# CHEMISTRY OF MATERIALS

# Influence of Structural Variation on the Solid-State Properties of Diketopyrrolopyrrole-Based Oligophenylenethiophenes: Single-Crystal Structures, Thermal Properties, Optical Bandgaps, Energy Levels, Film Morphology, and Hole Mobility

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**Supporting Information** 

**ABSTRACT:** Five new compounds, based on diketopyrrolopyrrole (DPP) and phenylene thiophene (PT) moieties, were synthesized to investigate the effect of structural variations on solid state properties, such as single-crystal structures, optical absorption, energy levels, thermal phase transitions, film morphology, and hole mobility. The molecular structures were modified by means of (i) backbone length by changing the number of thiophenes on both sides of DPP, (ii) alkyl substitution (*n*-hexyl or ethylhexyl) on DPP, and (iii) the presence of an *n*-hexyl group at the end of the molecular backbone. These DPP-based oligophenylenethiophenes were systematically characterized by UV–visible spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), cyclic voltammetry (CV), ultraviolet photoelectron spectroscopy (UPS), atomic force microscopy (AFM), and hole-only diodes. Single-crystal structures were provided to probe insight into structure–property relationships at a molecule level resolution. This work demonstrates the



significance of alkyl substitution as well as backbone length in tuning material's solid-state properties. **KEYWORDS:** diketopyrrolopyrrole, oligophenylenethiophene, structure–property relationships, single-crystal structure,

#### ■ INTRODUCTION

molecular packing, conjugated molecule

Bulk heterojunction (BHJ) organic solar cells, using conjugated polymers<sup>1-10</sup> or small molecules<sup>11-13</sup> as electron donors and fullerene derivatives as electron acceptors, have drawn much attention due to their potential as low-cost, flexible, and largearea renewable energy sources. To function as effective electron donors for high-performance BHJ organic solar cells, materials should exhibit broad absorption extending to the near-infrared region of the solar spectrum for light harvesting, high hole mobility for facile charge transport, energy levels well matched to those of electron acceptors for efficient charge separation and large open circuit voltage, and desirable phase separation to form continuous percolation pathways for charge transport and collection. A thorough understanding of structure–property relationships in the solid state is essential for developing materials to fulfill these requirements.

By a judicious design of molecular structures combined with material processing and device engineering, BHJ solar cells using a blend of a conjugated polymer and fullerene derivative, have reached power conversion efficiency (PCE) over 8%.<sup>14–20</sup> However, systematically elucidating structure–property relationships is challenging for conjugated polymers due to inherent polydispersity, batch-to-batch variation, and indistinct

intermolecular packing. For example, solar cell characteristics may change considerably when the utilized conjugated polymer has inconsistent molecular weights and polydispersity.<sup>21,22</sup> In addition, the end group effects of conjugated polymers should be considered, <sup>23,24</sup> which makes the investigation of structural variations complicated.

Solution processable small molecule donor materials have advantages over polymers in terms of well-defined structure, monodisperse molecular weight, and convenient purification methods. These assets allow for a clear understanding of structure–property relationships. BHJs comprising small molecule/fullerene derivatives have been developed rapidly over past few years, and small molecular donor materials with numerous structures have achieved comparable device performance with PCEs up to 7%.<sup>25–32</sup> Diketopyrrolopyrrole (DPP)based materials have demonstrated great potential as donor materials due to their desirable properties such as broad optical absorption, chemical and thermal stability, and ease of synthesis and modification.<sup>25,26,33–36</sup> Solution processed BHJ solar cells

Received:September 22, 2011Revised:April 22, 2012Published:May 4, 2012

based on DPP-containing small molecules have achieved high PCEs of up to 4.4%;<sup>35</sup> however, a systematic study of molecular donors especially DPP-based materials to establish structure—property relationships has not been investigated. This investigation of structure effects on the material's basic properties is critical not only for further developing DPP-based donor materials but also for the rational design of other small molecular donor materials.

In this work, we report the synthesis and characterizations of a series of DPP-based oligophenylenethiophenes focusing on structural effects on materials' properties such as molecular packing, thermal transitions, optical bandgaps, energy levels, film morphology, and hole mobility. The chemical structure of these DPP-based oligophenylenethiophenes is successfully varied by tuning (i) conjugated backbone length by changing the number of thiophene rings on both sides of DPP, (ii) alkyl substitution (*n*-hexyl or ethylhexyl) on DPP, and (iii) the presence of *n*-hexyl groups at the end of the rigid molecular backbone. In the solid state, both conjugated backbone and alkyl substitution significantly affect materials' various physical properties. Single-crystal structures of these compounds are provided as an efficient platform to understand these structural effects at a molecular level.

#### EXPERIMENTAL SECTION

**Material Synthesis.** 5-Hexyl-2-thiophene boronic acid pinacol ester, 2,2'-bithiophene-5-boronic acid pinacol ester, and 5-hexyl-2,2'-bithiophene-5'-boronic acid pinacol ester were purchased from Sigma-Aldrich Chemical Co. and used as received. Other chemicals and solvents were used as received from commercial sources without further purification. Tetrahydrofuran (THF) was distilled over sodium/benzophenone. 3,6-Bis(4-bromophenyl)-2,5-dihydropyrrolo-[3,4-c]pyrrolo-1,4-dione, 1, was synthesized following the previously published procedure.<sup>33</sup>

**2,5-Dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrolo-1,4-dione (2a).** To a solution of **1** (5.0 g, 11 mmol) in *N*,*N* dimethylformamide (DMF) (50 mL) were added 1-bromohexane (7.4 g, 45 mmol) and cesium carbonate (11 g, 34 mmol) at 40 °C. After stirring for 24 h, the reaction mixture was filtered to remove solid. The filtrate was extracted with chloroform and recrystallized from methanol to yield red needle-like crystal (4.1 g, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.66 (s, 8H), 3.70 (t, 4H, *J* = 7.6 Hz), 1.58 (m, 4H), 1.19 (m, 12H), 0.83 (t, 6H, *J* = 6.8 Hz).

**2,5-Dihexyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]-pyrrole-1,4-dione (2b).** The procedure for the synthesis of **2a** was followed to prepare **2b** using 2-ethylhexyl bromide (3.5 g, 18 mmol) instead of 1-bromohexane. The crude product was purified by column chromatography on a silica gel using gradient solvent with dichloromethane/hexane from 1/1 to 2.5/1 (v/v) to yield in 22% (0.66 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.65 (s, 8H), 3.72 (d, 4H, J = 4.4 Hz), 1.45 (m, 2H), 1.08–1.20 (m, 16H), 0.81 (t, 6H, J = 6.4 Hz), 0.73 (t, 6H, J = 7.2 Hz).

