# Conjugated Polymers of Rylene Diimide and Phenothiazine for n-Channel Organic Field-Effect Transistors

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**Supporting Information** 

**ABSTRACT:** A series of new n-type copolymers based on perylene diimide (PDI) or naphthalene diimide (NDI) and phenothiazine (PTZ) with different side chain length and molecular weight have been designed and synthesized by Pdcatalyzed Suzuki coupling polymerization with or without phasetransfer catalyst Aliquat 336. The effects of main chain, side chain, and molecular weight on the thermal, optical, electronic, and charge transport properties of the polymers have been investigated. Aliquat 336 improves molecular weight as well as reduces polydispersity index of the polymers. All the polymers exhibit a broad absorption extending from 300 to 900 nm. The main chain and side chain structure and molecular weight have minor effects on the HOMO (-5.8 to -5.9 eV) and LUMO



(-3.7 to -3.8 eV) levels of the polymers. n-Channel field-effect transistors with bottom-gate top-contact geometry based on these copolymers exhibit electron mobilities as high as 0.05 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and on/off ratios as high as 10<sup>5</sup> in nitrogen, which are among the best reported for rylene diimide-based polymers under the same test conditions.

# INTRODUCTION

Polymer semiconductors have been the subject of intensive academic and commercial interest over the past two decades. Electronic devices based on polymer semiconductors, such as polymer light-emitting diodes (PLEDs), polymer solar cells (PSCs), and organic field-effect transistors (OFETs), have advantages such as low cost, light weight, and flexibility. Polymer semiconductors are generally classified as p-type, ntype, and ambipolar materials according to the type of orderly transferring charge carriers. Most of polymer semiconductors are p-type that have seen a dramatic rise in performance over the past decade, and hole mobilities on the order of 1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> have been achieved in p-channel or ambipolar transistors.<sup>1</sup> n-Type polymers are essential for the fabrication of organic pn junctions, PSCs, n-channel OFETs, PLEDs, and complementary logic circuits.<sup>2</sup> Although some novel n-type conjugated polymers have been created recently,<sup>2-6</sup> development of this field has lagged behind their p-type counterparts. Most of ntype polymer semiconductors exhibited electron mobilities below 0.1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in OFETs.

Rylene diimides are one of the classical n-type semiconductor materials due to the substitution of rylene core with two sets of  $\pi$ -accepting six-membered dicarboxylic imide rings that are mutually conjugated. Rylene diimides exhibit relatively high electron affinities, high electron mobilities, and excellent thermal, chemical, and photochemical stabilities.<sup>4</sup> Perylene-3,4:9,10-tetracarboxylic diimide (PDI) and naphthalene-1,8:4,5-

tetracarboxylic diimide (NDI) are widely used building blocks for n-type polymers. Since Zhan et al. reported the first rylene diimide-based conjugated polymer in 2007,<sup>5a</sup> several n-type conjugated polymers-based PDI and NDI have been synthesized and used in n-channel OFETs and PSCs.<sup>5</sup> A few ladder polymers-based PDI and NDI were also reported.<sup>6</sup>

Owing to electron-rich nitrogen and sulfur heteroatoms in a heterocyclic structure, phenothiazine (PTZ) has been well-known as an excellent electron-donating chromophore. Phenothiazine-based semiconductors are widely utilized in organic electronic devices, such as light-emitting devices,<sup>7</sup> photovoltaic cells,<sup>8</sup> thin film transistors,<sup>9</sup> and dye-sensitized solar cells.<sup>10</sup> Nonplanar butterfly conformation in phenothia-zine can inhibit molecular aggregation and increase solubility of the polymers.

The molecular weight as well as conjugation length of a polymer semiconductor affects electronic and optical properties as well as morphology of the polymer thin film. There have been some reports addressing effect of molecular weight on carrier mobility of conjugated polymers,<sup>11</sup> suggesting that increasing molecular weight could significantly improve charge transporting ability of polymer semiconductors. However, most of these literatures discussed effect of molecular weight in p-

Received: March 12, 2012 Revised: April 27, 2012 Published: May 8, 2012

type polymers, while a few literatures referred to that in n-type polymers.

In this work, we designed and synthesized a series of n-type conjugated copolymers of PDI or NDI and PTZ with different side chains and different molecular weights (Figure 1). These



Figure 1. Chemical structures of copolymers discussed in this paper.

polymers exhibited electron mobilities as high as 0.05 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in OFETs in nitrogen. We also investigated effect of main chain, side chain, and molecular weight on electronic, optical, and electron transport properties of the polymers.

