Perylene Diimide Copolymers with Dithienothiophene and Dithienopyrrole: Use in n-Channel and Ambipolar Field-Effect Transistors

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ABSTRACT: Solution-processable polymers consisting of perylene diimide (PDI) acceptor moieties alternating with dithienothiophene (DTT), *N*-dodecyl-dithienopyrrole (DTP), or oligomers of these donor groups have been synthesized. We have, in addition to varying the donor, varied the *N*,*N* substituents of the PDIs. The thermal, optical, electrochemical, and charge-transport properties of the polymers have been investigated. The polymers show broad absorption extending from 300 to 1000 nm with optical band gaps as low as 1.2 eV; the band gap decreases with increasing the conjugation length of donor block, or by replacement of DTT by DTP. The electron affinities of the polymers, estimated from electrochemical data, range from -3.87 to -4.01 eV and are slightly affected by the specific choice of donor moiety, while the esti-

INTRODUCTION Organic electron-transport (ET) materials are essential for the fabrication of organic p-n junctions, photovoltaic cells, n-channel field-effect transistors (OFETs), and complementary logic circuits. High-performance ET materials must have high electron affinity to facilitate electron injection from electrodes in OFETs, good intermolecular electronic orbital overlap to facilitate high mobility, and good air stability, ideally both as neutral materials and under device operating conditions.¹ Good ET materials include acenes and oligothiophenes bearing electron-withdrawing substituents, such as fluoro, cyano, or acyl, fullerenes, and rylene and acene tetracarboxylic diimides.¹ In general, development of high-performance (stable, high-mobility) organic ET materials has lagged behind that of hole-transport (HT) materials. In particular, high-mobility n-type polymers remain rare.² Ambipolar OFETs, that is, OFETs based on materials that can function as either ET or HT materials depending on the gate voltage, are important for complementary inverters that enable robust, low-power circuits with wide noise margins withmated ionization potentials (–5.31 to –5.92 eV) are more sensitive to the choice of donor. Bottom-gate top-contact organic field-effect transistors based on the polymers generally exhibit n-channel behavior with electron mobilities as high as 1.7 \times 10⁻² cm²/V/s and on/off ratios as high as 10⁶; one PDI-DTP polymer is an ambipolar transport material with electron mobility of 4 \times 10⁻⁴ cm²/V/s and hole mobility of 4 \times 10⁻⁵ cm²/V/s in air. There is considerable variation in the charge transport properties of the polymers with the chemical structures. © 2013 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2013

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out using advanced patterning techniques to selectively deposit separate ET and HT materials.^{1(c)} Some singlecomponent organic materials exhibit ambipolar transport properties.³ In particular, a few diketopyrrolopyrrole (DPP)based polymers exhibit excellent ambipolar transport properties with both electron and hole mobilities as high as 1 cm²/V/s in nitrogen.⁴ However, air-stable ambipolar organic semiconductors remain very rare. Usta and Facchetti reported the first air-stable ambipolar OFET polymer based on indenofluorenebis(dicyanovinylene) core and having both electron and hole mobilities of about 2 \times 10⁻⁴ cm²/V/s.⁵

Perylene-3,4:9,10-tetracarboxydiimides (PDIs) are a robust, versatile class of materials with excellent stability, high electron affinities and, in some cases, high electron mobilities; they are, therefore, promising candidates for a variety of organic electronics applications.⁶ For example, OFETs based on PDI thin films and single crystals exhibited electron mobilities as high as 1–6 cm²/V/s in vacuum and in air.⁷ However,

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1



FIGURE 1 Chemical structures of PDI copolymers which is discussed in this article.

high-mobility PDI polymers remain rare. Several n-type conjugated polymers based PDI have been synthesized and used in n-channel OFETs and polymer solar cells.⁸ We reported the synthesis of the first soluble PDI-based fully conjugated polymer; this PDI-dithienothiophene (DTT) copolymer (1a, Fig. 1) exhibited a saturation electron mobility of 1.3 \times 10^{-2} cm²/V/s and a low threshold voltage of 4 V in nitrogen.^{8(a)} Later, a dithienopyrrole (DTP) analogue, 2a, was reported to show an electron mobility of 1.2 \times $10^{-3}~{\rm cm}^2/{\rm V/s}$ on annealing at 100 °C for 60 min under inert atmosphere.^{8(b)} Facchetti and coworkers have reported a PDI-bithiophene copolymer with a mobility of 2 \times 10⁻³ cm²/V/s in vacuum.^{8(g)} Thelakkat and coworkers have reported a polymer containing PDIs as pendant groups with a mobility of 1.2×10^{-3} cm²/V/s under inert atmosphere after thermal annealing at 210 °C for 60 min.9

