Donor–Acceptor Photovoltaic Polymers Based on 1,4-Dithienyl-2,5-Dialkoxybenzene with Intramolecular Noncovalent Interactions

Xue-Qiang Chen,¹ Xiang Yao,¹ Tianwen Bai,² Jun Ling,² Wen-Jing Xiao,¹ Jiandong Wang,¹ Si-Cheng Wu,¹ Li-Na Liu,¹ Guanghui Xie,³ Jingjing Li,³ Zhengquan Lu,³ Iris Visoly-Fisher,⁴ Eugene A. Katz,⁴ Wei-Shi Li ¹

¹Key Laboratory of Synthetic and Self-assembly Chemistry for Organic Functional Molecules, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China ²Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

³Engineering Research Center of Zhengzhou for High Performance Organic Functional Materials, Zhengzhou Institute of Technology, 6 Yingcai Street, Huiji District, Zhengzhou 450044, China

⁴Department of Solar Energy and Environmental Physics, Swiss Institute for Dryland Environmental and Energy Research, The Jacob Blaustein Institutes for Desert Research (BIDR), Ben-Gurion University of the Negev, Sede Boqer Campus, Midreshet Ben-Gurion 8499000, Israel

Correspondence to: W.-S. Li (E-mail: liws@mail.sioc.ac.cn)

Received 10 November 2017; accepted 8 January 2018; published online 00 Month 2018 DOI: 10.1002/pola.28959

ABSTRACT: Donor-acceptor (D-A) conjugated polymers bearing non-covalent configurationally locked backbones have a high potential to be good photovoltaic materials. Since 1,4-dithienyl-2,5-dialkoxybenzene (TBT) is a typical moiety possessing intramolecular S...O interactions and thus a restricted planar configuration, it was used in this work as an electron-donating unit to combine with the following electron-accepting units: 3fluorothieno[3,4-b]thiophene (TFT), thieno-[3,4-c]pyrrole-4,6-dione (TPD), and diketopyrrolopyrrole (DPP) for the construction of such D-A conjugated polymers. Therefore, the so-designed three polymers, PTBTTFT, PTBTTPD, and PTBTDPP, were synthesized and investigated on their basic optoelectronic properties in detail. Moreover, using [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC71BM) as acceptor material, polymer solar cells (PSCs) were fabricated for studying photovoltaic performances of these polymers. It was found that the optimized PTBTTPD cell gave the best

performance with a power conversion efficiency (PCE) of 4.49%, while that of **PTBTTFT** displayed the poorest one (PCE = 1.96%). The good photovoltaic behaviors of **PTBTTPD** come from its lowest-lying energy level of the highest occupied molecular orbital (HOMO) among the three polymers, and good hole mobility and favorable morphology for its PC₇₁BM-blended film. Although **PTBTDPP** displayed the widest absorption spectrum, the largest hole mobility, and regular chain packing structure when blended with PC₇₁BM, its unmatched HOMO energy level and disfavored blend film morphology finally limited its solar cell performance to a moderate level (PCE: 3.91%). © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2018**, *00*, 000–000

KEYWORDS: 1,4-dithienyl-2,5-dialkoxybenzene; donor–acceptor conjugated polymers; intramolecular non-covalent interactions; polymer solar cells

INTRODUCTION Polymer solar cells (PSCs) have attracted considerable attention for their potential to offer low-cost, lightweight, flexible, and large-area energy conversion devices.¹⁻⁴ With tremendous efforts in material innovation and device engineering, PSCs have achieved a substantial progress in the past decades.⁵⁻⁷ The power conversion efficiency (PCE) record of their single junction modules was raised from 3% to 5% before 2005 to over 13% nowadays.^{8,9} However, compared with that of crystalline-silicon-based inorganic solar cells, this efficiency still lags far behind and

needed to be further improved for PSC commercialization.¹⁰ Therefore, the development of novel high performance polymer photovoltaic materials is still highly desirable and would be one of the top challenges in the field. Besides material innovation, systematic investigations on their structure-property relationships are of primary importance because it can guide us in the design of new materials.¹¹

According to light-to-electricity conversion mechanisms operating in bulk heterojunction (BHJ) PSCs, high performance

Additional Supporting Information may be found in the online version of this article.

© 2018 Wiley Periodicals, Inc.



1

photovoltaic materials are generally required to possess the following properties and characteristics:^{3,12-14} (1) a narrow bandgap for efficient harvesting of solar photons in a wide spectral range, (2) matched molecular frontier orbital energy levels for providing a large open-circuit voltage ($V_{\rm OC}$) and sufficient driving force for exciton dissociation, and (3) strong interchain π - π stacking interactions for efficient charge transportation. For the former two requirements, donor-acceptor (D-A) conjugated polymers, which are composed of electron-donating (D) and -accepting (A) moieties in their backbones, have been developed in lieu of previously used conjugated homopolymers represented by poly(3hexylthiophene). Due to the existence of intramolecular charge transfer (ICT) between D and A units, such materials generally possess a narrow bandgap.^{15,16} Meanwhile, the material energy levels for both highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) can be easily tuned by the proper choice of D and A units and their mode of combination.¹⁷ For the third requirement, a planar structure of the conjugated backbone would be preferred. To reduce torsional angles between two neighboring moieties and make the backbone more planar, both covalent and noncovalent binding strategies have been reported.^{18,19} In the covalent approach, certain bridged bonds in addition to those in the backbone are used to lock two neighboring moieties in a planar geometry and thus form ladder-type moieties. $^{\rm 20-22}$ However, their syntheses generally need a tedious procedure. In an alternative approach, intramolecular non-covalent interactions can be adopted to induce conformation lock and backbone planarization. For example, non-covalent S...O coulomb attraction has been found between the sulfur of thienyl unit and the oxygen of alkoxyl or carbonyl substituents on adjacent aromatics, and was utilized in the design of a variety of conjugated polymers and small molecular semiconductors.23-25 Most of the works demonstrated that such non-covalent S...O interactions can improve the material performance and achieve a PCE over 9.39% and mobility higher than 5.37 cm² $V^{-1}\ s^{-1.26,27}$ Therefore, from the above analysis, one may conclude that D-A conjugated polymers with intramolecular non-covalent interactions would be promising photovoltaic materials with potential high performance.

