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PAPER

# Synthesis and thin-film transistor performance of benzodipyrrolinone and bithiophene donor-acceptor copolymers<sup>†</sup>

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Three novel benzodipyrrolinone–bithiophene based donor-acceptor polymers are synthesized and used as p-type semiconductors in organic thin-film transistors (OTFTs). Hole mobility of up to  $0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  is achieved. A new acetal-type branched substituent is introduced to significantly improve the solubility of the resulting polymer.

### Introduction

In recent years, polymer semiconductors have attracted considerable research interests because they enable solution-processing (or printing) organic thin film transistors (OTFTs),<sup>1</sup> organic photovoltaics (OPVs),<sup>2</sup> organic light-emitting diodes (OLEDs),<sup>3</sup> etc., which are essential components for inexpensive, flexible, and large-area organic opto-electronics. Charge carrier mobility is one of the most important parameters for OTFTs, which determines the performance of the electronic devices using OTFTs. Mobility for polymer semiconductors, which is typically less than  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , has long been inadequate for several applications such as backplane drivers for displays and radio-frequency identification (RFID) tags. In the last couple of years, however, a number of polymers were reported to show ultra-high mobility values close to or exceeding  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , even outperforming amorphous silicon (a-Si).<sup>4</sup> These high mobility polymer semiconductors are almost exclusively donor-acceptor (D-A)-type polymers,<sup>5</sup> which consist of an alternating arrangement of an electron-donating (D) unit and an electron-accepting (A) unit. Recently we found that combination of the electron-accepting pyrrolo[3,4-b]pyrrole-1,4(2H,5H)-dione or diketopyrrolopyrrole (DPP) and the electron-donating thieno[3,2-b]thiophene could form a p-type D-A polymer, PDBT-co-TT, which showed high hole mobility of  $\sim 0.94$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in OTFTs.<sup>6</sup> The strong intermolecular donor-acceptor interactions led to the reduced  $\pi$ - $\pi$  stacking distance (~3.71 Å) and the well-interconnected film morphology, which are responsible respectively for the improved interchain and interdomain charge hopping. Later, this polymer was reinvestigated in ambipolar OTFTs resulting in even higher

hole mobility up to  $1.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and electron mobility up to 2.0 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for polymer films annealed at high temperatures.<sup>7</sup> Within less than two years, a number of other DPP-based D-A polymers with mobility of ~1 to 2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> were reported,<sup>6,8</sup> demonstrating that DPP is indeed a very useful building block for high-performance polymer semiconductors for OTFTs.

DPP can be viewed as a fused aromatic ring of two pyrrolinones. A natural extension of DPP by fusing two pyrrolinones to cyclohexa-1,4-diene would form a larger conjugated moiety, pyrrolo[3,4-*f*]isoindole-1,5(2*H*,6*H*)-dione or benzodipyrrolinone (BDP) (Scheme 1). When used as a building block in polymer semiconductors, the more extended  $\pi$ -conjugation and the larger ring size of BDP could provide stronger intermolecular interactions and larger  $\pi$ - $\pi$  overlapping, which are desirable characteristics for efficient charge transport. While the preparation of BDP was proven to be a synthetic challenge, its isomeric structure, pyrrolo[2,3-*f*]indole-2,6(1*H*,5*H*)-dione (BDP') is readily accessible.<sup>9</sup> Based on its analogy with BDP in terms of its molecular geometry and electronic structure, BDP' is also highly likely a useful building block for high mobility D-A polymers for OTFTs.



Scheme 1 A structural comparison of various fused pyrrolinones, wherein *R* is hydrogen or a suitable substituent such as an alkyl group.

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Small molecules that comprise BDP' have been known for many years as pigments and dyes.9 Very recently, BDP'-based polymers comprising a thiophene unit (PBDP'DP-T) was reported.<sup>10a</sup> The resulting polymers showed ambipolar behaviour in OTFT devices. Electron mobility of up to  $3.5 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and hole mobility of up to  $6.4 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> were achieved. Another lately reported BDP'-thiophene copolymer containing N-acvlated side chains showed improved electron mobility of up to  $0.012 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>10b</sup> In this work, we report three new BDP'-based D-A polymers, PBDP'DP-BT's, synthesized via Stille coupling polymerization and their charge transport performance as channel semiconductors in OTFTs. The incorporation of the longer and more electron donating bithiophene (BT) unit aims to suppress the electron transport behaviour and promote hole transport of the resulting BDP' polymers. All polymers showed unipolar p-channel charge transport characteristics with the best hole mobility value of up to  $0.03 \text{ cm}^2$  $V^{-1}$  s<sup>-1</sup>. The use of a new acetal-type side-chain significantly improved the solubility of the resulting BDP'-based polymer. Our results demonstrate that BDP' is a promising acceptor building block for the construction of high performance D-A type polymer semiconductors and that an extension of the donor unit could be able to convert the BDP' based polymers into unipolar p-type semiconductors with improved charge transport mobility.