In this article, we compare the OFET behavior of a series of low band gap π -conjugated copolymers of PDI acceptors with DTT and DTP donors (Fig. 1), including the previously reported **1a** and **2a**, an additional polymer, **3a**, that we have previously examined as an electron acceptor for all-polymer solar cells,^{8(b)} and four new polymers. One of these materials shows stable ambipolar OFET behavior in air, while some of the other polymers show good n-channel OFET performance for solution-processed materials. As shown in Figure 1, within this series, we vary the number and nature of fused thiophene donor linkers, and the *N*-alkyl substituents. In addition to comparing OFET behavior, we also compare the optical and electrochemical properties of these polymers.

RESULTS AND DISCUSSION

Synthesis and Characterization

Polymers **1a**, **2a**, and **3a** were synthesized according to our previously published procedures.^{8(a,b)} The synthetic routes to the remaining polymers are outlined in Scheme 1. 1,7-Dibro-moperylene-3,4:9,10-tetracarboxylic dianhydride¹⁰ was condensed with the amines to yield the new N,N'-disubstituted 1,7-dibromoperylene-3,4:9,10-tetracarboxylic diimides (**Ia-b**) in 24–64% yields. The Stille coupling reaction between 2,6-distannyl DTT or DTP derivatives and **Ia-c** or a 1,7-bis(-bromo-DTT) PDI in the presence of a catalytic amount of Pd(PPh₃)₄ afforded the new copolymers **1b-c**, **2b**, and **3b** in 87–91% yields.

All these polymers have good solubility in chloroform. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) using polystyrene standards as calibrants with toluene as eluant. Table 1 shows the molecule weights of the polymers as well as their thermal property. All the polymers except **1b** (not measured due to poor solubility in toluene) exhibit weight-average molecular weight (M_w) of 16,000–82,000 with polydispersity index



SCHEME 1 Synthesis of the polymers.

 (M_w/M_n) of 1.5–1.8. All the polymers exhibit good thermal stability with decomposition temperatures (T_d) of 330–430°C, as estimated by thermogravimetric analysis (TGA) (Table 1).

Absorption Spectra

UV-vis-NIR absorption spectra of the polymers in chloroform are shown in Figure 2(a) with the maxima summarized in Table 2. We have previously assigned the lowest energy bands of 1a, 2a, and 3a to transitions with substantial donor-to-acceptor charge-transfer character, and suggested that the two strong higher energy bands are primarily PDI-based and donor-based (with overlap between these two transitions in the case of **3a**).^{8(b),11} The spectra of **1b-c** and **2b** are similar to those of 1a and 2a, respectively, indicating that 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.¹² In the case of **3b**, both bands are significantly redshifted relative to those of 3a; the shift of the charge-transfer-type band can be attributed to the greater donor strength of DTP vs. DTT.^{8(b),13,14} The UV-vis-NIR absorption spectra of the polymers in thin films are shown in Figure 2(b) and are generally similar to the solution spectra, with only minor red or blue shifts in the absorption maxima being observed.

Electrochemistry

To estimate the solid-state ionization potential (IP) and electron affinity (EA) of the polymers, we studied their electrochemical properties using cyclic voltammetry of films drop cast onto glassy carbon working electrodes. Figure 3 shows cyclic voltammograms of all polymers. The IP and EA values of the polymers are estimated from the onset oxidation and



reduction potentials, assuming the absolute energy level of $\text{FeCp}_2^{+/0}$ to be 4.8 eV below vacuum. As we have previously discussed for **1a**, **2a**, and **3a**, the estimated EAs are relatively insensitive to the choice of donor groups. The data for the new polymers are consistent with this picture and also show that, consistent with data for small-molecule PDIs,¹² the choice of *N*,*N'*-substituents does not significantly affect the EAs either (Table 3). The estimated IPs are relatively insensitive to the choice of *N*,*N'*-substituents. However, the estimated IPs decrease with increasing the number of DTT units or replacing DTT by DTP. The optical band gaps (E_g^{opt}) are relatively insensitive to the choice of *N*,*N'*-substituents, while decrease with increasing the number of DTT units or replacing DTT by DTP. The trend in IP-EA gaps (E_g^{ec}) obtained from electrochemistry is similar to E_g^{opt} . However, E_g^{ec} is