In this work, we were endeavored to develop D–A photovoltaic polymers based on 1,4-dithienyl-2,5-dialkoxybenzene moiety, as symbolized with **TBT**. Since it contains two thienyl units adjacent to a central phenylene unit bearing two alkoxyl substituents on its 2,5-positions, **TBT** is a typical building block that confers the occurrence of non-covalent S...O interactions and has an almost planar configuration.^{28,29} The first use of **TBT** as donor moiety can be dated back to 2007, when Andersson and coworkers reported a D– A conjugated polymer based on it and 2-thia-1,3,5,8-tetraazacyclopenta[*b*]naphthalene, a strong electron-deficient unit.³⁰ The polymer displayed an extremely narrow bandgap (~1.0 eV) and was demonstrated useful for near infrared photodetector application. However, its photovoltaic performance was poor, only 0.38% for its PSC devices. Later, **TBT** was

mainly combined with benzothiadiazole-derived acceptor units and a number of D-A conjugated polymers were produced.^{28,29,31-33} Among them, a polymer named PPDT2FBT, which was composed of 5,6-difluorobenzothiadiazole and TBT moieties in an alternative fashion, achieved a PCE of 9.39% for its optimized PSCs.²⁶ In the polymer, the existence of numerous intra- and intermolecular non-covalent interactions was demonstrated to endow the polymer tight interchain packing and high charge mobility, affording high photovoltaic performance. From these studies, one may learn that TBT is an excellent electron-donating moiety with intramolecular non-covalent S...O interactions. It has high potential for the construction of high performance photovoltaic polymers and the key is lying in the proper choice of electron-accepting unit. However, most of the reported works focused on benzothiadiazole-derived acceptor units. Only a few studies used other accepting unit, including thienopyrazine, diketopyrrolopyrrole (DPP), and isoindigo.^{34,35} To fully exploit the potential of TBT unit, this work investigated its combination with 3-fluorothieno[3,4-b]thiophene (TFT) and thieno-[3,4-c]pyrrole-4,6-dione (TPD), as well as DPP, for D-A photovoltaic polymers. Owing to their unique structures, all these newly chosen A moieties have excellent records in the field and produced a number of high performance photovoltaic polymers, such as PTB7, PBDTTPD, and PDPP3T. Thus, three polymers named PTBTTFT, PTBTTPD, and PTBTDPP were designed and synthesized in the work (Scheme 1). It was found that the different A combination produced polymers having different optical, electrochemical, and crystalline properties. Moreover, they also displayed quite different photovoltaic performances, in which an optimized PCE of 4.49% was achieved for PTBTTPD, while that of 3.91% was found for PTBTDPP and 1.96% for PTBTTFT.

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic routes for these polymers are outlined in Scheme 1. First, 2,5-dibromohydroquinone (compound 1) was alkylated with 2-ethylhexyl bromide, and then subjected to Stille coupling with 2-(tributylstannyl)thiophene in the presence of Pd(PPh₃)₄ catalyst. The obtained compound 3 was further stannylated with trimethyltin chloride, producing monomer M1 in a yield of 70%. Finally, this monomer was Stille-coupling polymerized with 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate (M2), 1,3-dibromo-5-heptyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (M3), or 3,6-bis(5-bromothiophen-2-yl)-2,5bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (M4), affording the polymers PTBTTFT, PTBTTPD, and PTBTDPP, respectively. It was found that all these polymers possess good solubility in common solvents such as chloroform, chlorobenzene, and o-dichlorobenzene at room temperature. Their number-average molecular weights (M_n) and dispersities (D)were analyzed by gel permeation chromatography (GPC) with monodispersed polystyrenes as standard and reported to be 10.3, 8.64, and 23.6 kDa for the M_n of **PTBTTFT**, **PTBTTPD**, and PTBTDPP, and 2.71, 1.70, and 2.11 for their dispersity, respectively (Table 1). Thermogravimetric analysis (TGA) revealed



SCHEME 1 Synthesis of PTBTTFT, PTBTTPD, and PTBTDPP. [Color figure can be viewed at wileyonlinelibrary.com]

that **PTBTTPD** and **PTBTDPP** start to decompose over 350 °C and have 5%-weight-loss temperature (T_d) at 397 and 412 °C, respectively (Table 1 and Supporting Information Fig. S9). While, **PTBTTFT** starts to decompose around 250 °C although it T_d is as high as 331 °C. Since the weight loss in its first stage of 250–280 °C is only 3–4%, the decomposition may be ascribed to loss fluoro-substituent on thieno[3,4-c]thiophene unit. In differential scanning calorimetry (DSC), all these polymers did not

show any thermal transition in the range of 0-250 °C (Supporting Information Fig. S10).

