Benzo[1,2-*b*:4,5-*b'*]dithiophene and Thieno[3,4-*c*]pyrrole-4,6-dione Based Donor- π -Acceptor Conjugated Polymers for High Performance Solar Cells by Rational Structure Modulation

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S Supporting Information

ABSTRACT: A series of benzo[1,2-*b*:4,5-*b'*]dithiophene and thieno[3,4-*c*]pyrrole-4,6-dione (BDT-TPD) based copolymers (P1–P4) with D- π -A structures are designed and synthesized. When the π bridges change from 2,2'-bithiophene to thieno[3,2-*b*]thiophene and then to 3-hexylthieno[3,2-*b*]thiophene, the performance of the polymer photovoltaic devices shows significant improvement. Especially, the device based on P4 with alkylthienyl-substituted BDT and π bridge of 3-hexylthieno[3,2-*b*]thiophene exhibits power conversion efficiency as high as 7.71%, and the short-circuit current of the cells is up to 13.70 mA cm⁻². The results indicate that the modulation of π bridges is a feasible way to achieve highly efficient polymer solar cells.

INTRODUCTION

Since the first introduction of bulk heterojunction (BHJ) architecture into organic photovoltaics (OPVs),¹ polymer solar cells (PSCs) have attracted much attention in both the academic and industrial communities due to their potential for lightweight, low-cost, and flexible fabrication in large area through solution processing techniques.^{2–10} Commonly, the active layer of PSCs is composed of a nanoscale bicontinuous interpenetrating network of conjugated polymers as donor materials and fullerene derivatives as acceptor materials. The conjugated polymers with donor–acceptor (D–A) structure have been reported to tune the energy levels effectively by choosing appropriate D and A building blocks, and the power conversion efficiency (PCE) of the PSCs has exceeded 10%.¹¹ Among the electron-donating monomers, benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) has been widely used owing to its good planarity and excellent electron mobility.^{12,13} Referring to the reported works, a series of BDT-based copolymers were designed with different acceptor units, such as thieno[3,4-*b*]thiophene (TT),^{14–16} thieno[3,4-*c*]pyrrole-4,6-dione (TPD),^{17–21} diketopyrrolopyrrole (DPP),^{22,23} benzodithiazole (BT),^{24–26} isoindigo (ID), and so on.^{27–31} Among the various efficient acceptor units, TPD is very attractive due to its relatively simple, symmetric, compact, and planar structure, which is beneficial for electron delocalization when incorporated into conjugated polymers.³²

Up to now, BDT-TPD based copolymers have been focused on altering the side chain on a donor or acceptor unit to modify the arrangement of polymers or inserting π bridges to form a

D- π -A structure with extended conjugated polymers. In 2011, the TPD moiety that was copolymerized with the octyldodecyloxy-substituted BDT moiety was first reported by Leclerc with a PCE of 5.5% in a conventional single junction device structure.³³ Afterward, alkyl chains modulation on the BDT-TPD based copolymers has been reported, with a PCE exceeding 8%.^{34–39} However, as to the studies of π bridges on BDT-TPD based polymers, thiophene and alkylthiophene are the only units that have been inserted between BDT donor and TPD acceptor units with a highest PCE of 6.08%.^{40–42} To the best of our knowledge, there is little research on other different π bridges in BDT-TPD based polymers.⁴³ It has been demonstrated that π bridge has a significant effect on the optical and electrochemical properties, charge transport, and device performance for the D- π -A conjugated polymers.¹² Hou et al. reported a significant enhancement of the short-circuit current (J_{sc}) and hole mobility when inserting thiophene as π bridge on the BDT-TT polymers.⁴⁴ By altering the π bridge from thiophene to thieno[3,2-*b*]thiophene on BDT-BT based polymers, the backbone conformations changed from a zigzag chain conformation to a straight one, which resulted in a high hole mobility and significant improvement of PCE.^{45,46} Therefore, it should have some room to optimize BDT-TPD based polymers by inserting suitable π bridges between BDT and TPD units.

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Scheme 1. Structures of the Polymers

Scheme 2. Syntheses of A1–A3^a

^aReagents and conditions: (i) *n*-BuLi, THF, $-78\text{ }^{\circ}\text{C}$; (ii) tributyltin chloride, rt; (iii) $\text{Pd}(\text{PPh}_3)_4$, toluene, $110\text{ }^{\circ}\text{C}$; (iv) *N*-bromosuccinimide, CHCl_3 , CH_3COOH .

Herein, we designed and synthesized a series of BDT-TPD based D- π -A conjugated polymers by introducing different π bridges of 2,2'-bithiophene (**P1**), thieno[3,2-*b*]thiophene (**P2**), or 3-hexylthieno[3,2-*b*]thiophene (**P3** and **P4**). As shown in Scheme 1, to ensure good solubility in organic solvents, we attached octyldodecyloxy substituents on BDT unit in **P1** and **P2**. Attributed to the introduction of the hexyl in 3-hexylthieno[3,2-*b*]thiophene, the solubility of the monomer is greatly improved. Thus, we just use 2-ethylhexyloxy substituents on BDT unit for **P3**. Since fine-tuning from alkoxy-substituted BDT to alkylthienyl-substituted BDT can enhance the hole mobility with two-dimensional structure, we replaced **P3** by alkylthienyl-substituted BDT for **P4**. Via the structure modulation, the PCE of the device based on **P4** reached 7.71% in a conventional single junction PSC.