TABLE 1 Molecular Weights and Thermal Properties of the

 Polymers

Polymer	Yield (%)	$M_{\rm n}^{\rm a}$	<i>M</i> _w ^a	$M_{\rm w}/M_{\rm n}^{\rm a}$	<i>T</i> d [°] (°C)
1b	88	_ ^b	-	-	334
1c	87	25,000	38,000	1.5	422
2b	89	44,800	82,300	1.8	342
3b	91	9,400	16,000	1.7	426

^a 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 toluene as eluant on the basis of polystyrene calibration.

^b Not measured due to poor solubility in toluene.

 $^{\rm c}$ Decomposition temperature (5% weight loss) estimated using TGA under $N_2.$



FIGURE 2 UV-vis-NIR spectra of the polymers in 10⁻⁶ M chloroform solution (a) and in film spin coated from chloroform solution (b).

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Polymer	Solution (nm)	Film (nm)	E_{g}^{opt} (eV) ^a
1a	351,485,619	350,490,630	1.59
1b	354,484,618	349,485,617	1.63
1c	357, 485, 620	354, 484, 608	1.60
2a	369,482,736	369,483,747	1.37
2b	369,486,714	372,492,754	1.30
3a	448,685	451,677	1.48
3b	492,770	490,773	1.24

^a Estimated from the onset edge of absorption in the film.

larger than E_{g}^{opt} . This phenomenon was usually observed for other type polymers in literatures.¹⁶

Film Morphology

Figure 4 shows atomic force microscope (AFM) height images of the polymer films on the OTS-modified Si/SiO_2 substrates spin coated from chloroform solution. All the

polymer films exhibit typical amorphous state without any crystalline domains. The root-mean-square (rms) roughness of these films is in the range of 1–2.1 nm. More uniform morphology (rms roughness of 1.065 nm) with lower defect density was observed for polymer **1a**, which is beneficial to electron transport. To further investigate the thin film organization of the copolymers, we carried out X-ray diffraction (XRD) measurements. None of the polymer thin films exhibit peaks in $2\theta = 2-30^{\circ}$ region (**1a** as an example shown in Fig. 5), suggesting no crystalline structure, which is consistent with AFM images.

Field-Effect Transistors

OFET devices were fabricated in a bottom-gate, top-contact configuration using Au as source and drain electrodes to study the charge-transport properties of these polymers; the transistor device parameters are summarized in Table 4. We have previously reported n-channel OFET data acquired in nitrogen for **1a** and **2a** using Al as top-contact source and drain electrodes.^{8(a,b)} Similar mobilities were observed in both cases to those found in this study. The threshold voltages were, however, significantly lower in the previous studies, presumably due to more facile electron injection from



FIGURE 3 Cyclic voltammograms of all polymers in CH₃CN/0.1 M [${}^{n}Bu_{4}N$] ${}^{+}$ [PF₆] ${}^{-}$ with ferrocenium/ferrocene as an internal standard, at 50 mV/s. The horizontal scale refers to an anodized Ag wire pseudo-reference electrode.

TABLE 3 Electrochemical Properties of the Polymers^a

Polymer	$E_{\rm ox}^{\ b}$ (eV)	$E_{\rm red}^{\rm b}$ (eV)	IP ^c (eV)	EA ^c (eV)	E_{g}^{ec} (eV)
1a	+1.03	-0.89	-5.83	-3.91	1.92
1b	+1.06	-0.84	-5.86	-3.96	1.90
1c	+1.12	-0.83	-5.92	-3.97	1.95
2a	+0.74	-0.90	-5.54	-3.90	1.64
2b	+0.51	-0.79	-5.31	-4.01	1.30
3a	+0.62	-0.91	-5.42	-3.89	1.53
3b	+0.58	-0.93	-5.38	-3.87	1.51

^a Thin films in CH₃CN/0.1 M [ⁿBu₄N]⁺[PF₆]⁻ at 50 mV/s.