**5-Hexyl-2,2':5',2"-terthiophene (4).** To a mixture of 2-bromothiophene (1.56 g, 9.57 mmol), 5-hexyl-2,2'-bithiophene-5'-boronic acid pinacol ester (3.0 g, 8.0 mmol), tri(dibenzylidene-acetone) palladium (0)  $(Pd_2(dba)_3)$  (0.15 g, 0.17 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.18 g, 0.65 mmol), and potassium phosphate (14 g, 64 mmol) was added degassed THF/water (30 mL/ 3 mL). After stirring under argon at 80 °C overnight, the reaction mixture was poured into methanol. The crude product was collected by filtration and purified by column chromatography on a silica gel with hexane to obtain 4 (2.1 g, 81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.21 (d, 1H, *J* = 4.0 Hz), 7.16 (d, 1H, *J* = 2.4 Hz), 7.06 (d, 1H, *J* = 3.6 Hz), 7.03 (m, 3H), 6.69 (d, 1H, *J* = 3.2 Hz), 2.79 (t, 2H, *J* = 8.0 Hz), 1.68 (quintet, 2H), 1.28–1.44 (m, 6H), 0.90 (t, 3H, *J* = 7.2 Hz).

5-Hexyl-2,2':5',2"-terthiophene-5"-boronic Acid Pinacol Ester (5). To a solution of 4 (1.8 g, 5.4 mmol) in 45 mL of THF was added *n*-BuLi (2.6 mL, 6.5 mmol, 2.5 M in hexane) dropwise at -78 °C. After stirring for 30 min at -78 °C, the solution was warmed to room temperature and stirred for 1 h. Then, the mixture was cooled to -78 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dixoaborolane (1.5 g, 8.1 mmol) was added at once. The mixture was warmed to room temperature and stirred overnight. After reaction was quenched with water, the organic layer was extracted by ethyl acetate and dried over magnesium sulfate. After solvent was removed under reduced pressure, the crude product was purified by column chromatography with 7% acetone in hexane to obtain **5** (1.9 g, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.53 (d, 1H, J = 2.8 Hz), 7.22 (d, 1H, J = 3.6 Hz), 7.12 (d, 1H, J = 4.0 Hz), 6.99 (t, 2H, J = 4.0 Hz), 6.69 (d, 1H, J = 2.8 Hz), 2.79 (t, 2H, J = 7.2 Hz), 1.68 (quintet, 2H), 1.29–1.41 (m, 18H), 0.90 (t, 3H, J = 6.8 Hz).

2,5-Dihexyl-3,6-bis[4-(5-hexylthiophene-2-yl)phenyl]pyrrolo[3,4-c]-pyrrole-1,4-dione, C6PT1C6. To a mixture of 2a (0.50 g, 0.81 mmol), 5-hexyl-2-thiophene boronic acid pinacol ester (0.60 g, 2.0 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.037 g, 0.041 mmol), tri-tertbutylphosphonium tetrafluoroborate (0.071 g, 0.24 mmol), and potassium phosphate (2.8 g, 13 mmol) was added into degassed THF/ water (27 mL/2.7 mL). After stirring under argon at 80 °C overnight, the reaction mixture was poured into methanol. The crude product was collected by filtration and purified by column chromatography on a silica gel with gradient chloroform/hexane from 2/1 to 5/1 (v/v) to obtain C6PT1C6 (0.46 g, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.86 (d, 4H, J = 8.8 Hz), 7.72 (d, 4H, J = 7.6 Hz), 7.26 (d, 2H, J = 4.0 Hz), 6.80 (d, 2H, J = 3.6 Hz), 3.79 (t, 4H, J = 7.6 Hz), 2.84 (t, 4H, J = 7.6 Hz), 1.60-1.77 (m, 8H), 1.18–1.45 (m, 24H), 0.90 (t, 6H, J = 6.8 Hz), 0.84 (t, 6H, J = 6.8 Hz). Anal. Calcd for C<sub>50</sub>H<sub>64</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> (%): C, 76.10; H, 8.17; N, 3.55. Found: C, 76.20; H, 8.20; N, 3.67.

**2,5-Dihexyl-3,6-bis[4-(5-hexyl-2,2'-bithiophene-5 yl)-phenyl]pyrrolo[3,4-c]-pyrrole-1,4-dione, C6PT2C6.** The procedure for the synthesis of **C6PT1C6** was followed using 5-hexyl-2,2'-bithiophene-5'-boronic acid pinacol ester (0.92 g, 2.4 mmol), instead of 5-hexyl thiophene boronic acid pinacol ester, to yield in 91% (0.85 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.88 (d, 4H, J = 8.4 Hz), 7.74 (d, 4H, J = 7.2 Hz), 7.33 (d, 2H, J = 3.6 Hz), 7.10 (d, 2H, J = 4.0 Hz), 7.05 (d, 2H, J = 3.2 Hz), 6.72 (d, 2H, J = 3.6 Hz), 3.80 (t, 4H, J = 7.6 Hz), 2.81 (t, 4H, J = 7.6 Hz), 1.60–1.75 (m, 8H), 1.18–1.45 (m, 24H), 0.90 (t, 6H, J = 6.8 Hz), 0.84 (t, 6H, J = 6.4 Hz). Anal. Calcd for C<sub>58</sub>H<sub>68</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub> (%): C, 73.06; H, 7.19; N, 2.94. Found: C, 73.10; H, 7.13; N, 3.04.

**2,5-Dihexyl-3,6-bis[4-(5-hexyl-2,2':5',2"-terthiophene-5"-yl)phenyl]pyrrolo[3,4-c]-pyrrole-1,4-dione, C6PT3C6.** The procedure for the synthesis of **C6PT1C6** was followed using 5-hexyl-2,2':5',2"-terthiophene-5"-boronic acid pinacol ester (0.90 g, 2.0 mmol), instead of 5-hexyl thiophene boronic acid pinacol ester, to yield in 78% (0.68 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.90 (d, 4H, J = 8.4 Hz), 7.75 (d, 4H, J = 8.4 Hz), 7.36 (d, 2H, J = 4.0 Hz), 7.17 (d, 2H, J = 3.6 Hz), 7.13 (d, 2H, J = 3.6 Hz), 7.03 (quartet, 4H), 6.71 (d, 2H, J = 3.6 Hz), 3.81 (t, 4H, J = 7.6 Hz), 2.81 (t, 4H, J = 7.6 Hz), 1.61–1.74 (m, 8H), 1.20–1.42 (m, 24H), 0.90 (t, 6H, J = 6.4 Hz), 0.84 (t, 6H, J = 7.0 Hz). Anal. Calcd for C<sub>66</sub>H<sub>72</sub>N<sub>2</sub>O<sub>2</sub>S<sub>6</sub> (%): C, 70.92; H, 6.49; N, 2.51. Found: C, 71.10; H, 6.45; N, 2.70.

