-Thieno[3,4-c]furan-1,3-dione (1)** In a 250 mL single-neck round-bottom flask equipped with reflux condenser, 3,4-thiophenedicarboxylic acid (Frontier Scientific, 5.1 g, 29.5 mmol) was heated to 140 °C with acetic anhydride for 6 hours. The reaction was then cooled to room temperature and the solvent was removed under reduced pressure to yield a dark brown solid. The crude product was recrystallized from toluene to yield pale brown needles. 4.07 g, 89% yield. ¹H NMR (400 MHz, Acetone-d₆): δ ppm 8.49 (s, 2H). ¹³C (100 MHz, Acetone-d₆): δ 158.59, 136.87, 132.18.

(ii) **4-[[1-(2-ethylhexyl)amino]carbonyl]-3-Thiophenecarboxylic acid (2)** In a 100 mL singleneck round-bottom flask, **1** (4.07 g, 26.4 mmol) was dissolved in DMF (40 ml) and 1-(2ethylhexyl)amine (Aldrich, 3.76 g, 29 mmol) was added dropwise (over 10-15 min) to the stirred solution (exothermic). The reaction mixture was then heated to 140 °C for 2 hours, cooled to room temperature, and then slowly precipitated into water. This crude amic-acid was filtered off and used without further purification. 5.4 g 72% yield, off-white solid. ¹H NMR (500 MHz, CDCl₃): δ ppm 8.41 (d, 1H), 8.16 (d, 1H), 7.87 (bs, 1H), 3.42 (t, 2H), 1.7 – 1.6 (m, 1H), 1.4 – 1.2 (m, 8H), 0.95 – 0.8 (m, 6H).

(iii) **5-(2-Ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3)** In a 100 mL single-neck round–bottom flask, **2** was dissolved in thionyl chloride (20 mL) and heated to 72 °C for 3 hours. The reaction was then cooled to room temperature and slowly precipitated into water (exothermic). The off-white solid was filtered off and used without further purification. 3.26 g, 87% yield. ¹H NMR (500 MHz, CDCl₃): δ ppm 7.83 (s, 2H), 3.54 (d, 2H), 1.8 – 1.75 (m, 1H), 1.4 – 1.2 (m, 8H), 1 – 0.8 (m, 6H). ¹³C (100 MHz): δ 162.96, 136.62, 125.47, 42.35, 38.15, 30.94, 30.47, 28.47, 23.80, 23.02, 14.07, 10.41.

(iv) **1,3-dibromo-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (4)** In a 100 mL round-bottom, **3** (2 g, 7.5 mmol) was dissolved in concentrated sulfuric acid with dibromocyanuric acid (2.6 g, 9 mmol) and heated to 60 °C for 12 hours. The reaction was then cooled to room temperature and precipitated into methanol:water (50:50), filtered off, and further purified by column chromatography (100% chloroform as eluant). 1.1 g, 34.5% yield. ¹H NMR (500 MHz, *CDCl*₃): d ppm 3.48 (d, J = 7.18 Hz, 2H), 1.83 – 1.70 (m, 1H), 1.38 – 1.17 (m, 8H), 0.94 – 0.84 (m, 6H). ¹³C (100 MHz): d 160.64, 134.67, 112.91, 42.60, 38.14, 30.48, 28.50, 23.79, 22.92, 14.06, 10.34. Melting Range: 115 - 117 °C. GC-MS t = 15.18 minutes, m/z = 423.0

1,3-dibromo-5-(3,7-dimethyloctyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (5)

¹H NMR (500 MHz, *CDCl*₃): d ppm 3.63-3.58 (t, 2H), 1.71 – 1.56 (m, 1H), 1.56 – 1.36 (m, 3H), 1.36 – 1.18 (m, 3H), 1.18 – 1.05 (t, 3H), 0.94 (d, J = 6.29 Hz, 3H), 0.85 (d, J = 6.61 Hz, 6H). ¹³C (125 MHz): d 160.31, 134.78, 112.87, 39.17, 37.06, 36.92, 35.18, 30.63, 27.89, 24.48, 22.66, 22.58, 19.31. Melting Range: 126 - 129 °C. GC-MS t = 16.22 minutes, m/z = 451.0