Optical and Electrochemical Properties

The absorption spectra of **PTBTTFT**, **PTBTTPD**, and **PTBTDPP** in dilute chlorobenzene solution and thin film state are shown in Figure 1(a), and their data are summarized in Table 1. It is clear that **PTBTDPP** displayed the

TADIE 1	Racia	Proportion	of DTDTTET	DTDTTDD	and DTRTDDD
IABLE I	Basic	Properties	OT PIBILFI.	PIBIIPD	and PIBIDPP

				λ_{\max} (nm)								
Polymer	<i>M</i> n (KDa)	Đ	<i>Т</i> _d (°С)	Solution	Film	λ _{onset} (nm)	E _{ox,onset} (V)	E _{red,onset} (V)	HOMO ^c (eV)	LUMO ^d (eV)	E _{g, opt} e (eV)	E _{g, CV} f (eV)
PTBTTFT	10.3 ^a	2.71 ^a	331	447, 564	459, 607	822	0.38	-1.24	-5.10	-3.48	1.51	1.62
PTBTTPD	8.64 ^b	1.70 ^b	397	502	382, 541, 592	671	0.49	-1.20	-5.21	-3.52	1.85	1.69
PTBTDPP	23.6 ^b	2.11 ^b	412	433, 676, 739	435, 675, 743	886	0.29	-1.17	-5.01	-3.55	1.40	1.46

 $^{\rm a}$ Measured by GPC operating with 1,2-dichlorobenzene as an eluent at room temperature.

 $^{\rm b}$ Measured by high temperature GPC operating with 1,2,4-trichlorobenzene as an eluent at 150 $^{\circ}\text{C}.$

 c HOMO = -e($E_{\text{ox,onset}}$ - $E_{\text{Fc/Fc+}}$ + 4.8 V).

^d LUMO = $-e(E_{red,onset}-E_{Fc/Fc+} + 4.8 \text{ V}).$

^e $E_{g,opt} = 1240/\lambda_{onset}$.

 $^{f}E_{g,CV} = E_{LUMO} - E_{HOMO}$





FIGURE 1 (a) UV-vis absorption spectra of **PTBTTFT**, **PTBTTPD**, and **PTBTDPP** in diluted chlorobenzene solutions and film state at room temperature. (b–d) The temperature-dependent UV-vis spectra of (b) **PTBTTFT**, (c) **PTBTTPD**, and (d) **PTBTDPP** in chlorobenzene solutions. [Color figure can be viewed at wileyonlinelibrary.com.]

broadest absorption spectrum among the three polymers in dilute chlorobenzene solution [Fig. 1(a)] in the range of 350-800 nm. Three absorption peaks were identified with apexes at 433, 676, and 739 nm. The first peak is attributed to $\pi - \pi^*$ transition of the conjugated backbone, while the middle one originates from ICT transition between the TBT and **DPP** units. The 739 nm peak may be due to interchain π -stacking interactions when considering its film spectral features as described below. Unlike PTBTDPP, PTBTTPD showed only a broad peak in the range of 350-600 nm with an apex at 502 nm, while PTBTTFT exhibited a similar broad peak in the range of 350-700 nm with an apex at 447 and a shoulder at 564 nm. This observation implies that the excitation energy for ICT transition in PTBTTPD and **PTBTTFT** may be close to that for their π - π * transitions. In film state, the polymer PTBTTFT showed absorption spectrum with a 43 nm-red-shifted band as compared with its solution one. In the case of PTBTTPD polymer, it displayed not only a \sim 40 nm-red shifted band but also a new peak at 592 nm. All these indicate the occurrence of interchain π - π stacking interactions in their films. However, PTBTDPP presented absorption peaks in film state with almost identical positions to their solution ones. This implies that interchain π - π stacking interactions take place even in dilute solution state.

To further confirm the interchain π - π interaction occurring in solution, temperature-dependent UV-vis spectroscopy was carried out on these polymer chlorobenzene solutions [Figs. 1(b-d)]. It was found that the spectra of **PTBTTFT** and **PTBTTPD** almost kept the same shape but with blue shifted ICT peaks, when the temperature was risen from 0 to 120 °C. Considering higher temperature generally activates conjugated backbone to take a more twisted configuration and leads to blue shift in absorption peaks, the observed phenomena suggest the occurrence of little interchain π - π interactions in **PTBTTFT** and **PTBTTPD** solutions. However, in the case of **PTBTDPP** solution, the spectral shape changed a lot with temperature increments. The peak around 739 nm was observed at low temperature (0–40 °C), but disappeared when the temperature was higher than 80 °C. This unambiguously proves that **PTBTDPP** polymer has strong π - π interchain interactions even in dilute solution.

The bandgap energy (E_g) and energy levels of the HOMO and LUMO (E_{HOMO} and E_{LUMO}) are important parameters for a photovoltaic material. They can be estimated from the absorption edges (λ_{onset}), and onset oxidation ($E_{ox,onset}$) and reduction potentials (Ered,onset) measured by cyclic voltammetry. From their film absorption spectra as shown in Figure 1(a), the λ_{onset} of **PTBTTFT**, **PTBTTPD**, and PTBTDPP was found to be 822, 671, and 886 nm, giving their $E_{g,opt}$ to be 1.51, 1.85, and 1.40 eV, respectively (Table 1). Meanwhile in their CV profiles (Figure 2a), apparent oxidation waves with onset points of 0.38, 0.49, and 0.29 V were identified for PTBTTFT, PTBTTPD, and PTBTDPP, respectively. Since the redox couple of ferrocene/ferrocenium (Fc/Fc⁺), having an absolute energy level of -4.8 eV with respect to the vacuum level, displayed the oxidation onset at 0.08 V under the same conditions, the E_{HOMO} of **PTBTTFT**, **PTBTTPD**, and **PTBTDPP** can be calculated to be -5.10, -5.21, and -5.01 eV, respectively [Table 1 and Figure 2(b)].



FIGURE 2 (a) CV curves of **PTBTTFT**, **PTBTTPD**, and **PTBTDPP** films deposited on glassy carbon electrodes and measured in acetonitrile solutions containing 0.1 mol L^{-1} Bu₄NPF₆ electrolyte at a scan rate of 50 mV s⁻¹. (b) Energy-level diagram of **PTBTTFT**, **PTBTTPD**, and **PTBTDPP**. [Color figure can be viewed at wileyonlinelibrary.com.]