### **Results and discussion**

The synthetic route to PBDP'DP-BT is outlined in Scheme 2. Compound 1 was prepared in good yields ( $\sim$ 87%) according to the established literature methods.<sup>9</sup> Ring-closure of compound 1

in concentrated sulphuric acid afforded 2 in 96% isolated vields. The<sup>1</sup>H NMR spectrum of 2 confirmed that it contains three stereoisomers. Oxidation of 2 with  $H_2O_2$  produced 3 in 45% yields. The subsequent alkylation of 3 with 2-octyldodecyl bromide, 2-decyltetradecyl bromide or 2,2-bis((3,7-dimethyloctyl)oxy)ethyl bromide was conveniently accomplished in anhydrous DMF in the presence of potassium carbonate, a procedure similar to the one for the preparation of alkylated DPP compounds.<sup>6,11</sup> The products M1-M3 were obtained in 57-68% yields. Substitution of the BDP' unit with long branched alkyl and acetal type side chains aims to provide sufficient solubility to resulting polymers. The precursor to novel acetal type side chain, 2,2-bis((3,7-dimethyloctyl)oxy)ethyl bromide, could be easily synthesized in high yields ( $\sim 90\%$ ) by heating the commercially available bromoacetaldehyde diethyl acetal and 3,7-dimethyl-1octanol in the presence of a catalytic amount of methanesulfonic acid.

Polymers P1 (PBDP'DP20-BT), P2 (PBDP'DP24-BT) and P3 (PBDP'DP24a-BT) were synthesized by Stille coupling reactions of 5,5'-bis(trimethylstannyl)-bithiophene with M1, M2, and M3, respectively, in the presence of a catalytic amount of Pd(PPh\_3)<sub>2</sub>Cl<sub>2</sub> in toluene at 90–110 °C. After being precipitated from methanol, the polymers were extensively purified by Soxhlet extraction successively with acetone and hexane to remove low molecular mass fractions and other impurities. The higher molecular weight polymer fractions were dissolved with refluxing chloroform. However, P1 substituted with 2-octyldodecyl groups was found only sparingly soluble in chloroform and thus 1,1,2,2-tetrachloroethane (TCE) that has a higher boiling point (146 °C) than that (61 °C) of chloroform was used to extract P1. The majority of P1 (73%) was dissolved in TCE, while



Scheme 2 Synthesis of (a) PBDP'DP-BT polymers (P1, P2, and P3) and (b) 2,2-bis((3,7-dimethyloctyl)oxy)ethyl bromide.

there still remained some insoluble mass in the extraction thimble. Polymer P2, which has longer side chains (2-decyltetradecyl groups), showed better solubility with 35% of the theoretical mass (as P2a) dissolved with refluxing chloroform. The remaining higher molecular-weight fraction was completely dissolved with refluxing TCE, affording another 59% yield of polymer as P2b. The lower solubility of these two polymers than that of DPP-based copolymers<sup>6,11</sup> could be attributed to the stronger intermolecular interactions in P1 and P2 due to the presence of larger fused BDP' rings. On the other hand, polymer **P3** substituted with the highly branched acetal-type side chain, 2,2-bis((3,7-dimethyloctyl)oxy)ethyl, showed significantly improved solubility with all the high molecular weight fractions (P3,  $\sim 90\%$  yield) being dissolved in refluxing chloroform. Besides chloroform, P3 is also soluble in tetrahydrofuran (THF), chlorobenzene, 1,2-dichlorobenzene, 1,1,2-trichloroethane, and TCE. Since P1 and P2 showed very poor solubility in THF, the molecular weights of all polymers were determined by hightemperature gel permeation chromatography (HT-GPC) with polystyrene as standards and 1,2,4-trichlorobenzene as an eluent at a high temperature of 140 °C. For P1, the number average molecular weight  $(M_n)$  was found to be 6.0 kDa, while its weight average molecular weight  $(M_w)$  is 27.4 kDa (with a polydispersity index, PDI, of 4.57). The average number of repeat unit for P1 is calculated to be 5.7, indicating that P1 consists of a significant portion of oligomers. P2a, which was extracted with chloroform, is also mainly composed of oligomers with a low  $M_{\rm n}$  of 4.3 kDa (PDI = 3.51). The molecular weights of the TCE extracted fraction, **P2b**, are much higher with a  $M_n$  of 19.8 kDa (PDI = 1.78). The chloroform extracted P3 has an even higher  $M_{\rm n}$  of 22.8 kDa (PDI = 2.89), which is close to that  $(M_n = 25.4 \text{ kDa}, \text{PDI} =$ 2.39) of a DPP-based high mobility polymer PDQT<sup>11</sup> measured using a HT-GPC system.

