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Bithieno[3,4-c]pyrrole-4,6-dione-Mediated Crystallinity in Large-Bandgap Polymer **Donors Directs Charge Transportation and Recombination in Efficient Nonfullerene Polymer Solar Cells**

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Cite This: ACS Energy Lett. 2020, 5, 367-375 **Read Online** ACCESS S Supporting Information **Metrics & More** Article Recommendations ABSTRACT: Solution-processed nonfullerene bulk-heterojunction (BHJ) polymer solar cells (PSCs), which are composed of polymer

donors and organic acceptors, are proven to manifest promising performance and long-term stability. In this concise contribution, bithieno[3,4-c]pyrrole-4,6-dione (BiTPD), which is a TPD derivative but presents a large planar structure and strong electron-withdrawing ability, was used to construct a large-bandgap polymer donor PBiTPD. Results show that the polymer donor PBiTPD realized power conversion efficiency (PCE) as high as 14.2% in fullerene-free BHJ solar cells. Larger ionization potential value, more favorable face-on backbone orientation, and stronger crystallinity were concurrently obtained in PBiTPD. Correspondingly, improved and more balanced charge transportation; less nongeminate and trap-assisted recombina-



tion losses; and thus high fill factor (FF) of 67%, short-circuit current density (J_{SC}) of 25.6 mA·cm⁻², and high open-circuit voltage $(V_{\Omega C})$ of 0.83 V were concurrently achieved in PBiTPD-based devices. PBiTPD does clear the way for a novel and promising class of large-bandgap polymer donor candidates.

ith recently achieved power conversion efficiency (PCE) of $>16\%^{1-6}$ and lifetime of >10 years,⁷, solution-processed nonfullerene bulk-heterojunction (BHJ) polymer solar cells (PSCs), consisting of smallmolecule acceptors and polymer donors, as well as all-polymer solar cells,⁹⁻¹¹ are very promising alternatives to the more studied fullerene (e.g., PC60BM, PC70BM) acceptor-based PSCs. As an alternative to fullerene-based PSCs, nonfullerene BHJ PSCs possess some practical advantages, spanning complementary optical absorption between the donor and acceptor counterparts and straightforward design of their photoelectronic properties through the chemical structure modification.¹²⁻¹⁴ Thus, considerable efforts, including novel donor and acceptor materials design, meticulous BHJ morphology optimization, novel device architecture, in tandem with effective electrode interlayers, have been made in the development of nonfullerene PSCs.^{1-6,12-15}

In principle, the complementary absorption and broad absorption band of the BHJ active layer are a substantial benefit for enhancing photon absorption and exciton generation to increase short-circuit current density (J_{SC}) of BHJ solar cells.^{1-6,12-15} To date, most of the efficient smallmolecule acceptors are 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone)-5,5,11,11-tetrakis(4-hexylphenyl)dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']-dithiophene (ITIC)¹⁵ and its analogues (IEICO,¹⁶ Y6,¹⁷ chlorinated¹⁸ or fluorinated¹⁹ ITIC, etc.) with strong optical absorption in the near-infrared (NIR) range of 600-1000 nm. When considering the complementary optical absorption between donor and



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Chart 1. Chemical Structures of (a) Electron-Withdrawing Motifs and (b) Electron-Donating Motifs That Are Used To Construct High-Performing Polymer Donor Materials in BHJ Devices with PCE > $14\%^{1-6}$



Chart 2. Chemical Structures of BiTPD- and TPD-Based Polymers PBiTPD, PTPD, and Model System Molecule Acceptor Y6 Used in PSC Device Studies



acceptor counterparts, it is particularly important to take considerable efforts to develop large optical bandgap (LBG) $(E_{opt} > 1.7 \text{ eV})$ polymer donors with strong photon absorption in the short wavelength range of 400-700 nm. Currently, a number of LBG polymer donors are widely used in nonfullerene BHJ PSCs and have demonstrated efficient photovoltaic performance. For example, electron-withdrawing motifs benzo-[1,2-c:4,5-c']dithiophene-4,8-dione (BDD),^{1–5} benzotriazole (BTA),^{20,21} pyrrolo[3,4-f]benzotriazole-5,7(6H)-dione (TzBI),^{6–8} fluorinated thiophene,²² ester-substituted thiophene²³ and thieno[3,2-b]thiophene,²⁴ thiazole,²⁵ etc. have been extensively employed in constructing numerous LBG polymer donors for efficient nonfullerene BHJ PSCs. However, as shown in Chart 1, only several classes of LBG polymer donors have been shown to achieve PCEs of >14% in single-junction binary-blend BHJ PSCs with selected small-molecule acceptors to date.¹⁻⁶ Thus, at this stage, broadening the class of high-performing polymer donor material systems and determining the relationship between the chemical structure design parameters and LBG polymer donor performance in fullerene-free BHJ solar cells are critically important steps to take in the improvement of device photovoltaic performance beyond current state-of-the-art efficiency.

Thieno[3.4-*c*]pyrrole-4,6-dione (TPD) units have been widely and successfully used to construct LBG polymer donors

with $E_{opt} > 1.7$ eV and yield efficient PSCs with PCEs over 10% when PCBM was used as the acceptor.²⁶ Moreover, the types of alkyl side-chains that append at the imide site of TPD motifs can be facilely tuned. Generally, the alkyl side-chains in TPDbased polymers not only provide the solubility in organic solvent and thus solution processability but also furnish a meaningful strategy that tailors the self-assembly capability of polymers.²⁶ However, as implied in recent studies, the TPDbased LBG polymer donors did not exhibit high photovoltaic performance like the benchmark LBG polymer donors J51, PBDB-T, PTzBI, and their analogues in nonfullerene BHJ PSCs.²⁶ Large open-circuit voltages (V_{OC}), small energy loss (E_{loss}), but low quantum efficiencies were observed in nonfullerene solar cells when TPD-based polymers were used as donors. To some extent, this primary design rule, pairs of polymer donor and small-molecule acceptor with complementary absorption, is however not a sufficient condition for achieving efficient PSCs, mostly because morphological, energetic, and charge transport properties are also critically important to the photovoltaic performance. Recently, Jang and co-workers have reported the PCE of $\sim 10\%$ for the fullerenefree BHJ PSCs made with a TPD-based polymer donor and an ITIC acceptor.²⁷ A meticulous cross-link strategy was used to tune the BHJ morphology phase separation, and the TPD polymer donor-based BHJ solar cells exhibited promising performance with PCE of $\sim 12\%$.²⁸ A few studies indicate that Scheme 1. Synthesis of BiTPD (M1) Monomer and Polymer Donor PBiTPD^a