^b E_{ox} is the onset potential for oxidation vs. $FeCp_2^{+/0}$; E_{red} is the onset potential for reduction vs. $FeCp_2^{+/0}$.

 $^{\rm c}$ IP and EA estimated from the onset oxidation and reduction potentials, respectively, assuming the absolute energy level of ferrocenium/ ferrocene to be 4.8 eV below vacuum.

the lower work function Al electrodes. Comparing behavior between the different compounds, we note the following:

The charge-transport properties of the polymers vary considerably with the variation of the *N,N'*-substituents of the PDI, with the electron mobility in nitrogen varying by nearly two orders of magnitude within the series of PDI-DTT, **1a-c**. The highest mobility is found in **1a** and may possibly be related to stronger interchain interactions in this polymer, which also exhibits a relatively larger red shift of the low-energy absorption band between solution and film. The highest mobility in **1a** is also attributed to more uniform morphology with smaller rms roughness and lower defect density. Polymers **1a-c** do not function in n-channel FET in air. For the PDI-DTP polymers, **2a** (with swallow-tail groups) exhibits only n-channel FET behavior in nitrogen, but **2b** (with propoxyethyl groups)



FIGURE 5 X-ray diffraction pattern of 1a thin film on OTS-modified Si/SiO₂ substrate.

exhibits ambipolar transport properties in air (Fig. 6). Polymer **2b** exhibits the largest EA (-4.01 eV) and the smallest IP (-5.31 eV) among all the polymers, which facilitates electron and hole injection and ambipolar transport. Moreover, strong intermolecular interaction [evidenced by the large red shift (40 nm) of low-energy absorption band that we observed between solution and film] of **2b** perhaps contributes to the ambipolar transport. To the best of our knowledge, this is the first example of a PDI-based polymer to exhibit ambipolar transport.

 The charge-transport properties also vary with the choice of donor. Replacing DTT with DTP in **1a** to give **2a** leads to fourfold lower electron mobility and two orders of magnitude lower on/off ratio. Increasing the number of



FIGURE 4 AFM topographic images (5 μ m \times 5 μ m) of thin films of all polymers on OTS-modified Si/SiO₂ substrates. The scale of height images are 0 to 8 nm.



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TABLE 4 Performance of OFETs Based on the Polymers

	<i>n</i> -Channel			p-Channel			
	Mobility (e) (cm²/V/s)	I _{on} /I _{off}	V _T (V)	Mobility (h) (cm²/V/s)	I _{on} /I _{off}	V _T (V)	
1a ^a	$1.7 imes 10^{-2}$	10 ⁶	13	-			
1b ^a	$4 imes 10^{-3}$	10 ⁵	15	-			
1c ^a	3×10^{-4}	10 ³	14	_			
2a ^a	$5 imes 10^{-3}$	10 ⁴	13	-			
2b ^b	4×10^{-4}	10 ⁴	17	4×10^{-5}	10 ³	0	
3a ^a	$7 imes 10^{-4}$	10 ⁴	18	_			
3b ^c	3×10^{-4}	10 ³	27	4×10^{-5}	10 ³	-15	

^a In nitrogen.

^b In air.

^c In air for p-channel FET but in nitrogen for *n*-channel FET.

DTT units in the donor bridges between the PDIs from 1 (1a) to 3 (3a) leads to a two orders of magnitude decrease in the electron mobility and in the on/off ratio. Again, replacing DTT with DTP in the PDI-3DTT polymer (3b) leads to a lower electron mobility and a lower on/off ratio. It is possible that intrachain ET is hindered by the more electron-rich DTP groups (in 2) and/or by the longer bridges (in 3), while the overall dilution of electron-transporting PDI content by the *N*-alkyl groups of the DTPs or by using longer bridges may hinder interchain ET. Interestingly, 3a (with three DTT units) does not exhibit p-channel FET behavior in nitrogen and in air although it has a longer electron donating block. However,

its DTP-containing counterpart (3b) exhibits p-channel FET behavior in air, which may be related to the smaller IP of **3b** due to more electron-rich character of DTP vs. DTT.¹³

