

Molecular Design toward Highly Efficient Photovoltaic Polymers Based on Two-Dimensional Conjugated Benzodithiophene

Long Ye,^{†,‡} Shaoqing Zhang,[†] Lijun Huo,[†] Maojie Zhang,[†] and Jianhui Hou^{*,†}

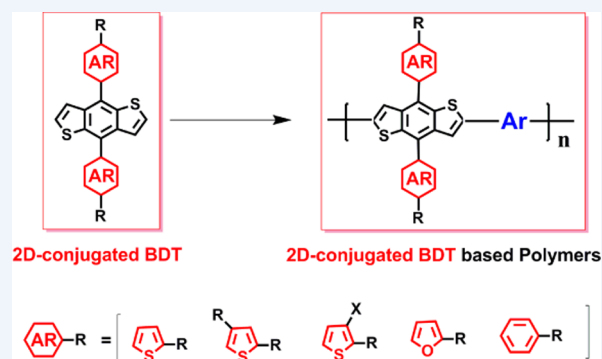
[†]State Key Laboratory of Polymer Physics and Chemistry, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

[‡]University of Chinese Academy of Sciences, Beijing 100049, P. R. China

CONSPECTUS: As researchers continue to develop new organic materials for solar cells, benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT)-based polymers have come to the fore. To improve the photovoltaic properties of BDT-based polymers, researchers have developed and applied various strategies leading to the successful molecular design of highly efficient photovoltaic polymers. Novel polymer materials composed of two-dimensional conjugated BDT (2D-conjugated BDT) have boosted the power conversion efficiency of polymer solar cells (PSCs) to levels that exceed 9%.

In this Account, we summarize recent progress related to the design and synthesis of 2D-conjugated BDT-based polymers and discuss their applications in highly efficient photovoltaic devices. We introduce the basic considerations for the construction of 2D-conjugated BDT-based polymers and systematic molecular design guidelines. For example, simply modifying an alkoxy-substituted BDT to form an alkylthienyl-substituted BDT can improve the polymer hole mobilities substantially with little effect on their molecular energy level. Secondly, the addition of a variety of chemical moieties to the polymer can produce a 2D-conjugated BDT unit with more functions. For example, the introduction of a conjugated side chain with electron deficient groups (such as *para*-alkyl-phenyl, *meta*-alkoxy-phenyl, and 2-alkyl-3-fluoro-thienyl) allowed us to modulate the molecular energy levels of 2D-conjugated BDT-based polymers. Through the rational design of BDT analogues such as dithienobenzodithiophene (DTBDT) or the insertion of larger π bridges, we can tune the backbone conformations of these polymers and modulate their photovoltaic properties. We also discuss the influence of 2D-conjugated BDT on polymer morphology and the blends of these polymers with phenyl-C₆₁ (or C₇₁)-butyric acid methyl ester (PCBM). Finally, we summarize the various applications of the 2D-conjugated BDT-based polymers in highly efficient PSC devices.

Overall, this Account correlates the molecular structures of the 2D-conjugated BDT-based polymers with their photovoltaic properties. As a result, this Account can guide the molecular design of organic photovoltaic materials and the development of organic materials for other types of optoelectronic devices.



1. INTRODUCTION

Polymer solar cells (PSCs) have attracted considerable interests from both the academic and industrial communities over the past decade due to potentials such as low cost, tunable flexibility, and high specific weight.¹ More encouragingly, PSCs with record power conversion efficiencies (PCEs) up to 10.6% were also reported.² As a useful tool, molecular engineering of conjugated polymers has become one of the main driving forces to promote the development of the field of PSCs.^{3–6} To develop new strategies for improving photovoltaic properties of conjugated polymers has been deemed to be of crucial importance to the field. As donor material in the PSCs with the bulk heterojunction (BHJ) structure,^{7,8} a high-performance conjugated polymer should possess at least three intrinsic features: (i) a broad and strong absorption band for ensuring efficient harvest of solar light; (ii) appropriate highest occupied molecular orbital (HOMO) level and lowest unoccupied molecular orbital (LUMO) level for realizing efficient charge

separation with low energy loss; (iii) high hole mobility for facilitating charge transport.⁹ Besides of these requirements, they also should have excellent solubility in organic solvents, and when they are blended with [6,6]-phenyl-C₆₁(or C₇₁)-butyric acid methyl ester (PC₆₁BM or PC₇₁BM), bicontinuous networks with nanoscale phase separation should be formed.^{10–12} Therefore, in order to meet all these specific requirements, structural components in conjugated polymers, including their backbones and side groups, should be designed and modified very carefully. If we look back at the developments of PSCs, molecular design strategies of conjugated polymers played important roles in exploring highly efficient photovoltaic materials and thus in achieving the milestones of PCEs.^{2–6,13–15}