"(i) DMAP, 2-hexyldecan-1-amine, 1,4-dioxane, 50 °C, 20 h; acetic anhydride, 80 °C, 4 h, 76%. (ii) Cu, DMF, 140 °C, 48 h, 68%. (iii) NBS, CF₃COOH, H_2SO_4 , RT, 12 h, 94%. (iv) 2-(Tributylstannyl)thiophene, $Pd_2(dba)_3$, $P(t-tol)_3$, chlorobenzene, 140 °C, 12 h, 94%. (v) NBS, chloroform/AcOH, 50 °C, 24 h, 78%. (vi) $Pd_2(dba)_3$, $P(t-tol)_3$, chlorobenzene, 150 °C, 24 h, 74%.

polymers combining TPD motifs along the backbone may be a class of potential high-performing LBG polymer donor candidates for efficient nonfullerene PSCs as long as the energetic, morphological, and charge transport parameters are all taken into consideration.

TPD dimer (bithieno[3,4-*c*]pyrrole-4,6-dione, BiTPD) is a derivative of TPD but has a larger planar skeleton and stronger electron-withdrawing ability than that of TPD, making it a potential useful planar building block for efficient polymer donors and acceptors. In our previous report, we showed that the BiTPD motifs in polymers can be used to simultaneously increase the ionization potential (IP) and electron affinity (EA) values, narrow the E_{opt} and enhance charge transportation properties.²⁹ The similar phenomenon in BiTPD-based polymers was also observed independently by Li and coworkers.³⁰ Therefore, the BiTPD may be a useful motif to develop LBG polymer donors that deliver promising photovoltaic performance in nonfullerene BHJ PSCs.

In this Letter, to understand the large-bandgap polymer donor design rules and further boost the TPD derivativesbased polymer donors' photovoltaic performance in nonfullerene PSCs, the LBG polymer donor design strategies, material properties, and photovoltaic performance in BHJ solar cells based on two analogous polymer donors composed of benzo[1,2-b:4,5-b']dithiophene derivative (BDT) and TPD or BiTPD motifs are reported. The effect of TPD or BiTPD motifs in the polymer main chains on the optical, electronic, carrier transport, morphology, and photovoltaic properties are also systematically examined. It was found that the two analogues, presented in Chart 2 (PTPD and PBiTPD), exhibit significantly different photovoltaic performance patterns in BHJ devices with the nonfullerene acceptor Y6 as a model system (Chart 2). Our detailed device analysis demonstrates that the PBiTPD with BiTPD motifs in the main chain largely outperform the analogue PTPD, which results from (i) larger ionization potential (IP, coinciding with the lower-lying highest occupied molecular orbital (HOMO) energy levels) of PBiTPD that contributes to larger $V_{\rm OC}$ in BHJ devices and (ii) more favorable face-on backbone orientation and stronger crystallinity of PBiTPD:Y6 BHJ blend that contribute to increase of charge transportation and suppression of carrier recombination in BHJ solar cells. Thus, the PBiTPD reaches

PCEs as high as 14.2% in optimized BHJ devices with acceptor Y6. Importantly, the PBiTPD does enable a new kind of LBG polymer donors with tunable optical spectra, electronic properties, and crystallinity for efficient fullerene-free BHJ solar cells; to the best of our knowledge, only a few classes of polymer donors showed PCEs over 14% in single-junction binary-blend BHJ PSCs to date.¹⁻⁶

To obtain efficient BHJ solar cells, the design of solutionprocessable polymer donors with large optical bandgap is critically important because the state-of-the-art fused ringbased molecule acceptors possess strong optical absorption in the NIR range of 600-1000 nm. Previous studies showed that TPD-based polymer donors exhibit strong optical absorption ranging from 400 to 700 nm. According to prior single-crystal structure analyses³¹ and DFT predictions (Figures S1 and S2), BiTPD, in which the two TPDs are coplanar and have an anticonformation, has larger planar structure and stronger electron-withdrawing ability in comparison to TPD.³² The BiTPD-based polymer donor (PBiTPD), depicted in Chart 2, probably tends to backbone planarization; has larger IP; and may concurrently benefit charge transportation and improvement of V_{OC} , FF, and J_{SC} in BHJ devices. Herein, the PBiTPD and PTPD were developed to exam how the BiTPD motif in the polymer backbone affect the optical absorption, energy level, charge transport, and thus photovoltaic properties.

Scheme 1 provides the key routes for the synthesis of BiTPD derivative (M1) according to our previously reported methods²⁹ and their polymerization with BDT derivative (M2), affording the titled polymer analogue PBiTPD. The key monomer M1 was prepared from the precursor 4-iodothieno-[3,4-c] furan-1,3-dione (1) by a multiple-step procedure. First, the solubilizing alkyl chain 2-hexyloctyl (2HD) was appended at the imide site of intermediate (2), which was then converted to the TPD dimer (3) by copper-mediated Ullmann coupling. Near-quantitative bromination (94%) of 3 to the intermediate 4, followed by Stille cross-coupling reaction (75%), yields intermediate 5, which was then brominated using NBS to form the monomer M1 in relatively high yields (78%). The polymer PBiTPD was synthesized from monomer M1 and M2 by palladium (Pd)-mediated Stille coupling and was further purified by an established procedure.³³ For comparison, the analogue PTPD, with the same solubilizing alkyl chain 2hexyloctyl (2HD) for consistency in this study, was also developed. The PBiTPD and PTPD possess similar numberaverage molecular weight (MW) (22.2–24.6 kDa) and polydispersity indexes (PDI = 2.2–2.6), which can minimize the MW effect on BHJ morphology, carrier transport, and photovoltaic performance in BHJ solar cells. The two polymers possess good solubility in toluene, chlorobenzene, and chloroform that are commonly used for the solution processing of BHJ active layers. Thermogravimetric analysis (TGA, Figure S4) and differential scanning calorimetry (DSC, Figure S5) suggest that PBiTPD and PTPD exhibit good thermal stability up to ca. 400 °C (ca. 5% loss of weight at 424 and 440 °C, respectively), which is beneficial for the long-term operation of BHJ solar cells.