CONCLUSIONS

We have shown that electron-transporting polymers with good solution processability, excellent thermal stability, high electron affinities, and in some cases high electron mobilities can be obtained based on copolymerization of perylene diimide and dithienothiophene, dithienopyrrole, or related oligomeric building blocks. One of these materials is the first example of an ambipolar PDI-based polymer. In particular, we have investigated the effects of main chain structure and side chain structure on the thermal, electronic, and charge transport properties of the polymers. To summarize:

- 1. The absorption spectra red shift and the band gap decreases with increasing the conjugation length of donor block, or by replacement of DTT by DTP. Increasing the number of DTT units, or replacing DTT with DTP, leads to more facile oxidation (smaller IP), but affects the ease of reduction (EA) to a lesser extent, suggesting that the LUMOs are strongly PDI-localized. Increasing the number of DTT units, or replacing DTT with DTP, also leads to lower electron mobilities. However, in some cases, replacing DTT with DTP leads to ambipolar transport, probably related to the more electron-rich character of DTP vs. DTT.
- 2. The *N*-substituents on PDI unit exhibit little effect on the absorption of the polymers in solution, but exhibit considerable effect on the low-energy charge transfer bands and



FIGURE 6 Ambipolar OFET properties of **2b**: (a) n-type output; (b) n-type transfer; (c) p-type output; (d) p-type transfer curves for a top contact device (annealing at 140 °C for 1 h, W = 3 mm, $L = 50 \mu$ m, 100 nm film).

6

intermolecular interaction in film. The substituents on the imide exhibit little impact on energy levels but significant effect on charge transport properties of the polymers.

EXPERIMENTAL

Materials

Monomers N,N'-bis(2-decyl-tetradecyl)-1,7-dibromo-3,4:9,10perylene diimide,^{8(a)} 2,6-bis(tri-n-butylstannyl)dithieno [3,2-b:2',3'-d]thiophene,^{8(a)} 2,6-bis(tri-n-butylstannayl)-N-(ndodecyl) dithieno[3,2-b:2',3'-d]pyrrole,^{8(b)} 1,7-bis(6-bromodithieno[3,2-b:2',3'-d]thiophene-2-yl)-N,N' – bis(2-decyl-tetradecyl)-3,4:9,10-perylene diimide,^{8(b)} and N,N'-bis(2-propoxyethyl)-1,7-dibromo –3,4:9,10-perylene diimide (**Ic**),^{8(d)} and polymers **1a**,^{8(a)} **2a**,^{8(b)} and **3a**^{8(b)} were synthesized according to our published procedures. 3,4,5-Tris(n-dodecyloxy)aniline^{17(a)} and 2-hexyl-decylamine^{17(b)} were synthesized according to the literature methods. Toluene was distilled from sodium-benzophenone under nitrogen prior to use. All other reagents were used as received.

Characterization

The ¹H and ¹³C 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 GCT-MS micromass spectrometer using the electron impact (EI) mode or 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 thin-film (on quartz substrate) UV-vis-NIR 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. Potentials were referenced to the ferrocenium/ferrocene (FeCp $_2^{+/0}$) couple by using ferrocene as an internal standard. Thermogravimetric analysis (TGA) measurements were performed on Shimadzu thermogravimetric analyzer (model DTG-60) under a nitrogen flow at a heating rate of 20 °C/min. The gel permeation chromatography (GPC) measurements were performed on a Waters 515 chromatograph connected to a Waters 2414 refractive index detector, using toluene as eluant and polystyrene standards as calibrants. Three Waters Styragel columns (HT2, 3, 4) connected in series were used. AFM images of organic thin films were obtained on a NanoMan VS microscope (Digital Instruments) in tapping mode. 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 Ka radiation. The samples for XRD and AFM measurements were prepared by spin-coating chloroform solution of the polymers on the OTS-modified Si/SiO₂ substrates.

Fabrication and Characterization of Field-Effect Transistors

FET devices were fabricated with a bottom-gate top-contact configuration. A heavily doped *n*-type Si wafer with a SiO₂ layer of 500 nm and a capacitance of 7.5 nF/cm² was used as the gate. Octadecyltrichlorosilane (OTS) was used as a self-assembled surface modifier for SiO₂. A 100-nm thick (\pm 10 nm) semiconductor film was spin-coated on top of the OTS-treated SiO₂ from 10 mg/mL chloroform solution of the polymers. Gold source and drain contacts (50 nm) were deposited on the organic layer through a shadow mask under high vacuum. The channel length (*L*) and width (*W*) were 50 μ m and 3 mm, respectively. All the measurement of electric property was carried out in nitrogen or air using a Keithley 4200 SCS semiconductor parameter analyzer. **2b**-Based device annealing was carried out at 140 °C for 1 h in a vacuum oven under a pressure of 0.1 Pa.