RESULTS AND DISCUSSION

Synthesis and Thermal Properties. The synthetic routes of monomers 1,3-bis(5'-bromo-[2,2'-bithiophen]-5-yl)-5-(2-octyldodecyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(*SH*)-dione (**A1**),

1,3-bis(5-bromo-thieno[3,2-*b*]thiophen-2-yl)-5-(2-octyldodecyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(*SH*)-dione (**A2**), and 1,3-bis(5-bromo-6-hexylthieno[3,2-*b*]thiophen-2-yl)-5-(2-octyldodecyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(*SH*)-dione (**A3**) are depicted in Scheme 2. Compounds **8–10** were prepared by the Stille coupling reaction of 1,3-dibromo-5-(2-octyldodecyl)-4*H*-thieno[3,4-*c*]pyrrole-4,6(*SH*)-dione (**7**) and the corresponding monostannylated compounds **4–6**. Then **A1–A3** were obtained by the bromination of compounds **8–10**, respectively. BDT based monomers (**D1–D3**, shown in Scheme 3) were purchased from Suna Tech Inc. and Derthon. The syntheses of **P1–P4** are shown in Scheme 3. Under nitrogen atmosphere, monomers **D1–D3** were copolymerized with different acceptors (**A1–A3**) in toluene by using $\text{Pd}(\text{PPh}_3)_4$ as the catalyst to afford the four polymers with high yields and moderate molecular weights. The number-average molecular weights (M_n) and polydispersity index (PDI) of **P1–P4** were analyzed by gel permeation chromatography (GPC). The M_n of **P1** and **P3** are 5.3 and 19.5 kDa with 1,2,4-trichlorobenzene as the eluent at $150\text{ }^{\circ}\text{C}$, and the M_n of **P2** and **P4** are 42.3 and 23.2 kDa with tetrahydrofuran (THF) as the eluent, respectively.

Scheme 3. Syntheses of P1–P4

The PDI of the four polymers are 1.6, 2.1, 8.6, and 2.2, respectively. All the polymers have good solubility in chloroform (CHCl_3), chlorobenzene (CB), and 1,2-dichlorobenzene (*o*-DCB).

The thermal properties of **P1–P4** were investigated by thermogravimetric analysis (TGA). As shown in Figure 1, the thermal decomposition temperatures (T_d) (corresponding to

Figure 1. TGA plots of P1–P4.

5% weight loss in the thermogravimetric analysis) of **P1–P4** are 341, 328, 328, and 429 °C, respectively. **P1–P4** have good thermal stability with decomposition temperatures over 320 °C, which are adequate for their application in photovoltaic applications. Obviously, **P4** shows a decomposition temperature at 429 °C, i.e., 100 °C higher than that of **P3**, owing to the introduction of thiophene into the BDT unit. It means that two-dimensional conjugated polymer with alkylthienyl-substituted BDT is more thermally stable than that with alkoxy-substituted BDT.^{14,47}

Optical Properties. The normalized UV–vis absorption spectra of **P1–P4** in diluted chloroform solution and thin film are shown in Figure 2, and the data of the optical property are listed in Table 1. The absorption peaks of **P1–P4** in diluted chloroform solution are located at 546, 565, 550, and 574 nm, respectively. Compared with **P1**, the absorption band of **P2** is 20 nm red-shifted because the π bridge of thieno[3,2-*b*]thiophene in **P2** has more excellent electron-donating ability than that of 2,2'-bithiophene in **P1**. Compared with **P2**, there is a blue-shifted absorption of the main peak of **P3** with the π bridge of 3-hexylthieno[3,2-*b*]thiophene. This may originate from the large steric hindrance by the introduction of the hexyl chain on π bridge, which can break the planarity of the conjugated backbone. After replacing 2-ethylhexyloxy group with 2-ethylhexyloxythienyl group on the BDT unit, **P4** shows a

Figure 2. Normalized UV-vis absorption spectra of P1–P4: (a) measured in CHCl₃ solution and (b) in thin film on quartz plate cast from CHCl₃.

Table 1. Optical Properties and Energy Levels of the Polymers

polymers	$\lambda_{\max}^a$ (nm)	$\lambda_{\max}^b$ (nm)	λ_{onset}^b (nm)	E_g^{opt} (eV)	E_{HOMO}^c (eV)	E_{LUMO}^c (eV)
P1	545	555, 601	674	1.84	−5.39	−3.52
P2	565	565, 604	680	1.82	−5.47	−3.40
P3	550	554, 604	650	1.89	−5.42	−3.52
P4	574	573, 618	672	1.85	−5.38	−3.47

^aIn CHCl₃ solution. ^bPolymer films on quartz plate. ^cResults from cyclic voltammetry.

red-shifted absorption spectrum, and an extra absorption band centralized at 350 nm, which is consistent with other 2-alkylthienyl-substituted BDT-based polymers.^{37,46,47} In comparison with their absorption in chloroform solution, the spectra of the four polymers in solid film are slightly red-shifted, and new absorption peaks over 600 nm appear, indicating the presence of stronger aggregation or more ordered π – π stacking in the solid-state films. Therefore, it is helpful to improve the charge transport in the films. The absorption edges of P1–P4 films are at 674, 680, 650, and 672 nm, corresponding to the optical band gaps of 1.84, 1.82, 1.89, and 1.85 eV, respectively.

Electrochemical Properties. The cyclic voltammograms (CV) were carried out for the films of polymers to evaluate the electronic energy levels. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the onset oxidation potentials and the onset reduction potentials, respectively. As shown in Table 1, the HOMO/LUMO energy levels of P1–P4 are −5.39/−3.52, −5.47/−3.40, −5.42/−3.52, and −5.38/−3.47 eV, respectively. Thus, their band gaps measured from CV are 1.87, 2.07, 1.90, and 1.91 eV, respectively. These values were slightly higher than those obtained from the absorption edges in solid state, which are consistent with the other TPD-based polymers.^{17,41} When the π bridge changes from 2,2'-bithiophene to thieno[3,2-*b*]thiophene, there is an obvious decrease of ca. 0.08 eV of HOMO levels from P1 to P2. Although P4 has higher HOMO and LUMO levels than those of P3, its bandgap is nearly identical to that of P3.