Similarly, the E_{LUMO} of **PTBTTFT**, **PTBTTPD**, and **PTBTDPP** was estimated from their $E_{red,onset}$ (-1.24, -1.10, and -1.17 V) and found to be -3.48, -3.52, and -3.55 eV, respectively. With both E_{HOMO} and E_{LUMO} data, the energy bandgap can be also derived to be 1.62, 1.69, and 1.46 eV for **PTBTTFT**, **PTBTTPD**, and **PTBTDPP**, respectively. From these data, one may see that **PTBTTPD** has the lowest-lying HOMO energy level, which would benefit to obtain a large open-circuit voltage (V_{OC}) in combination with fullerene acceptor for PSCs. However, polymer **PTBTDPP** possesses the smallest bandgap. This is consistent with the observations in absorption spectroscopy and would be favorable for achieving a large short-circuit current (J_{SC}) in PSC application.

Theoretical Studies

To gain insight into the fundamental structure and electronic properties of these three polymers, density functional theory (DFT) was employed to simulate on their trimer segments by using Gaussian 09 program with B3LYP/6-31G(d,p) methods.³⁶ To simplify the calculation, all of the

alkyl side chains were replaced with methyl units and the optimized backbone geometries are displayed in Figure 3. It is clear that the TBT moieties in all three polymers adopt a planar configuration with all dihedral angles less than 15°. More importantly, all sulfur atoms of thienyl units are residing in the same side of alkoxyl substituents of central benzene units. The distances between S and O are estimated to be around 2.7 Å, much smaller than the sum of their van der Waals radius (O: 1.52 Å, S: 1.8 Å).³⁷ Although lacks of direct experimental supports, the DFT optimized backbone geometries prove the existence of non-covalent S...O interactions in TBT moieties for all three polymers. It is valuable to point out that PTBTTPD polymer has the most planar backbone structure among the three polymers. This is because the concurrence of another set of noncovalent of S...O interactions, which is existing between thienyl sulfur and imide oxygen in TPD unit and evidenced by a small S...O distance (3 Å) and almost flat configuration between thienyl and TPD units with dihedral angles less than $<1^{\circ}$.



FIGURE 3 Optimized backbone geometries and electron wave functions of HOMO and LUMO orbitals of the trimer models of **PTBTTFT**, **PTBTTPD**, and **PTBTDPP** via DFT calculation. [Color figure can be viewed at wileyonlinelibrary.com.]





FIGURE 4 (a) *J*–*V* curves and (b) EQE spectra of the optimized **PTBTTFT**/PC₇₁BM, **PTBTTPD**/PC₇₁BM, and **PTBTDPP**/PC₇₁BM-based PSC devices. [Color figure can be viewed at wileyonlinelibrary.com.]

Figure 3 also displays the simulated electron wave functions of HOMO and LUMO orbitals for these three polymer models. For both HOMO and LUMO orbitals, electron delocalizes through a wide range of backbone units, suggesting the good π -electron conjugation in all these polymers. But their delocalizing centers are different, suggesting certain D–A nature for all three polymers.

Photovoltaic Performance

To investigate the photovoltaic properties of these polymers, PSC devices with a conventional configuration of ITO/ PEDOT:PSS/BHJ active layer/Ca/Al were fabricated. The BHJ active layer was composed of the tested donor polymer and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as acceptor material. To know the best performance of each polymer, their fabrication processes were individually optimized on polymer/PC71BM weight ratio, solvent, and additive. The experiments found that chlorobenzene as solvent and polymer/PC71BM weight ratio of 1:1 were suitable for fabrication of both PTBTTFT- and PTBTTPD-based cells, while 1,2-dichlorobenzene and polymer/PC₇₁BM weight ratio of 1:1.5 were good for PTBTDPP cell fabrication. Moreover, 3% (v/v) 1-chloronaphthalene (CN) as an additive to the processing solvent was found to effectively improve PTBTTPD cell performance, while the tested additives (1,8diiodooctane and 1-chloronaphthalene) did not enhance the performances of **PTBTTFT** and **PTBTDPP** cells. After optimization, the J-V curves of their best cells are displayed in Figure 4(a) and their device parameters are listed in Table 2. It can be seen that the optimized PTBTTPD cell with a PCE of 4.49% displayed the best performance among these polymer devices. This should result from its largest $V_{\rm OC}$ (0.88 V), which is closely associated with its lowest lying HOMO

energy level. Compared with **PTBTTPD** cell, **PTBTDPP** device showed a higher J_{SC} (11.11 vs. 8.70 mA cm⁻²) and a slightly larger FF (62.2% vs. 58.5%). However, the smallest V_{OC} (0.57 V) limited its final power conversion efficiency to a moderate level (3.91%). For the **PTBTTFT** device, it displayed the smallest PCE (1.96%) with a V_{OC} of 0.67 V, a J_{SC} of 5.83 mA cm⁻² and a FF of 50.1%.

In their external quantum efficiency (EQE) spectra, as shown in Figure 4(b), PTBTDPP cell was found to display the widest photo-response range, from 300 to 800 nm, but with moderate EQEs among the three optimized devices. The PTBTTPD cell showed the largest EQE values in the region of 400-600 nm but with the narrowest photo-response range, while PTBTTFT cell displayed the smallest EQEs in its photo-response range of 300-750 nm. Therefore, these EQE spectra are well consistent with light-absorption behaviors of the polymers and can well explain the order of J_{SC} . In addition to PC71BM, [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM) was also used as acceptor material blended with the polymers for PSCs and achieved similar photovoltaic performances with PCEs of 4.41% for PTBTTPD-, 2.85% for PTBTDPP-, and 1.68% for PTBTTFT-based devices (Supporting Information Table S1).