Figure 1a superimposes the normalized thin-film ultraviolet-visible (UV-vis) light absorption spectra of PBiTPD



Figure 1. Normalized UV-vis absorption spectra of (a) neat PTPD film, neat PBiTPD film, and neat Y6 film and (b) BHJ blend films fabricated from the corresponding polymer donors and Y6 acceptor (model system), polymer donor:Y6 = 1:1.2, w/w.

and PTPD, and that of the small-molecule acceptor Y6 (later used in BHJ solar cells studies), with corresponding data provided in Table 1. As presented in Figure 1a, PTPD's spectral absorption falls in the visible range: 400-670 nm. The E_{opt} value of PTPD was calculated to be ca. 1.86 eV from its absorption onset at ca. 667 nm. In comparison, the PBiTPD possesses strong optical absorption in the range of 400-700 nm and shows a red-shifted optical absorption spectrum by ca. 30 nm, which can be attributed to the more pronounced electron-deficient character, and more effective π -electron delocalization along the backbone. The red-shift absorption spectrum indicates that the BiTPD motif indeed narrows the optical bandgap from 1.86 eV for PTPD to 1.78 eV for PBiTPD. The stronger 0-0 transition peak in PBiTPD suggests stronger aggregation feature in PBiTPD thin film. When considering the absorption spectrum of the acceptor conterpart, Y6 has spectral absorption in the NIR range of 600-950 nm, which is highly complementary to the spectral absorption (400-700 nm) of polymer donors PBiTPD and PTPD. In addition, Figure 1b further confirms that the BHJ blend films made with Y6 and PBiTPD or PTPD exihibit complementary absorption and a broad absorption band,

which are essential for improving photon harvesting, exciton generation, and thus increasing the J_{SC} of the devices.

The IPs of PTPD and PBiTPD polymers were estimated through photoelectron spectroscopy in air (PESA) measurement: ca. 5.05 eV for PTPD, and ca. 5.20 eV for PBiTPD (Figure 2a and Table 1). The larger IP value of polymer



Figure 2. (a) Photoelectron spectroscopy in air (PESA) curves for PTPD, PBiTPD, and Y6. PESA-inferred IPs are reported on the plots, and the traces are offset for clarity. (b) Energy level alignments (IP and EA) of electron acceptor Y6 and electron donors PTPD and PBiTPD.

PBiTPD is consistent with the more pronounced electrondeficient properties of BiTPD motifs. It should be noted that the larger IP value measured for donor polymer PBiTPD should translate into higher $V_{\rm OC}$ values in BHJ solar cells.^{34,35} The first-level EA values, inferred from IPs and $E_{\rm opt}$, were 3.19 eV for PTPD, 3.45 eV for PBiTPD, and 4.30 eV for Y6 (see Table 1 and Figure 2b), respectively. As provided in the energy level alignments (Figure 2b), the energy offsets for electron and hole transfer between donor PBiTPD and acceptor Y6, which are derived from EA and IP values, are ca. 0.98 and 0.43 eV, respectively, which are greater than 0.3 eV and thus arguably sufficient to ensure efficient exciton dissociation and promote hole/electron transfer at the donor–acceptor interface (detailed in photoluminescence quenching studies, Figure S10).³⁶

Given the optical and electronic parameter differences between polymers PTPD and PBiTPD, we turned to a systematic analysis of device photovoltaic performance patterns across those two polymer-based BHJ solar cells. Solution-processed thin-film BHJ polymer solar cells were fabricated with the conventional device structure ITO/ PEDOT:PSS/Polymer Donor:Y6/PFN-Br/Ag (indium tin oxide (ITO); poly(3,4-ethylenedioxythiophene)-poly-(styrenesulfonate) (PEDOT:PSS); poly[(9,9-bis(3-(N,N-dimethyl)-N-ethylammonium)-propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)]dibromide (PFN-Br); device area [mask]: 0.04 cm²), and tested under AM 1.5G solar illumination (100 mW·cm⁻²). The BHJ active layers with the optimized donor:acceptor blend ratio of 1:1.2 (w/w) were spin-coated from chloroform (CF) solution with 0.5 vol% 1,8diiodoctane (DIO). The thicknesses of the optimized BHJ

Table 1. Molecular Weight and Thermal, Electronic, and Optical Properties of PTPD, PBiTPD, and Y6

polymer	$M_{\rm n}^{\ a}$ (kDa)	PDI ^a	$T_{\rm d(95\%)}^{b}$ (°C)	$\lambda_{\rm abs}/{\rm sol}^c$ (nm)	$\lambda_{abs}/\text{film} (nm)$	$\mathrm{IP}_{\mathrm{PESA}}^{d}(\mathrm{eV})$	$E_{\rm opt}^{e}$ (eV)	$\mathrm{EA}^{f}\left(\mathrm{eV}\right)$
PTPD	22.2	2.2	424	564, 612	562, 613	5.05	1.86	3.19
PBiTPD	24.6	2.6	440	582, 610	586, 630	5.20	1.78	3.45
Y6	_	_	-	_	825	5.63	1.33	4.30

^{*a*}Determined by GPC. ^{*b*}Measured by TGA. ^{*c*}In chlorobenzene at 100 °C. ^{*d*}Evaluated via PESA measurement. ^{*e*}Optical gaps evaluated from the onset of the thin-film UV–vis absorption spectra. $E_{opt} = 1240/\lambda_{onset}$ (in units of eV). ^{*f*}EA = IP_{PESA} – E_{opt} .

active layer were ca. 100 nm. Figure 3a depicts the current density-voltage (J-V) curves of BHJ solar cells, with the key



Figure 3. (a) J-V curves and (b) EQE spectra for "as spun" (no DIO, curves with unfilled symbols) and optimized (DIO added, curves with solid symbols) PTPD- and PBiTPD-based BHJ polymer solar cells with the benchmark acceptor Y6; AM1.5G solar illumination (100 mW·cm⁻²).

figure of merits provided in Table 2. Further solar cell optimizations are presented in Tables S1-S6 (Supporting Information).