Received: February 20, 2014

Published: April 29, 2014

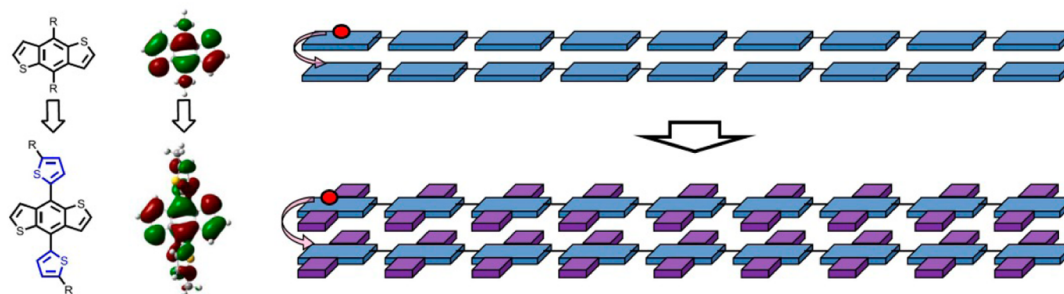


Figure 1. Design considerations of photovoltaic polymers based on 2D-conjugated BDT.

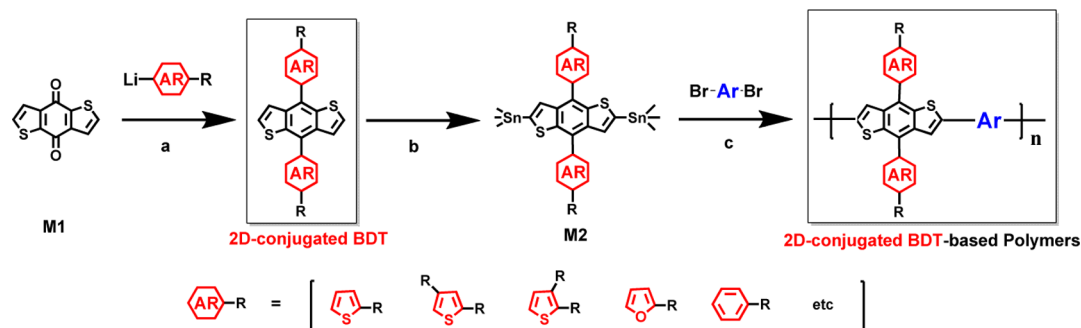


Figure 2. General synthesis routes of 2D-conjugated BDT-based polymers. (a) 0 °C, 10 min and then 50 °C, 30 min; SnCl₂/HCl/H₂O, 50 °C, 1 h. (b) *n*-Butyllithium, -78 °C, 30 min; trimethyltin chloride, ambient temperature, 30 min. (c) Pd(PPh₃)₄, toluene/DMF, 110 °C, 16 h.

Among various types of conjugated polymers, the polymers based on benzo[1,2-*b*:4,5-*b'*]dithiophene units (BDT) exhibit promising photovoltaic properties. Since the first introduction¹⁶ as photovoltaic materials into PSCs, hundreds of new BDT-based polymers have been designed, synthesized, and applied in PSCs within the past 5 years. More interestingly, many important progresses of PCEs achieved in recent years were associated with the BDT-based polymers, and currently the BDT-based polymers have become one of the major families of polymeric photovoltaic materials.^{17–29} According to the reported works, efficient photovoltaic materials can be obtained by copolymerizing BDT units with other types of conjugated building blocks.¹⁷ For example, 8–9% PCEs have been obtained by using the BDT and thieno[3,4-*b*]thiophene (TT) copolymers,^{22–27} the BDT and TPD copolymers,²⁸ the BDT and diketopyrrolopyrrole (DPP) copolymers,^{14,29} and so on. Therefore, how to improve photovoltaic properties of the BDT-based polymers is a very important topic for molecular engineering.