Hole Mobility, Film Structure, and Morphology

To get insights into the observed photovoltaic performance differences of these three polymers, their BHJ films with $PC_{71}BM$ were investigated for hole mobility, chain packing structure and as well as morphology. Charge mobility in the BHJ active layer is an important factor that determines PSC performance, especially for J_{SC} and FF. In this work, hole transporting only devices with a configuration of

TABLE 2 Device Parameters of the Optimized PTBTTFT-, PTBTTPD-, and PTBTDPP-Based PSCs as Shown in Figure 4(a)

Polymer	Polymer/PC ₇₁ BM (w/w)	CN (v/v)	Thickness (nm)	V _{oc} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE ^a (%)	${{{\mu_{\rm h}}^{\rm b}}\over{({ m cm}^2~{ m V}^{-1}~{ m S}^{-1})}}$
PTBTTFT	1:1	0	85	0.67	5.83	50.1	1.96 (1.84)	$9.62 imes 10^{-4}$
PTBTTPD	1:1	3%	80	0.88	8.70	58.5	4.49 (4.27)	$1.96 imes10^{-3}$
PTBTDPP	1:1.5	0	150	0.57	11.11	62.2	3.91 (3.70)	$5.25 imes10^{-3}$

^a The date in parentheses are average value.

^b Measured by SCLC method.



FIGURE 5 XRD profiles of polymer/PC₇₁BM BHJ films. [Color figure can be viewed at wileyonlinelibrary.com.]

ITO/PEDOT:PSS/BHJ active layer/Au were fabricated for the three polymers (Table 2 and Supporting Information Fig. S8). Here, the compositions and fabrication methods of the BHJ active layers were the same as for their optimized PSCs. *J–V* curves were measured in the dark and fitted by a space charge-limited current theory (Supporting Information Fig. S11), and the hole mobilities were calculated to be 9.62×10^{-4} , 1.96×10^{-3} , and 5.25×10^{-3} cm² V⁻¹ S⁻¹ for **PTBTTFT-**, **PTBTTPD-**, and **PTBTDPP**-based BHJ films, respectively (Table 2). It is clear that **PTBTDPP**/PC₇₁BM blend film gave the largest hole mobility, while that of **PTBTTFT** was the smallest one. So, it is not surprising that

the **PTBTDPP** PSC displayed the best J_{SC} and FF value, while **PTBTTFT** cell exhibited the poorest performances in these two parameters.

Besides hole mobility, the BHJ film structure was investigated by X-ray diffraction (XRD). As shown in Figure 5, only **PTBTDPP**/PC₇₁BM (1/1.5, w/w) BHJ film gave a set of diffraction peaks at 2 θ of 4.9, 9.8, and 18.6°. The former two peaks can be assigned to (100) and (200) diffraction from a lamellar structure with layer distance of 1.74 nm, while the last broad peak may originate from (010) π – π stacking diffraction. However, no obvious diffraction peaks were found for **PTBTTFT**/PC₇₁BM (1/1, w/w) and **PTBTTPD**/PC₇₁BM (1/1, w/w) BHJ films. This result illustrates that only **PTBTDPP** polymer could form a regular packing structure with strong π – π interchain interactions in its BHJ film, and thus contribute to its good hole transport.

Atomic force microscopy was also used to investigate the BHJ film morphology. As shown in Figure 6, the blend films of **PTBTTFT**/PC₇₁BM (1/1, w/w) and **PTBTTPD**/PC₇₁BM (1/1, w/w) appeared to be rather flat. Their root-mean-square roughnesses were estimated to be 0.60 and 0.72 nm, respectively. However, the appearance of the blend film of **PTBTDPP**/PC₇₁BM (1/1.5, w/w) was very rough, with a RMS roughness of 11.57 nm [Note the height scale in Figure 6(c) is different from those of Figs. 6(a,b)]. Moreover, its phase image revealed that the film was full of dot-like domains with the size of 40–70 nm, while the phase image of **PTBTTPD** blend film suggested short rod-like structures.



FIGURE 6 (a–c) AFM height and (d–f) phase topographical images (5 μ m × 5 μ m) of (a, d) **PTBTTFT**/PC₇₁BM, (b, e) **PTBTTPD**/PC₇₁BM, and (c, f) **PTBTDPP**/PC₇₁BM BHJ films. [Color figure can be viewed at wileyonlinelibrary.com.]



Therefore, it is possible that the coarse morphology of the **PTBTDPP** BHJ film is adds to the HOMO energy level consideration in explaining the inferior performance of **PTBTDPP** PSCs compared to **PTBTTPD** cells.

CONCLUSIONS

In this contribution, three D-A conjugated polymers namely PTBTTFT, PTBTTPD, and PTBTDPP, which are composed of 1,4-dithienyl-2,5-di(2-ethylhexyoxyl)-benzene (TBT) electron-donating moiety and one of following electronaccepting units: 3-fluorothieno[3,4-*b*]thiophene (TFT), thieno-[3,4-c]pyrrole-4,6-dione (TPD), and diketopyrrolopyrrole (DPP), are reported. Owing to its unique structure, TBT has typical intramolecular S...O interactions and thus a noncovalent conformation-locked backbone. When it was combined with TPD, the produced PTBTTPD polymer has a low-lying HOMO energy level (-5.21 eV), thus affording the largest V_{OC} (0.88 V) for its PSCs. Moreover, its blend film with PC71BM possessed good hole mobility and a favorable morphology. Therefore, its optimized PSC showed a PCE of 4.49%, the best among the three polymer devices. In comparison, PTBTDPP displayed a wider absorption spectrum and a larger hole mobility than PTBTTPD, thus giving its PSC device the largest J_{SC} and FF value. However, its unmatched HOMO energy level and disfavored blend film morphology limited the performance of its PSC device, which displayed a PCE of 3.91%, slightly smaller than that of **PTBTTPD** cell. In the case of **PTBTTFT** polymer, high lying HOMO energy level, the smallest hole mobility, and irregular chain-packing structure in the blend film are all disfavor to its photovoltaic performance, thus leading to the smallest PCE (1.96%) for its PSC device in this family.