Synthesis

N,N'-Bis(2-hexyl-decyl)-1,7-dibromo-3,4:9,10-perylene diimide (Ia)

1,7-Dibromoperylene-3,4:9,10-tetracarboxylic acid dianhydride (1.63 g, 2.96 mmol) in 120 mL of $^{n}BuOH/H_{2}O$ (1:1, v/ v) was sonicated for 10 min. 2-Hexyl-decylamine (2.73 g, 11.33 mmol) 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 the extracts were dried over anhydrous MgSO₄. The solvent was removed and the residue was purified by column chromatography over silica gel eluting with CH₂Cl₂/ petroleum ether (1:1) to give a red solid (1.9 g, 64%). 1 H NMR (400 MHz, $CDCl_3$): δ 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). ¹³C NMR (100 MHz, CDCl₃): 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⁺). Anal. Calcd for $C_{56}H_{72}Br_2N_2O_4$: C, 67.46; H, 7.28; N, 2.81. Found: C, 67.53; H, 7.25; N, 2.91%.

N,N'-Bis(3,4,5-tris(n-dodecyloxy)phenyl)-1,7dibromo-3,4:9,10-perylene diimide (lb)

1,7-Dibromoperylene-3,4:9,10-tetracarboxylic acid dianhydride (142 mg, 0.26 mmol) in 112 mL propionic acid was sonicated for 10 min. 3,4,5-Tris(*n*-dodecyloxy)aniline (540 mg, 0.84 mmol) was added and the reaction mixture was stirred at 80 °C for 48 h under nitrogen. The mixture cooled down to room temperature, and then was extracted with chloroform (2 × 100 mL); the extracts were washed with aqueous sodium bicarbonate (2 × 150 mL) and water (2 × 150 mL), and dried over anhydrous MgSO₄. The solvent was removed and the residue was purified by column chromatography over silica gel eluting with CH₂Cl₂/ petroleum ether (3:1) to give a red solid (110 mg, 24%). ¹H NMR (400 MHz, CDCl₃): δ 9.45 (d, *J* = 8.2 Hz, 2H), 8.91 (s, 2H), 8.68 (d, *J* = 8.2 Hz, 2H), 6.52 (s, 4H), 4.04 (t, *J* = 6.2 Hz, 4H), 3.90 (t, *J* = 6.2 Hz, 8H), 1.85 (m, 12H), 1.55–1.20 (m, 108H), 0.87 (t, *J* =



6.2 Hz, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 162.6, 162.0, 153.6, 138.5, 137.9, 132.2,129.6, 129.2, 128.5, 128.1, 126.5, 123.0, 122.6, 121.2, 106.7, 73.4, 68.9, 31.9, 30.6, 29.929.8, 29.7, 29.5, 29.4, 29.3, 26.2, 26.1, 22.7, 14.1. MS (MALDI): m/z 1807 (MH⁺). Anal. Calcd for C₁₀₈H₁₆₀Br₂N₂O₁₀: C, 71.82; H, 8.93; N, 1.55. Found: C, 71.38; H, 8.94; N, 1.64%.

Poly{[*N*,*N*'-bis(2-hexyl-decyl)-3,4:9,10-perylenediimide-1,7diyl]-alt-(dithieno[3,2-b:2',3'-d] thiophene-2,6-diyl)} (1b)