1,3-dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (6)

¹H NMR (500 MHz, CDCl₃): δ ppm 3.64-3.53 (m, 2H), 1.66 – 1.57 (m, 2H), 1.35-1.18 (m, 10H), 0.89 – 0.84 (m, 3H). ¹³C (125 MHz): δ 160.35, 134.76, 112.89, 38.81, 31.75, 29.09, 28.23, 26.77, 22.60, 14.06. Melting Range: 104 - 108 °C. GC-MS t = 15.51 minutes, m/z = 423.0

2,6-bis(trimethylstannyl)-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (7)

Details related to the synthesis and characterization of 7 can be found in *Macromolecules*, **2008**, 41, 6012-6018.

Representative procedure for the polymerizations:

Copolymer P1: Compound 7 (350 mg, 0.453 mmol), compound 4 (191.73 mg, 0.453 mmol), Pd2(dba)₃ (2 mol %) and P(o-tol)₃ (8 mol %) were cycled and subsequently dissolved in 8 mL of dry chlorobenzene. The mixture was stirred for 36 hours at 110 °C. A strongly complexing ligand (N,N-Diethylphenylazothioformamide, CAS# 39484-81-6) was then stirred with the polymer to remove any residual catalyst before being precipitated into methanol (200 mL). The precipitate was filtered through a Soxhlet thimble and purified via Soxhlet extraction for 12 hours with methanol, 2 hours with hexanes and finally was collected with chloroform. The chloroform solution was then concentrated by evaporation and precipitated into methanol (200 mL) and filtered off as a dark purple solid (274 mg).

SEC analysis: Mn = 42 kDa, Mw = 105 kDa, PDI = 2.5.

Device Fabrication:

All devices were fabricated on ITO-coated glass substrates (pre-patterned, R = 20 Ω^{-1} , Thin Film Devices, Inc.). A thin-layer (30-40 nm) of PEDOT:PSS (Baytron PH) was spin-coated onto UV-ozone treated ITO substrates at 4000 RPM for 40 s and then baked at 140 °C for 15 min in air. The photoactive layer containing the polymers (15 mg/ml) and fullerene (40 mg/ml) in different ratios was spun cast from chlorobenzene solution after passing through a 0.45 µm polytetrafluoroethylene filter. Different concentrations for the blend solutions were tested in order to obtain the optimized thicknesses. 1,8-Diodooctane (purchased from Sigma Aldrich, used as received) with 2% volume ratio for P1 and 1% volume ratio for P2 and P3 was then added to the solution and stirred overnight before spin-coating. The active layers were spin-coated inside a glove-box at 1200 rpm for 40 sec. The cathode, consisting of Ca (20nm) and Al (100 nm), was then thermally evaporated under vacuum ($\sim 10^{-7}$ torr) through a shadow mask defining an active device area of ~ 0.03 cm². The current-voltage (*J-V*) curves were measured using a Keithlev 2400 source-measure unit under AM 1.5 G solar illumination at 100 mW cm⁻² (1 sun) using a Thermal-Oriel 150W solar simulator. In order to optimize the various parameters for all three polymers (concentration, blend ratio and DIO percentage) more than 300 devices were tested and experiments were repeated multiple times in order to check the reproducibility of the data. External quantum efficiency (EQE) values were obtained with a monochromator and calibrated with a silicon photodiode.

Instrumentation:

All small molecules were characterized by ¹H NMR (400 MHz or 500 MHz) and ¹³C NMR (100 MHz or 125 MHz) on a Bruker AVB-400, AVQ-400 or DRX-500.