In 2006, Li's group developed the concept of two-dimensional conjugated polythiophenes (2D-PTs).³⁰ After the full scan of tens of 2D-PTs, Li et al. summarized the progresses of the 2D-PTs in a review paper in 2008.³¹ They found that, by using the 2D-structure, not only the absorption spectra but also the hole mobilities of PTs can be enhanced effectively. In 2009, Yang and Hou et al. introduced 2,4-dioctylthienyl substituents onto BDT units and constructed the first polymer³² based on 2D-conjugated BDT units, named as PBDTTBT-T. Although PBDTTBT-T showed one of the outstanding photovoltaic data then, the steric hindrance caused by the alkyls at 4-position of the thiophene units is too strong to get effective conjugation effect of the side groups.

In 2011, we first used 2-alkylthienyl groups to replace the commonly used alkoxy groups at 4- and 8-positions of BDT units and designed two pairs of polymers based on BDT and

TT units.³³ The results clearly indicated that photovoltaic properties of the BDT-based polymers can be significantly improved by adding the conjugated side groups onto the BDT units. Furthermore, we also used these 2-alkylthienyl substituted BDT units to build several polymers.^{33–35,40,42–47}

As is well-known, for the polymer donors with a given absorption band, a deeper HOMO level is helpful to get higher open-circuit voltage (V_{oc}) in BHJ PSCs.⁷ Therefore, we designed and synthesized a series of new BDT-based polymers with varied conjugated side groups, including *para*-alkylphenyl, *meta*-alkoxyphenyl, and 2-alkyl-3-fluoro-thienyl, and these polymers exhibited deeper HOMO levels so that enhanced PCEs can be realized in PSCs due to the significantly improved V_{oc} . In recent years, many novel BDT-based polymers with conjugated side groups have been reported and these polymers have been employed in the studies of device engineering as well as morphology fine-tuning.

In this Account, we will focus our attention mainly on molecular design of BDT-based polymers with conjugated side groups. The influences of the 2D-conjugated structures on the band gaps, the molecular energy levels, the morphologies, and the photovoltaic properties of the BDT-based polymers will be discussed in detail. Moreover, the applications of the 2D-conjugated BDT-based polymers in highly efficient PSCs with various device structures will also be summarized.

2. DESIGN CONSIDERATIONS AND SYNTHESIS APPROACHES OF THE 2D-CONJUGATED BDT-BASED POLYMERS

Transport properties of π -electrons in polymeric semiconductors are of crucial importance to almost all types of polymeric electronic devices, like polymer field-effect transistors (PFETs), polymer light-emitting diodes (PLEDs), and PSCs.⁵ As is known, in order to achieve high mobilities in conjugated polymers, both intermolecular and intramolecular charge

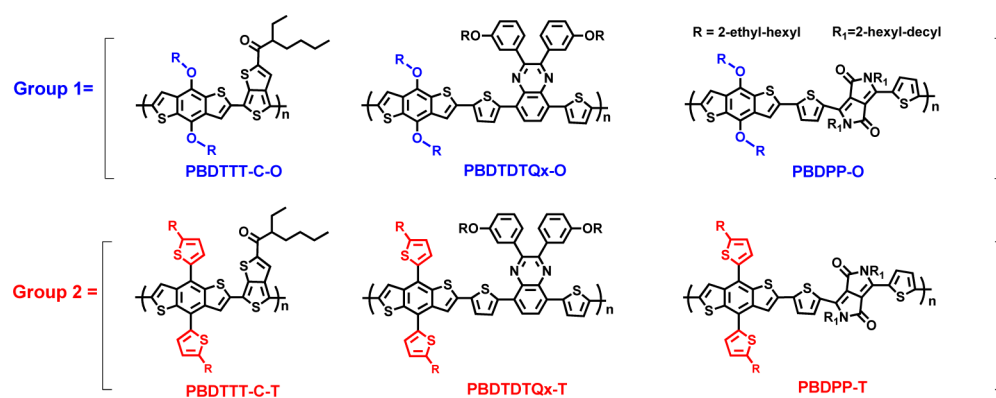


Figure 3. Evolution of molecular structures for three BDT-based polymers from alkoxy substitution to 2-alkylthienyl substitution.