To a 100-mL three-necked round-bottomed flask, Ia (415 mg, 0.42 mmol), 2,6-bis(tri-n-butylstannyl)dithieno[3,2b:2',3'-d]thiophene (325 mg, 0.42 mmol), and dry toluene (20 mL) were added. The mixture was deoxygenated with nitrogen for 30 min. Pd(PPh₃)₄ (11 mg, 10 μ mol) was added under nitrogen. The dark red solution was stirred at 110 °C for 2 days. The resulting black sticky solution was cooled down to room temperature. A solution of KF (5 g) in water (10 mL) was added and stirred at room temperature for 2 h to destroy the tin side products. The mixture was extracted with CH_2Cl_2 (2 \times 150 mL), washed with water (2 \times 300 mL), and the extracts were dried over anhydrous MgSO₄. The solution was concentrated to 15 mL, then dropped into 300 mL of methanol. The black precipitate was filtered, and washed with methanol. The black solid was redissolved in 60 mL of CH₂Cl₂, then dropped into 500 mL of acetone. The black precipitate was filtered, and Soxhlet extracted with acetone for 2 days. Finally, the polymer was purified by size exclusion column chromatography over Bio-Rad Bio-Beads S-X1 eluting with CHCl₃. Polymer **1b** was dissolved in chloroform and filtered through a 0.22 μ m Nylon 6 filter to remove the insoluble impurities. Removal of the solvent afforded a black solid (387 mg, 88%). ¹H NMR (400 MHz, CDCl₃): δ 8.7 (br, 2H), 8.3 (br, 4H), 7.6 (br, 2H), 4.1 (br, 4H), 2.0 (br, 2H), 1.2 (br, 48H), 0.8 (br, 12H). Anal. Calcd for $(C_{64}H_{74}N_2O_4S_3)_n$: C, 74.52; H, 7.23; N, 2.72. Found: C, 73.59; H, 7.16; N, 2.63%.

Poly{[N,N'-bis(3,4,5-tris(n-dodecyloxy)phenyl)-3,4:9,10-perylene diimide-1,7-diyl]-alt- (dithieno [3,2-b:2',3'-d]thiophene-2,6-diyl)} (1c)

To a 100-mL three-necked round-bottomed flask, Ib (722 mg, 0.4 mmol), 2,6-bis(tri-n-butylstannyl)dithieno[3,2-b:2',3'd]thiophene (310 mg, 0.4 mmol), and dry toluene (20 mL) were added. The mixture was deoxygenated with nitrogen for 30 min. Pd(PPh₃)₄ (47 mg, 40 μ mol) was added under nitrogen. The dark red solution was stirred at 110 $^\circ\text{C}$ for 2 days. The black sticky solution was cooled down to room temperature. A solution of KF (5 g) in water (10 mL) was added and stirred at room temperature for 2 h to destroy the tin side products. The mixture was extracted with CH₂Cl₂ $(2 \times 150 \text{ mL})$, washed with water $(2 \times 300 \text{ mL})$, and the extracts were dried over anhydrous MgSO₄. The solution was concentrated to 15 mL, then dropped into 300 mL of methanol. The black precipitate was filtered and washed with methanol. The black solid was redissolved in 60 mL of CH₂Cl₂, and then dropped into 500 mL of acetone. The black precipitate was filtered, and Soxhlet extracted with acetone for 2 days. Finally, the polymer was purified by size exclusion column chromatography over Bio-Rad Bio-Beads S-X1 eluting with THF. Polymer 1c was dissolved in chloroform and filtered through a 0.22 μ m Nylon 6 filter to remove the insoluble impurities. Removal of the solvent afforded a black solid (640 mg, 87%). ¹H NMR (400 MHz, CDCl₃): δ 8.7 (br, 2H), 8.3 (br, 4H), 7.6 (br, 2H), 6.5 (br, 4H), 4.0 (br, 12H), 1.9-1.2 (br, 120H), 0.8 (br, 18H). $M_{\rm w}$ 3.8 \times 10⁴; $M_{\rm w}/M_{\rm n}$, 1.5. Anal. Calcd for (C₁₁₆H₁₆₂N₂O₁₀S₃)_n: C, 75.69; H, 8.87; N, 1.52. Found: C, 74.81; H, 8.75; N, 1.41%.

Poly{[N,N'-bis(2-propoxyethyl)-3,4:9,10perylenediimide-1,7-diyl]-alt-(N-n-dodecyl-dithieno [3,2-b:2',3'-d]pyrrole-2,6-diyl)} (2b)