Theoretical Calculations. Theoretical calculations based on density functional theory (DFT) (BY3LIP/6-31G(d)) were used to get an insight into electronic structures of the polymers. The alkyl chains were replaced by methyl group, and the backbones of the polymers were also replaced by three repeating units for computational simplification. As shown in Figure S2, the computational results showed that P1–P4 with the HOMO/LUMO energy levels were −4.92/−2.70, −5.04/−2.78, −5.03/−2.63, and −4.96/−2.60 eV, respectively.

Different π bridges between donor units and acceptor units can affect the molecular structures. As shown in Figure S2, the calculated dihedral angles (θ_1) between BDT units and π bridges are 7.20° for P1, 6.45° for P2, −29.93° for P3, and −29.10° for P4, respectively. The dihedral angles (θ_2) between TPD units and π bridges are 0.54° for P1, 0.34° for P2, 1.17° for P3, and −0.81° for P4, respectively. The torsion angles between BDT units and π bridges and between TPD units and π bridges are less than 10° for P1 and P2, indicating that P1 and P2 have planar structures.⁴⁸ It is noted that the dihedral angles θ_1 of P3 and P4 are larger than those of P1 and P2, owing to the introduction of hexyl chain on thieno[3,2-*b*]thiophene as the π bridge. The molecular structures may affect the hole mobilities of the polymers, and this will be discussed below.

Photovoltaic Performance and Film Morphology. To evaluate the photovoltaic performance, the PSCs were fabricated with the device structure of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/active layer/Ca/Al. The active layer was prepared by spin-coating the blend solution of P1, P2, P3, or P4 as a donor material and PC₆₁BM or PC₇₁BM as an acceptor material in *o*-DCB, respectively. Different donor:acceptor (D:A) ratios of 1:0.5, 1:1, 1:2, and 1:3, different acceptors of PC₆₁BM or PC₇₁BM, and the high boiling point additive of 1,8-diiodooctane (DIO) with volume fraction from 2% to 4% were tested for a better understanding of the optimized condition for the photovoltaic devices. The devices with PC₆₁BM as the acceptor were initially fabricated with different D:A blend ratios from 1:0.5 to 1:3. As shown in Figure S3 and Table S1, without any further treatment, the devices based on P1–P4 achieved their best PCEs of 1.39% for P1, 2.05% for P2, 4.56% for P3, and 3.51% for P4 at the D:A ratio of 1:1 (Table S2). Then, the active layer composed of the polymer and PC₇₁BM at the ratio of 1:1 was adopted. Meanwhile the additive of DIO from 2 to 4 vol % fraction was also added for the further optimization of the performance. Table 2 summarizes the performance of the devices without and with 3% DIO additive treatment. It could be concluded that the best PCEs are all achieved with the same donor and acceptor ratio at 1:1 and 3% DIO additive for the four polymers, which is consistent with the fact that most TPD-based polymers have the similar ratios with their best photovoltaic performance at the condition of 3% DIO.^{36,42}

Figure 3 presents the current density–voltage (*J*–*V*) curves of these solar cells with the blends of polymers and PC₇₁BM. Since the DIO helps to tune the morphology in BHJ polymer solar cells effectively,^{49,50} the devices of P1–P4 show

Table 2. Photovoltaic Properties of PSCs and Hole Mobilities Based on the Blend Films

polymer	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	thickness (nm)	hole mobility (cm ² V ⁻¹ s ⁻¹)
P1	0.86	3.53	60	1.82	103	
P1 ^a	0.81	6.11	67	3.30	98	3.56×10^{-4}
P2	0.80	4.06	65	2.32	95	
P2 ^a	0.88	9.30	68	5.55	107	2.40×10^{-4}
P3	0.84	9.73	59	4.81	100	
P3 ^a	0.83	10.60	65	5.77	94	5.18×10^{-5}
P4	0.88	6.12	57	3.08	94	
P4 ^a	0.86	13.70	66	7.71	104	1.56×10^{-4}

^aProcessed with 3% DIO.

simultaneously substantial enhancement of J_{sc} and fill factor (FF), which are beneficial for higher PCEs. When the π bridges changed from 2,2'-bithiophene to thieno[3,2-*b*]thiophene and then to 3-hexylthieno[3,2-*b*]thiophene, the PCEs were enhanced from 3.30% for P1, to 5.55% for P2, and then to 5.77% for P3, accompanied by an obvious increase of J_{sc} from 6.11 to 9.30 and then to 10.6 mA cm⁻², respectively. Meanwhile, all the devices achieve high open-circuit voltages (V_{oc}) over 0.8 V. For P1, P3, and P4, the V_{oc} decreased accordingly in the presence of DIO, which is a common phenomenon for PSCs.^{23,32} Interestingly, the V_{oc} increased from 0.80 to 0.88 V after the addition of DIO. This could be due to the presence of pinholes in the active layer before the addition of DIO,⁵¹ which will be discussed below. The V_{oc} cannot be simply expressed by the difference between the HOMO level of the donor and the LUMO level of the acceptor. A more precise description of the V_{oc} should follow eq 1.^{52,53}

$$V_{oc} = \frac{E_{LUMO}(A) - E_{HOMO}(D)}{q} - \frac{kT}{q} \times \ln \frac{N_{LUMO}(A) - N_{HOMO}(D)}{np} \quad (1)$$

where $E_{LUMO}(A)$ and $E_{HOMO}(D)$ are the energetic position of the LUMO and HOMO levels of the acceptor and the donor, respectively. $N_{LUMO}(A)$ and $N_{HOMO}(D)$ are the densities of states of the LUMO and HOMO levels of the acceptor and the donor, respectively. n and p are the densities of the charge carriers of the acceptor and the donor, respectively. q is the elementary charge, k is the Boltzmann's constant, and T is the temperature in kelvin.

The mobility of P4 is significantly higher than that of P3, and thus higher J_{sc} can be achieved (Table 2). According to eq 1, regarding the device with the donor P4, a higher $N_{HOMO}(D)$ and/or p is predictable. Therefore, compared to the device with P3, a lower loss of V_{oc} can be expected for the device with P4 although the first term of eq 1 is somewhat smaller.