Table 1. Properties and Photovoltaic Results of Three Pairs of BDT-Based Polymers with Alkoxy Substitution and 2-Alkylthienyl Substitution

material	properties of the polymers				photovoltaic data of the corresponding PSCs						ref
	λ_{edge} [nm]	$E_{\text{g}}^{\text{opt}}$ [eV]	HOMO [eV]	T_{d} [°C]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]	μ_{h} [cm ² /(Vs)]		
PBDTTT-C-O	776	1.60	−5.07	320	0.70	15.51	59.2	6.43	5.53×10^{-4}	33	
PBDTTT-C-T	788	1.58	−5.11	428	0.74	17.48	58.7	7.59	0.27	33	
PBDTDTQx-O	714	1.74	−5.12	320	0.71	7.00	61.5	3.06	4×10^{-5}	34	
PBDTDTQx-T	740	1.67	−5.12	430	0.76	10.13	64.3	5.00	1.04×10^{-4}	34	
PBDPP-O	880	1.45	−5.29	330	0.69	6.50	63	2.83	4.48×10^{-2}	35	
PBDPP-T	880	1.45	−5.29	390	0.73	8.42	68	4.23	2.45×10^{-2}	35	

transport properties should be taken into account. Basically, the π -electrons of conjugated polymers can be transported along their conjugated backbones efficiently, because their HOMO surfaces can be well delocalized along their backbones. Considering that the intermolecular charge transport in conjugated polymers occurs by the hopping model through the overlapped π -electron orbits between the adjacent backbones,⁷ to enhance the intermolecular π - π interaction will be the key to improve their mobilities. Therefore, in order to extend the conjugation of the backbones and thus to increase the probability of forming effective interchain π - π overlaps, the 2D-conjugated BDT-based polymers were designed.

As shown in Figure 1, for a BDT unit substituted with nonconjugated side groups, the π -electrons can only delocalize on its conjugated skeleton. However, when 2-alkylthienyl groups are introduced, the π -electrons will delocalize to the conjugated side groups so that the π -conjugation will be enlarged effectively. Therefore, compared to the polymers based on the BDT with nonconjugated side groups, the 2-alkylthienyl-substituted BDT-based polymers will possess larger conjugated area and thus more effective interchain π - π overlap will be ensured, which will be beneficial to facilitate exciton diffusion and charge transport.

As shown in Figure 2, the conjugated side groups, like thienyls and phenyls, can be easily introduced onto BDT by an one-step reaction starting from a commercial available intermediate, benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (M1). The representative synthesis methods of 2-alkylthienyl-substituted BDT units and the corresponding polymers have been reported in our recent works.^{17,33} This method can be used to introduce different types of conjugated side groups onto BDT-based polymers.

3. DESIGN STRATEGIES OF THE 2D-CONJUGATED BDT-BASED POLYMERS

3.1. From Alkoxy-Substituted BDT to 2-Alkylthienyl-Substituted BDT

In Figure 3, six BDT-based polymers are put into two groups. In Group 1, the BDT units in the polymers are substituted by alkoxy groups; in Group 2, the three polymers possess identical backbone structures and alkyl side groups as the analogues in Group 1, but the alkoxy groups linked with their BDT units are replaced by 2-alkylthienyl groups, so that the conjugation area of their backbones can be expanded toward the vertical direction to the backbones. Obviously, the comparisons between the polymers in these two groups will provide information for the effects of the 2D-conjugated structure.^{33–35}

According to the data collected in Table 1, it can be concluded that, after the replacement of the alkoxy groups with the 2-alkylthienyl groups, the absorption bands of the polymers are slightly red-shifted, while their HOMO levels are little changed. The thermal decomposition temperatures (T_{d}) of the polymers in Group 2 are significantly improved. Moreover, the polymers in Group 2 showed higher hole mobilities and improved PCEs in PSCs compared to the polymers in Group 1.

For making clear comparisons, the absorption spectra and the thermogravimetric analysis (TGA) plots of PBDTTT-C-O and PBDTTT-C-T, and the current density–voltage (J - V) and the external quantum efficiency (EQE) curves of the corresponding PSCs are shown in Figure 4. From PBDTTT-C-O to PBDTTT-C-T, the absorption peak red-shifts for 20 nm. PBDTTT-C-O shows a moderate T_{d} of 320 °C, while that of PBDTTT-C-T is located at 428 °C. Compared to the PSC based on PBDTTT-C-O, the PBDTTT-C-T-based device shows a slightly higher V_{oc} of 0.74 V, a higher J_{sc} of 17.48 mA/cm², and a similar FF of 59%, so that an improved PCE of 7.59% can be achieved.³³ For charge transport properties, the