## RESULTS AND DISCUSSION

**Synthesis and Characterization.** The synthetic routes to the polymers are outlined in Scheme 1. 1,7-Dibromoperylene dianhydride was condensed with 2-hexyldecylamine to yield a new compound N,N'-bis(2-hexyldecyl)-1,7-dibromoperylene-

Article

3,4:9,10-tetracarboxylic diimide (1) in 64% yield. The new monomer, N,N'-bis(2-decyl-tetradecyl)-2,6-dibromonaphthalene-1,4:5,8-tetracarboxylic diimide (2), was synthesized by condensation of 2,6-dibromonaphthalene dianhydride with 2decyltetradecylamine in 13% yield. Suzuki coupling reactions between N,N'-bis(2-decyl-tetradecyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic diimide,<sup>5a</sup> 1, or 2 and the known compound 10-hexyl-2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenothiazine (3)<sup>12</sup> afforded new copolymers **PPP24-L, PPP16-L**, and **PNP24-L** in 88%, 60%, and 73% yields. Then other three copolymers **PPP24-H, PPP16-H**, and **PNP24-H** with higher molecular weights were obtained by Suzuki coupling reactions in the presence of phase-transfer catalyst Aliquat 336.

All the polymers have good solubility in common organic solvents such as chloroform, THF, and chlorobenzene. Molecular weights of the polymers were determined by gel permeation chromatography (GPC), using polystyrene standards as calibrants with THF as eluent (Table 1). The three copolymers synthesized without Aliquat 336 (PPP24-L, PPP16-L, and PNP24-L) exhibit number-average molecular weights  $(M_n)$  below 7000 with polydispersity index  $(M_w/M_n)$  up to 2.77, while the three copolymers synthesized with Aliquat 336 (PPP24-H, PPP16-H, and PNP24-H) exhibit relatively larger  $M_n$  of 7800–11 800 with lower  $M_w/M_n$  below 1.7. Thus, phase-transfer catalyst Aliquat 336 can improve degree of polymerization and molecular weight as well as reduce polydispersity index in Suzuki coupling polymerization.

The thermal properties of the polymers were determined by thermogravimetric analysis (TGA) under nitrogen. The decomposition temperatures ( $T_d$ ) at 5% weight loss for higher molecular weight polymers **PPP24-H**, **PPP16-H**, and **PNP24**-

Scheme 1. Synthesis of the Polymers



 Table 1. Molecular Weights and Thermal Properties of the

 Polymers

polymer	yield (%)	$M_{\rm n}^{\ a}$	$M_{\rm w}^{\ a}$	$M_{\rm w}/M_{\rm n}^{\ a}$	$T_{\rm d}^{\ b}$ (°C)
PPP24-L	88	4830	9414	1.95	404
PPP24-H	54	9971	15278	1.53	407
PPP16-L	60	2621	3596	1.37	322
PPP16-H	57	7850	13273	1.69	397
PNP24-L	73	6823	18966	2.77	281
PNP24-H	76	11821	18540	1.57	405

<sup>*a*</sup>Number-average molecular weight  $(M_n)$ , weight-average molecular weight  $(M_w)$ , and polydispersity index  $(M_w/M_n)$  determined by means of GPC with THF as eluent on the basis of polystyrene calibration. <sup>*b*</sup>Decomposition temperature (5% weight loss) estimated using TGA under N<sub>2</sub>.

H are 397–407 °C, while lower molecular weight polymers **PPP24-L**, **PPP16-L**, and **PNP24-L** exhibit relatively lower  $T_d$  of 281–404 °C (Table 1).