Because of two-dimensional conjugated BDT unit, the device based on P4 shows an excellent performance with the PCE of 7.71%, V_{oc} of 0.86 V, J_{sc} of 13.70 mA cm⁻², and FF of 66%. The higher performance of the P4-based device can be attributed to the favorable film morphology as well as high hole mobility. To our best knowledge, the PCE of 7.71% is the highest among the BDT-TPD based polymers by inserting π bridges (Table 3). We note that Hwang's group reported a similar copolymer (PBDTT-tt-TPD) to P4, and the corresponding PSC achieved the average PCE of 6.76% (Table 3). We would like to point out the differences between them. On one hand, although the two copolymers have the similar donor, acceptor and π bridge, the alkyl chains on TPD unit are different. The 2-hexyldodecyl chain is attached on the TPD unit in the copolymer of PBDTT-tt-TPD, whereas the 2-octyldodecyl chain is used on P4 in this

Figure 3. J - V curves of polymer:PC₇₁BM (1:1, w/w) solar cells under illumination of AM 1.5G, 100 mW cm⁻²: (a) without DIO; (b) with 3% DIO, and EQE curves of the corresponding solar cells (c) without DIO and (d) with 3% DIO.

Table 3. Photovoltaic Properties of PSCs on BDT-TPD Based Polymers with Different π Bridges

active layer	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	ref
P5:PC ₆₁ BM	0.76	2.9	43	0.95	40
P7:PC ₆₁ BM	0.89	7.6	57	3.9	40
P11:PC ₆₁ BM	0.92	2.3	34	0.7	40
PBDTPD-HT:PC ₇₁ BM	0.92	10.94	60.4	6.08	41
PBDTTP2:PC ₇₁ BM	0.83	5.28	61	2.68	42
PBDTT-tt-TPD:PC ₇₁ BM	0.84	11.05	73	6.76	43
P4:PC ₇₁ BM	0.86	13.7	66	7.71	this work

work. Long alkyl chains may benefit the solubility and film morphology of the copolymer. On the other hand, the PSC structures are different. The PCE of 6.76% for the PBDTT-tt-TPD based device was obtained in an inverted single junction structure of ITO/ZnO NPs/PBDTT-tt-TPD:PC₇₁BM/MoO₃/Ag, whereas the PCE of 7.71% for the **P4**-based device was achieved in a conventional single junction structure of ITO/PEDOT:PSS/P4:PC₇₁BM/Ca/Al.

The external quantum efficiencies (EQEs) of the devices with or without DIO were measured to evaluate the photoresponse of the polymers and calibrate the J_{sc} . As shown in Figure 3c,d, when 3% DIO was added to control the nanoscale morphology, the EQE values of the devices based on **P1**, **P2**, and **P4** are double of those without DIO, which are consistent with their doubled J_{sc} . In contrast, the EQE value for **P3** device is only about 10% higher than its device without DIO. The EQE of the **P4** based device is above 70% and the peak value is up to 80%, which is consistent with high J_{sc} . In comparison with other TPD-based polymers, the device based on **P4** exhibits the higher EQE in the wavelength range from 350 to 650 nm.

Atomic force microscopy (AFM) imaging was carried out to study the relationship between the film morphology and device performance. As shown in Figure 4b, without the addition of DIO, the blend film of **P2** shows serious aggregation with spherical shapes. The serious aggregation could form some pinholes in the active layer and consequently induce the decrease of V_{oc} in the polymer solar cells. For simplification, the V_{oc} can also be described in the other form as⁵⁴

$$V_{oc} = \frac{mkT}{q} \ln \frac{J_{sc}}{J_0} \quad (2)$$

where m is the ideality factor, k the Boltzmann's constant, T the temperature, and J_0 the reverse saturation current density. The pinhole will likely induce large leakage current, i.e., J_0 , and consequently some loss of the V_{oc} , and vice versa. As mentioned above, the V_{oc} of the device with **P2** increased unordinarily from 0.80 to 0.88 V after the addition of DIO. This is likely due to the presence of the pinholes (see Figure 4b) in the active layer without the addition of DIO.⁵¹ However, the film showed reduced lateral phase separation after the DIO treatment (see Figure 4f) and thus pinhole-free morphology and a lower leakage current. According to eq 2, a lower leakage current will improve the V_{oc} after the DIO treatment.

It is clear that the serious aggregations were improved with the addition of the DIO for **P1** and **P2**, and the J_{sc} of **P1** and **P2** are twice as much as those without DIO. Generally, a reduction in lateral phase separation but an increase of the RMS after adding the DIO were observed in **P1** and **P2**. The

improved performances are resulted from better percolating pathways for the charge carriers.^{55–57} Unlike the other donors, there is no significant change of the lateral phase separation of the film with **P3** before and after the DIO treatment even though a big shift of RMS is observed (see Figure 4c,g). Therefore, only a small improvement of J_{sc} is achieved. As shown in Table 2, there is nearly no change of V_{oc} (0.84 V vs 0.83 V) without and with the DIO additive. Based on the J – V curves and FF, the small improvement of PCE for the device with **P3** is reasonable (see Figure 3a,b). In contrast, for **P4** with two-dimensional structure, the RMS value decreased to 2.93 nm, slightly lower than the value of 3.23 nm in the case without DIO. The more uniform film after adding the DIO indicated good miscibility between **P4** and PC₇₁BM and subsequently formation of interpenetrating networks within the blends. The other reason for the dramatic improvement of the photovoltaic performance of **P4** is that the two-dimensional molecular structure of **P4** refrained the enrichment of the polymer on the top surface after the DIO treatment. Therefore, more favorable extraction of the two kinds of charge carriers was achieved in the noninverted device structure.⁵⁸