**2,5-Dihexyl-3,6-bis[4-(5-hexyl-2,2'-bithiophene-5-yl)phenyl]pyrrolo[3,4-c]-pyrrole-1,4-dione, EHPT2C6.** The procedure for the synthesis of C6PT1C6 was followed, using 2b (0.58 g, 0.87 mmol) and 5-hexyl-2,2'-bithiophene-5'-boronic acid pinacol ester (0.81 g, 2.2 mmol) instead of 2a and 5-hexyl thiophene boronic acid pinacol ester to yield in 86% (0.75 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.83 (d, 4H, J = 8.4 Hz), 7.71 (d, 4H, J = 8.4 Hz), 7.30 (d, 2H, J = 3.6Hz), 7.08 (d, 2H, J = 4.0 Hz), 7.04 (d, 2H, J = 3.6 Hz), 6.71 (d, 2H, J = 3.6 Hz), 3.80 (d, 4H, J = 7.6 Hz), 2.81 (t, 4H, J = 7.6 Hz), 1.70 (quintet, 4H), 1.30–1.43 (m, 12H), 1.03–1.28 (m, 16H), 0.91 (t, 6H, J = 6.8 Hz), 0.70–0.81 (m, 12H). Anal. Calcd for C<sub>62</sub>H<sub>76</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub> (%): C, 73.76; H, 7.59; N, 2.77. Found: C, 74.00; H, 7.40; N, 2.89.

**2,5-Dihexyl-3,6-bis[4-(2,2'-bithiophene-5-yl)phenyl]pyrrolo-**[**3,4-c]-pyrrole-1,4-dione, C6PT2.** The procedure for the synthesis of **C6PT1C6** was followed using 2,2'-bithiophene-5'-boronic acid pinacol ester (0.89 g, 3.1 mmol), instead of 5-hexyl thiophene boronic Chart 1. Molecular Structures of All DPP-Based Oligophenylenethiophenes



acid pinacol ester to yield in 78% (0.75 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.88 (d, 4H, J = 8.4 Hz), 7.74 (d, 4H, J = 8.4 Hz), 7.34 (d, 2H, J = 4.0 Hz), 7.24 (quartet, 4H), 7.18 (d, 2H, J = 3.6 Hz), 7.06 (quartet, 2H), 3.80 (t, 4H, J = 7.6 Hz), 1.66 (quintet, 4H), 1.18–1.32 (m, 12H), 0.84 (t, 6H, J = 6.4 Hz). Anal. Calcd for C<sub>46</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub> (%): C, 70.37; H, 5.65; N, 3.57. Found: C, 70.40; H, 5.54; N, 3.66.

Characterization. <sup>1</sup>H NMR spectra were recorded with a 400 MHz spectrometer (Varian, ASM-100). Elemental analyses were performed by the UC Santa Barbara Marine Science Institute Analytical Laboratory. Thermal properties of the compounds were determined by differential scanning calorimetry (DSC) at 10 °C/min under N<sub>2</sub> purge (TA Instrument, Q20). Thermogravimetric analyses (TGA) were carried out at a heating rate of 10 °C/min under N<sub>2</sub> purge (Mettler Toledo, TGA/SDTA851e). UV-vis absorption spectra were measured at a concentration at  $0.9-2.2 \times 10^{-5}$  M in chloroform (CHCl<sub>3</sub>). UV-vis absorption spectra were collected with a UV-vis spectrophotometer (Beckman Coulter, DU 800). Thin films for UV-vis absorption spectra were prepared by spin coating on quartz substrate. Atomic force microscopy (AFM) images were collected in air under ambient conditions using the MultiMode scanning probe microscope and the controller IIIa (BrukerNano). Silicon probes with resonant frequencies of 75 kHz (Budget Sensors) were used for tapping mode AFM measurements. The hole mobility for pristine films was measured by fabricating a hole-only diode with a device architecture of ITO/PEDOT:PSS/DPP-based oligophenylenethiophene/Au. PEDOT:PSS is poly(3,4-ethylenedioxythiophene) poly-(styrenesulfonate). Current density as a function of voltage was recorded on a Keithly 4200 in a nitrogen atmosphere. The value of mobility was extracted by fitting the current density-voltage curve with a Mott-Gurney relationship (space charge limited current, SCLC). Cyclic voltammetry (CV) was performed using an electrochemical analyzer (CH Instrument, CHI730B) to study the electrochemical properties of the materials in dilute solution. The experiment was carried out in a chloroform solution of 0.1 M tertra-nbutylammonium hexafluorophosphate (Bu4NPF6) at a scan rate of 50 mV/s using a glassy carbon electrode as a working electrode, platinum wire as a counter electrode, and Ag/Ag<sup>+</sup> electrode as a reference electrode. The electrochemical potential was calibrated against Fc/Fc<sup>+</sup>, whose oxidation potential was located at 0.24 V to the Ag/Ag<sup>+</sup>. The energy levels of HOMO and LUMO were calculated according to the equations HOMO =  $-(E_{ox} + 4.56)$  (eV) and LUMO =  $-(E_{red} + 4.56)$  (eV), where  $E_{ox}$  and  $E_{red}$  are oxidation potential onset and reduction potential onset versus Ag/Ag<sup>+</sup>, respectively. For ultraviolet photoelectron spectroscopy (UPS), 75 nm thick Au films were thermally deposited onto precleaned Si substrates with a thin native oxide, followed by spin coating of the 2 mg/mL of small molecules in chloroform at 3000 rpm in the glovebox under nitrogen.

The UPS measurement was carried out, using a He I ( $h\nu = 21.2 \text{ eV}$ ) source, equipped with a hemispherical electron energy analyzer (Kratos Ultra Spectrometer).

Single-crystal X-ray diffraction was collected on a Bruker Kappa Apex II diffractometer using a graphite monochromator with a Mo K $\alpha$ X-ray source ( $\lambda = 0.71073$  Å). The crystals were mounted on a nylon loop under Paratone-N oil, and all data were collected at 100 K using an Oxford nitrogen gas cryostream system. Data collection, cell parameter determination, data integration, and parameter refinement were performed using Apex2 software (V2011). Absorption correction of the data was applied using SADABS software. Structure determination was done using direct method and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom of attachment. Structure solution and refinement were performed using SHELXTL. Powder X-ray diffraction was recorded on a Bruker D8 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). The powder samples were prepared by scratching thin films that were casted from chloroform solutions.

#### RESULTS AND DISCUSSION

Material Design and Synthesis. The molecular structure of each compound is displayed in Chart 1. The compounds were assigned names with a form of APTBC based on their topologies, where A refers to the alkyl substitution on DPP, PT represents the phenylene thiophene linkage, B refers to the number of thiophene rings, and C denotes the presence or absence of an alkyl chain at the end of the terminal thiophene rings. The synthetic routes for these compounds are illustrated in Scheme 1. Diphenyl-DPP precursor (1) was prepared according to a reported literature.<sup>33</sup> Precursors 2a and 2b were synthesized via N-alkylation of 1. This process has been reported to suffer a lower yield (less than 50%),<sup>37,38</sup> compared to the highly efficient N-alkylation of dithienyl-DPP.<sup>39</sup> An enhanced yield (up to 60%) was achieved by carrying out the reaction with Cs<sub>2</sub>CO<sub>3</sub> as a base catalyst at 40 °C when using 1-bromohexane for the N-alkylation; however, the yield still remains less than 30% when using 2-ethylhexyl bromide. The final products were achieved by reacting precursor 2a or 2b with oligothiophene boronates via a palladium-catalyzed Suzuki coupling. The yield of this reaction was found to be insensitive to the base used, such as K<sub>2</sub>CO<sub>3</sub> and K<sub>3</sub>PO<sub>4</sub>, but significantly affected by solvents. A THF/water (10/1, v/v) mixing solvent can give optimal yields up to 90%.