Table 2. Photovoltaic Performance of BHJ Solar Cells Made with Polymers PTPD and PBiTPD as Donors and the Small Molecule Y6 as Model System Acceptor^{a,b,c}

BHJ active layer	DIO ^d	$V_{\rm OC}\left({\rm V}\right)$	$(mA \cdot cm^{-2})$	FF (%)	max PCE %
PTPD:Y6	no	0.65	20.8	37.7	5.1
	yes	0.66	19.5	46.0	5.9
PBiTPD:Y6	no	0.84	25.6	59.7	12.8
	yes	0.83	25.6	66.7	14.2

^{*a*}Device structure: ITO/PEDOT:PSS/Polymer_Donor:Y6/PFN-Br/ Ag. ^{*b*}Device area [mask]: 0.04 cm². ^{*c*}Device statistics in the Supporting Information, Table S4. ^{*d*}The DIO ratio is 0.5 vol %.

As provided in Figure 3a and Table 2, BHJ devices fabricated from polymer donors (PTPD and PBiTPD) with various backbones and the small-molecule acceptor Y6 achieve very distinct performance characteristics. "As-cast" BHJ polymer solar cells composed of PTPD and Y6 can yield only modest PCE of 5.1%, mainly limited by concurrently low $V_{\rm OC}$ (0.65 V) and FF (37.7%) values. Optimized devices, which were made from a blend solution containing 0.5% DIO (v/v), showed improved FF (46.0%) but decreased J_{SC} (19.5 $mA \cdot cm^{-2}$) and thus did not exhibit any significant promising performance with still modest PCE of less than 6%. Smallmolecule additive DIO is now commonly used in the regulation of BHJ film morphologies.³⁷ In comparison, the as-cast BHJ devices made with PBiTPD and Y6 presented remarkably enhanced PCE of 12.8%, with concurrently improved $V_{\rm OC}$ (0.84 V), FFs (59.7%), and $J_{\rm SC}$ (25.6 mA· cm⁻²) compared to PTPD-based as-cast BHJ solar cells. The significant and almost 0.2 V increase in V_{OC} (0.65 V in PTPD devices, 0.84 V in PBiTPD devices) agrees well with the larger PESA-estimated IP value (corresponding to the downshifted HOMO energy level) of PBiTPD.^{34,35} Upon addition of 0.5% DIO (v/v) in the PBiTPD blend solution (cf. additive optimization study in Table S3), the FF improves significantly from 59.7% to 66.7% (~12% improvement), indicating that favorable morphologies are formed in BHJ photoactive layers. The optimized BHJ devices made with PBiTPD yielded higher FF value of 66.7%, while retaining almost the same J_{SC} and V_{OC} values of $\approx 25.6 \text{ mA} \cdot \text{cm}^{-2}$ and 0.83 V, respectively, resulting in PCEs of up to ~14.2%. Overall, BHJ devices made with polymer PBiTPD reach an impressive ca. 2.5-fold PCE enhancement over BHJ solar cells based on the analogous polymer PTPD. As far as we know, the PBiTPD-based BHJ solar cell with PCE of 14.2% is one of the highest-performing photovoltaic BHJ solar cells made with imide- and amidefunctionalized polymers, such as thieno [3,4-c]pyrrole-4,6dione (TPD)-based, diketopyrrolopyrrole (DPP)-based, isoindigo (IID)-based, phthalimide (PhI)-based, and bithiophene imide (BTI)-based polymers, as electron donor materials.¹² Importantly, the PBiTPD broadens the class of high-performing polymer donor materials system, while to date, only a few classes of polymer donors showed PCEs of over 14% in singlejunction binary-blend BHJ PSCs (stated in earlier sections).¹

The varied J_{SC} values (Table 2) reached in PTDP- and PBiTPD-based BHJ solar cells are highlighted in the J-Vcurves (Figure 3a) and are further verified in the external quantum efficiency (EQE) spectra (Figure 3b). The J_{SC} values integrated from EQE curves agree well ($\pm 0.4 \text{ mA} \cdot \text{cm}^{-2}$) with the J_{SC} values provided in Table 2. It can be seen from Figure 3b that all the BHJ solar cells exhibit a broad photo response from 300 to 1000 nm as result of the established complementary optical absorption (Figure 1) of narrowbandgap small-molecule acceptor Y6 and large-bandgap polymer donors, with balanced EQE contributions from polymer donors (300-650 nm) and from the Y6 acceptor (600–1000 nm). The higher J_{SC} values of 25.6 mA·cm⁻² achieved in PBiTPD-based BHJ devices are in line with the EQE spectra. The PBiTPD-based BHJ devices showed EQE values higher by >30% in the broad range of 400-1000 nm (peaking ca. 83% at 610 nm), whereas the EQE responses of PTPD-based solar cells remain less than 70% in the same broad range of 400-1000 nm, in accordance with the modest $J_{\rm SC}$ values (19.5–20.8 mA·cm⁻²) estimated from the J-Vcurves.

Given that the solvent additive DIO can induce efficiency improvement, we examined the BHJ morphology effect via atomic-force microscopy (AFM) and transmission electron microscopy (TEM).^{38,39} Figure S6 presents the film surface variations by AFM, suggesting that the as-cast and "optimized" (DIO processed) BHJ active layers are comparatively smooth. All the BHJ films showed root-mean-square (RMS) roughness values of less than 1.5 nm. The smoothest surface was obtained in the "optimized" PBiTPD BHJ active layer with RMS of 0.88 nm, indicating the good miscibility between PBiTPD and Y6. As shown in Figure 4, the TEM images further suggest that the donor and acceptor components in PTPD:Y6 and PBiTPD:Y6 BHJ films are finely mixed. The finely mixed BHJ films and sufficient energy offset (Figure 2b) contribute to efficient exciton dissociation, hole/electron transfer at the donor and acceptor interface, which agrees well with the near unity photoluminescence quenching efficiencies of >98% (Figure S10).