The hole mobility of the blend films composed of PC₇₁BM:**P1** (**P2**, **P3**, or **P4**) at 1:1 (w/w) were measured by the space-charge-limited current (SCLC) method with the structure of ITO/PEDOT:PSS/polymer:PC₇₁BM/MoO₃/Ag. As shown in Figure S6 and Table 2, the hole mobility of each blend film for **P1**–**P4** was 3.56×10^{-4} , 2.40×10^{-4} , 5.18×10^{-5} , and 1.56×10^{-4} cm² V⁻¹ s⁻¹, respectively. Although the blend films of **P1** and **P2** possessed high hole mobilities, the devices based on **P1** and **P2** achieved poor photovoltaic performances compared with those of **P3** and **P4**, which can be mainly attributed to the poor morphology with serious aggregations. The blend film of **P3** showed a relatively low hole mobility, which should result from the side chain of hexyl on the π bridge. Obviously, as discussed above, there is a slight twist in the whole backbone of **P3**, which would affect the arrangement of polymers. Because of the two-dimensional conjugation by introduction thiophene on BDT unit, the blend film of **P4** still had a high hole mobility that helps to reach a high J_{sc} . The large improvement of the photovoltaic performance from **P3** to **P4** can be partially attributed to the enhancement of hole mobility from 5.18×10^{-5} to 1.56×10^{-4} cm² V⁻¹ s⁻¹. Combined with the favorable film morphology and high hole mobility, the J_{sc} of the device based on **P4** boosts to 13.70 mA cm⁻², which is one of the highest values in the BDT-TPD based polymers ever reported.

CONCLUSION

We have synthesized a series of BDT-TPD based copolymers (**P1**–**P4**) with D- π -A structures by inserting different π bridges of 2,2'-bithiophene, thieno[3,2-*b*]thiophene, and 3-hexylthieno[3,2-*b*]thiophene between the BDT and TPD units. The four polymers exhibit good thermal stabilities, broad absorptions, suitable energy levels, and appropriate mobilities, which make them the promising donor materials for photovoltaic application. When the π bridges change from 2,2'-bithiophene to thieno[3,2-*b*]thiophene and then to 3-hexylthieno[3,2-*b*]thiophene, the PCEs of the polymer-based devices vary from 3.30% to 5.55% and then to 5.77%. After tuning an alkoxyl-substituted BDT to be an alkythienyl-substituted BDT, i.e., **P4**, the device achieves the highest PCE of 7.71% in a conventional device structure. Besides, the peak EQE of the **P4** based device is approaching to 80%, and the J_{sc} is up to 13.70

Figure 4. Tapping mode AFM height images of PC₇₁BM blended with (a) P1, (b) P2, (c) P3, and (d) P4 without DIO; (e) P1, (f) P2, (g) P3, and (h) P4 with 3% DIO.

mA cm^{-2} . The results indicate that the rational structure modulation by altering π bridges is an effective method to achieve high device performance, and two-dimensional conjugated polymers with 3-hexylthieno[3,2-*b*]thiophene coupled TPD monomers are the promising donor materials for further enhancement of the photovoltaic performance in PSCs.

EXPERIMENTAL SECTION

Materials and Synthesis. Compounds 3 and 7 were synthesized according to the known procedures.^{59–61} The polymers were prepared by the Stille coupling reaction, and the precipitations were filtered into a Soxhlet extractor. Methanol and hexane were used as solvents to remove the residual catalyst and the oligomers,⁶² successively. Then the polymers were extracted by chloroform. The dry toluene and THF were prepared by refluxing with the alloy of potassium/sodium under

an argon atmosphere. Unless stated, other reagents were purchased commercially and used without further purification.

Synthesis of Tributyl[2,2'-bithiophen]-5-yltributylstannane (4). 1 (1 g, 6.02 mmol) was dissolved into anhydrous tetrahydrofuran (60 mL) in a Schlenk flask in an argon atmosphere. *n*-Butyllithium (2.41 mL, 6.02 mmol) was added into the solution by dropwise at the temperature of -78°C and keep stirring for another 2 h. Then, tributyltin chloride (2.55 g, 7.83 mmol) was added quickly. After that, the solution was reacted at room temperature for another 12 h. 50 mL of potassium fluoride solution was poured to quench the reaction, and 200 mL of diethyl ether was used to extract the organic phase. The mixture was dried by anhydrous sodium sulfate, and the solvent was removed under reduced pressure to get the crude product (3.50 g). Without any further purification, the product was used into the following reaction.

Synthesis of Tributyl(thieno[3,2-*b*]thiophen-2-yl)stannane (5). 2 (1 g, 7.13 mmol) was dissolved into anhydrous tetrahydrofuran (70 mL) in a Schlenk flask in an argon atmosphere. *n*-Butyllithium (2.85 mL, 7.13 mmol) was added into the solution by dropwise at the temperature of -78°C and keep stirring for another 2 h. Then, tributyltin chloride (3.01 g, 9.27 mmol) was added quickly. The solution was reacted at room temperature for another 12 h. The solvent was evaporated to get the crude product (2.94 g). Without any further purification, the product was used into the following reaction.

Synthesis of Tributyl(6-hexylthieno[3,2-*b*]thiophen-2-yl)stannane (6). 2 (1 g, 4.46 mmol) was dissolved into anhydrous tetrahydrofuran (50 mL) in a Schlenk flask under an argon atmosphere. *n*-Butyllithium (1.78 mL, 4.46 mmol) was added into the solution by dropwise at the temperature of -78°C and keep stirring for another 2 h. Then, tributyltin chloride (1.89 g, 5.80 mmol) was added quickly. The solution was reacted at room temperature for another 12 h. The solvent was evaporated to get the crude product (4.06 g).