Scheme 1. Synthesis Routes for DPP-Based Oligophenylenethiophenes<sup>a</sup>



<sup>*a*</sup>Conditions: (i) cesium carbonate, alkylbromide, DMF, 40 °C; (ii) appropriate thiophene boronic acid pinacol ester,  $Pd_2(dba)_3$ ,  $HP('Bu)_3BF_4$ ,  $K_3PO_4$ , THF; (iii) 2-bromothiophene,  $Pd_2(dba)_3$ ,  $HP('Bu)_3BF_4$ ,  $K_3PO_4$ , THF; (iv) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

crystal	C6PT1C6	C6PT2C6	C6PT3C6	EHPT2C6	C6PT2
empirical formula crystal habit, color	C <sub>50</sub> H <sub>64</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub> plate, red	C <sub>58</sub> H <sub>68</sub> N <sub>2</sub> O <sub>2</sub> S <sub>4</sub> plate, red	C <sub>66</sub> H <sub>72</sub> N <sub>2</sub> O <sub>2</sub> S <sub>6</sub> plate, dark red	C <sub>62</sub> H <sub>76</sub> N <sub>2</sub> O <sub>2</sub> S <sub>4</sub> needle, light red	C <sub>46</sub> H <sub>44</sub> N <sub>2</sub> O <sub>2</sub> S <sub>4</sub> plate, red
crystal size (mm <sup>3</sup> ) crystal system	$1.0 \times 1.0 \times 0.3$ monoclinic	$0.4 \times 0.3 \times 0.1$ monoclinic	$0.4 \times 0.1 \times 0.05$ monoclinic	$0.5 \times 0.4 \times 0.2$ monoclinic	$0.4 \times 0.2 \times 0.05$ monoclinic
space group	$P2_1/c$	$P2_{1}/c$	$P2_{1}/c$	C2/c	$P2_1/c$
a (Å)	15.215(3)	18.236(1)	19.462(2)	57.201(8)	13.414(2)
b (Å)	14.797(3)	14.338(1)	15.099(1)	10.523(2)	14.427(2)
c (Å)	10.103(2)	9.876 (1)	9.847 (1)	9.102(1)	10.079(2)
α (°)	90.00	90.00	90.00	90.00	90.00
$\beta$ (°)	101.369(4)	96.891(5)	96.944(6)	97.505(3)	92.804(9)
γ (°)	90.00	90.00	90.00	90.00	90.00
Ζ	2	2	2	4	2
R factor	5.85	5.40	5.49	6.3	8.5
density	1.18	1.24	1.29	1.23	1.34

Table 1. Crystallographic Data for DPP-Based Oligophenylenethiophenes

Crystallography. To gain insight into how molecular structures affect the material's properties in the solid state, single-crystal structures of these DPP-based oligophenylthiophenes were investigated. The single crystals of these compounds were successfully grown by an interface diffusion method, using chloroform and acetone as the good solvent and nonsolvent, respectively. Table 1 summarizes the basic information of these single-crystal structures. The details can be viewed from the crystallographic information files (CIFs) (Supporting Information). As shown in Table 1, all DPP-based oligophenylthiophenes have the monoclinic crystal system regardless of different unit cell parameters (axis length and angle). Moreover, all compounds with *n*-hexyl side chains attached on DPP have the same space group  $(P2_1/c)$  and a similar molecular packing style in their unit cells as shown in Figure 1(a)-(c). The compound with a branched ethylhexyl side chains (EHPT2C6) has a C2/c space group and a difference packing style as shown in Figure 1(d)-(f). Increasing the backbone length (i.e., from **C6PT1C6** to **C6PT3C6**) and removing the end-capping *n*-hexyl groups (C6PT2C6 vs C6PT2) do not change their packing style; however, using branched side chains leads to a big difference in the intermolecular packing (Table 2).

Besides these packing styles, the intermolecular backbone overlapping can be revealed from their single-crystal structures. Table 2 provides a simple summary of the intermolecular backbone overlapping (area and distance) of all DPP-based oligophenylthiophenes. The overlapping areas are highlighted by red rectangles. Due to the nonplanar conformation of these compounds (vide infra), it is difficult to get the interplanar overlapping distances for entire molecules. For reference, the interplanar distances calculated from phenyl rings, which are parallel to each other and have the shortest overlapping distance, are listed in Table 2. For compound **EHPT2C6**, the interplanar distance is calculated from DPP rings because the overlapping only exists on the DPP moieties.

As shown in Table 2, when increasing the conjugated backbone length from C6PT1C6 to C6PT2C6, the overlapping area increases concomitantly; however, further increasing the backbone length from C6PT2C6 to C6PT3C6 does not lead to the corresponding enlargement in the overlapping area. A possible reason is the nonplanar conformations of these compounds. Compared to C6PT2C6, EHPT2C6 shows a significant effect from the side chains. The ethylhexyl groups substituted on the DPP ring dramatically reduce the intermolecular overlapping. In contrast, removing the end-capping *n*-hexyl groups (from C6PT2C6 to C6PT2) almost does not change the overlapping location but leads to a slight offset in vertical direction of overlapping. Comparing to the overlapping areas, the overlapping distances as listed in Table 2 are not sensitive to the molecular structures possibly because these overlapping distances are mainly calculated from stacked phenyl rings.



**Figure 1.** Two typical molecular packing styles observed in single crystals as illustrated by **C6PT1C6** ((a)–(c); a unit cell viewed from side (a), *a* axis (b), and *c* axis (c)) and **EHPT2C6** ((d)–(f); a unit cell viewed from side (d), *b* axis (e), and *c* axis (f)). Due to the chirality of the ethylhexyl side chains, only the mesomer of **EHPT2C6** was shown in the unit cell. All hydrogen atoms were omitted for clarity. Atoms of C, O, N, and S are shown in gray, red, cyan, and yellow, respectively.