Compared to PTPD, PBiTPD preferentially promotes backbone planarization and presents strong molecular level aggregation in the thin film (stated in previous discussion), and thus, PBiTPD and its BHJ films may have strong ordering and crystallinity. Herein, 2D grazing incidence wide-angle X-ray scattering (GIWAXS) was used to compare the crystallinity and crystallite orientation of both polymers and their BHJ blend films, with corresponding GIWAXS patterns for neat



Figure 4. TEM images (bright-field) of BHJ active layers made up of (a) PTPD:Y6, as-cast BHJ film, without DIO; (b) PTPD:Y6, optimized BHJ film, with 0.5% DIO; (c) PBiTPD:Y6, as-cast BHJ films, without DIO; (d) PBiTPD:Y6, optimized BHJ film, with 0.5% DIO.

materials and BHJ films provided in Figures S7 and 5, respectively. As presented in Figure 5a,b, PTPD:Y6 BHJ films



Figure 5. (a-d) 2D GIWAXS patterns for PTPD:Y6 and PBiTPD:Y6 BHJ blend films without or with DIO solvent additive, as labeled. (e) 1D profiles of PTPD:Y6 and PBiTPD:Y6 BHJ blend films. Dashed lines represent the out-of-plane direction, and solid lines show the in-plane profiles.

adopt very weak preferential orientation, as evidenced by the mostly isotropic diffraction ring of lamellar stacking (100), regardless of whether DIO is used as solvent additive during solution processing. As shown in Figure 5c, PBiTPD:Y6 BHJ film adopts a face-on orientation relative to the substrate, as indicated by the simultaneous existence of in-plane lamellar (100) diffraction and out-of-plane (010) $\pi - \pi$ diffraction. The crystallite orientation distribution functions related to pole angles, which are provided in Figure S8, also confirm that the dominant crystallite orientation of PBiTPD:Y6 BHJ films is face-on. Interestingly, the application of DIO does not bring up noticeable differences in nanoscale crystallization as resolved by GIWAXS measurement. Upon using DIO for optimizing the BHJ morphology, the PBiTPD:Y6 BHJ film showed even stronger $\pi - \pi$ stacking, as indicated by the sharper $\pi - \pi$ diffraction peak (010). Moreover, higher-order lamellar

diffraction of (200) can be vaguely observed. The stronger $\pi-\pi$ stacking and crystallinity in DIO-processed PBiTPD:Y6 BHJ films are consistent with the red-shifted UV-vis absorption spectra (Figure S9). The face-on backbone orientation and stronger crystallinity in PBiTPD:Y6 blend are generally preferable for the increase of charge transportation and suppression of carrier recombination and thereby yield a higher FF (~67%) in comparison to that of the PTPD:Y6 devices (FF of only 46%).

To further shed light on the large distinction in photovoltaic performance between PBiTPD- and PTPD-based BHJ devices, charge generation, transportation, and extraction in tandem with recombination were studied. Figure 6a depicts photocurrent density $(J_{\rm ph})$ versus internal voltage $(V_{\rm int})$ for the optimized BHJ solar cells. The V_{int} corresponding to the electric field's strength is associated with charge carrier extraction. As presented in Figure 6a, the $J_{\rm ph}$ of PBiTPD BHJ devices increases rapidly in the low-voltage range (V_{int} < 0.2 V) and then gradually saturates and shows fieldindependent behavior at higher voltage ranges ($V_{int} > 0.2 V$), suggesting that all the photogenerated charges can be effectively extracted in PBiTPD devices at $V_{int} > 0.2$ V. For the analogue polymer PTPD-based BHJ devices, J_{ph} shows a distinctive slope within the same V_{int} range. J_{ph} shows a strong dependence on the voltage even at short-circuit (>0.7 V), and saturates gradually in the extremely higher voltage range (V_{int} > 2 V), indicating that charge collection remains hindered probably by charge recombination and unfavorable charge transportation in PTPD BHJ devices. In the saturation regime, PTPD- and PBiTPD-based BHJ cells presented comparable high $J_{\rm ph}$ values of 30 mA·cm⁻², suggesting high efficiency of charge generation in the two BHJ devices, which is consistent with the broad photo response from 300 to 1000 nm of BHJ films (Figures 1b and 3b) and high photoluminescence quenching efficiencies of >98% (Figure S10).

From our space-charge-limited current (SCLC) analyses (Figure 6b,c and Table S7), we also highlight that hole ($\mu_{\rm h}$) and electron ($\mu_{\rm e}$) mobilities, which are estimated from single-carrier devices using the SCLC model, are higher and more balanced in the optimized PBiTPD BHJ devices, in which $\mu_{\rm h}$ achieves 4.61 × 10⁻⁴ cm²·V⁻¹s⁻¹ (vs 0.87 × 10⁻⁴ cm²·V⁻¹s⁻¹ for PTPD) and $\mu_{\rm e}$ achieves 2.42 × 10⁻⁴ cm²·V⁻¹s⁻¹ (vs 1.32 × 10⁻⁴ cm²·V⁻¹s⁻¹ for PTPD), which represents another important parameter in explaining the photovoltaic performance, charge collection, and carrier recombination (discussed later) differences observed between PBiTPD and PTPD BHJ solar cells.