The UV-Vis absorption properties of P1-P3, as well as their monomers M1-M3 in TCE solutions and in thin films are shown in Fig. 1 and Table 1. In solutions, all three monomers showed almost an identical maximum absorption wavelength ( $\lambda_{max}$ ) at ~471 nm. In thin films, their  $\lambda_{max}$  red-shifted to 519–522 nm, suggesting that these molecules are more coplanar and have strong intermolecular interactions in the solid state. As expected, polymers P1-P3 displayed large redshifts in their absorption spectra in comparison to their corresponding monomers M1-M3. Redshifts of  $\sim$ 22 to 47 nm in the  $\lambda_{max}$  from solution to the solid thin film for all polymers are observed, which are indicative of the more coplanar conformation of the polymer chains and the stronger intermolecular interactions (such as the D-A interactions) in the solid state. P1 showed a  $\lambda_{max}$  at 590 nm in solution, while the  $\lambda_{max}$  of **P2b** in solution is 605 nm, 15 nm longer than that of P1. This difference is apparently a result of their different molecular weights; P2b with a higher molecular weight has a more extended  $\pi$ -conjugation length and thus a smaller band gap. Interestingly, in the solid state, P1 and P2b exhibited almost identical absorption maxima (637 nm for P1 and 639 nm for P2b). This result might be interpreted by the enhanced intermolecular interactions and polymer chain aggregation of P1 in the thin films. On the other hand, P3 showed a longer  $\lambda_{max}$  at 653 nm in the thin film. The red-shifted absorption profile of the P3 thin film compared with those of P1 and P2 might be due to the stronger intermolecular interactions



Fig. 1 Normalized UV-Vis absorption spectra of M1–M3 and polymers P1–P3: (a)  $\sim 10^{-5}$  M solutions in 1,1,2,2-tetrachloroethane; and (b): thin films spin-coated from 1,1,2,2-tetrachloroethane solutions on glass substrates.

enhanced by the polar acetal side chains in the solid state. The optical band gaps  $(E_g^{opt})$  of **P1**, **P2b** and **P3** thin-films are calculated to be 1.61, 1.62 and 1.59 eV from their absorption edges of 769, 766 and 779 nm, respectively, which are narrower than that (1.68 eV) of BDP'-thiophene copolymer (PBDP'DP-T) reported previously.<sup>10a</sup>

The electrochemical properties of P1, P2b, and P3 thin films were examined with cyclic voltammetry (CV) in 0.1 M Bu<sub>4</sub>NPF<sub>4</sub> solution in anhydrous acetonitrile, using ferrocene (with a highest occupied energy molecular orbital (HOMO) energy level,  $E_{\rm HOMO} = \sim -4.8 \text{ eV}^{12}$  as an external standard. For all the polymers, a reversible oxidation process was observed (Fig. 2). The HOMO energy levels of P1, P2b, and P3 were calculated from their onset oxidation potentials to be -5.64, -5.66 eV, and -5.62 eV, respectively (Table 1). On the other hand, the reduction processes of these polymers showed weak and irreversible I-V loops, indicating that these polymers are unstable during the reduction processes under our experimental conditions. Therefore the lowest unoccupied molecular orbital (LUMO) energy levels (E<sub>LUMO</sub>) of P1, P2b, and P3 were calculated using their HOMO levels and optical band gaps to be -4.03, -4.04, and -4.03 eV, respectively, which are comparable to that of their analogous DPP-bithiophene copolymer PDQT (-4.0 eV).<sup>11</sup> The

Table 1 Properties of BDP'-containing monomers M1-M2 and polymers P1-P3

	$\lambda_{\max}^{abs\ a}$ (nm)		$\lambda_{\text{onset}}^{\text{abs}}{}^{a}$ (nm)				Energy levels <sup>e</sup>		OTFT performance	
Compounds	Solution <sup><i>a</i></sup>	Film <sup>b</sup>	Solution <sup>a</sup>	Film <sup>b</sup>	$E_{\rm g}^{{ m opt}c}~({ m eV})$	$E_{\mathrm{ox}}^{\mathrm{onset}d}$ (eV)	$E_{\mathrm{HOMO}}\left(\mathrm{eV}\right)$	$E_{\rm LUMO}~({\rm eV})$	$(\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ range (average)	$I_{\rm on}/I_{\rm off}$
M1	471	519	535	560	_	_	_	_	_	_
M2	470	519	537	556						
M3	471	522	536	558					_	_
P1	590	637	707	769	1.61	0.84	-5.64	-4.03	0.003-0.030(0.015)	$\sim 10^{3-6}$
P2b	605	639	738	766	1.62	0.86	-5.66	-4.04	0.007-0.027(0.018)	$\sim 10^{3-5}$
P3	631	653	750	779	1.59	0.82	-5.62	-4.03	0.024-0.030(0.026)	$\sim 10^{5-6}$