Table 2. Intermolecular Backbone Overlapping Area and Distance of All DPP-Based Compounds Derived from Their Single-Crystal Structures

Name	Intermolecular backbone overlapping <sup>a</sup>	Interplane distance <sup>b</sup> (Å)
C6PT1C6	so to the second	3.28
C6PT2C6		3.26
C6PT3C6	00304040000	3.37
EHPT3C6		3.27°
С6РТ2	000000000000000000000000000000000000000	3.23

<sup>*a*</sup>The backbone overlapping is determined from their single-crystal structures. Images here show the stacked molecules as viewed orthogonally to the molecular backbones with red rectangles highlighting the overlapping area. All alkyl chains are simplified into methyl groups for clarity. <sup>*b*</sup>The interplanar distance is calculated from phenyl–phenyl rings. <sup>*c*</sup>Calculated from overlapped DPP rings.

Intramolecular conformation can also be obtained from the single-crystal structures of these DPP-based oligophenylthiophenes. Figure 2 shows a simplified molecular backbone structure of these DPP compounds with two primary  $\sigma$  bond linkages (DPP-phenyl linkage and phenyl-thiophene linkage). The dihedral angles of these two linkages ( $\varphi 1$  and  $\varphi 2$ ) obtained from single-crystal structures were listed in a table in Figure 2. Both  $\varphi 1$  and  $\varphi 2$  are not coplanar;  $\varphi 1$  has a larger value than  $\varphi 2$  for all compounds. Therefore, the molecular

R <sub>2</sub> $\phi^2$		S S R <sub>2</sub>
Name	φ1 (°)	φ2 (°)
C6PT1C6	26.2	22.8
C6PT2C6	23.7	10.2
C6PT3C6	25.1	16.5
EHPT2C6	37.6	17.4
C6PT2	26.2	14.2

**Figure 2.** Primary backbone structure (top) indicating two dihedral angles of DPP-phenyl ( $\varphi$ 1) and phenyl-thiophene ( $\varphi$ 2) linkages and a table (bottom) summary of  $\varphi$ 1 and  $\varphi$ 2 from single-crystal structures.

planarity is primarily dominated by  $\varphi 1$ . All *n*-hexyl-substituted compounds have very similar  $\varphi 1$  values  $(23-27^{\circ})$ , while the ethylhexyl-substituted compound (EHPT2C6) has a much larger  $\varphi 1$  (37.6°) indicating the least planarity among these compounds. The single-crystal structures clearly indicate effects of structural moieties in these DPP-based oligophenylenethiophenes. The phenyl groups incorporated in conjugated backbones lead to nonplanar conformation due to steric hindrance. Bulky alkyl side chains (2-ethylhexyl) attached on DPP further twist this nonplanar conformation, leading to a weak intermolecular  $\pi - \pi$  interaction. Therefore, EHPT2C6 should have a large optical bandgap and low charge carrier mobility in the solid state (vide infra).

Due to the polymorphism of crystals, the crystal structures solved from solution-grown single crystals can be different from the crystal structures existing in the polycrystalline films. To evaluate this possible difference, the thin film XRD of these compounds was compared with theoretical XRD patterns simulated from their single-crystal structures. As shown in Figure 3, the experimental peaks in a region of  $3-20^{\circ}$  match



**Figure 3.** Measured thin film XRD (a, c, e, g, and i) and corresponding simulated patterns (b, d, f, h, and j) of DPP-based oligophenylene-thiophenes.

well with simulated ones for these compounds. **EHPT2C6** and **C6PT2** films show very weak diffraction peaks in the region of  $3-20^{\circ}$ , indicating a low degree of crystallinity in the film state. In a wider angle region (> $20^{\circ}$ ), a deviation on peak positions can also be observed. This indicates a slight difference between molecular packing in the film state and single crystals. However, given this qualitative comparison, it can be concluded that the molecular packing in thin films is similar to that in single crystals. Surface morphology and charge carrier mobility of these films will be discussed later.

**Thermal Properties.** Generally, thermal properties of a material depend on its molecular weight and the strength of the intermolecular interactions. The thermal properties of these DPP-based oligophenylenethiophenes were evaluated by DSC. To remove the effect of thermal history, the third heating and cooling scan loop of each compound was employed to determine thermal transition temperatures. The DSC thermograms as shown in Figure 4 exhibit clear melting and crystallization phase



Figure 4. DSC thermograms of DPP-based materials with a scanning rate of 10  $^\circ C/min$  under  $N_2.$ 

transitions. The corresponding melting temperatures are listed in Table 3.

The effect of the conjugated backbone length is observed by comparing C6PT1C6, C6PT2C6, and C6PT3C6, which have

the same linear alkyl substitution both on DPP and at the end of the molecular backbone. As the conjugation length increases from C6PT1C6 to C6PT3C6, the melting temperature  $(T_m)$  is elevated from 181 to 263 °C, concomitantly with a strong tendency to crystallize during the cooling scan. The highest melting temperature of C6PT3C6 is mainly due to its highest molecular weight among the three compounds. While C6PT2C6 and C6PT3C6 show only one transition upon heating, C6PT1C6 shows two transitions at 125 and 181 °C, respectively. This double transition indicates a possible liquid crystal state of C6PT1C6. The smaller transition that occurs at low temperature is due to a liquid crystal phase transition. The liquid crystal phase disappears on other compounds probably because the ratio of flexible alkyl chain to rigid backbone that is required for the liquid crystal phase is reduced.

Changing the alkyl substitution on the compounds with the same conjugated backbone drastically affects the thermal properties, as clearly evidenced by C6PT2C6, EHPT2C6, and C6PT2. Compared to n-hexyl substitution on DPP (C6PT2C6), 2-ethylhexyl substitution (EHPT2C6) effectively reduces both  $T_{\rm m}$  (from 231 to 164 °C) and  $T_{\rm c}$  (from 194 to 77 °C). Unlike C6PT2C6 which has sharp and large melting and crystallization peaks, EHPT2C6 exhibits wide and small melting and crystallization peaks. This difference in phase transition is especially significant in the cooling scan in which EHPT2C6 has only a very tiny crystallization peak at 77 °C. Moreover, EHPT2C6 shows a cold crystallization peak at 70 °C upon heating. All these characteristics observed in EHPT2C6's thermogram indicate a low degree of crystallinity in the solid state, which is due to its inferior intermolecular  $\pi - \pi$  interaction as revealed from the single-crystal structure (Figure 1d-f and Table 2). Removing the alkyl chains at the end of the conjugated backbone (C6PT2C6 versus C6PT2) causes similar effects including the reduced  $T_{\rm m}$ , a broad crystallization peak, and cold crystallization upon heating. However, such effects are not as significant as the ones observed when replacing the *n*-hexyl substituent with 2-ethylhexyl (C6PT2C6 versus EHPT2C6) on DPP rings. In addition, compared to that of C6PT2C6, the  $T_{\rm m}$  of C6PT2 has not decreased but increases from 231 to 249 °C because both reduced flexible alkyl chains and intermolecular packing remained the same as shown in single-crystal structures.

The thermal stability of all the compounds was investigated by TGA at a heating rate of 10 °C/min under N<sub>2</sub>. The table lists 5% weight loss temperatures ( $T_d$ ) of these compounds determined from TGA curves (Figure S1, Supporting Information). Each compound exhibits high thermal stability with a  $T_d$  of greater than 410 °C.