The charge recombination behaviors in optimized PTPDand PBiTPD-based BHJ devices were investigated by examining the variations of $V_{\rm OC}$ and $J_{\rm SC}$ under various light intensities. As provided in Figure 7a, the dependence of $J_{\rm SC}$ against incident light intensity (I) is plotted in a log–log scale and fitted to a power law (solid lines). In general, the light intensity (I) dependence of the photocurrent, which is described by $J_{\rm SC} \propto I^{\alpha}$, can be used to estimate the extent of nongeminate charge recombination loss in BHJ devices.⁴⁰ Here, an $\alpha = 1$ (or near unity) indicates that carrier extraction is effective before recombination at short circuit, where $\alpha < 1$ indicates nongeminate charge recombination loss is not negligible at short-circuit conditions. For PTPD BHJ cells, the α value is 0.92; for PBiTPD BHJ devices, the α value is 0.98, which is close to unity, indicating that carrier extraction



Figure 6. (a) Photocurrent density (J_{ph}) vs internal voltage (V_{int}) for the PBiTPD- and PTPD-based BHJ devices with Y6 as the acceptor. Here, $J_{ph} = J_L - J_D$, in which J_L is the light current density and J_D is the dark current density; $V_{int} = V_0 - V_{appl}$, in which V_0 and V_{appl} are the voltage when $J_{ph} = 0$ and the applied voltage, respectively. Dark J-V curves for (b) electron-only and (c) hole-only diodes made with optimized PTPD:Y6 and PBiTPD:Y6 BHJ active layers. The experimental data (hollow symbols) are fitted using the space-charge-limited current (SCLC) model (solid lines).



Figure 7. Dependence of (a) J_{SC} and (b) V_{OC} of PTPD- and PBiTPD-based devices as a function of incident light intensity (I) (symbols) on a logarithmic scale and fitted to a power law (solid lines).

suffers from less nongeminate recombination losses in PBiTPD BHJ solar cells.

As shown in Figure 7b, the dependence of $V_{\rm OC}$ against incident light intensity (I) is depicted in a natural log-linear scale and described by $V_{\rm OC} \propto nkT/q\ln(I)$, in which k is Boltzmann constant, T temperature in Kelvin, and q the elementary charge. The parameter n (usually 1 < n < 2) illustrates the degree of trap-assisted recombination across the BHJ active layers or interfaces with the electrodes. Any deviations from n = 1 (trap-free condition) indicate the presence of trap-assisted recombination at open-circuit.⁴¹ As shown in Figure 7b, n = 1.27 and 1.59 were estimated for PBiTPD and PTPD BHJ solar cells, respectively, suggesting less trap-assisted recombination at open-circuit condition in PBiTPD optimized BHJ devices and serious trap-assisted recombination in PTPD BHJ devices. In PBiTPD:Y6 BHJ, the face-on backbone orientation, stronger crystallinity, and thereby the higher and more balanced charge transportation, together with less nongeminate and trap-assisted recombination losses, are deemed to be the most important reasons for the higher FF in BHJ solar cells and thus the improved device PCE.

To summarize, bithieno[3,4-*c*]pyrrole-4,6-dione (BiTPD), which is a derivative of thieno[3.4-*c*]pyrrole-4,6-dione (TPD) but has a larger planar skeleton and stronger electron-withdrawing capability, was used for constructing the large-bandgap polymer donor PBiTPD. The electron-withdrawing ability of the BiTPD motif can enlarge the ionization potential value of PBiTPD, and a correspondingly larger $V_{\rm OC}$ of 0.83 V

(vs 0.66 V for PTPD-based devices) was obtained in PBiTPDbased BHJ devices. As confirmed by 2D GIWAXS results, the PBiTPD and PBiTPD:Y6 BHJ blend film exhibited more favorable face-on backbone orientation and stronger crystallinity. As a result, charge transportation was enhanced, whereas the charge recombination was suppressed in the BHJ device, which contributed to the higher FF of 67%. Thereby, the PBiTPD-based BHJ solar cells exhibited high PCE of 14.2%, which is an approximately 2.5-fold efficiency enhancement over BHJ devices made with the analogous polymer PTPD with efficiency of only 5.9%. PBiTPD does broaden the family of high-performing polymer donor materials, while only a few classes of polymer donors showed efficiency of over 14% in single-junction binary-blend polymer solar cells to date. In all, this concise contribution demonstrates that polymers based on bithieno[3,4-c]pyrrole-4,6-dione (BiTPD) motifs are a prospective class of large-bandgap donors for fullerene-free polymer solar cells.

Letter

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.9b02842.

Synthetic details, polymer solar cell device fabrication, and polymer solar cell characterization; charge carrier mobility measurements; GIWAXS measurement, AFM, and TEM experimental methods; and additional figures and tables (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Cui, Y.; Yao, H.; Zhang, J.; Zhang, T.; Wang, Y.; Hong, L.; Xian, K.; Xu, B.; Zhang, S.; Peng, J.; Wei, Z.; Gao, F.; Hou, J. Over 16% efficiency organic photovoltaic cells enabled by a chlorinated acceptor with increased open-circuit voltages. *Nat. Commun.* **2019**, *10*, 2515.

(2) Hong, L.; Yao, H.; Wu, Z.; Cui, Y.; Zhang, T.; Xu, Y.; Yu, R.; Liao, Q.; Gao, B.; Xian, K.; Woo, H. Y.; Ge, Z.; Hou, J. Eco-Compatible Solvent-Processed Organic Photovoltaic Cells with Over 16% Efficiency. *Adv. Mater.* **2019**, *31*, 1903441.

(3) Li, K.; Wu, Y.; Tang, Y.; Pan, M. A.; Ma, W.; Fu, H.; Zhan, C.; Yao, J. Ternary Blended Fullerene-Free Polymer Solar Cells with 16.5% Efficiency Enabled with a Higher-LUMO-Level Acceptor to Improve Film Morphology. *Adv. Energy Mater.* **2019**, *9*, 1901728.

(4) Meng, L. X.; Zhang, Y. M.; Wan, X. J.; Li, C. X.; Zhang, X.; Wang, Y. B.; Ke, X.; Xiao, Z.; Ding, L. M.; Xia, R. X.; Yip, H. L.; Cao, Y.; Chen, Y. S. Organic and solution-processed tandem solar cells with 17.3% efficiency. *Science* **2018**, *361*, 1094.

(5) Yan, T.; Song, W.; Huang, J.; Peng, R.; Huang, L.; Ge, Z. 16.67% Rigid and 14.06% Flexible Organic Solar Cells Enabled by Ternary Heterojunction Strategy. *Adv. Mater.* **2019**, *31*, 1902210.

(6) Fan, B.; Zhang, D.; Li, M.; Zhong, W.; Zeng, Z.; Ying, L.; Huang, F.; Cao, Y. Achieving over 16% efficiency for single-junction organic solar cells. *Sci. China: Chem.* **2019**, *62*, 746–752.