 $^{a} \sim 10^{-5}$  M in 1,1,2,2-tetrachloroethane.  $^{b}$  Spin-coated films from 1,1,2,2-tetrachloroethane solutions on glass substrates.  $^{c}$  Calculated from the onset absorption,  $E_{g}^{opt} = 1240/\lambda_{onset}^{abs}$ .  $^{d}$  Calculated using the equation  $E_{ox}^{onset}$  (*vs.* Fc/Fc<sup>+</sup>) =  $E_{ox}^{onset}$  (*vs.* Ag/AgCl) –  $E_{ox}^{onset}$  (Fc/Fc<sup>+</sup> *vs.* Ag/AgCl).  $^{e}$  Calculated using the equation  $E_{HOMO}$  (eV) =  $-E_{ox}^{onset}$  (*vs.* Fc/Fc<sup>+</sup>) – 4.8 eV,  $E_{LUMO} = E_{HOMO} + E_{g}^{opt}$ .



Fig. 2 Cyclic voltammograms of films of P1, P2b, and P3 in 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile at a sweeping rate of 50 mV s<sup>-1</sup> under nitrogen, using ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple as a standard.

low LUMO levels of **P1**, **P2b**, and **P3** indicate that BDP' is a strong electron accepting building block. The very similar HOMO and LUMO levels measured for these three polymers indicate that the energy levels are mainly determined by their conjugated backbone, while different side chain substitutions only exerted slight effects.

To investigate the molecular organization of these polymers in the thin film state, X-ray diffraction (XRD) analysis of the polymer thin films spin-coated on glass substrates was performed. As shown in Fig. 3, the as-spun P1 thin film showed a primary reflection peak at  $2\theta = \sim 4.9^\circ$ , which remained similar after the film was annealed at 150 and 200 °C, respectively. The as-spun **P2b** film showed a noticeable peak at  $2\theta = \sim 4.8^{\circ}$ . The intensity of this peak increased as the film was annealed at 150 °C. Further raising the annealing temperature to 200 °C had little effect on increasing the intensity of this peak. Very weak reflections were observed for the as-spun P3 film. After the film was annealed at 150 °C, a primary peak at  $2\theta = \sim 4.1^{\circ}$  appeared. Interestingly, the reflection intensity of this peak decreased when the sample was annealed at 200 °C, which might be due to the side chain motion at this temperature.<sup>13</sup> The diffraction patterns of these polymers resemble those of many other conjugated polymers with a layer-by-layer lamellar packing structure.<sup>6,8,11</sup>



**Fig. 3** XRD diagrams obtained from spin-coating polymer thin films on glass substrates annealed at different temperatures.

The low angle diffraction peak represents the interlayer *d*-spacing distance, which was calculated to be ~18.0 Å for **P1**, ~18.4 Å for **P2b**, and 21.5 Å for **P3**, respectively. The broad peak in the region of  $2\theta = \sim 20$  to  $30^{\circ}$  is mainly due to the glass substrate since no such intense peaks were observed for samples prepared on the Si/SiO<sub>2</sub> wafer substrates (ESI†). The polymer thin film samples on the Si/SiO<sub>2</sub> substrates was also found to be less crystalline.

The surface morphology of **P1**, **P2b**, and **P3** thin films ( $\sim$ 30 to 40 nm) spin-coated using their solutions in TCE on glass substrates was characterized with the atomic force microscopy (AFM) technique (Fig. 4). For the as-spun **P1** thin film, spherical grains with an average diameter of  $\sim$ 50 nm formed. Thermal annealing at 150 and 200 °C improved the granular connectivity,

but large gaps between grains remained. The as-spun **P2b** thin film showed smaller grains than those in the as-spun **P1** thin film. Some grains have joined to form clusters when the film was annealed at 150 °C. For the film annealed at 200 °C, all grains are well connected. On the other hand, the AFM image of the asspun **P3** thin film showed a much smoother surface, which consists of tightly packed grains of ~50 nm in diameter. The grains become well defined for the film annealed at 150 °C, but turned less discernible again once the annealing temperature was increased to 200 °C. The changes in the morphology with annealing temperature observed for the thin films of all three polymers are in good agreement with the changes in crystallinity shown in their XRD diagrams (Fig. 3). It seems that the film consisting of more defined grains is more crystalline. The



Fig. 4 AFM height images ( $2 \times 2 \mu m$ ) of polymer thin films (~30 to 40 nm) on glass substrates annealed at different temperatures: (a) P1/r. t., (b) P1/150 °C; (c) P1/200 °C, (d) P2b/r. t., (e) P2b/150 °C, (f) P2b/200 °C, (g) P3/r. t., (h) P3/150 °C, and (i) P3/200 °C.