Synthesis of 1-([2,2'-Bithiophen]-4-yl)-3-([2,2'-bithiophen]-5-yl)-5-(2-octyldodecyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (8). 4 (1.14 g, 2.5 mmol) and 7 (0.59 g, 1 mmol) were dissolved into anhydrous methylbenzene (30 mL) in a round-bottom flask under an argon atmosphere, and a catalytic amount $\text{Pd}(\text{PPh}_3)_4$ was added into the flask. Then the solution was refluxed for 48 h at the temperature of 110°C . After cooling down, the mixture was washed with potassium fluoride solution and diethyl ether. The solvent was evaporated, and the crude product was purified via column chromatography using dichloromethane:hexane = 1:2 by volume as the eluent to afford 8 (533 mg) as a dark red solid. Yield: 70%. ^1H NMR (CD_2Cl_2 , 300 MHz, δ): 7.87 (d, J = 3.9 Hz, 2H), 7.31–7.21 (m, 4H), 7.13 (d, J = 3.9 Hz, 2H), 7.01 (t, J = 4.2 Hz, 2H), 3.47 (d, J = 6.6 Hz, 2H), 1.84–1.74 (m, 1H), 1.38–1.10 (m, 32H), 0.82–0.74 (m, 6H). ^{13}C NMR (CDCl_3 , 75 Hz, δ): 162.6, 140.6, 136.3, 135.6, 130.8, 130.7, 128.2, 128.0, 125.5, 124.7, 124.5, 42.8, 36.9, 31.8, 31.5, 29.6, 29.5, 29.3, 29.2, 26.3, 22.6, 14.0. MS (MALDI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{42}\text{H}_{51}\text{NO}_2\text{S}_5$, 761.25; found, 761.56. Anal. Calcd for $\text{C}_{42}\text{H}_{51}\text{NO}_2\text{S}_5$: C 66.19, H 6.74, N 1.84, S 21.03. Found: C 66.31, H 6.52, N 1.91, S 21.12.

Synthesis of 5-(2-Octyldodecyl)-1,3-bis(thieno[3,2-*b*]thiophen-2-yl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (9). 5 (1.07 g, 2.5 mmol), 7 (0.59 g, 1 mmol), and a catalytic amount $\text{Pd}(\text{PPh}_3)_4$ were dissolved into anhydrous methylbenzene (30 mL), and then the solution was refluxed for 48 h at the temperature of 110°C . An orange solid 9 (426 mg) was obtained via column chromatography using dichloromethane:hexane = 1:2 by volume as eluent. Yield: 60%. ^1H NMR (300 MHz, CD_2Cl_2 , δ): 8.33 (s, 2H), 7.48 (d, J = 5.4 Hz, 2H), 7.23 (d, J = 5.1 Hz, 2H), 3.49 (d, J = 7.2 Hz, 2H), 1.84–1.74 (m, 1H), 1.38–1.01 (m, 32H), 0.84–0.64 (m, 6H). ^{13}C NMR (75 Hz, CDCl_3 , δ): 162.6, 140.8, 140.2, 136.5, 133.5, 130.1, 128.5, 122.2, 119.2, 42.8, 37.0, 31.8, 31.5, 30.0, 29.6, 29.5, 29.3, 26.3, 22.6, 14.0. MS (MALDI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{38}\text{H}_{47}\text{NO}_2\text{S}_5$, 709.22; found 709.22. Anal. Calcd for $\text{C}_{38}\text{H}_{47}\text{NO}_2\text{S}_5$: C 64.28, H 6.67, N 1.97, S 22.57. Found: C 64.05, H 6.53, N 2.04, S 22.41.

Synthesis of 1,3-Bis(6-hexylthieno[3,2-*b*]thiophen-2-yl)-5-(2-octyldodecyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (10). 6 (1.16 g, 2.5 mmol), 8 (0.59 g, 1 mmol), and a catalytic amount $\text{Pd}(\text{PPh}_3)_4$

were dissolved into anhydrous methylbenzene (30 mL), and then the solution was refluxed for 48 h at the temperature of 110°C . A dark yellow solid 10 (791 mg) was obtained via column chromatography using dichloromethane:hexane = 1:2 by volume as eluent. Yield: 90%. ^1H NMR (300 MHz, CDCl_3 , δ): 8.38 (s, 2H), 7.11 (s, 2H), 3.60 (d, J = 7.2 Hz, 2H), 2.74 (t, J = 7.8 Hz, 4H), 1.98–1.84 (m, 1H), 1.82–1.65 (m, 4H), 1.46–1.19 (m, 44H), 0.95–0.80 (m, 12H). ^{13}C NMR (75 Hz, CDCl_3 , δ): 162.7, 141.4, 139.5, 136.7, 134.9, 133.0, 128.3, 124.6, 122.8, 42.9, 37.0, 31.8, 31.5, 30.0, 29.7, 29.6, 29.5, 29.3, 29.2, 29.0, 28.4, 26.3, 22.6, 22.5, 22.4, 14.0. MS (MALDI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{50}\text{H}_{71}\text{NO}_2\text{S}_5$, 877.41, found, 877.64. Anal. Calcd for $\text{C}_{50}\text{H}_{71}\text{NO}_2\text{S}_5$: C 68.37, H 8.15, N 1.59, S 18.25. Found: C 68.21, H 8.31, N 1.63, S 18.10.