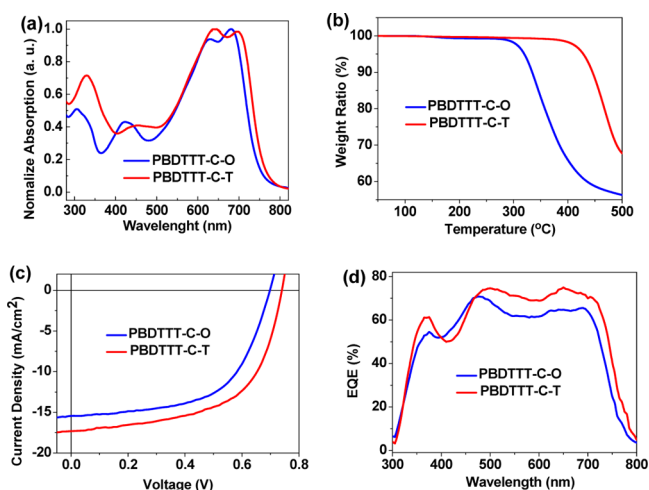


Figure 4. (a) Absorption spectra and (b) TGA plots of PBDTTT-C-O and PBDTTT-C-T. (c) J - V curves and (d) EQE curves of the PSCs based on PBDTTT-C-O:PC₇₁BM and PBDTTT-C-T:PC₇₁BM.

blend of PBDTTT-C-T:PC₇₁BM (1:1.5, w/w) delivered a significantly improved hole mobilities, which is 3 orders of magnitude higher than the blend of PBDTTT-C-O:PC₇₁BM (1:1.5, w/w). Overall, according to the reported works, the polymers based on the 2-alkylthienyl-substituted BDT units exhibit better thermal stabilities, slightly red-shifted absorption spectra, higher hole mobilities and significantly improved photovoltaic properties, in comparison with their corresponding alkoxy-substituted analogues.

3.2. Molecular Energy Level Modulation of the 2D-Conjugated BDT-Based Polymers

Recent progresses in molecular design of the 2D-conjugated BDT-based polymers show that molecular energy levels of this type of polymers can be tuned effectively by changing or modifying the conjugated side groups. From alkoxy substitution to 2-alkylthienyl substitution, little change in their HOMO levels can be observed, meaning that the 2-alkylthienyl groups have similar influence on molecular energy levels of the BDT-based polymers as the alkoxy groups.

Yang et al. synthesized two BDT and DPP copolymers¹⁴ in which thienyls and phenyls were respectively used as the conjugated side groups. In order to make clear comparisons,

the analogous polymers based on alkoxy-substituted BDT³⁶ are also shown in Figure 5, and their photovoltaic properties are collected in Table 2. For the polymers based on BDT and DPP, when the substituents on BDT were changed from alkoxy to 2-alkylthienyl and then to *para*-alkylphenyl, their HOMO levels were reduced gradually, from -5.16 to -5.30 eV and then to -5.35 eV; V_{oc} 's of the corresponding PSCs are increased from 0.68 to 0.73 V and then to 0.76 V. Our group also introduced *para*-alkylphenyl groups onto a BDT-based polymer and designed a polymer named as PBDTDTBT-P,³⁷ and the HOMO level of this polymer is 0.11 eV lower than the analogue polymer based on alkoxy-substituted BDT, named as PBDTDTBT-O.³⁸ Correspondingly, the PSC based on PBDTDTBT-P reached 0.88 V, which is ~ 0.1 V higher than that of the PSC based on PBDTDTBT-O, and after detailed device optimization, an outstanding PCE of 8.07% can be obtained.

Molecular energy level of the 2D-conjugated BDT-based polymers can also be affected by changing the substitution positions of the alkyls. For example, the polymer PBDTTBT-T having two octyls at 2- and 4-positions on each of the thiophene side groups has a deep HOMO level at -5.31 eV, and the corresponding PSC showed a V_{oc} of 0.92 V.³² Recently, Huang et al. did a systematic study on the influence of alkyl substitution position on molecular energy levels of the 2D-conjugated BDT-based polymers and realized a PCE of 7.1% with a high V_{oc} of 0.9 V.³⁹ In their work, three polymers with identical backbone structures were synthesized and the results showed that when the alkyls were introduced in different positions, varied HOMO levels and thus different V_{oc} values can be obtained.