**Fig. 5** Output (left) and transfer (right) curves of a typical OTFT device with a **P3** thin film annealed at 120 °C. Device dimensions: channel length  $L = 50 \mu \text{m}$ ; channel width  $W = 500 \mu \text{m}$ .

formation of smoother and well interconnected morphology observed for P3 is probably due to the better solubility and the amorphous nature of the as-spun thin films of this polymer as compared to P1 and P2b. AFM images of polymer thin films on Si/SiO<sub>2</sub> substrates were also measured (ESI†). P1 films on Si/SiO<sub>2</sub> are similar as on the glass substrates, but P2b and P3 films showed dramatically different surface morphology. This again affirms that the substrate surface plays an important role in the molecular organization.

Polymers P1, P2b, and P3 were evaluated as channel semiconductors in the top-gate, bottom-contact OTFT device architecture. A glass substrate was first patterned with gold sourcedrain pairs with a channel length (L) of 50  $\mu$ m and a channel width (W) of 500  $\mu$ m. A polymer thin film (~30 nm) was then deposited by spin-coating a polymer solution in 1,2-dichlorobenzene on the substrate, followed by thermal annealing at 120 °C for 5 min on a hotplate. Next, a polyolefin-polyacrylate dielectric layer (capacitance =  $4.2 \text{ nF cm}^{-2}$ ) was deposited by spin-coating a Polyera ActivInkTM D2200 solution and baked at 120 °C for 5 min. Finally a ~30 nm gold thin film was deposited as a top gate electrode to complete the device fabrication. OTFT devices were characterized under ambient conditions. All polymers tested showed typical p-type field effect behaviour. The hole mobility  $(\mu_h)$  and current on-to-off ratio  $(I_{\rm on}/I_{\rm off})$  are summarized in Table 1. The average mobility values for **P1**, **P2b**, and **P3** are 0.015, 0.018, and 0.026 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. The mobility values for these polymers are greater than the ones reported for the BDP' copolymer having one thiophene unit (PBDP'DP-T).<sup>10</sup> In addition, the electron transport characteristics of P1-P3 are minimal, indicating that the incorporation of the stronger electron-donating bithiophene unit effectively suppressed the electron transport and enhanced the hole transport performance. OTFTs with P1 and P2b showed large variations in mobility and current on-to-off ratio. This is due to the poor quality of the P1 and P2b thin films as shown in their AFM images, where there are large gaps between grains. On the other hand, the mobility and the current on-to-off ratio of the P3 based OTFTs are very consistent, which is due to the smoother morphology of the P3 thin films consisting of tightly joined grains (Fig. 4). The output and transfer curves of a typical

device based on P3 are shown in Fig. 5. The hole mobility in the saturation regime at  $V_{\rm DS} = -60$  V is 0.03 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, with a high current on-to-off ratio of ~10<sup>6</sup>.

### Conclusions

Three new pyrrolo[2,3-f]indole-2,6(1H,5H)-dione (BDP')bithiophene copolymers P1, P2, and P3 were synthesized by Stille coupling polymerization. The BDP' moiety showed similar electron-accepting effects as the DPP unit in conjugated polymers, but it induced stronger intermolecular interactions due to its large ring size. All three polymers showed good hole mobility up to  $\sim 0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , demonstrating that BDP' is a potentially useful acceptor building block for polymer semiconductors for OTFTs. The incorporation of an electron-donating bithiophene unit in these polymers could suppress the electron transport characteristics, making these polymers explicit in hole transport. The phenylene units adjacent to BDP' are found to cause unfavoured twisting of the polymer backbone.<sup>10a</sup> It is expected that replacing the phenylene units with sterically less encumbered thiophene or furan rings would planarize the polymer backbone and thus greatly enhance the charge transport properties, as similarly observed in the analogous DPP-based polymers. It was found that the long branched alkyl side chain, 2octyldecyl and even 2-decyltetradecyl, which are sufficient for solubilising the analogous DPP-based polymers, are unable to offset the strong aggregation tendency enhanced by the BDP' units to render the resulting polymers soluble. A novel acetaltype side chain substituent, 2,2-bis((3,7-dimethyloctyl)oxy)ethyl, was found to be an excellent solubilising group for the BDP'based polymers. Besides solubility, the acetal substitution has significant impacts on the molecular ordering, thin film morphology, and OTFT performance of the resulting polymers.