For polymer molecular weight determination, polymer samples were dissolved in HPLC grade THF at a concentration of 1 mg/ml, briefly heated and then allowed to return to room temperature prior to filtering through a 0.2 m PVDF filter. Size exclusion chromatography (SEC) was performed with HPLC grade THF eluant at 1.0 mL/min by using three PLgel columns (7.5 x 300 mm) with pore sizes of 10^5 , 10^3 , and 500 Å, respectively. The particle size in columns was 5 µm and the columns were thermostatted at 35 °C. The SEC system consisted of a Waters 510 pump, a Waters 717 auto-sampler, a Waters 486 UV-Vis detector, and a Wyatt Optilab DSP differential refractive index detector. The apparent molecular weights and polydispersities (M_w/M_n) were determined with a calibration based on linear polystyrene standards using Empower software from Waters.

GC-MS data was collected on an Agilent 7890A GC system fitted with an Agilent HP-5 chromatography column. Helium carrier gas at a flow rate of 2.2 mL/min was used as the mobile phase. The sample inlet was set at 250 °C and a pressure of 8.8 PSI was used to load the vaporized compounds onto the column at a split ratio of 50:1. The oven temperature was equilibrated at 50 °C for 30 seconds, and then a temperature program was run as follows: 50 °C for 1 minute, ramp to 310 °C at 20 °C/min, hold at 310 °C for 5 minutes. The total run time is 19 minutes. An auxiliary heater is kept at 150 °C between the GC column and the Agilent 5975C VL MSD system (electron impact (EI)), in order to keep the separated compounds from precipitating from the He carrier gas at the MSD system inlet. MS information was collected by the 5975C system and analyzed with the Agilent Chemstation software.

UV-vis absorption spectra were recorded at room temperature using a Varian Cary 50 Conc UV-Visible spectrophotometer. The polymers were spin-coated on quartz substrates from chlorobenzene solutions (15 mg/ml). The thickness of the thin films was about 100 nm and a blank quartz substrate was used as reference.

Cyclic voltammograms were collected using a Solartron 1285 potentiostat under the control of CorrWare II software. A standard three electrode cell based on a Pt wire working electrode, a silver wire pseudo reference electrode (calibrated vs. Fc/Fc^+), and a Pt wire counter electrode was purged with nitrogen and maintained under a nitrogen atmosphere during all measurements. Acetonitrile was purchased anhydrous from Aldrich and tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. Polymer films were drop cast onto a Pt wire working electrode from a 1% (w/w) chloroform solution and dried under nitrogen prior to measurement.

Tapping-mode atomic force microscopy (AFM) was performed on a Veeco Nanoscope V scanning probe microscope.

Grazing-Incidence X-ray Scattering (GIXS) experiments were conducted at the Stanford Synchrotron Radiation Laboratory on beamline 11-3. The sample was irradiated at a fixed incident angle on the order of 0.1° and the GIXS patterns were recorded with a 2-D image detector (MAR345 image plate detector). GIXS patterns were recorded with an X-ray energy of

12.72 keV ($\lambda = 0.975$ Å). To maximize the intensity from the polymer sample, the incident angle (~0.1°-0.12°) was carefully chosen such that the X-ray beam penetrates the polymer sample completely but does not interact with the silicon substrate. Typical exposure times were 30-180 s. To produce identical surface condition for samples as those used for device fabrication, a thin layer (~40 nm) of PEDOT:PSS was cast onto silicon substrates that were pretreated with UV-ozone for 30 min. Then the GIXS samples were prepared by spin-coating the same polymer solutions used for fabricating devices onto the silicon substrates at 1200 RPM for 40 s.

Melting points were measured on an Electrothermal Melt-Temp apparatus.



M&M Figure 1. *J-V* curves of bulk-heterojunction solar cells fabricated from **P1**, **P2** and **P3** from CB solutions, with and without DIO, under illumination of AM 1.5G, 100 mW/cm².



M&M Figure 2. Tapping mode AFM images of the polymer: $PC_{61}BM$ blend film from CB/DIO solution in the optimized conditions. Topography is shown on the left with the corresponding phase image on the right. a) and b) **P1**: $PC_{61}BM$ 1:2 CB/DIO (98/2) (v/v); c) and d) **P2**: $PC_{61}BM$ 1:1.5 CB/DIO (99/1) (v/v); e) and f) **P3**: $PC_{61}BM$ 1:1.5 CB/DIO (99/1) (v/v).