Optical Properties. The UV-vis absorption spectra of all polymers were measured in CHCl<sub>3</sub> (ca. 10<sup>-6</sup> M) solution and in thin films (Figure 2). The detailed absorption data, including maximum absorption wavelength of solutions and films and the optical band gap deduced from the absorption edge in films, are summarized in Table 2. Four PDI-based copolymers (PPP24-L, PPP16-L, PPP24-H, and PPP16-H) in solution exhibit similar absorption spectra with three absorption maxima, which are reminiscent of those of PDI with dithienothiophene (DTT)<sup>13</sup> in the 1,7-positions and PDI–DTT copolymers.<sup>5c</sup> These similarities suggest that the band at ca. 330 nm can be assigned to a PTZ-centered transition, the 520 nm band to a principally PDI-based transition, and the low-energy band located at ca. 600 nm to a transition with significant PTZ-to-PDI charge-transfer character. In absorption spectra of solutions of two NDI-based copolymers (PNP24-L and PNP24-H), there are also three characteristic bands located at ca. 330, 360, and 620 nm, related to a PTZ-centered transition, a principally NDI-based transition, and a significant PTZ-to-NDI charge-transfer transition, respectively. The PTZcentered and PDI/NDI-based transition bands are not susceptible to the polymer molecular weights, while the lowenergy charge-transfer bands of the copolymers with higher molecular weights red-shift ca. 10 nm in comparison with those with lower molecular weights. The N,N'-substituents on the PDI have only minor effects on the spectra, as is also seen in the case of small-molecule PDIs.<sup>14</sup>

 Table 2. Absorption Maxima and Energy Levels of the Polymers

polymer	$\lambda_{\max,s}^{a} (\mathrm{nm})$	$\lambda_{\max, \mathrm{f}}^{} b} (\mathrm{nm})$	$(eV)^{E_g^c}$	$HOMO^d$ (eV)	$LUMO^d$ (eV)	$E_{g}^{CV e}$ (eV)
PPP24-L	330, 518, 600	336, 522, 610	1.5	-5.82	-3.73	2.1
PPP24-H	328, 518, 610	332, 522, 630	1.5	-5.85	-3.75	2.1
PPP16-L	330, 522, 600	320, 526, 610	1.4	-5.84	-3.68	2.1
РРР16-Н	324, 518, 610	342, 524, 630	1.5	-5.81	-3.74	2.1
PNP24-L	328, 362, 616	342, 364, 670	1.4	-5.89	-3.72	2.2
PNP24-H	328, 362, 628	342, 364, 682	1.4	-5.83	-3.79	2.0

<sup>*a*</sup>Absorption maxima in solution. <sup>*b*</sup>Absorption maxima in film. <sup>*c*</sup>Optical band gap estimated from the absorption edge in film. <sup>*d*</sup>HOMO and LUMO estimated from the onset oxidation and reduction potentials, respectively, assuming the absolute energy level of ferrocene/ ferrocenium to be 4.8 eV below vacuum. <sup>*e*</sup>HOMO–LUMO gap estimated electrochemistry.

The UV-vis spectra of thin films of all polymers show absorption throughout the visible region. Moreover, there is significant absorption extending into the near-IR region (as far as ca. 900 nm, equivalent to optical band gaps as low as ca. 1.5 eV). The absorption spectra (particularly the low-energy charge-transfer bands) of the polymer films show red-shift relative to those of their chloroform solutions, which is a common phenomenon for conjugated polymers owing to the aggregation of the conjugated polymer main chains in the solid films. The low-energy charge-transfer band of NDI-based copolymers red-shifts 54 nm, larger than those for the PDIbased copolymers (10-20 nm), indicating that there are stronger intermolecular interactions in more planar NDI-based copolymers.

**Electrochemistry.** To estimate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the conjugated copolymers, we studied electrochemical properties using cyclic voltammetry (CV) of films drop-cast onto glassy carbon working electrodes. The cyclic voltammograms of all polymers are shown in Figure 3. The HOMO and LUMO values of the polymers are estimated from the onset oxidation and reduction potentials, assuming the absolute energy level of  $FeCp_2^{+/0}$  to be 4.8 eV below vacuum (Table 3). Six rylene-based copolymers



Figure 2. UV-vis spectra of the polymers in chloroform (left) and in film (right).



Figure 3. Cyclic voltammograms of polymer films in  $CH_3CN/0.1 \text{ M}$  [ ${}^nBu_4N$ ]<sup>+</sup>[ $PF_6$ ]<sup>-</sup> at 50 mV s<sup>-1</sup>. The horizontal scale refers to an anodized Ag wire pseudoreference electrode.