EXPERIMENTAL

Measurements and Characterization

All reagents from commercial sources were used as received. All reactions were carried out under argon atmosphere using solvents dehydrated following standard methods. Compound 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate (M2) and 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2hexyldecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (M4)were purchased from Suna Tech, Inc. 1,3-Dibromo-5-heptyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (M3) was synthesized according to reported procedures. 38,39 $^{1}\mathrm{H}$ NMR (400 MHz) and ¹³C NMR (100 MHz) were recorded on a Varian Mercury spectrometer with tetramethylsilane (TMS) as an internal reference. The spectra of small molecular compounds were measured in CDCl₃ at room temperature, while those of polymers were recorded in 1,1,2,2-tetrachloroethane- d_2 at 100 °C. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy was carried out on a Shimadzu Biotech Axima Mass Spectrometer using dithranol as a matrix. The average molecular weights and dispersities (D) of PTBTTPD and PTBTDPP were estimated by hightemperature gel permeation chromatography (GPC) operating at 150 °C using 1,2,4-trichlorobenzene as an eluent and monodispersed polystyrenes as standards, while those of PTBTTFT was measured by room temperature GPC using o-dichlorobenzene as an eluent. Thermogravimetric analysis (TGA) was carried out by a TGA Q500 instrument with a temperature rate of 10 $^\circ C \ min^{-1}$ under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a Q2000 modulated DSC instrument with a heating rate of 10 °C min⁻¹ and a cooling rate of 15 °C min⁻¹ under a nitrogen atmosphere. UV-vis absorption spectroscopy was performed on a Hitachi U-3310 spectrophotometer. Cyclic voltammetry (CV) measurements were performed on a CHI 660C instrument with a three-electrode cell using glassy carbon as a working electrode, platinum wire as a counter electrode, and Ag/AgNO₃ as a reference electrode. Samples were prepared by casting their chlorobenzene solutions onto glassy carbon electrodes. The measurements were carried out in dehydrated acetonitrile solutions containing 0.1 M Bu₄NPF₆ electrolyte at a scan rate of 50 mV s⁻¹. Atomic force microscopy (AFM) was performed on a JPK NanoWizard AFM system in tapping mode. X-ray diffraction (XRD) was carried out on a PANalytical X'Pert Pro diffractometer with Cu K α beam (40 kV, 40 mA) in θ -2 θ scans (0.026 Å step size, 50 s/step).

Photovoltaic Device Fabrication and Characterization

All solar cell devices were fabricated with a structure of ITO/PEDOT:PSS/BHJ active layer/Ca/Al. First, ITO-coated glass substrates were cleaned by deionized water, acetone, and isopropanol. Then the substrates were dried with pressurized nitrogen and exposed to UV-ozone plasma for 15 min. A thin layer (25 nm) of filtered PEDOT:PSS (Heraeus Clevios PVP. Al 4083) was spin-casted on the top of cleaned ITO at 4000 rpm and baked at 140 °C for 15 min. Afterwards, the substrates were transferred into a dry nitrogen glovebox ($0_2 < 0.1$ ppm, $H_20 < 0.1$ ppm) for active layer deposition. The active layer of PTBTTFT or PTBTTPD was spin-coated from a chlorobenzene solution of the polymer and PC₇₁BM with a total weight concentration of 20 mg mL^{-1} , while that of **PTBTDPP** was from an *o*-dichlorobenzene solution of PTBTDPP and PC71BM with a total weight concentration of 25 mg mL^{-1} . In the fabrication of **PTBTTPD**/PC₇₁BM BHJ active layer, 1-chloronaphthalene (CN) in a volume fraction of 3% was added as additive to solvent. Finally, the devices were finished by thermal deposition of 8 nm-thick Ca and 80 nm-thick Al cathode under a vacuum of 10^{-5} mbar. The thicknesses of all the films were measured by a Veeco Dektak 150 profilometer. Current density-voltage (I-V) curves were recorded with a Keithley 2420 source meter. Photocurrent was acquired upon irradiation using an AAA solar simulator (Oriel 94043A, 450 W) with an AM 1.5G filter. Light intensity was adjusted to 100 mW cm⁻² using a standard NRE-certified silicon cell. External quantum efficiency (EQE) was detected with a 75 W Xe lamp, an Oriel monochromator (74125), an optical chopper, a lock-in amplifier, and a NREL-calibrated crystalline silicon cell.

Hole Mobility Measurement

Hole-transporting only devices were fabricated with a structure of ITO/PEDOT:PSS/polymer:PC₇₁BM/Au. The mobility was determined by fitting the dark current to single carrier SCLC, as described by the following equation:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h \frac{\left(V_a - V_{bi}\right)^2}{d^3}$$

where *J* is the current density, $\mu_{\rm h}$ is the hole mobility, ε_0 and $\varepsilon_{\rm r}$ are the permittivity of free space and the relative permittivity of the materials, respectively, *d* is the thickness of the active layer, $V_{\rm a}$ is the applied voltage, and $V_{\rm bi}$ is the built-in voltage.