**Solubility and Optical Properties.** The conjugated backbone length has a large impact on the solubility. As listed in Table 3, C6PT1C6 is soluble in CHCl<sub>3</sub> up to 228 mg/mL; however, adding thiophene rings (C6PT2C6 and C6PT3C6) reduces the solubility substantially to 11 and 1.5 mg/mL, respectively. Replacing the linear alkyl chain (C6PT2C6) with the ethylhexyl chain (EHPT2C6) increases the solubility to 53 mg/mL. Eliminating the terminal alkyl chain (C6PT2) also affects the solubility (6.3 mg/mL).

UV-vis absorption spectra in  $CHCl_3$  solution were obtained at 0.9–2.2 × 10<sup>-5</sup> M. Films were prepared by spin coating 1 mg/mL CHCl<sub>3</sub> solutions on quartz substrates. All absorption spectra are presented in Figure 5; the related optical data are summarized in Table 3.

Table 3. Op	ptical and	Thermal	Properties of	f DPP–Based	Oligopheny	lenethiophenes
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	solution <sup>a</sup>				$\operatorname{film}^b$						
name	$\lambda_{\max}$ (nm)	$\lambda_{\mathrm{onset}}$ (nm)	$E_{\rm g}^{\rm opt}  ({\rm eV})^c$	$\varepsilon (M^{-1} cm^{-1})$	$\lambda_{\max}$ (nm)	$\lambda_{\mathrm{onset}}$ (nm)	$E_{\rm g}^{\rm opt}  ({\rm eV})^c$	$T_{\rm m}  (^{\circ}{\rm C})^d$	$T_{\rm c}  (^{\circ}{\rm C})^d$	$T_{\rm d} (^{\circ}{\rm C})^e$	solubility (mg/mL) <sup>f</sup>
C6PT1C6	505	571	2.17	$3.2 \times 10^{4}$	582	629	1.97	181	143	411	228
C6PT2C6	521	591	2.09	$4.6 \times 10^{4}$	614	674	1.84	231	194	415	11
C6PT3C6	528	602	2.06	$5.6 \times 10^{4}$	608	667	1.86	263	229	425	1.5
EHPT2C6	514	584	2.12	$4.8 \times 10^{4}$	532	626	1.98	164	77	413	53
C6PT2	516	587	2.11	$4.4 \times 10^{4}$	554	671	1.85	249	184	422	6.3

<sup>a</sup>Measured in chloroform solution. <sup>b</sup>Cast from chloroform solution. <sup>c</sup>The optical bandgap calculated from  $E_g^{opt} = 1240/\lambda_{onset}$  in the absorption spectrum. <sup>d</sup>Melting point on heating scan by DSC under N<sub>2</sub>. <sup>e</sup>Temperature with 5% weight loss by TGA under N<sub>2</sub>. <sup>f</sup>In chloroform at room temperature determined by the method in ref 40.



**Figure 5.** Absorption spectra of all DPP-based oligophenylenethiophenes (C6PT1C6: black solid line; C6PT2C6: red dashed line; C6PT3C6: blue dash-dotted line; EHPT2C6: green dash-dot-dotted line; C6PT2: olive short dashed line) in (a) dilute CHCl<sub>3</sub> solution at a concentration of  $10^{-5}$  M and (b) as-cast films on a quartz plate.

Figure 5(a) shows the solution absorption spectra of all compounds in CHCl<sub>3</sub>. One absorption maximum is apparent in the range of 300–450 nm for the  $\pi$ – $\pi$ \* transition of the phenylenethiophene moiety, and the other absorption maximum in the 450–600 nm range is for the intramolecular charge transfer (ICT) transition. As the incorporated thiophene units increase from C6PT1C6 to C6PT2C6 and C6PT3C6, the wavelength of maxima absorption ( $\lambda_{max}$ ) shifts from 505 to 521 and 528 nm, respectively. However, the alkyl substitution on conjugated backbones has much less impact on spectral shift, which is demonstrated by the similar absorption of C6PT2C6, EHPT2C6, and C6PT2 in solution. Thus, the optical absorptions of dilute solutions of these compounds are determined mainly by the conjugated backbone.

Figure 5(b) displays the absorption spectra of all compounds in the film state. Compared with their absorption in solution, C6PT1C6, C6PT2C6, and C6PT3C6 exhibit a strong red shift (77–97 nm) on  $\lambda_{\rm max}$ . In addition, unlike the absorption spectra of dilute solutions which exhibit broad featureless absorption in the long-wavelength region, the film absorption of each compound shows a shoulder peak in the long-wavelength region. The red shift on  $\lambda_{\max}$  is due to strong intermolecular interactions and more planar conformation of the conjugated backbone in the solid state, which results in a longer effective conjugation length than in the solution state. The accompanied shoulder peaks result from vibronic coupling related to the solid-state packing.<sup>41</sup> Compared to C6PT2C6, EHPT2C6 shows a much smaller red shift (18 nm) on  $\lambda_{max}$  (532 nm) without a shoulder peak. The twisted conformation due to the presence of the ethylhexyl groups as revealed by its singlecrystal structure and the low crystallinity demonstrated by thinfilm XRD and DSC, which significantly reduce the effective conjugation length and intermolecular interactions, is the main reason for the weakest red shift, featureless absorption in the solid state, and a slightly larger optical bandgap. Similar to **EHPT2C6**, **C6PT2** also shows a weak red shift (38 nm) on  $\lambda_{max}$  from the solution to film state. The absence of straight alkyl substitution at the end of the conjugated backbone in **C6PT2** reduces intermolecular interactions in films leading to a loss of vibronic shoulder in the absorption. This observation agrees with DSC results that the material's crystallinity is reduced for **C6PT2** as compared to **C6PT2C6**.

For the compounds with *n*-hexyl substitutions on DPPs, an effective conjugation between DPP and thiophene moieties still exists when the dihedral angle is about  $25-27^{\circ}$  as revealed from their single crystals. A similar result was observed in polyfluorene derivatives in which the dihedral angle is about  $20^{\circ}$ .<sup>42</sup> The conjugation seems to be retarded when the dihedral angle is  $37^{\circ}$ , as demonstrated by **EHPT2C6** which has a much larger optical bandgap in the solid state, although the less intermolecular overlapping may also attribute to the large optical bandgap. In addition, compared with **C6PT3C6**, **C6PT2C6** has a larger optical bandgap in solution but a slightly narrower optical bandgap in the solid state probably due to its more planar conformation (smallest dihedral angle) and better intermolecular overlapping (shortest interplanar distance).