 Table 3. Performance of n-Channel OFETs Based on the

 Polymers in Nitrogen

polymer	$\mu_{\rm e}~({\rm cm}^2~{\rm V}^{-1}~{\rm s}^{-1})$	$I_{\rm on}/I_{\rm off}$	$V_{\rm T}$ (V)
PPP24-L	0.02	10 <sup>4</sup>	21
PPP24-H	0.05	10 <sup>5</sup>	8
PPP16-L	10 <sup>-4</sup>	10 <sup>4</sup>	9
PPP16-H	0.02	10 <sup>5</sup>	17
PNP24-L	0.02	10 <sup>5</sup>	4
PNP24-H	0.05	$10^{4}$	14

exhibit an irreversible oxidation peak and one or two quasireversible reduction waves. All of the copolymers exhibit similar LUMO levels of ca. -3.7 eV and HOMO levels of ca. -5.8 eV. The energies of LUMO and HOMO for these polymers are relatively insensitive to the main chain structure, side chain structure, and molecular weight.

**Field-Effect Transistors.** Electron transport properties of these polymers were investigated using OFET devices with a bottom-gate top-contact configuration using Au as source and drain electrodes. The output and transfer plots of all polymers in nitrogen are shown in Figure 4 and Figure S1 (Supporting Information), and the performance data of OFETs based on the polymers are listed in Table 3.

The highest electron mobility obtained from the PDI-based copolymers is up to 0.05 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (**PPP24-H**), higher than those of the PDI-DTT copolymer (0.013 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>)<sup>5a</sup> and the PDI-bithiophene copolymer (0.002 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>)<sup>5e</sup> in the same device geometry and in the same atmosphere. The highest electron mobility obtained from the NDI-based copolymers is up to 0.05 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (**PNP24-H**), similar to that of the NDI–bithiophene copolymer (0.06 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>)<sup>5e</sup> in the same device geometry and in the same atmosphere. However, the same OFET arrays do not function in air since the LUMOs of the polymers are not deep enough.

The copolymers with higher molecular weights show higher electron mobilities than their lower molecular weight counterparts. Generally, electron transport in polymer films has two pathways: transport along the main chain and interchain hopping. Electron transport in conjugated polymers along an individual chain is easier than transport through interchain hopping.<sup>11a</sup> Since the carriers are frequently trapped in the chain ends, increasing molecular weight means decreasing chain end density, leading to improved carrier mobility.<sup>11e</sup> On the other hand, increasing molecular weight improves the coalescence between molecular chains and optimizes the film



**Figure 4.** Current–voltage characteristics ( $I_{ds}$  vs  $V_{ds}$ ) at several values of the gate voltage ( $V_g$ ) (left) and  $I_{ds}$  and ( $I_{ds}$ )<sup>1/2</sup> vs  $V_g$  plots (right) for a top contact device based on **PPP24-H** (top) and **PNP24-H** (bottom).

morphology in FET devices, finally enhancing interchain hopping of carriers since the probability of this hopping is related to the density of low activation energy pathways for crossing between polymer chains whose number should increase with the chain length.<sup>11a</sup>

Replacing the shorter 2-hexyldecyl groups in **PPP16-L** and **PPP16-H** with longer 2-decyltetradecyl groups (**PPP24-L** and **PPP24-H**) in the *N*-position of the PDI moiety leads to significant enhancement in electron mobility, which could be attributed to stronger intermolecular interaction and/or higher molecular weight in the copolymers with longer side chains.

Figure 5 and Figure S2 show AFM height images of the polymer films. All the polymer films exhibited typical



**Figure 5.** AFM topographic images (5  $\mu$ m × 5  $\mu$ m) of thin films of **PPP24-H** and **PPP24-L**.

amorphous state without any crystalline domains. The rootmean-square (rms) roughness of these films is in the range of 0.3-0.9 nm. More uniform morphology with lower defect density was observed for the polymers with higher molecular weight relative to those with lower molecular weight, which is beneficial to electron transport.

In order to further investigate the thin film organization of the copolymers, we carried out X-ray diffraction measurements as shown in Figures 6 and Figure S3. All thin films of the



Figure 6. X-ray diffraction patterns of thin films of PPP24-H and PPP24-L.

polymers with higher molecular weights exhibit a broad peak in  $2\theta = 15^{\circ}-25^{\circ}$  region accompanied by one sharp peak at 21.4° corresponding to  $\pi-\pi$  stacking distance of 0.41 nm. Thin films of polymers **PPP24** and **PNP24** with lower molecular weights do not exhibit a broad peak in  $2\theta = 15^{\circ}-25^{\circ}$  region. Thus, high molecular weight is beneficial to  $\pi-\pi$  stacking of the polymer chain and electron transport.