Alternatively, the molecular energy levels can be tuned by introducing functional groups onto their conjugated side groups. In a previous work, our group revealed that when *meta*-alkoxy-phenyl was used as side groups instead of *para*-alkoxy-phenyl in a conjugated polymer, deeper HOMO level and thus improved V_{oc} can be realized, which is ascribed to the inductive electron-withdrawing effect of the alkoxy groups at *meta*-positions.⁴¹ Therefore, as shown in Figure 6, we applied this design method in the BDT-based polymers.⁴⁰ As listed in Table 2, compared with the 2-alkylthienyl-substituted polymer (PBT-T), the HOMO level of the *meta*-alkoxy-phenyl-substituted polymer (PBT-OP) is much lower and thus the corresponding

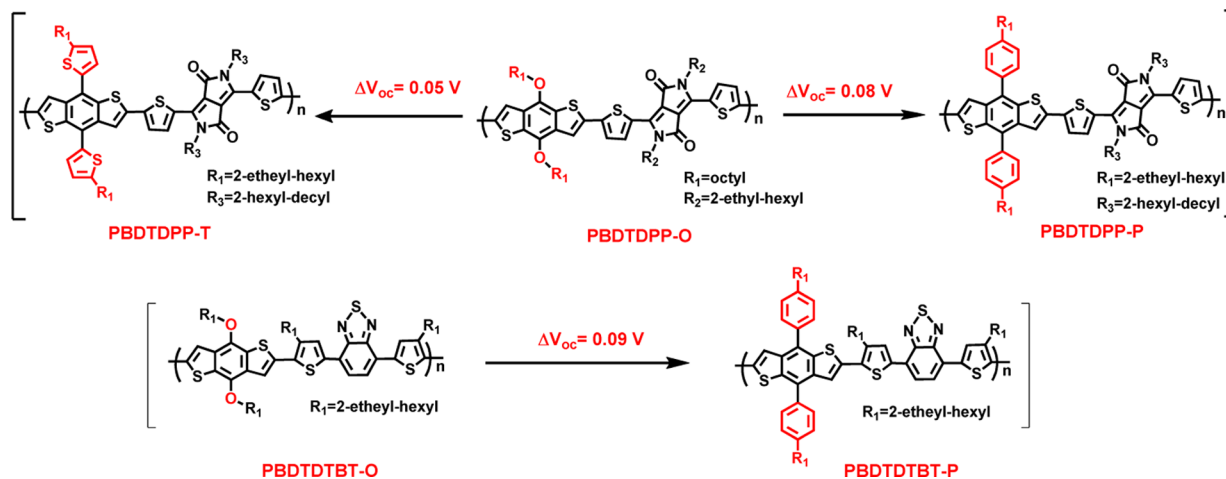
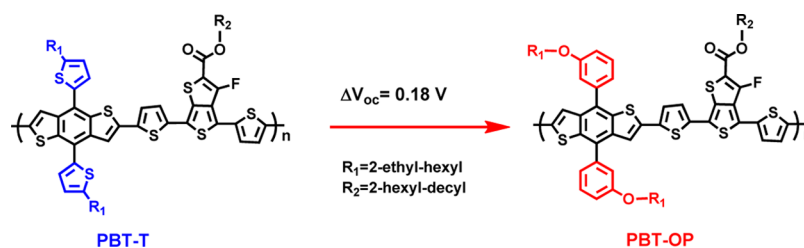
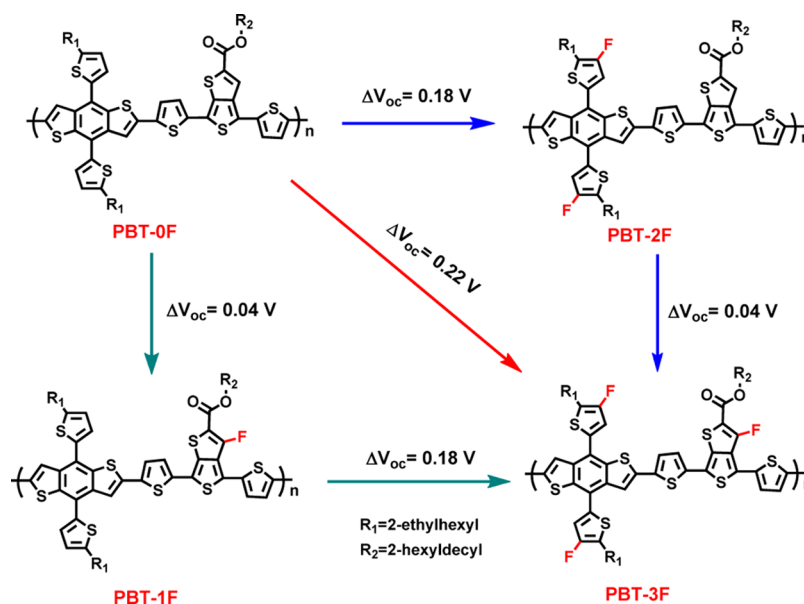


Figure 5. Evolution of molecular structures for BDT-based polymers with different conjugated side groups.