Active layer	V _{OC} [V]	J _{SC} [mA cm ⁻²]	FF[%]	PCE [%]
P1 :PC ₆₁ BM	0.86	-5.2	57.0	2.5
P1 :PC ₆₁ BM +2% DIO	0.87	-8.0	57.0	4.0
P2 :PC ₆₁ BM	0.81	-8.4	62.3	4.3
P2 :PC ₆₁ BM +1% DIO	0.81	-10.4	67.8	5.7
P3 :PC ₆₁ BM	0.86	-10.9	68.7	6.4
P3 :PCBM +1% DIO	0.85	-11.5	69.8	6.8

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Chapter 9

A Direct Route to Cyclic Organic Nanostructures via Ring-Expansion Metathesis Polymerization of a Dendronized Macromonomer

Abstract

Cyclic organic nanostructures were prepared via ring-expansion metathesis polymerization of a dendronized norbornene macromonomer. This strategy provides a direct, efficient route to nanoscale rings in a single operation. AFM imaging confirmed toroidal features, with diameters of approximately 35-40 nm.

1. Introduction

Controlling polymer topology presents challenging synthetic obstacles, as well as exciting opportunities for tuning macromolecular properties.¹ In particular, nanoscale molecular architectures with well-defined shapes and dimensions may provide significant advancements in areas such as drug delivery and nanotechnology. Over the past decade, breakthroughs in polymer syntheses have greatly increased the variety of macromolecular architectures that may be obtained. These architectures now include dendronized, cylindrical, star, hyperbranched, and cyclic polymers, as well as various block copolymers.^{2,3} However, the synthesis of circular nanostructures remains challenging, due in large part to the difficulty in preparing functionalized cyclic polymers.⁴ Furthermore, reliance on macrocyclization routes to cyclic polymers restricts the attachment of large side chains or dendrons to a postpolymerization step, and an efficient route to cyclic hybrid architectures of high purity is yet to be realized. Given recent developments in ring-expansion metathesis polymerization (REMP)⁵ and linear dendronized polymers,⁶ it follows that joining these two advances to achieve a direct, efficient route to cyclic organic nanostructures is logical.⁷

2. Results and Discussion

REMP utilizes Ru-based metathesis catalysts (Figure 1) capable of producing cyclic polymers directly from cyclic olefin monomers, thus avoiding linear polymeric synthons. Earlier studies revealed that N-heterocyclic carbene backbone saturation greatly increased overall catalyst activity, while the tether length influenced the relative rates of propagation versus catalyst release. With access to a range of catalyst activities, it was envisioned that REMP of dendronized MMs may achieve dendronized cyclic polymers in a single operation. In addition, REMP can produce high molecular weight (MW) cyclic polymers, a goal not easily accomplished using macrocyclization processes.



Figure 1. Structures of the cyclic REMP catalysts and dendronized macromonomer used in this study.

While the polymerization of sterically hindered MMs presents an inherent challenge, it was shown that 1 (Figure 1) could be efficiently polymerized via ROMP using a highly active Rubased metathesis catalyst. This approach to dendritic polymers is particularly attractive, in that

post-polymerization modifications are unnecessary, ensuring that complete dendron functionality is present along the polymer backbone.^{2c} The efficiency of REMP using 1, in combination with cyclic catalysts SC-5 and UC-6, was examined. Note: SC and UC are acronyms for Saturated Carbene and Unsaturated Carbene (referring to the N-heterocyclic carbene ligand) with a five and six carbon linker to the Ru metal center.