### Experimental

#### Instrumentation and materials

Reagents and anhydrous solvents were purchased from Sigma-Aldrich or Alfa Aesar and used as received. N, N'-(1,4-Phenylene) bis(2-(4-bromophenyl)-2-hydroxyacetamide) (1) and 3,7-bis(4bromophenyl)-5,7-dihydropyrrolo[2,3-f]indole-2,6(1H,3H)-dione (2) were prepared using the literature method<sup>9</sup> in comparable yields as reported previously.<sup>10</sup> 2-Octyldodecyl bromide and 2decyltetradecyl bromide14 and 5,5'-bis(trimethylstannyl)bithiophene<sup>15</sup> were synthesized according to the literature. NMR data were collected on a Bruker DPX 300 MHz spectrometer with chemical shifts relative to tetramethylsilane (TMS, 0 ppm). UV-Vis spectra were recorded on a Shimadzu Mandel 2501-PC instrument. Cyclic voltammetry (CV) measurements were performed on a potentiostat/galvanostat model EPP-4000 (Princeton Applied Research) using an Ag/AgCl reference electrode, a platinum wire counter electrode, and a platinum foil working electrode. The working electrode was coated with a polymer film by drop-casting a polymer solution in 1,1,2,2-tetrachloroethane (TCE). CV measurements were recorded in 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile at a sweeping rate of 50 mV s<sup>-1</sup> under nitrogen, using ferrocene as a ref. 12 The HOMO energy levels were calculated using the equations of  $E_{\text{HOMO}}$  (eV) =  $-\{E_{\text{ox}}^{\text{onset}} - E_{\text{Fc}}\}$  - 4.8 eV, respectively, where  $E_{\rm ox}^{\rm onset}$  and  $E_{\rm Fc}$  are the onset oxidation potentials of the polymer and ferrocene, respectively, relative to the Ag/AgCl reference electrode. The LUMO energy levels are estimated by using HOMO levels and optical band gaps. XRD diagrams of polymer thin films (~100 nm) on glass substrates or DTS-modified Si/SiO<sub>2</sub> substrates deposited by drop-casting polymer solutions in TCE were obtained with a Bruker D8 Advance powder diffractometer using standard Bragg-Brentano geometry with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). Data were collected from 2 to  $35^{\circ}$  in  $2\theta$ , using a step size of  $0.02^{\circ}$  and a count time of 0.7 s. High-temperature gel-permeation chromatography (HT-GPC) measurements were performed on a Malvern 350 HT-GPC system using 1,2,4-trichlorobenzene (stabilized with butylated hydroxytoluene) as an eluent with polystyrene as standards at column temperature of 140 °C. AFM images of polymer thin films were obtained on a Dimension 3100 Scanning Probe Microscope. The polymer thin films (~30 to 40 nm) for AFM measurements were deposited by spin-coating polymer solutions in TCE (0.4 wt%) on glass substrates or DTS-modified Si/SiO2 substrates.

#### Synthesis of 2,2-bis((3,7-dimethyloctyl)oxy)ethyl bromide

2-Bromoacetaldehyde diethyl acetal (3.3 mL, 20 mmol) was dissolved in 42 mL of 3,7-dimethyl-1-octanol, and 3 drops of methanesulfonic acid was added. The mixture was heated at 120 °C overnight with a slow stream of argon to remove the ethanol formed. The mixture was cooled down and sodium bicarbonate (0.84 g, 10 mmol) was added to neutralize the acid. Upon filtration and removal of solvent, the excess 3,7-dimethyl-1-octanol was removed under a reduced pressure (95 °C, 2 mbar) to give a brown oil, which was passed through a flash silica gel column with hexane as an eluent to give the title compound as a light yellow liquid (7.59 g, 90.0%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  ppm 4.65 (t, J = 5.4 Hz, 1H), 3.72–3.57 (m, 2H), 3.57–3.45 (m, 2H), 3.36 (d, J = 5.4 Hz, 2H), 1.70–1.05 (m, 20H), 0.88 (t, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  ppm 101.91, 65.29, 39.42, 37.44, 36.90, 31.86, 29.84, 28.10, 24.80, 22.84, 22.75, 19.74.

### Synthesis of 3,7-bis(4-bromophenyl)pyrrolo[2,3-*f*]indole-2,6(1*H*,5*H*)-dione (3)

A 2 M aqueous NaOH solution (24 mmol, 12 mL) was added dropwise to a suspension of 3,7-bis(4-bromophenyl)-5,7-dihydropyrrolo[2,3-*f*]indole-2,6(1*H*,3*H*)-dione (**2**) (4.4 g, 8.83 mmol) in ethanol (75 mL) at 20 °C. After 15 min, hydrogen peroxide (15 mL, 30 wt%) was added and the mixture was stirred at room temperature overnight. The reaction mixture was filtered, washed with a saturated NH<sub>4</sub>Cl aq. solution, water, i-PrOH and MeOH, then dried *in vacuo* to give compound **3** as a brown powder (1.98 g, yield 45%). <sup>1</sup>H NMR (DMSO, 300 MHz)  $\delta$  ppm 10.35 (s, 2H), 6.36 (s, 2H), 7.71 (d, *J* = 8.4 Hz, 4H), 7.61 (d, *J* = 8.4 Hz, 4H).