Table 2. Band Gaps and HOMO Levels of the BDT-Based Polymers with Different Conjugated Side Groups and the Corresponding Photovoltaic Results

material	E_g^{opt} [eV]	HOMO level [eV]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]	ref
PBDTDPP-O	1.31	-5.16	0.68	8.4	44.3	2.53	36
PBDTDPP-T	1.44	-5.30	0.73	14.0	65	6.6	14
PBDTDPP-P	1.46	-5.35	0.76	13.6	60	6.2	14
PBDTDTBT-O	1.72	-5.24	0.79	13.56	69.1	7.40	38
PBDTDTBT-P	1.70	-5.35	0.88	12.94	70.9	8.07	37
PBT-T	1.67	-4.95	0.60	13.7	67.7	5.6	40
PBT-OP	1.70	-5.17	0.78	13.4	71.8	7.5	40
PBT-OF	1.61	-4.90	0.56	12.2	66.7	4.5	22
PBT-2F	1.64	-5.15	0.74	14.4	67.7	7.2	22
PBT-1F	1.65	-4.95	0.60	14.3	65.7	5.6	22
PBT-3F	1.64	-5.20	0.78	15.2	72.4	8.6	22

**Figure 6.** Evolution of molecular structures from PBT-T to PBT-OP.**Figure 7.** Evolution of molecular structures from PBT-OF to PBT-3F.

PSC exhibited a V_{oc} of 0.78 V, which is 0.18 V higher than that of the PBT-T-based PSC.

By introducing fluorine atoms onto the polymers with donor–acceptor structures (D-A polymer), fine-tuning of molecular energy levels can be realized.^{19,20} As shown in Figure 7, four BDT-based polymers with 2D-conjugation were synthesized to investigate the synergistic effect of the fluorine atoms at different substitution positions.²² As listed in Table 2, the V_{oc} of the PSC based on the trifluorinated polymer, PBT-3F, is 0.22 V higher than that of the PSC based on the nonfluorinated analogue polymer, PBT-OF. Accordingly, the PSC based on PBT-3F showed an enhanced PCE of 8.6%. Therefore, according to the discussion in this section, it can be

concluded that molecular energy levels of the 2D-conjugated BDT-based polymers can be effectively tuned.

3.3. Backbone Conformation Modulation of the 2D-Conjugated BDT-Based Polymers

As known, to get bicontinuous nanoscale phase separation in the blends of polymer and PC₇₁BM is one of the key issues to realize efficient PCE. Sometimes, the formation of large size aggregations of polymer or/and PC₇₁BM in the blends is one of the main obstacles to realizing high photovoltaic performance. For example, as shown in Figure 8, the PBDPP-O:PC₇₁BM blend showed very large aggregations (>100 nm), so that the excitons generated in the polymer and PC₇₁BM domains cannot diffuse to the D/A interface efficiently due to the limited

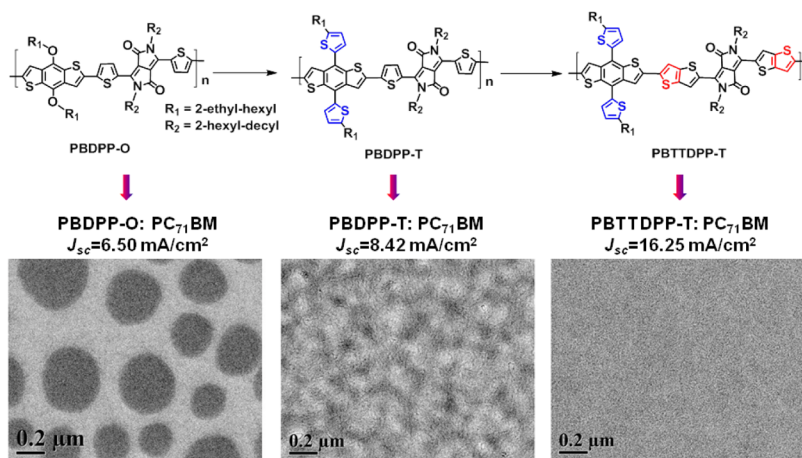


Figure 8. Molecular structures of three polymers based on BDT and DPP units, and TEM images of the corresponding polymer:PC₇₁BM blends.