Annealing these films at 100 °C for 10 min reveals another remarkable effect of alkyl substitution, as shown in Figure S2 (Supporting Information); while no obvious change was observed with C6PT2C6, EHPT2C6 exhibits an enhanced absorption in the short-wavelength region (300–450 nm) and a decreased absorption in the long-wavelength region (450–600 nm). C6PT2 shows a red shift on  $\lambda_{max}$  as well as a shoulder peak, similar to the optical absorption of C6PT2C6. Such different annealing effects between C6PT2 and EHPT2C6 imply that the branched alkyl chains (2-ethylhexyl) on DPP have different impact on the conjugation length and molecular packing in solid state from terminal linear alkyl chains (*n*-hexyl).

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In addition to the thermal annealing, the effect of concentration on absorption spectra of as-cast films was investigated by comparison of films prepared from 0.5, 1.0, and 5.0 mg/mL solutions in chloroform. The related absorption spectra are provided in Figure S3 (Supporting Information). The **C6PT2C6** films prepared from higher concentrations show a slight increase of the aggregation (shoulder) peak at 613 nm and similar absorption onsets. **EHPT2C6** films prepared from higher concentrations show very similar spectral change as that observed in the annealed films: (1) the peak at 365 nm was shifted by 10 nm, and absorption intensity was increased, and (2) absorption at 550 nm was decreased (Figure S3, Supporting Information). In contrast to **C6PT2C6** and **EHPT2C6**, **C6PT2** exhibits weak concentration dependence of absorption spectra with nearly the same absorption maximum and onset.

**Energy Levels.** To determine the HOMO and LUMO levels of all compounds under different environments, cyclic voltammetry (CV, see Figure 6) and UPS measurements (see



Figure 6. Cyclic voltammograms of all DPP-based oligophenylenethiophenes in 0.1 M  $Bu_4NPF_6$  chloroform solution at a scan rate of 50 mV/s.

Figure S4, Supporting Information) were performed on the chloroform solutions and the films, respectively. The results are summarized in Table 4.

From the values of oxidation potential onset and reduction potential onset obtained by CV, HOMO and LUMO as well as electrochemical band gap ( $E_g^{ec}$ ) were calculated. As the number of thiophenes increases from **C6PT1C6** to **C6PT2C6** and **C6PT3C6**, the LUMO changes very slightly from -3.30 to -3.39 eV. **C6PT3C6** has a higher-lying HOMO (-5.19 eV) than **C6PT1C6** (-5.48 eV) and **C6PT2C6** (-5.46 eV). Similar results have been observed in DPP-based donor–acceptor

copolymers, in which the LUMO was determined by the DPP and the HOMO was dependent on the donor moiety.<sup>43</sup> The effect of alkyl substitution on energy levels in solution is negligible, as evidenced from C6PT2C6, EHPT2C6, and C6PT2. The energy levels in solution are largely determined by the conjugation length, which is consistent with the solution UV–vis absorptions.

To obtain energy levels in the solid state, UPS was used to determine the ionization potential (IP) of each compound. The optical band gap  $(E_g^{opt})$  was determined by the absorption onset and used to calculate the electron affinity (EA) from EA =  $E_g^{opt}$  – IIPI. Figure 7 shows the  $E_g^{opt}$ , IP, and EA of each



**Figure 7.** Optical band gap and energy levels of ionization potential (IP) and electron affinity (EA) of all DPP-based oligophenylenethiophenes. IP determined by UPS and EA obtained by EA =  $E_e^{\text{opt}} - |\text{IP}|$ .

compound. As the number of thiophenes increases from C6PT1C6 to C6PT2C6, the IP and EA are elevated, and the band gap decreases. Further addition of thiophenes (from C6PT2C6 to C6PT3C6) causes a much smaller change in energy levels. UPS measurements of C6PT1C6, C6PT2C6, and C6PT3C6 indicate that the electronic properties such as band gap, IP, and EA are saturated after the addition of two thiophenes on each side of the DPP (C6PT2C6). This observation is consistent with the film UV–vis spectra, where similar absorption onsets are observed for C6PT2C6 and C6PT3C6.

Comparison of the solid-state energy levels among C6PT2C6, EHPT2C6, and C6PT2 reveals remarkable effects of alkyl substitution. EHPT2C6 and C6PT2 possess deeper IPs and EAs than those of C6PT2C6. The absence of a straight alkyl chain at the end of the conjugated backbone almost does not change the bandgaps (1.84 vs 1.85 eV) but lowers the IP and EA levels, as shown for C6PT2C6 and C6PT2 (Table 4). In addition, replacing linear alkyl chains on the DPP with 2-ethylhexyl chains (EHPT2C6) leads to much deeper IP (5.49 versus 5.16 eV) and EA (3.51 versus 3.32 eV) than those of C6PT2C6. Considering the same conjugated backbone of C6PT2C6, EHPT2C6, and C6PT2, these variations in energy

Table 4. Energy Levels and Band Gaps of DPP-Based Oligophenylenethiophenes

			soluti	$\operatorname{film}^b$					
	$E_{\text{onset}}^{\text{ox}}$ (V) <sup>c</sup>	$E_{\text{onset}}^{\text{red}}$ (V) <sup>c</sup>	HOMO $(eV)^d$	LUMO $(eV)^d$	$E_{\rm g}^{\rm ec}~({\rm eV})^e$	$E_{g}^{opt} (eV)^{f}$	HOMO (eV) <sup>g</sup>	LUMO $(eV)^h$	$E_{\rm g}^{\rm opt} \ ({\rm eV})^f$
C6PT1C6	0.92	-1.26	-5.48	-3.30	2.18	2.17	-5.63	-3.66	1.97
C6PT2C6	0.90	-1.17	-5.46	-3.39	2.07	2.09	-5.16	-3.32	1.84
C6PT3C6	0.63	-1.26	-5.19	-3.30	1.89	2.06	-5.24	-3.38	1.86
EHPT2C6	0.86	-1.27	-5.42	-3.29	2.13	2.12	-5.49	-3.51	1.98
C6PT2	0.90	-1.24	-5.46	-3.32	2.14	2.11	-5.37	-3.52	1.85

<sup>*a*</sup>Measured in chloroform solution. <sup>*b*</sup>Cast from chloroform solution. <sup>*c*</sup>Determined by cyclic voltammetry to Ag/Ag<sup>+</sup>. <sup>*d*</sup>Calibrated based on the oxidation potential of Fc/Fc<sup>+</sup>. <sup>*e*</sup>E<sub>g</sub><sup>ec</sup> = LUMO – HOMO. <sup>*f*</sup>The optical band gap calculated from  $E_g^{opt} = 1240/\lambda_{onset}$  in the absorption spectrum. <sup>*g*</sup>Measured by UPS. <sup>*h*</sup>EA obtained by EA =  $E_g^{opt}$  – IIPI.

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levels suggest that the molecular packing in the solid state, which is strongly influenced by alkyl substituents, is one of the critical factors that determine the resulting energy levels. Such results are consistent with a study on pentacene and 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS pentacene) in which the solid state electronic properties were reported to be significantly affected by the substitutions on the conjugated backbone.<sup>44</sup> While pentacene and TIPS pentacene showed similar HOMO levels by CV measurements in solutions, UPS measurements performed on TIPS pentacene thin films exhibited a much (ca. 1.0 eV) larger IP than that of pentacene.