### Synthesis of 3,7-bis(4-bromophenyl)-1,5-bis(2-octyldodecyl) pyrrolo[2,3-f]indole-2,6(1H,5H)-dione (M1)

To a mixture of 3(1.0 g, 2 mmol) and  $K_2CO_3(0.830 \text{ g}, 6 \text{ mmol})$  in anhydrous *N*,*N*-dimethylformamide (DMF) (30 mL) was added portion-wise 2-octyl-1-dodecylbromide (2.241 g, 6.2 mmol) at

130 °C. The reaction mixture was further heated at 130 °C under stirring overnight. Then the reaction mixture was allowed to cool down to room temperature, poured into water (200 mL), and stirred for 5 min. The product was extracted with ethyl acetate (100 mL for 3 times), then washed with water. Upon removal of solvent, the crude product was further purified using column chromatography on silica gel (eluted with CH<sub>2</sub>Cl<sub>2</sub>) to give compound **M1** as a deep-green solid (1.33 g, 62.9%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  ppm 7.61 (d, *J* = 8.7 Hz, 4H), 7.57 (d, *J* = 8.7 Hz, 4H), 6.29 (s, 2H), 3.50 (d, *J* = 6.9 Hz, 4H), 1.65–1.85 (m, 2H), 1.15–1.45(m, 66H), 0.80–0.95 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  ppm 169.71, 144.47, 134.64, 132.20, 131.08, 130.19, 126.47, 123.74, 97.29, 44.18, 37.26, 32.06, 32.04, 31.91, 30.15, 29.78, 29.75, 29.50, 26.83, 22.82, 14.26. UV-Vis:  $\lambda_{max} = 471$  (in TCE), 519 (film).

### Synthesis of 3,7-bis(4-bromophenyl)-1,5-bis(2-decyltetradecyl) pyrrolo[2,3-f]indole-2,6(1*H*,5*H*)-dione (M2)

Compound **M2** was prepared from compound **3** and 2-decyltetradecyl bromide following a procedure as described for compound **M1**. Data for **M2** follow. Yield: 68.4% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  ppm 7.61 (d, J = 8.7 Hz, 4H), 7.56 (d, J = 8.7 Hz, 4H), 6.29 (s, 2H), 3.50 (d, J = 7.2 Hz, 4H), 1.65–1.85 (m, 2H), 1.15–1.45(m, 80H), 0.80–0.95 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  ppm 169.68, 144.43, 134.61, 132.18, 131.06, 130.16, 126.43, 123.72, 97.28, 44.14, 37.23, 32.06, 31.88, 30.14, 29.80, 29.50, 26.82, 22.83, 14.26. UV-Vis:  $\lambda_{max} = 470$  nm (in TCE); 519 nm (film).

### Synthesis of 1,5-bis(2,2-bis((3,7-dimethyloctyl)oxy)ethyl)-3,7bis(4-bromophenyl)pyrrolo[2,3-f]indole-2,6(1*H*,5*H*)-dione (M3)

Compound **M3** was prepared from compound **3** and 2,2-bis((3,7dimethyloctyl)oxy)ethyl bromide following a procedure as described for compound **M1**. Data for **M3** follow. Yield: 56.7%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  ppm 7.59 (s, 8H), 6.58 (s, 2H), 4.58 (t, *J* = 5.4 Hz, 2H), 3.80–3.60 (m, 8H), 3.60–3.42 (m, 4H), 1.70–0.95 (m, 40H), 0.90–0.75 (m, 36H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  ppm 169.72, 144.25, 135.12, 132.22, 131.09, 130.03, 126.48, 123.76, 98.97, 67.02, 66.93, 43.32, 39.41, 37.40, 37.07, 29.89, 28.09, 24.81, 24.77, 22.84, 22.74, 19.68, 19.63. UV-Vis:  $\lambda_{max} = 471$  nm (in TCE), 522 nm (film).