### CONCLUSION

A series of new copolymers based on perylene diimide (PDI) or naphthalene diimide (NDI) and phenothiazine (PTZ) with different side chain length and molecular weight have been synthesized by Pd-catalyzed Suzuki coupling polymerization with or without phase-transfer catalyst Aliquat 336. Aliquat 336 improves molecular weight as well as reduces polydispersity index of the polymers. The PDI-based polymers with longer side chains have higher molecular weights than those with shorter side chains. The polymers with higher molecular weights exhibit relatively higher decomposition temperature, red-shift of low-energy absorption band, more uniform film morphology, stronger  $\pi - \pi$  stacking, and higher electron mobility than those with lower molecular weights. The main chain and side chain structure and molecular weight have minor effects on the HOMO and LUMO levels of the polymers. The electron mobilities obtained from the PDI or NDI-based copolymers are as high as 0.05 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which are among the best reported for rylene diimide-based polymers under the same test conditions.

#### EXPERIMENTAL SECTION

**Materials.** Unless stated otherwise, starting materials were obtained from Aldrich or Acros and were used without further purification. 1,7-Dibromoperylene dianhydride,<sup>15</sup> 2,6-dibromonaph-thalene-1,4:5,8-tetracarboxydianhydride,<sup>16</sup> 2-decyltetradecylamine,<sup>5a</sup> 2-hexyldecylamine,<sup>5a</sup> 10-hexyl-2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxabor-olan-2-yl)-phenothiazine,<sup>12</sup> and *N*,*N'*-bis(2-decyl-tetradecyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic diimide<sup>5a</sup> were synthesized according to the literature methods.

Characterization. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker AVANCE 400 MHz spectrometer using tetramethylsilane (TMS;  $\delta = 0$  ppm) as an internal standard. Mass spectra were measured on a Bruker Daltonics BIFLEX III MALDI-TOF analyzer using MALDI mode. Elemental analyses were carried out using a FLASH EA1112 elemental analyzer. Solution (chloroform) and thinfilm (on quartz substrate) UV-vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-n-butylammonium hexafluorophosphate (0.1 M) in acetonitrile using a computer-controlled Zahner IM6e electrochemical workstation, a glassy-carbon working electrode coated with polymer films, a platinum-wire auxiliary electrode, and an Ag wire anodized with AgCl as a pseudoreference electrode. Thermogravimetric analysis (TGA) measurements were performed on Shimadzu thermogravimetric analyzer (model DTG-60) under a nitrogen flow at a heating rate of 10 °C min<sup>-1</sup>. The gel permeation chromatography (GPC) measurements were performed on a Waters 515 chromatograph connected to a Waters 2410 refractive index detector, using THF as eluent and polystyrene standards as calibrants; three Waters Styragel columns (HT3, 5, 6E) connected in series were used. The X-ray diffraction (XRD) pattern was recorded by a Rigaku D/max-2500 diffractometer operated at 40 kV voltage and a 200 mA current with Cu K $\alpha$  radiation. The samples for XRD measurements were prepared by spin-coating chloroform solution of the polymers on the OTS-modified SiO2.

**Fabrication and Characterization of Field-Effect Transistors.** FET devices were fabricated with a top-contact bottom-gate configuration. A heavily doped n-type Si wafer with a SiO<sub>2</sub> layer of 500 nm and a capacitance of 11.5 nF cm<sup>-2</sup> was used as the gate. Octadecyltrichlorosilane (OTS) was used as a self-assembled surface modifier for SiO<sub>2</sub>. A 60 nm thick ( $\pm$ 10 nm) semiconductor film was spin-coated on top of the OTS-treated SiO<sub>2</sub> from 10 mg mL<sup>-1</sup> chloroform solution of the polymers. Gold source and drain contacts (40 nm) were deposited on the organic layer through a shadow mask under high vacuum. The channel length (*L*) and width (*W*) were 80  $\mu$ m and 8.8 mm, respectively. All the measurement of electric property was carried out in nitrogen using a Keithley 4200 SCS semiconductor parameter analyzer. The mobility in the saturated regime was extracted from the following equation:  $I_{\rm ds} = C_i \mu_{\rm e} (W/2L) (V_{\rm g} - V_{\rm T})^2$ , where  $I_{\rm ds}$  is the drain current,  $C_i$  is the capacitance per unit area of the gate dielectric layer,  $\mu_{\rm e}$  is field-effect electron mobility, W and L are the channel width and length, and  $V_{\rm g}$  and  $V_{\rm T}$  are the gate voltage and threshold voltage, respectively. AFM images of organic thin films were obtained on a NanoMan VS microscope (Digital Instruments) in tapping mode.