**Film Morphology and Hole Mobility.** Figure 8 displays the AFM images of as-cast and thermal annealed (100 °C) films



Figure 8. Tapping mode AFM height images of C6PT1C6 (a and b), C6PT2C6 (c and d), C6PT3C6 (e and f), EHPT2C6 (g and h), and C6PT2C6 (i and j) films at conditions of as-cast (left) and after thermal annealing (right). Annealing conditions: 100 °C for 10 min. Scan size: 2  $\mu$ m × 2  $\mu$ m.

of all compounds. The AFM images of the annealed films at 80 °C are shown in Figure S5 (Supporting Information). C6PT1C6 and C6PT2C6 and C6PT3C6 have plate-like structures, which are fused together. The surface roughnesses of the as-cast C6PT1C6 and C6PT2C6 and C6PT3C6 films are 0.87, 1.29, and 0.79 nm, respectively. The plate-like structures grow larger and show clear domain boundaries after thermal annealing. Upon thermal annealing, the surface roughness reduces to 0.73 and 1.06 nm for C6PT1C6 and C6PT2C6, respectively. In contrast, the surface roughness of the annealed C6PT3C6 film increases to 1.11 nm. One expects that the molecular packing in the plate-like domains is similar to that of their single crystals as confirmed by having similar XRD patterns (Figure 3). The crystalline domain size in these films is influenced by the molecular structure of the compounds. A larger conjugated backbone results in smaller crystalline domains in both as-cast and annealed films, which is demonstrated by comparing the surface morphology of C6PT1C6, C6PT2C6, and C6PT3C6. The domain sizes for C6PT1C6 and C6PT2C6 are 162-270 nm and 128-167 nm, respectively. Besides the molecular structures, thermal annealing can increase the domain size effectively. In particular, C6PTC6 shows a large domain size (380-500 nm) in the annealed films, whereas for C6PT2C6 the domain size increases to 183-218 nm. For C6PT3C6, the domain size is very small for the as-cast film but grows up to 100 nm. In contrast, the as-cast and annealed films of C6PT2 show featureless with surface roughness of 0.31 and 0.75 nm, respectively, which can be ascribed to the low crystallinity as demonstrated by thin-film XRD and DSC. The as-cast EHPT2C6 surface is comprised of wavy structures with high surface roughness of 3.86 nm, which reduces to 2.99 nm upon thermal annealing at 100 °C. Overall, the surface morphology is dependent on the molecular structure and thermal annealing and is correlated well with the thin film XRD and DSC results.

The hole mobility of each material was determined from holeonly diodes using the space charge limited current (SCLC) model. Figure 9 shows the hole mobility of as-cast and annealed



Figure 9. Hole mobility measured using hole-only diodes with as-cast (25  $^{\circ}\rm C)$  and thermal annealing (80 and 100  $^{\circ}\rm C)$  films.

films at different temperatures for the five DPP compounds. The as-cast film of **C6PT2** does not exhibit SCLC dependence, thus the mobility cannot be extracted. Among the as-cast films, **C6PT2C6** has the best hole mobility of  $7.8 \times 10^{-6} \text{ cm}^2/(\text{V s})$ , while **EHPT2C6** has the lowest mobility ( $8.9 \times 10^{-7} \text{ cm}^2/(\text{V s})$ ), as a result of adding branched alkyl chains. This observation agrees well with the XRD, DSC, and AFM results. The hole

mobility of the as-cast C6PT1C6 film is slightly higher than that of the as-cast C6PT3C6 film  $(4.6 \times 10^{-6} \text{ vs } 2.4 \times 10$  $cm^2/(Vs)$ ). Thermal annealing of C6PT1C6, C6PT3C6, and C6PT2 at 80 and 100 °C leads to a slight increase of hole mobility possibly due to a higher degree of crystallinity. However, EHPT2C6 and C6PT2C6 exhibit a slight decrease in hole mobility upon thermal annealing at 100 °C. Overall, the hole mobilities among these compounds do not change significantly upon thermal annealing. Due to the 2-ethylhexyl substitution, EHPT2C6 has the smallest intermolecular  $\pi - \pi$  overlapping area in the crystal structure and amorphous-like as-cast film, therefore resulting in the lowest hole mobility. Comparing the linear alkyl chain series, C6PT2C6 has a balanced intermolecular overlapping and crystalline film morphology, resulting in highest hole mobility. These observations indicate a strong correlation among molecular structure, crystal structure, film morphology, and hole mobility.

# CONCLUSION

To understand the effect of structural variation on solid state properties, a series of DPP-based oligophenylenethiophenes were synthesized and characterized. Structural variation is found to have remarkable effects on the materials' fundamental properties including molecular packing, thermal transitions, crystallinity, optical absorption, energy levels, film morphology, and hole mobility. Single-crystal structures of these DPP-based oligophenylenethiophenes were resolved and compared in terms of molecular packing style, intermolecular overlapping (areas and distance), and intramolecular conformation. The polycrystalline films have molecular packing similar to their single crystals. The observed structural effects on properties can be explained according to the single-crystal structures. Branched alkyl chain substitution can dramatically decrease melting temperature and crystallinity. While the molecular backbone determines the optical absorption in solution, the optical absorption in the solid state is affected by both conjugated backbone and alkyl substitution. CV conducted in solution confirms that alkyl substitution does not affect energy levels in the solution state. In contrast, UPS measurements indicate that the position of energy levels in given materials with the same conjugation length can be tuned by changing alkyl substitution on the DPP unit as well as at the end of the conjugation backbone. The film morphology and hole mobilities measured using hole-only diodes show strong correlations with their molecular structures and single-crystal structures. This systematic investigation of structural effect on the evolution of materials' fundamental properties provides an effective approach to establish structure-property relationships and guidelines to design new molecules for use in BHJ solar cells. The alkyl chains attached on the conjugated backbone affect not only the solubility but also the molecular packing in the solid state and hence film absorption and energy levels. Effects of chemical structure on solar cell performance will be published elsewhere.

## ASSOCIATED CONTENT

#### **Supporting Information**

Absorption spectra of as-cast and annealed film of C6PT2C6, EHPT2C6, and C6PT2; TGA profiles, UPS spectra, AFM images (PDF), and crystallographic information files (CIFs) of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

C.K. thanks the Department of Energy, Office of Basic Research, for financial support. J. Liu and J. Lin are supported by the NSF-CAREER/SPECIAL CREATIVITY and NSF-SOLAR, respectively. B.W. is supported by the Office of Naval Research. T.-Q.N. thanks the Camille Dreyfus Teacher Scholar and the Alfred Sloan programs. We thank J. Sherman and Dr. S. R. Parkin for helping with initial single-crystal structures of C6PT2C6 and C6PT3C6.

## DEDICATION

This paper is dedicated to the memory of Mananya Tantiwiwat.

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