Saturated catalyst SC-5 was found to mediate REMP of 1, and key data are summarized in Table 1. In general, polymerizations required higher temperatures (55 °C) and higher loadings of $[1]_0/[SC-5]_0$ than used in previous studies involving cyclooctene monomers, which is ascribed to the steric bulk of MM 1.⁵ Interestingly, an inverse relationship between reaction concentration and degree of polymerization (DP) of polymer P1 was observed. Specifically, REMP of 1 ($[1]_0/[SC-5]_0 = 50:1$) at $[1]_0 = 0.05$, 0.10, 0.20, and 0.33 M resulted in polymers having DPs of 5840, 4510, 4330, and 2190, respectively (entries 1, 2, 5, and 6). Since each polymerization reached full monomer conversion, this trend suggests that the initiation rate increases more with increased reaction concentration than does the propagation rate. Additionally, because incomplete initiation is observed with catalyst SC-5, the increased reaction concentration essentially led to a greater number of growing polymer rings and therefore a lower average MW.

Increasing the ratio $[1]_0/[SC-5]_0$ resulted in incomplete monomer conversion due to catalyst death over the extended reaction periods. However, as expected, increased $[1]_0/[SC-5]_0$ ratios resulted in higher M_w values. Specifically, using $[1]_0/[SC-5]_0 = 100:1$ results in polymer P1 with $M_w = 4.47$ MDa (entry 3), whereas $M_w = 5.33$ MDa was obtained with $[1]_0/[SC-5]_0$ (entry 4). Notably, catalyst UC-6 efficiently polymerized 1 to >95% conversion at $[1]_0/[UC-6]_0 = 250:1$. These conditions provided P1 with an $M_w = 3.79$ MDa (entry 7).

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Entry	Catalyst	[1]₀ (M)	[1] ₀ /[C] ₀	<i>M</i> _w (MDa) [♭]	DP/1000	PDI ^b
1	SC-5	0.05	50	5.26	5.84	1.29
2	SC-5	0.10	50	4.06	4.51	1.25
3^{c}	SC-5	0.10	100	4.47	4.97	1.51
4^d	SC-5	0.10	200	5.33	5.92	1.49
5	SC-5	0.20	50	3.90	4.33	1.33
6	SC-5	0.33	50	1.97	2.19	1.17
7	UC-6	0.10	250	3.79	4.21	1.18

Table 1. REMP of 1 to give cyclic dendronized polymer P1.^a

^aUnless noted otherwise, reactions were conducted under dry N₂ and monitored via ¹H NMR spectroscopy until conversions were >90%. [1]₀ = initial concentration of 1; [C]₀ = initial catalyst concentration. ^bMolecular weight data obtained via GPC with multiangle laser light scattering. ^cMaximum conversion = 60%. ^dMaximum conversion = 39%.

Catalyst release and re-incorporation have been shown to guide the thermodynamically driven MW of REMP polymers.⁵ In the present case, catalyst re-incorporation and chain transfer are unlikely considering the steric bulk of MM **1**. Notably, the MW of **P1** did not change upon prolonged standing after 100% monomer conversion or upon injection of fresh catalyst into the reaction mixtures; this indicates that thermodynamic equilibration of ring sizes is not taking place. Furthermore, the MW of isolated **P1** did not increase upon treatment with additional **1**, suggesting that no significant amount of active Ru species remain in the cyclic polymer. Collectively these data suggest efficient, irreversible catalyst release and an absence of chain transfer events. These experiments provide an initial investigation into the kinetically controlled MW profile of REMP.

Visualization of the polymers via AFM was also performed.⁸ Samples of **P1** were prepared by spin-coating a 9 ng/mL solution of the polymer in CHCl₃ onto freshly cleaved mica. As shown in Figure 2, toroidal features were observed with external diameters of approximately 35 - 40 nm, heights ranging from 5 - 9 Å, and internal diameters of approximately 5 - 7 nm. Multiple rings were observed (Figure 2A) without any detectable linear polymers. Analysis of the line scans of the toroids revealed highly uniform profile features (Figure 2D). Considering the high DP values obtained for **P1**, the dimensions observed via AFM suggested that the polymer backbone is not fully extended and may be adopting a zigzag orientation.