Material Synthesis Synthesis of 1,4-Dibromo-2,5-Bis((2-Ethylhexyl)Oxy) Benzene (Compound 2)

A mixture of 2,5-dibromobenzene-1,4-diol (compound 1, 2.0 g, 7.52 mmol), K₂CO₃ (4.14 g, 30 mmol) was put into a 250 mL flask under the protection of argon. After addition of 100 mL DMF, the reaction mixture was stirred for 1 h. Then, 3-(bromomethyl)heptane (5.76 g, 30 mmol) were added into the reaction mixture. After refluxing at 100 °C for 24 h, the solvent was removed under reduced pressure. The crude product washed with water and extracted with dichloromethane. The product was separated by silica column chromatography using hexane as the eluent to afford compound **2** as colorless oil liquid (3.263 g, yield 88%). ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.084 (s, 2H), 3.831 (d, *J* = 7.2 Hz, 4H), 1.788–1.711 (br, 2H), 1.571–1.398 (m, 8H), 1.342–1.268 (m, 8H), 0.962–0.892 (m, 12H).

Synthesis of 2,2'-(2,5-Bis((2-Ethylhexyl)Oxy)-1,4-Phenylene)Dithiophene (Compound 3)

A mixture of compound 2 (1.65 g, 3.36 mmol), tributyl(thiophen-2-yl)stannane was dissolved in dry toluene under the protection of Ar atmosphere. After the solution was frozen by liquid nitrogen, tetrakis(triphenylphosphine) palladium(0) (194 mg) was added quickly into the flask. The resulted mixture was then subjected to thoroughly degassed with three freeze-pump-thaw cycles and filled back with Ar. After stirring at 110 °C for 8 h, the solvent was removed under reduced pressure. The residue was added with water and extracted with dichloromethane for three times. The organic phases were combined, washed with brine, dried over anhydrous MgSO₄, and concentrated under vacuum. The crude product was finally separated by silica column chromatography using hexane as eluent to afford compound 3 as yellow solid (1.43 g, yield 86%). ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.531 (d, *J* = 4.8 Hz, 2H), 7.347 (d, *J* = 6.8 Hz, 2H), 7.260 (s, 2H), 7.102 (dd, J = 6.8 Hz, J = 4.8 Hz, 2H), 3.979 (d, J = 6.8 Hz, 4H), 1.882–1.799 (br, 2H), 1.629–1.460 (m, 8H), 1.344-1.312 (m, 8H), 0.969-0.899 (m, 12H).

Synthesis of ((2,5-Bis((2-Ethylhexyl)Oxy)-1,4-Phenylene) Bis(Thiophene-5,2-Diyl))Bis(Trimethylstannane) (M1)

Compound **3** (1.25 g, 2.5 mmol) was dissolved in 30 mL dry THF under the protection of argon. After the solution was cooled down to -78 °C using a dry iceacetone bath, *n*-butyl-lithium (3 mL, 2.5 M in *n*-hexane, 7.5 mmol) was added dropwise. Then, the reaction mixture was slowly warmed up to



General Procedure for Synthesis of Polymers PTBTTFT, PTBTTPD, and PTBTDPP

To a two-necked flask was added dry toluene (12 mL), monomer **M1** (0.2 mmol) and one of following monomers: **M2**, **M3**, or **M4** (0.2 mmol). After the solution was frozen by liquid nitrogen, Pd(PPh₃)₄ (12 mg) was added quickly into the flask. The resulted mixture was then subjected to thoroughly degassed with three freeze-pump-thaw cycles and filled back with Ar. After stirring at 110 °C for 36 h, the reaction mixture was poured into 150 mL methanol to precipitate the produced polymers. After filtration, the crude polymer was subjected to Soxhlet extraction with methanol, acetone, hexane, and chloroform in sequence, and finally purified by SEC column with S-X1 Biobeads using chloroform as an eluent. The yields for all polymers were 70–80%.

ACKNOWLEDGMENTS

This work was financially supported by National Natural Science Foundation of China (21474129, 21674125, and 51761145043), International Science and Technology Cooperation Program of China (2015DFG62680), Strategic Priority Research Program of Chinese Academy of Sciences (XDB20020000), Science and Technology Open Cooperation Projects of Henan Province (162106000018 and 172106000067) and Zhengzhou Institute of Technology. IVF and EAK are grateful to Israel's Ministry of Science and Technology for the China-Israel Cooperative Scientific Research Grant number 3–12387.

AUTHOR CONTRIBUTIONS

X.-Q. Chen was mainly in charge of research experiments. X. Yao, J. Wang, and S.-C. Wu fabricated solar cells and characterized device performance. W.-J. Xiao and L.-N. Liu helped in polymer syntheses. G. Xie, J. Li, and Z. Lu helped in polymer characterizations. I. Visoly-Fisher and E. A. Katz helped in device characterization and data analysis. T. Bai and J. Lin carried out DFT calculations. W.-S. Li supervised the research. X.-Q. Chen and W.-S. Li wrote the manuscript, while I. Visoly-Fisher and E. A. Katz proofread the manuscript.



9

REFERENCES AND NOTES

1 S. Günes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* **2007**, *107*, 1324.

2 T. M. Clarke, J. R. Durrant, Chem. Rev. 2010, 110, 6736.

3 L. Lu, T. Zheng, Q. Wu, A. M. Schneider, D. Zhao, L. Yu, *Chem. Rev.* **2015**, *115*, 12666.

4 C.-Y. Mei, L. Liang, F.-G. Zhao, J.-T. Wang, L.-F. Yu, Y.-X. Li, W.-S. Li, *Macromolecules* 2013, *46*, 7920.

5 Y. Deng, W. Li, L. Liu, H. Tian, Z. Xie, Y. Geng, F. Wang, *Energy Environ. Sci.* **2015**, *8*, 585.

6 Y. F. Li, Acc. Chem. Res. 2012, 45, 723.

7 J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante, A. J. Heeger, *Science* **2007**, *317*, 222.

8 M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. J. Brabec, *Adv. Mater.* 2006, *18*, 789.

9 W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang, J. Hou, *J. Am. Chem. Soc.* **2017**, *139*, 7148.

10 A. Polman, M. Knight, E. C. Garnett, B. Ehrler, W. C. Sinke, *Science* **2016**, *352*, 307.

11 P. Gao, J. Tong, P. Guo, J. Li, N. Wang, C. Li, X. Ma, P. Zhang,

C. Wang, Y. Xia, J. Polym. Sci. Part A: Polym. Chem. 2018, 56, 85.
 12 L. Dou, Y. Liu, Z. Hong, G. Li, Y. Yang, Chem. Rev. 2015,

115, 12633.