To a 100-mL three-necked round-bottomed flask, Ic (216 mg, 0.30 mmol), 2,6-bis(tri-n-butylstannyl)-N-n-dodecyldithieno[3,2-b:2',3'-d]pyrrole (278 mg, 0.30 mmol), and dry toluene (10 mL) were added. The mixture was deoxygenated with nitrogen for 30 min. $Pd(PPh_3)_4$ (40 mg, 36 μ mol) was added under nitrogen. The dark red solution was stirred at 110 °C for 3 days. The black solution was cooled down to room temperature. A solution of KF (5 g) in water (10 mL) was added and stirred at room temperature for 2.5 h to destroy the tin side products. The mixture was extracted with $CHCl_3$ (2 × 150 mL), washed with water (2 × 300 mL), and the extracts were dried over anhydrous MgSO₄. The solution was concentrated to 5 mL, and then dropped into 200 mL of methanol. The black precipitate was filtered, and washed with methanol. The black solid was Soxhlet extracted with acetone for 2 days. Finally, the polymer was purified by size exclusion column chromatography over Bio-Rad Bio-Beads S-X1 eluting with CHCl₃. Polymer 2b was dissolved in chloroform and filtered through a 0.22 μ m Nylon 6 filter to remove the insoluble impurities. Removal of the solvent afforded a black solid (240 mg, 89%). ¹H NMR (400 MHz, CDCl₃): δ 8.7 (br, 2H), 8.3 (br, 4H), 7.4 (br, 2H), 4.5 (br, 6H), 3.8 (br, 4H), 3.5 (br, 4H), 1.9 (br, 2H), 1.7-1.2 (br, 22H), 0.8 (br, 9H). $M_{\rm w}$ 8.2 \times 10⁴; $M_{\rm w}/M_{\rm n}$, 1.8. Anal. Calcd for C₅₄H₅₅N₃O₆S₂: C, 71.57; H, 6.12; N, 4.64. Found: C, 70.56; H, 6.05; N, 4.48%.

Poly{[1,7-bis-2-dithieno[3,2-b:2',3'-d]thiophene-N,N'-bis (2-decyl-tetradecyl)-3,4:9,10-perylene -diimide-6,6'-diyl]-

alt-(N-n-dodecyl-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)} (3b) To a 100-mL three-necked round bottom flask, 1,7-bis (6-bromodithieno[3,2-b:2',3'-d]thiophene-2-yl)-N,N'-bis(2decyl-tetradecyl)-3,4:9,10-perylene diimide (403 mg, 0.25 mmol), 2,6-bis(tri-n-butylstannyl)-N-n-dodecyl-dithieno[3,2b:2',3'-d]pyrrole (232 mg, 0.25 mmol), and dry toluene (10 mL) were added. The mixture was deoxygenated with nitrogen for 30 min. $Pd(PPh_3)_4$ (22 mg, 20 μ mol) was added under nitrogen. The dark red solution was stirred at 110 $^\circ\text{C}$ for 3 days. A solution of KF (5 g) in water (10 mL) was added and stirred at room temperature for 2.5 h to destroy the tin side products. The mixture was extracted with CHCl₃ (2 \times 150 mL), washed with water (2 \times 300 mL), and the extracts were dried over anhydrous MgSO₄. The solution was concentrated to 5 mL, and then dropped into 200 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 CHCl₃. Polymer **3b** was dissolved in chloroform and filtered through a 0.22 μ m Nylon 6 filter to remove the insoluble impurities. Removal of the solvent afforded a black solid (406 mg, 91%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.8 (br, 2H), 8.4 (br, 4H), 7.4 (br, 2H), 7.1 (br, 4H), 4.4-4.1 (br, 6H), 2.0 (br, 4H), 1.3 (br, 98H), 0.8 (br, 15H). M_{wo} 1.6 \times 10⁴; M_w/M_n , 1.7. Anal. Calcd for C₁₀₈H₁₃₅N₃O₄S₈: C, 72.23; H, 7.58; N, 2.34. Found: C, 71.20; H, 7.51; N, 2.17%.

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10 Actually a mixture of 1,7 and 1,6-dibromo isomers was used and only 1,7-dibromo isomer is shown for simplicity.

11 DFT calculations show that the LUMO for a small-molecule analogue of 1a is strongly PDI localized, while the HOMO has significant contributions from both DTT and PDI, albeit with higher coefficients on the former (Ref. 15). The bands assigned to the PDI unit are somewhat blue-shifted relative to those of isolated PDIs [Ref. 6(b)], while the primarily donor-based bands are red-shifted relative to isolated DTT and DTP units (ref. 14), reflecting the delocalization of orbitals over both donor and acceptor.

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