Synthesis of 1,3-Bis(5'-bromo-2,2'-bithiophen-5-yl)-5-(2-octyldodecyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (A1). 8 (533 mg, 0.70 mmol) was dissolved in a mixed solution of chloroform and acetic acid, and then in dark conditions, *N*-bromosuccinimide (311 mg, 1.74 mmol) was added into the mixture in several portions. After stirring for 2 h, the reaction solution was poured into brine and extracted three times by chloroform. The organic solvent was evaporated, and the crude product was purified via column chromatograph using dichloromethane:hexane = 1:2 by volume as the eluent to afford A1 (572 mg) as a viscous red solid. Yield: 89%. ^1H NMR (300 MHz, CDCl_3 , δ): 7.89 (d, J = 3.9 Hz, 2H), 7.08 (d, J = 3.6 Hz, 2H), 7.00 (s, 4H), 3.55 (d, J = 7.2 Hz, 2H), 1.95–1.83 (m, 1H), 1.38–1.08 (m, 32H), 0.94–0.80 (m, 6H). ^{13}C NMR (75 Hz, CDCl_3 , δ): 162.5, 39.4, 137.7, 135.4, 131.1, 130.8, 130.7, 128.4, 124.7, 124.6, 121.1, 43.0, 36.9, 31.8, 31.4, 30.0, 29.6, 29.5, 29.3, 29.2, 26.3, 22.6, 14.0. MS (MALDI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{42}\text{H}_{49}\text{Br}_2\text{NO}_2\text{S}_5$, 919.07, found, 919.26. Anal. Calcd for $\text{C}_{42}\text{H}_{49}\text{Br}_2\text{NO}_2\text{S}_5$: C 54.83, H 5.37, N 1.52, S 17.42. Found: C 54.55, H 5.19, N 1.79, S 17.61.

Synthesis of 1,3-Bis(5-Bromothieno[3,2-*b*]thiophen-2-yl)-5-(2-octyldodecyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (A2). A2 (479 mg) was synthesized as orange solid according to the method used for the preparation of A1. Yield: 92%. ^1H NMR (300 MHz, CD_2Cl_2 , δ): 8.17 (s, 2H), 7.19 (s, 2H), 3.44 (d, J = 7.2 Hz, 2H), 1.82–1.72 (m, 1H), 1.36–1.04 (m, 32H), 0.84–0.66 (m, 6H). ^{13}C NMR (75 Hz, CDCl_3 , δ): 162.6, 140.3, 139.6, 136.1, 132.9, 128.7, 121.9, 121.6, 116.9, 43.0, 37.0, 31.8, 31.5, 29.9, 29.6, 29.2, 26.3, 22.6, 14.0. MS (MALDI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{38}\text{H}_{45}\text{Br}_2\text{NO}_2\text{S}_5$, 867.04, found, 867.22. Anal. Calcd for $\text{C}_{38}\text{H}_{45}\text{Br}_2\text{NO}_2\text{S}_5$: C 52.59, H 5.23, N 1.61, S 18.47. Found: C 52.68, H 5.28, N 1.85, S 18.25.

Synthesis of 1,3-Bis(5-bromo-6-hexylthieno[3,2-*b*]thiophen-2-yl)-5-(2-octyldodecyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (A3). A3 (914 mg) was synthesized as yellow solid according to the method used for the preparation of A1. Yield: 98%. ^1H NMR (300 MHz, CDCl_3 , δ): 8.31 (s, 2H), 3.57 (d, J = 6.6 Hz, 2H), 2.76 (t, J = 6.9 Hz, 4H), 1.95–1.85 (m, 1H), 1.78–1.64 (m, 4H), 1.42–1.19 (m, 44H), 0.98–0.81 (m, 12H). ^{13}C NMR (75 Hz, CDCl_3 , δ): 162.5, 139.8, 137.9, 136.1, 134.1, 132.3, 128.5, 113.7, 43.1, 37.2, 31.8, 31.5, 30.0, 29.6, 29.5, 29.3, 29.0, 27.9, 26.3, 22.6, 22.5, 14.0. MS (MALDI-TOF) m/z : $[\text{M}]^+$ calcd for $\text{C}_{50}\text{H}_{69}\text{Br}_2\text{NO}_2\text{S}_5$, 1035.23, found, 1035.40. Anal. Calcd for $\text{C}_{50}\text{H}_{69}\text{Br}_2\text{NO}_2\text{S}_5$: C 57.96, H 6.71, N 1.35, S 15.47. Found: C 57.93, H 6.91, N 1.33, S 15.77.

Synthesis of Poly[1-(5'-(6-methyl-4,8-bis(2-octyldodecyloxy)-benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)-[2,2'-bithiophen]-5-yl)-3-(5'-methyl-[2,2'-bithiophen]-5-yl)-5-(2-octyldodecyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione) (P1). D1 (155 mg, 0.14 mmol), A1 (129 mg, 0.14 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (8.1 mg, 0.007 mmol) was added into 10 mL of anhydrous toluene under an atmosphere of argon. The solution was refluxed for 10 h at the temperature of 110°C , and then 0.5 mL of 4-bromotoluene was injected into the solution. Stirred overnight for the completion of end-capping reaction, the mixture was cooled down and poured into 300 mL of methanol. The precipitate was filtered into a Soxhlet extractor; methanol and hexane were used as solvents successively to remove the residual catalyst and the oligomers. Finally, the polymer was extracted by chloroform. The solution was concentrated and precipitated into 200 mL of methanol. The polymer was collected as a dark purple solid (145 mg). Yield: 67%. GPC: M_n = 5.3 kDa, M_w = 8.4 kDa, PDI = 1.6. ^1H NMR (400 MHz, CDCl_3 , δ):

7.51 (br, Ar–H), 7.04–6.40 (br, Ar–H), 4.16–3.77 (br, –OCH₂–), 3.66–3.30 (br, –NCH₂–), 2.17 (br, –CH–), 1.52–0.81 (br, –CH₂– and –CH₃).

Synthesis of Poly{1-(5-(4,8-bis(2-octyldodecyloxy)-6-methylbenzo[1,2-b:4,5-b']dithiophen-2-yl)thieno[3,2-b]thiophen-2-yl)-3-(5-methylthieno[3,2-b]thiophen-2-yl)-5-(2-octyldodecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione} (P2). P2 (144 mg) was prepared using the same procedure as P1. Yield: 69%. GPC: $M_n = 42.3$ kDa, $M_w = 88.0$ kDa, PDI = 2.1. ¹H NMR (400 MHz, CDCl₃, δ): 8.09 (br, Ar–H), 7.50 (br, Ar–H), 6.90 (br, Ar–H), 4.24–3.81 (br, –OCH₂–), 3.69–3.38 (br, –NCH₂–), 2.17 (br, –CH–), 1.48–0.80 (br, –CH₂– and –CH₃).