Figure 2. (A) AFM images of **P1** (Table 1, entry 7) on mica. (B) 3-D plot of toroidal feature. (C) Three toroids from image (A). (D) Line scans of toroids in image (C).

For comparison, we also examined linear analogues via AFM. Because the high DPs obtained via REMP were difficult to achieve using acyclic ROMP catalysts, we investigated ring opening of **P1** via sonication. Given that polymer chain scission can be induced via ultrasound⁹ and that the steric congestion may weaken the backbone of **P1**, we subjected a solution of cyclic polymer $(M_w = 2.99 \text{ MDa}, 1 \text{ mg/mL} \text{ in THF})$ to ultrasound irradiation for 30 min to yield **P1**_{son}. GPC analysis of **P1**_{son} revealed $M_w = 959 \text{ kDa}$, which suggests that chain scission accompanied ring opening. In addition, **P1**_{son} displayed shorter elution times at the same MW, in comparison with **P1**, consistent with linear and cyclic topologies, respectively (Figure 3).¹⁰ AFM imaging of **P1**_{son} revealed features consistent with a linear topology (Figure 4). Notably, some features resembled those of the cyclic polymers in diameter and shape; however, these did not appear toroidal, as no central void was observed. This may be ascribed to aggregation, which is more commonly observed upon AFM imaging of the linear polymers in comparison with cyclic **P1**.



Figure 3. GPC data for P1 (black) and P1_{son} (blue): normalized refractive index detector intensities (solid lines) and M_w values (dashed lines) vs retention times.



Figure 4. AFM images of $P1_{son}$ prepared as described above. Scale bars = 100 nm. There are no observable toroidal structures.

3. Conclusions

The first direct synthesis of cyclic dendronized polymers via REMP of a dendronized macromonomer was demonstrated. AFM imaging has confirmed the cyclic topology, revealing uniform cyclic features with no detectable linear polymer contaminants. The kinetically controlled molecular weight profiles and relative initiation versus propagation rates of REMP resulted in polymer M_w values that increased with decreasing initial concentrations. Despite the steric challenges inherent to the polymerization of these dendronized monomers, very high molecular weights were achieved for this novel class of hybrid macromolecules.

4. Methods and Materials

Cyclic catalysts **SC-5** and **UC-6** and macromonomer **1** were prepared as previously described and stored in a N₂-filled glove-box.^{5,6} C₆D₆ was obtained from a solvent purification column¹¹ and stored in a N₂-filled glove-box. All polymerization reactions were conducted using dry, degassed solvents under N₂ atmosphere. Gel permeation chromatography (GPC) was carried out in THF on two PLgel 10 m mixed-B LS columns (Polymer Labs) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). Molecular weights were determined from light scattering and considered to be absolute. Atomic force microscopy was performed using a Veeco (Digital Instruments) Multimode microscope with a Nanoscope V controller. Imaging was performed in semi-contact (tapping) mode using Veeco RTESP tips. AFM samples were prepared by spin-coating 300 μ L of a solution of **P1** in CHCl₃ onto freshly cleaved mica at 1000 rpm for 18 seconds. Sonicated polymer samples were prepared for imaging by sonicating the same **P1** solution used for cyclic imaging for 30 seconds, and then a sample was prepared and imaged following the same protocol for cyclic samples.

Representative Polymerization Procedure. In a N₂-filled glove-box, a screw-cap NMR tube was charged with macromonomer **1** (126 mg, 0.14 mmol) and C₆D₆ (0.65 mL). The NMR tube was sealed with a septum-lined screw cap and placed in an oil bath at 55 °C until complete macromonomer dissolution was achieved. A stock solution of cyclic catalyst **SC-5** (0.06 M in C₆D₆) was prepared and 50 L of this solution was injected into the NMR tube containing **1**. The reaction solution was maintained at 55 °C and monitored by ¹H NMR spectroscopy. Upon completion, the solution was added dropwise into MeOH (15 mL), causing precipitation of polymer **P1**. The product was isolated via vacuum filtration and dried under high vacuum to provide 122 mg (97% yield) of **P1**.

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