Synthesis. N,N'-Bis(2-hexyldecyl)-1,7-dibromo-3,4:9,10-perylene Diimide (1). 1,7-Dibromoperylene-3,4:9,10-tetracarboxylic acid dianhydride (2.96 mmol, 1.63 g) in 120 mL of "BuOH/H<sub>2</sub>O (1:1, v/v) was sonicated for 10 min. 2-Hexyldecylamine (11.33 mmol, 2.73 g) was added, and the reaction mixture was stirred at 80 °C for 24 h under nitrogen. Concentrated aqueous HCl (13 mL) was added, and the mixture was stirred at room temperature for 30 min. The mixture was extracted with chloroform (2  $\times$  90 mL), washed with water (2  $\times$ 180 mL), and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed and the residue was purified by column chromatography over silica gel eluting with  $CH_2Cl_2$ /petroleum ether (1:1) to give a red solid (1.90 g, 64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.36 (d, J = 8.1 Hz, 2H), 8.81 (s, 2H), 8.59 (d, J = 8.2 Hz, 2H), 4.12 (d, J = 7.1 Hz, 4H), 1.98 (m, 2H), 1.5-1.1 (m, 48H), 0.85 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *δ* 163.0, 162.5, 138.0, 132.9, 132.6, 129.8, 129.0, 128.3, 126.8, 123.0, 122.6, 120.8, 44.8, 36.6, 32.0, 31.8, 31.6, 30.0, 29.7, 29.6, 29.3, 26.5, 22.6, 14.1. MS (MALDI): m/z 996 (M<sup>+</sup>). Anal. Calcd for C<sub>56</sub>H<sub>72</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>4</sub>: C, 67.46; H, 7.28; N, 2.81. Found: C, 67.53; H, 7.25; N. 2.91.

N,N'-Bis(2-decyltetradecyl)-2,6-dibromo-1,4:5,8-naphthalene Diimide (2). A mixture of 2,6-dibromonaphthalene-1,4:5,8tetracarboxylic acid dianhydride (1.85 mmol, 789 mg), 2-decyltetradecylamine (5.08 mmol, 1.80 g), o-xylene (5 mL), and propionic acid (3 mL) was stirred overnight at 140 °C. Upon cooling to room temperature, the mixture was extracted with chloroform  $(2 \times 90 \text{ mL})$ , washed with water (2  $\times$  180 mL), and dried over anhydrous MgSO<sub>4</sub>. The residue was purified by column chromatography on silica gel with a mixture of chloroform:petroleum ether (1:1, v/v) as eluent, affording a pale yellow solid (271 mg, 13.4%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 8.99 (s, 2H), 4.14 (d, J = 7.3 Hz, 4H), 1.98 (m, 2H), 1.20–1.40 (m, 80H), 0.84–0.89 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.3, 161.1, 139.3, 128.5, 127.9, 125.4, 124.2, 45.6, 36.6, 32.1, 32.0, 31.7, 30.2, 29.8, 29.7, 29.5, 26.5, 22.8, 14.3. MS (MALDI): m/z 1095 (M<sup>+</sup>). Anal. Calcd for C<sub>62</sub>H<sub>100</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>4</sub>: C, 67.86; H, 9.19; N, 2.55. Found: C, 67.73; H. 9.04; N. 2.59.