Synthesis of Poly{1-(5-(4,8-bis(2-ethylhexyloxy)-6-methylbenzo[1,2-b:4,5-b']dithiophen-2-yl)-6-hexylthieno[3,2-b]thiophen-2-yl)-3-(6-hexyl-5-methylthieno[3,2-b]thiophen-2-yl)-5-(2-octyldodecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione} (P3). P3 (130 mg) was prepared using the same procedure as P1. Yield: 70%. GPC: $M_n = 19.5$ kDa, $M_w = 167.5$ kDa, PDI = 8.6. ¹H NMR (400 MHz, CDCl₃, δ): 8.43–8.00 (br, Ar–H), 7.54 (br, Ar–H), 4.30–3.88 (br, –OCH₂–), 3.72–3.39 (br, –NCH₂–), 3.10–2.79 (br, –CH₂–), 2.19 (br, –CH–), 1.51–0.81 (br, –CH₂– and –CH₃).

Synthesis of Poly{1-(5-(4,8-bis(2-ethylhexyl)thiophen-2-yl)-6-methylbenzo[1,2-b:4,5-b']dithiophen-2-yl)-6-hexylthieno[3,2-b]thiophen-2-yl)-3-(6-hexyl-5-methylthieno[3,2-b]thiophen-2-yl)-5-(2-octyldodecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione} (P4). P4 (128 mg) was prepared using the same procedure as P1. Yield: 63%. GPC: $M_n = 23.2$ kDa, $M_w = 51.2$ kDa, PDI = 2.2. ¹H NMR (400 MHz, CDCl₃, δ): 8.22 (br, Ar–H), 7.51 (br, Ar–H), 7.00 (br, Ar–H), 6.96–6.52 (br, Ar–H), 3.77–3.41 (br, –NCH₂–), 3.15–2.56 (br, –CH₂–), 2.17 (br, –CH–), 1.50–0.83 (br, –CH₂– and –CH₃).

Measurements. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Unity 300 MHz spectrometer using CDCl₃ or CD₂Cl₂ as solvent and tetramethylsilane as internal reference, and ¹H NMR spectra of polymers were recorded on Bruker ADVANCE III 400 MHz NMR spectrometer. Elemental analysis of hydrogen, carbon, and nitrogen was performed on Vario EL-III microanalyzer. EI-MS spectra were recorded on VJ-ZAB-3F mass spectrometer. Gel permeation chromatography was carried out at 308 K using a Waters 2690 D system using a refractive detector and THF as the eluent or was performed on a Polymer Laboratories PL-GPC220 at 150 °C using 1,2,4-trichlorobenzene as eluent. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument, and the thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss, heated at a rate of 10 °C min^{−1} from 25 to 650 °C. UV–vis absorption spectra were recorded on Shimadzu UV-2550 spectrophotometer. Cyclic voltammetric measurements were carried out on a computer-controlled EG&G potentiostat/galvanostat model 283 using tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte in acetonitrile and conventional three-electrode cell with a Pt work electrode of 2 mm diameter, a platinum-wire counter electrode, and a Ag/AgCl reference electrode was employed. The polymer was deposited on the Pt work electrode as a thin film before the measurement.

Fabrication and Characterization of Solar Cells. Polymer solar cells with the conventional structure of ITO/PEDOT:PSS/polymer:fullerene/Ca/Al were fabricated. After being cleaned in ultrasonic bath by acetone, toluene, methanol, and isopropyl alcohol sequentially, the ITO-coated glass substrates were treated in an oxygen plasma for 6 min and then spin-coated with a 40 nm thick layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). After that, the substrates were baked at 150 °C for 20 min and then transferred into a N₂-filled glovebox. o-DCB solutions consisting of polymers and fullerene (PC₆₁BM or PC₇₁BM) in different blend ratios with or without DIO additive were stirred overnight at room temperature. The solution was spin-coated to form the active layer on the ITO/PEDOT:PSS substrate. Finally, the substrates were transferred to a vacuum chamber, and Ca (10 nm)/Al (100 nm) bilayer cathode electrode was thermally deposited onto the active layer under a base pressure of 4 × 10^{−4} Pa. The photoactive area of the device was 0.1 cm² defined by the shadow mask. The thickness of the active layer was determined by Dektak 150 profilometer. Surface

morphological characterizations of the films were conducted by a tapping-mode atomic force microscope (AFM, Agilent 5400). The current density–voltage (*J*–*V*) curves were measured by using Keithley 2420 source measurement unit under simulated AM1.5G (100 mW cm^{−2}, Newport solar simulator). Light intensity was calibrated with a standard silicon solar cell. The external quantum efficiencies (EQE) of solar cells were analyzed by using a certified Newport incident photon conversion efficiency (IPCE) measurement system. Hole mobility was measured by following the space charge limited current (SCLC) method with the device structure of ITO/PEDOT:PSS/polymer:PC₇₁BM/MoO₃/Ag. The SCLC is described as

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_h \frac{V^2}{L^3} \quad (3)$$

where *J* is the current density, ϵ_0 the permittivity of the free space, ϵ_r the relative dielectric constant of the transport medium, μ_h the hole mobility, *V* the internal potential in the device, and *L* the active layer thickness. The internal potential *V* is obtained by subtracting the built-in voltage (*V*_{bi}) and the voltage drop (*V*_s) from the series resistance of the substrate, from the applied voltage (*V*_{appl}), according to *V* = *V*_{appl} − *V*_{bi} − *V*_s.

■ ASSOCIATED CONTENT

Supporting Information

¹H NMR spectra for all the compounds, cyclic voltammograms, theoretical calculations, *J*–*V* curves and EQE curves of PSCs, current voltage characteristics of P1–P4 blends with PC₇₁BM in SCLC devices, photovoltaic properties of PSCs. 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.

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