13 P. Guo, G. Luo, Q. Su, J. Li, P. Zhang, J. Tong, C. Yang, Y. Xia, H. Wu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 10937.

14 A. J. Heeger, Adv. Mater. 2014, 26, 10.

15 P.-L. T. Boudreault, A. Najari, M. Leclerc, *Chem. Mater.* **2011**, *23*, 456.

16 L. Dou, J. You, Z. Hong, Z. Xu, G. Li, R. A. Street, Y. Yang, *Adv. Mater.* **2013**, *25*, 6642.

17 P. Guo, J. Sun, S. Sun, J. Li, J. Tong, C. Zhao, L. Zhu, P. Zhang, C. Yang, Y. Xia, *RSC Adv.* **2017**, *7*, 22845.

18 C. Liu, K. Wang, X. Gong, A. J. Heeger, *Chem. Soc. Rev.* **2016**, *45*, 4825.

19 H. Huang, L. Yang, A. Facchetti, T. J. Marks, *Chem. Rev.* 2017, *117*, 10291.

20 J. Aragó, P. M. Viruela, J. Gierschner, E. Ortí, B. M. Medina, *Phys. Chem. Chem. Phys.* 2011, *13*, 1457.

21 J. Tong, J. Li, P. Zhang, X. Ma, M. Wang, L. An, J. Sun, P. Guo, C. Yang, Y. Xia, *Polymer* **2017**, *121*, 183.

22 Y. Wu, Z. Li, W. Ma, Y. Huang, L. Huo, X. Guo, M. Zhang, H. Ade, J. Hou, *Adv. Mater.* **2013**, *25*, 3449.

23 X. Guo, Q. Liao, E. F. Manley, Z. Wu, Y. Wang, W. Wang, T. Yang, Y.-E. Shin, X. Cheng, Y. Liang, L. X. Chen, K.-J. Baeg, T.

J. Marks, X. Guo, *Chem. Mater.* **2016**, *28*, 2449.

24 H. G. Kim, B. Kang, H. Ko, J. Lee, J. Shin, K. Cho, *Chem. Mater.* 2015, *27*, 829.

25 H. Huang, N. Zhou, R. P. Ortiz, Z. Chen, S. Loser, S. Zhang, X. Guo, J. Casado, J. T. L. Navarrete, X. Yu, A. Facchetti, T. J. Marks, *Adv. Funct. Mater.* **2014**, *24*, 2782.

26 T. L. Nguyen, H. Choi, S.-J. Ko, M. A. Uddin, B. Walker, S. Yum, J.-E. Jeong, M. H. Yun, T. J. Shin, S. Hwang, J. Y. Kim, H. Y. Woo, *Energy Environ. Sci.* **2014**, *7*, 3040.

27 W. Zhang, Z. Mao, J. Huang, D. Gao, G. Yu, *Macromole-cules* 2016, *49*, 6401.

28 M. A. Uddin, T. H. Lee, S. Xu, S. Y. Park, T. Kim, S. Song, T. L. Nguyen, S-j. Ko, S. Hwang, J. Y. Kim, H. Y. Woo, *Chem. Mater.* **2015**, *27*, 5997.

29 F. Livi, N. K. Zawacka, D. Angmo, M. Jørgensen, F. C. Krebs, E. Bundgaard, *Macromolecules* **2015**, *48*, 3481.

30 E. Perzon, F. Zhang, M. Andersson, W. Mammo, O. Inganäs, M. R. Andersson, *Adv. Mater.* **2007**, *19*, 3308.

31 A. Operamolla, S. Colella, R. Musio, A. Loiudice, O. H. Omar, G. Melcarne, M. Mazzeo, G. Gigli, G. M. Farinola, F. Babudri, *Solar Energy Mater. Solar Cells* **2011**, *95*, 3490.

32 J. E. Carlé, J. W. Andreasen, M. Jørgensen, F. C. Krebs, Solar Energy Mater. Solar Cells 2010, 94, 774.

33 F. Livi, N. S. Gobalasingham, B. C. Thompson, E. Bundgaard, *J. Polym. Sci. Part A: Polym. Chem.* **2016**, *54*, 2907.

34 M. Helgesen, F. C. Krebs, *Macromolecules* 2010, 43, 1253.

35 R. Hou, B. Zhao, F. Wu, G. Wang, T. Shen, H. Guo, J. Zhang, H. Chen, S. Tan, *Org. Electron.* **2015**, *20*, 142.

36 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A.01; Gaussian, Inc.: Wallingford, CT, 2009.

37 R. S. Rowland, R. Taylor, J. Phys. Chem. 1996, 100, 7384.

38 X.-Q. Chen, X. Yao, X. Xiang, L. Liang, W. Shao, F.-G. Zhao, Z. Lu, W. Wang, J. Li, W.-S. Li, *J. Mater. Chem. A* **2016**, *4*, 9286.

39 C. Piliego, T. W. Holcombe, J. D. Douglas, C. H. Woo, P. M. Beaujuge, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2010**, *132*, 7595.