Poly{[N,N'-bis(2-decyltetradecyl)-3,4:9,10-perylenediimide-1,7-diyl]-alt-(10-hexyl-phenothiazine-2,8-diyl)}. To a 50 mL three-neck round-bottom flask were added N,N'-bis(2-decyltetradecyl)-1,7-dibromo-3,4:9,10-perylene diimide (0.25 mmol, 308 mg) and 10-hexyl-2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenothiazine (0.25 mmol, 135 mg), and the mixture was deoxygenated with nitrogen for 30 min.  $Pd(PPh_3)_4$  (18 µmol, 21 mg), toluene (15 mL), and an aqueous solution of K2CO3 (1.36 g) in deoxygenated water (25 mL) were added under nitrogen. The dark red solution was stirred at 95 °C for 3 days. Phenylboronic acid (46 µmol, 5.6 mg) was added under nitrogen. The brown sticky mixture was stirred at 95 °C for 5 h. Bromobenzene (1.8 mmol, 290 mg) was added under nitrogen. The brown sticky mixture was stirred at 95 °C for 10 h. The brown sticky mixture was cooled down to room temperature. The mixture was extracted with  $CH_2Cl_2$  (2 × 100 mL), washed with water (2 × 100 mL), and dried over anhydrous MgSO4. The solution was concentrated to 15 mL and then dropped into 200 mL of methanol. The brown precipitate was filtered and washed with methanol. Finally, the polymer was purified by size exclusion column chromatography over Bio-Rad Bio-Beads S-X1 eluting with chloroform to afford a dark red-brown solid. PPP24-L: 300 mg, 88%. GPC: M<sub>n</sub>, 4830; M<sub>w</sub>, 9414;  $M_{\rm w}/M_{\rm n}$ , 1.95. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.6 (br, 2H), 8.3 (br, 4H), 7.8 (br, 2H), 7.5 (br, 4H), 4.1-3.9 (br, 6H), 2.00 (br, 4H), 1.6-1.0 (br, 86H), 0.9–0.6 (br, 15H). Anal. Calcd for (C<sub>90</sub>H<sub>123</sub>N<sub>3</sub>O<sub>4</sub>S)<sub>n</sub>: C, 80.49; H, 9.23; N, 3.13. Found: C, 74.70; H, 8.82; N, 2.83. PPP24-H: with Aliquat 336 (37  $\mu$ mol, 15 mg) in the reaction mixture, 181 mg, 54%. GPC:  $M_{\rm p}$ , 9971;  $M_{\rm w}$ , 15278;  $M_{\rm w}/M_{\rm p}$ , 1.53. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.5 (br, 2H), 8.3 (br, 4H), 7.8 (br, 2H), 7.6 (br, 4H), 4.1–3.9 (br, 6H), 2.00 (br, 4H), 1.6–1.0 (br, 86H), 0.9–0.6 (br, 15H). Anal. Calcd for  $(C_{90}H_{123}N_3O_4S)_n$ : C, 80.49; H, 9.23; N, 3.13. Found: C, 76.04; H, 8.86; N, 2.82.

Poly{[N,N'-bis(2-hexyldecyl)-3,4:9,10-perylenediimide-1,7diyl]-alt-(10-hexyl- phenothiazine-2,8-diyl)}. To a 50 mL threeneck round-bottom flask were added N,N'-bis(2-hexyldecyl)-1,7dibromo-3,4:9,10-perylene diimide (0.51 mmol, 505 mg) and 10hexyl-2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenothiazine (0.51 mmol, 271 mg), and the mixture was deoxygenated with nitrogen for 30 min.  $Pd(PPh_3)_4$  (59  $\mu$ mol, 68 mg), toluene (15 mL), and a solution of  $K_2CO_3$  (0.57 g) in deoxygenated water (5 mL) were added under nitrogen. The dark red solution was stirred at 95 °C for 3 days. Phenylboronic acid (87  $\mu$ mol, 10.6 mg) was added under nitrogen. The brown sticky mixture was stirred at 95 °C for 5 h. Bromobenzene (0.3 mL) was added under nitrogen. The mixture was stirred at 95 °C for 10 h. The brown sticky mixture was cooled down to room temperature. The mixture was extracted with  $CH_2Cl_2$  (2 × 100 mL), washed with water  $(2 \times 100 \text{ mL})$ , and dried over anhydrous MgSO<sub>4</sub>. The solution was concentrated to 15 mL and then dropped into 100 mL of methanol. The black precipitate was filtered and washed with methanol. Finally, the polymer was purified by size exclusion column chromatography over Bio-Rad Bio-Beads S-X1 eluting with chloroform to afford a dark red-brown solid. PPP16-L: 340 mg, 60%. GPC:  $M_{\rm pl}$  2621;  $M_{\rm wl}$  3596;  $M_{\rm w}/M_{\rm pl}$  1.37. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.6 (br, 2H), 8.3 (br, 4H), 7.7 (br, 2H), 7.5 (br, 4H), 4.1-3.9 (br, 6H), 2.00 (br, 4H), 1.6-1.0 (br, 54H), 0.9-0.7 (br, 15H). Anal. Calcd for (C<sub>74</sub>H<sub>91</sub>N<sub>3</sub>O<sub>4</sub>S)<sub>n</sub>: C, 79.46; H, 8.20; N, 3.76. Found: C, 70.59; H, 8.43; N, 2.75. PPP16-H: with Aliquat 336 (190  $\mu$ mol, 76 mg) in the reaction mixture, 320 mg, 57%. GPC:  $M_n$ , 7850;  $M_{\rm w}$ , 13273;  $M_{\rm w}/M_{\rm n}$ , 1.69. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.5 (br, 2H), 8.3 (br, 4H), 7.8 (br, 2H), 7.6 (br, 4H), 4.1-3.9 (br, 6H), 2.00 (br, 4H), 1.6-1.0 (br, 54H), 0.9-0.6 (br, 15H). Anal. Calcd for (C<sub>74</sub>H<sub>91</sub>N<sub>3</sub>O<sub>4</sub>S)<sub>n</sub>: C, 79.46; H, 8.20; N, 3.76. Found: C, 70.71; H, 7.90; N, 3.09