(7) Mateker, W. R.; McGehee, M. D. Progress in Understanding Degradation Mechanisms and Improving Stability in Organic Photovoltaics. *Adv. Mater.* **2017**, *29*, 1603940.

(8) Fan, B.; Du, X.; Liu, F.; Zhong, W.; Ying, L.; Xie, R.; Tang, X.; An, K.; Xin, J.; Li, N.; Ma, W.; Brabec, C. J.; Huang, F.; Cao, Y. Finetuning of the chemical structure of photoactive materials for highly efficient organic photovoltaics. *Nat. Energy* **2018**, *3*, 1051–1058. (9) Wang, G.; Melkonyan, F. S.; Facchetti, A.; Marks, T. J. All-Polymer Solar Cells: Recent Progress, Challenges, and Prospects. *Angew. Chem., Int. Ed.* **2019**, *58*, 4129–4142.

(10) Wang, G.; Eastham, N. D.; Aldrich, T. J.; Ma, B.; Manley, E. F.; Chen, Z.; Chen, L. X.; de la Cruz, M. O.; Chang, R. P. H.; Melkonyan, F. S.; Facchetti, A.; Marks, T. J. Photoactive Blend Morphology Engineering through Systematically Tuning Aggregation in All-Polymer Solar Cells. *Adv. Energy Mater.* **2018**, *8*, 1702173.

(11) Huang, F.; Bo, Z.-s.; Geng, Y.-h.; Wang, X.-h.; Wang, L.-x.; Ma, Y.-g.; Hou, J.-h.; Hu, W.-p.; Pei, J.; Dong, H.-l.; Wang, S.; Li, Z.; Shuai, Z.-g.; Li, Y.-f.; Cao, Y. Study on Optoelectronic Polymers: An Overview and Outlook. *Acta Polym. Sin.* **2019**, *50*, 988–1046.

(12) Yan, C.; Barlow, S.; Wang, Z.; Yan, H.; Jen, A. K. Y.; Marder, S. R.; Zhan, X. Non-fullerene acceptors for organic solar cells. *Nat. Ret. Mater.* **2018**, *3*, 18003.

(13) Nielsen, C. B.; Holliday, S.; Chen, H.-Y.; Cryer, S. J.; McCulloch, I. Non-Fullerene Electron Acceptors for Use in Organic Solar Cells. *Acc. Chem. Res.* **2015**, *48*, 2803–2812.

(14) Zhang, G.; Zhao, J.; Chow, P. C. Y.; Jiang, K.; Zhang, J.; Zhu, Z.; Zhang, J.; Huang, F.; Yan, H. Nonfullerene Acceptor Molecules for Bulk Heterojunction Organic Solar Cells. *Chem. Rev.* **2018**, *118*, 3447–3507.

(15) Lin, Y. Z.; Wang, J. Y.; Zhang, Z. G.; Bai, H. T.; Li, Y. F.; Zhu, D. B.; Zhan, X. W. An Electron Acceptor Challenging Fullerenes for Efficient Polymer Solar Cells. *Adv. Mater.* **2015**, *27*, 1170–1174.

(16) Yao, H.; Chen, Y.; Qin, Y.; Yu, R.; Cui, Y.; Yang, B.; Li, S.; Zhang, K.; Hou, J. Design and Synthesis of a Low Bandgap Small Molecule Acceptor for Efficient Polymer Solar Cells. *Adv. Mater.* **2016**, *28*, 8283–8287.

(17) Yuan, J.; Zhang, Y.; Zhou, L.; Zhang, G.; Yip, H.-L.; Lau, T.-K.; Lu, X.; Zhu, C.; Peng, H.; Johnson, P. A.; Leclerc, M.; Cao, Y.; Ulanski, J.; Li, Y.; Zou, Y. Single-Junction Organic Solar Cell with over 15% Efficiency Using Fused-Ring Acceptor with Electron-Deficient Core. *Joule* **2019**, *3*, 1140.

(18) Zhang, H.; Yao, H.; Hou, J.; Zhu, J.; Zhang, J.; Li, W.; Yu, R.; Gao, B.; Zhang, S.; Hou, J. Over 14% Efficiency in Organic Solar Cells Enabled by Chlorinated Nonfullerene Small-Molecule Acceptors. *Adv. Mater.* **2018**, *30*, 1800613.

(19) Li, W.; Ye, L.; Li, S.; Yao, H.; Ade, H.; Hou, J. A High-Efficiency Organic Solar Cell Enabled by the Strong Intramolecular Electron Push–Pull Effect of the Nonfullerene Acceptor. *Adv. Mater.* **2018**, *30*, 1707170.

(20) Tang, A.; Xiao, B.; Chen, F.; Zhang, J.; Wei, Z.; Zhou, E. The Introduction of Fluorine and Sulfur Atoms into Benzotriazole-Based p-Type Polymers to Match with a Benzotriazole-Containing n-Type Small Molecule: "The Same-Acceptor-Strategy" to Realize High Open-Circuit Voltage. *Adv. Energy Mater.* **2018**, *8*, 1801582.

(21) Lin, Y.; Zhao, F.; Prasad, S. K. K.; Chen, J.-D.; Cai, W.; Zhang, Q.; Chen, K.; Wu, Y.; Ma, W.; Gao, F.; Tang, J.-X.; Wang, C.; You, W.; Hodgkiss, J. M.; Zhan, X. Balanced Partnership between Donor and Acceptor Components in Nonfullerene Organic Solar Cells with > 12% Efficiency. *Adv. Mater.* **2018**, *30*, 1706363.

(22) Firdaus, Y.; Maffei, L. P.; Cruciani, F.; Müller, M. A.; Liu, S.; Lopatin, S.; Wehbe, N.; Ndjawa, G. O. N.; Amassian, A.; Laquai, F.; Beaujuge, P. M. Polymer Main-Chain Substitution Effects on the Efficiency of Nonfullerene BHJ Solar Cells. *Adv. Energy Mater.* **2017**, 7, 1700834.