### Synthesis of PBDP'DP20-BT (P1)

**M1** (0.3172 g, 0.3 mmol) and 5,5'-bis(trimethylstannyl)-bithiophene (0.1476 g, 0.3 mmol) were charged into a 50 mL dry flask. After degassing and refilling argon for 3 times, anhydrous toluene (20 mL) and bis(triphenylphosphine)palladium(II) dichloride (7 mg) were added and the reaction mixture was heated to 90 °C and stirred for 48 h. The temperature of reaction was raised to 100 °C and reacted for another 10 h. Then 0.5 mL of bromobenzene was added and the mixture was further stirred at 100 °C for 8 h to eliminate unreacted trimethylstannyl end groups. The mixture was then poured into 200 mL of stirring methanol. The solid was filtered off, washed with methanol, and dried. The solid was further purified by Soxhlet extraction using acetone, hexane, and then dissolved with chloroform. A low molecular weight polymer fraction was obtained from the

chloroform extract as a blue-purple solid (40 mg, 12.5%). The remaining material was extracted with TCE, to give polymer P1 as a deep-blue solid film (234 mg, 73.4%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ ppm 7.90-7.50, 7.30-7.10, 6.70-6.10 (aromatic), 3.65-3.35 (NCH<sub>2</sub>), 1.90-1.65, 1.65-1.40, 1.40-1.00 (CH<sub>2</sub> and CH in the chains), 0.95–0.65 (CH<sub>3</sub>). HT-GPC:  $M_n = 6032$ ;  $M_w = 27$ , 426;  $M_{\rm w}/M_{\rm n} = 4.54$ . UV-Vis:  $\lambda_{\rm max} = 590$  nm (in TCE), 637 nm (film).

### Synthesis of PBDP'DP24-BT (P2)

P2 was prepared as described above for P1 from M2 (0.3508 g. 0.3 mmol) and 5,5'-bis(trimethylstannyl)-bithiophene (0.1476 g, 0.3 mmol). After Soxhlet extraction with acetone and hexane, the first polymer fraction P2a was obtained by extraction with chloroform as a blue-purple solid (124 mg, 34.9%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ ppm 7.90-7.50, 7.50-7.25, 7.00-6.15 (aromatic), 3.65-3.35 (NCH<sub>2</sub>), 1.90-1.60, 1.60-1.40, 1.40-0.95 (CH<sub>2</sub> and CH in the chains), 0.95-0.70 (CH<sub>3</sub>). HT-GPC results for **P2a**:  $M_{\rm n} = 4293$ ;  $M_{\rm w} = 15,061$ ;  $M_{\rm w}/M_{\rm n} = 3.50$ . The higher molecular weight polymer P2b was obtained as a deep-blue solid film by extraction with TCE (208 mg, 59.0%). HT-GPC:  $M_{\rm n} =$ 19, 841;  $M_{\rm w} = 35$ , 301;  $M_{\rm w}/M_{\rm n} = 1.78$ . UV-Vis:  $\lambda_{\rm max} = 605$  nm (in TCE), 639 nm (film).

### Synthesis of PBDP'DP24a-BT (P3)

P3 was prepared as described above for P1 from M3 (0.2943 g, 0.25 mmol) and 5,5'-bis(trimethylstannyl)-bithiophene (0.1230 g, 0.25 mmol). After Soxhlet extraction with acetone and hexane, P3 was obtained as a deep-blue solid by extraction with chloroform (265 mg, 89.7%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ ppm 8.00-7.45, 7.45-7.25, 7.10-6.35 (aromatic), 4.75-4.50 (O-CH-O), 3.90-3.65 (OCH<sub>2</sub>), 3.65-3.40 (NCH<sub>2</sub>), 1.75-1.30, 1.30-0.95 (CH<sub>2</sub> and CH in the chains), 0.95–0.70 (CH<sub>3</sub>). HT-GPC:  $M_{\rm p} =$ 22 826;  $M_{\rm w} = 65\ 975$ ;  $M_{\rm w}/M_{\rm n} = 2.89$ .  $\lambda_{\rm max}$ : 631 nm (in TCE), 653 nm (film).

#### Fabrication and characterization of OTFT devices

The top-gate, bottom-contact OTFT devices were fabricated on glass substrates (Precision Glass & Optics, Eagle 2000). The gold source and drain electrodes ( $\sim$ 30 nm) were deposited by thermal evaporation using a shadow mask ( $L = 50 \mu m$ , W =500 µm). The polymer semiconductor films were deposited onto the substrates by spin-coating a polymer solution in 1,2dichlorobenzene (DCB) (4 mg mL<sup>-1</sup>) at 1000 rpm for 60 s and were annealed on a 120 °C on a hotplate for 5 min. Then a polyolefin-polyacrylate dielectric layer (Polyera ActivInkTM D2200, capacitance =  $4.2 \text{ nF cm}^{-2}$ ) was spin-coated on top of the polymer semiconductor film. The dielectric film was then baked at 120 °C on a hotplate for 5 min before the deposition of a  $\sim$ 30 nm gold thin film as the gate electrode on top of the dielectric layer. The finished devices were tested under ambient conditions.

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