Poly{[N,N'-bis(2-decyltetradecyl)-1,4:5,8-naphthalenediimide-2,6-diyl]-alt-(10-hexylphenothiazine-2,8-diyl)}. To a 25 mL three-neck round-bottom flask were added N,N'-bis(2-decyltetradecyl)-2,6-dibromo-1,4:5,8-naphthalene diimide (0.15 mmol, 166 mg) and 10-hexyl-2,8-bis(4,4,5,5-tetramethyl-1,3,2- dioxaborolan-2yl)-phenothiazine (0.15 mmol, 81 mg), and the mixture was deoxygenated with nitrogen for 30 min.  $Pd(PPh_3)_4$  (31 µmol, 36 mg), toluene (4 mL), and a solution of  $K_2CO_3$  (131 mg) in deoxygenated water (0.5 mL) were added under nitrogen. The yellow solution was stirred at 95 °C for 3 days. Phenylboronic acid (8.1 mg) was added under nitrogen. The dark green mixture was stirred at 95 °C for 5 h. Bromobenzene (0.1 mL) was added under nitrogen. The dark green mixture was stirred at 95 °C for 10 h. The dark green mixture was cooled down to room temperature. The mixture was extracted with  $CH_2Cl_2$  (2 × 100 mL), washed with water (2 × 100 mL), and dried over anhydrous MgSO<sub>4</sub>. The solution was concentrated to 15 mL and then dropped into 100 mL of methanol. The dark green precipitate was filtered and washed with methanol. The dark green precipitate was filtered and purified by size exclusion column chromatography over Bio-Rad Bio-Beads S-X1 eluting with chloroform to afford a dark green solid. PNP24-L: 134 mg, 73%. GPC:  $M_{\rm pl}$  6823;  $M_{\rm wl}$  18 966;  $M_{\rm wl}/M_{\rm pl}$  2.77. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 8.6 (br, 2H), 7.2 (br, 2H), 7.0 (br, 4H), 4.2-4.0 (br, 6H), 2.00 (br, 4H), 1.6-1.1 (br, 86H), 0.9-0.7 (br, 15H). Anal. Calcd for (C<sub>80</sub>H<sub>119</sub>N<sub>3</sub>O<sub>4</sub>S)<sub>n</sub>: C, 78.83; H, 9.84; N, 3.45. Found: C, 72.89; H, 8.74; N, 2.95. **PNP24-H**: with Aliquat 336 (108  $\mu$ mol, 44 mg) in the reaction mixture, 140 mg, 76%. GPC:  $M_{\rm n}$ , 11821;  $M_{\rm w}$ , 18 540;  $M_{\rm w}/M_{\rm n}$ , 1.57. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.6 (br, 2H), 7.2 (br, 2H), 7.0 (br, 4H), 4.1-3.9 (br, 6H), 2.00 (br, 4H), 1.6-1.0 (br, 86H), 0.9-0.7 (br, 15H). Anal. Calcd for (C<sub>80</sub>H<sub>119</sub>N<sub>3</sub>O<sub>4</sub>S)<sub>n</sub>: C, 78.83; H, 9.84; N, 3.45. Found: C, 71.84; H, 9.42; N, 3.01.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Output and transfer curves of OFETs; AFM images of **PPP16-H**, **PPP16-L**, **PNP24-H**, and **PNP24-L**; XRD patterns of **PPP16-H**, **PPP16-L**, **PNP24-H**, and **PNP24-L**. 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

This material is based upon work supported in part by the NSFC (Grants 21025418, 50873107, and 21021091), 973 Project (Grant 2011CB808401), the Chinese Academy of Sciences, and Solvay S. A.

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