(23) Liu, D.; Yang, B.; Jang, B.; Xu, B.; Zhang, S.; He, C.; Woo, H. Y.; Hou, J. Molecular design of a wide-band-gap conjugated polymer for efficient fullerene-free polymer solar cells. *Energy Environ. Sci.* **2017**, *10*, 546–551.

(24) Liao, X.; Yao, Z.; Gao, K.; Shi, X.; Zuo, L.; Zhu, Z.; Chen, L.; Liu, F.; Chen, Y.; Jen, A. K. Y. Mapping Nonfullerene Acceptors with a Novel Wide Bandgap Polymer for High Performance Polymer Solar Cells. *Adv. Energy Mater.* **2018**, *8*, 1801214.

(25) Xu, X.; Yu, T.; Bi, Z.; Ma, W.; Li, Y.; Peng, Q. Realizing Over 13% Efficiency in Green-Solvent-Processed Nonfullerene Organic Solar Cells Enabled by 1,3,4-Thiadiazole-Based Wide-Bandgap Copolymers. *Adv. Mater.* **2018**, *30*, 1703973. (26) Guo, X.; Facchetti; Marks, T. J. Imide- and Amide-Functionalized Polymer Semiconductors. *Chem. Rev.* 2014, 114, 8943-9021.

(27) Hadmojo, W. T.; Wibowo, F. T. A.; Ryu, D. Y.; Jung, I. H.; Jang, S.-Y. Fullerene-Free Organic Solar Cells with an Efficiency of 10.2% and an Energy Loss of 0.59 eV Based on a Thieno 3,4-c Pyrrole-4,6-dione-Containing Wide Band Gap Polymer Donor. ACS Appl. Mater. Interfaces 2017, 9, 32939–32945.

(28) Yang, F.; Zhao, W.; Zhu, Q.; Li, C.; Ma, W.; Hou, J.; Li, W. Boosting the Performance of Non-Fullerene Organic Solar Cells via Cross-Linked Donor Polymers Design. *Macromolecules* **2019**, *52*, 2214–2221.

(29) Liu, S.; Song, X.; Thomas, S.; Kan, Z.; Cruciani, F.; Laquai, F.; Bredas, J.-L.; Beaujuge, P. M. Thieno[3,4-c]Pyrrole-4,6-Dione-Based Polymer Acceptors for High Open-Circuit Voltage All-Polymer Solar Cells. *Adv. Energy Mater.* **2017**, *7*, 1602574.

(30) Qiao, X.; Wu, Q.; Wu, H.; Zhang, J.; Li, H. Bithienopyrroledione-Based Copolymers, Versatile Semiconductors for Balanced Ambipolar Thin-Film Transistors and Organic Solar Cells with Voc > 1 V. Adv. Funct. Mater. 2017, 27, 1604286.

(31) Berrouard, P.; Grenier, F.; Pouliot, J.-R.; Gagnon, E.; Tessier, C.; Leclerc, M. Synthesis and Characterization of 5-Octylthieno[3,4-c]pyrrole-4,6-dione Derivatives As New Monomers for Conjugated Copolymers. *Org. Lett.* **2011**, *13*, 38–41.

(32) Pépin-Donat, B.; Ottone, C.; Morell, C.; Lombard, C.; Lefrançois, A.; Reiss, P.; Leclerc, M.; Sadki, S. Electron Paramagnetic Resonance Tracing of Electronic Transfers in Push–Pull Copolymers/PCBM or Nanocrystal Composites. J. Phys. Chem. C 2014, 118, 20647–20660.

(33) Cao, Z.; Chen, J.; Liu, S.; Qin, M.; Jia, T.; Zhao, J.; Li, Q.; Ying, L.; Cai, Y.-P.; Lu, X.; Huang, F.; Cao, Y. Understanding of Imine Substitution in Wide Bandgap Polymer Donor–Induced Efficiency Enhancement in All-Polymer Solar Cells. *Chem. Mater.* **2019**, *31*, 8533–8542.

(34) Blom, P. W. M.; Mihailetchi, V. D.; Koster, L. J. A.; Markov, D. E. Device Physics of Polymer:Fullerene Bulk Heterojunction Solar Cells. *Adv. Mater.* **2007**, *19*, 1551–1566.

(35) Noriega, R.; Rivnay, J.; Vandewal, K.; Koch, F. P. V.; Stingelin, N.; Smith, P.; Toney, M. F.; Salleo, A. A general relationship between disorder, aggregation and charge transport in conjugated polymers. *Nat. Mater.* **2013**, *12*, 1038–1044.

(36) Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. Design Rules for Donors in Bulk-Heterojunction Solar Cells—Towards 10% Energy-Conversion Efficiency. *Adv. Mater.* **2006**, *18*, 789–794.

(37) McDowell, C.; Abdelsamie, M.; Toney, M. F.; Bazan, G. C. Solvent Additives: Key Morphology-Directing Agents for Solution-Processed Organic Solar Cells. *Adv. Mater.* **2018**, *30*, 1707114.

(38) Huang, Y.; Kramer, E. J.; Heeger, A. J.; Bazan, G. C. Bulk Heterojunction Solar Cells: Morphology and Performance Relationships. *Chem. Rev.* **2014**, *114*, 7006–7043.

(39) Li, Q.; Wang, L.; Liu, S.; Zhan, X.; Zhu, T.; Cao, Z.; Lai, H.; Zhao, J.; Cai, Y.-P.; Xie, W.; Huang, F. Impact of Donor–Acceptor Interaction and Solvent Additive on the Vertical Composition Distribution of Bulk-Heterojunction Polymer Solar Cells. ACS Appl. Mater. Interfaces 2019, 11, 45979.

(40) Riedel, I.; Parisi, J.; Dyakonov, V.; Lutsen, L.; Vanderzande, D.; Hummelen, J. C. Effect of Temperature and Illumination on the Electrical Characteristics of Polymer–Fullerene Bulk-Heterojunction Solar Cells. *Adv. Funct. Mater.* **2004**, *14*, 38–44.

(41) Koster, L. J. A.; Mihailetchi, V. D.; Ramaker, R.; Blom, P. W. M. Light intensity dependence of open-circuit voltage of polymer:-fullerene solar cells. *Appl. Phys. Lett.* **2005**, *86*, 123509.