exciton diffusion length^{8,9} and also the D/A interface in the blend is not big enough to perform efficient charge separation. In our recent work,³⁵ when the alkoxy groups on the BDT units were replaced by 2-alkylthienyls, the polymer PBDPP-T showed better compatibility with PC₇₁BM in solid film; that is, the size of the aggregations in the PBDPP-T:PC₇₁BM blend reduced significantly. As a result, J_{sc} of the corresponding PSC increased from 6.50 to 8.42 mA/cm². Furthermore, when the thiophene units between the BDT and the DPP units in PBDPP-T were replaced by thieno[3,2-*b*]thiophene units, the aggregation size in the blend can be further reduced. Therefore, the EQE of the PSC based on PBTTDPP-T reached over 55%, and hence, J_{sc} of the device reached 16.25 mA/cm².

Although the replacement of the alkoxy groups with the 2-alkylthienyls has positive influence on improving compatibility between PCBM and the polymer based on DPP and BDT,³⁵ this method has little effect on tuning crystallinities of the BDT-based polymers. Recently, our group carried out a series of studies on modulating crystallinities of the 2D-conjugated BDT-based polymers through changing the curvatures of their backbones.^{42–45} As shown in Figure 9, a few pairs of polymers based on the 2D-conjugated BDT units with zigzagged and straight backbone conformations were designed. The study on one pair of polymers, PBDDTBT-T and PBDDTTBT-T, reveals the correlations among the curvatures of the backbones, the morphological and the photovoltaic properties of the polymers.⁴² The polymer PBDDTBT-T has a typical zigzagged backbone in which the included angle is ca. 56°, while the polymer PBDDTTBT-T has a straight backbone. In X-ray diffraction (XRD) measurements, no clear diffraction peak can be observed in the PBDDTBT-T film, while the PBDDTTBT-T film shows two diffraction peaks at $2\theta = 4.78^\circ$ (100) and 24.62° (010), corresponding to the lamellar packing with a *d*-spacing of 18.4 Å and the π - π stacking distance of 3.61 Å, respectively. Benefiting from the stronger intermolecular π - π stacking and improved absorption at long wavelength direction, the PBDDTTBT-T-based PSC exhibited a higher PCE of 6.3% and an enhanced hole mobility of 5.63×10^{-3} cm²/(Vs) than the PBDDTBT-T-based device. As collected in Table 3, the similar trend can also be confirmed in another pair of polymers,⁴³ PBDDTBT-T and PBDDTBT-T.

More straight backbone conformation can also be realized by other methods. For example, the polymer PBDDTTT-S-T⁴⁵ has a zigzagged backbone with an included angle of 36°, and in

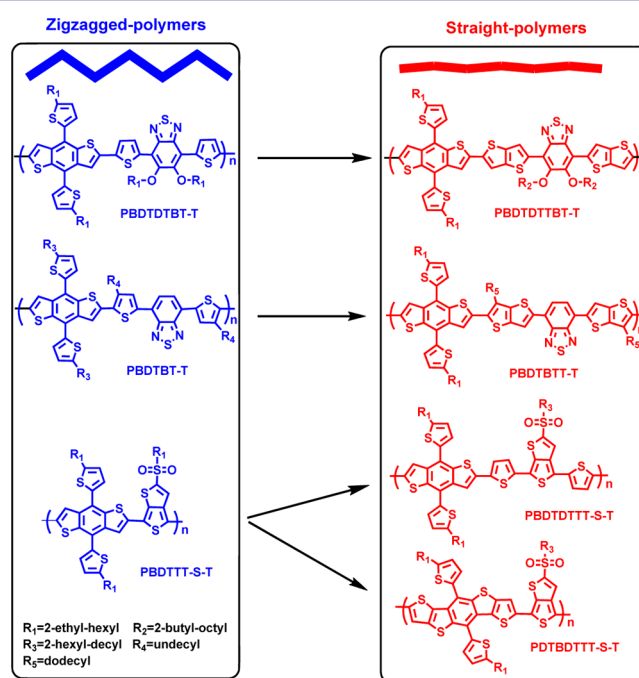
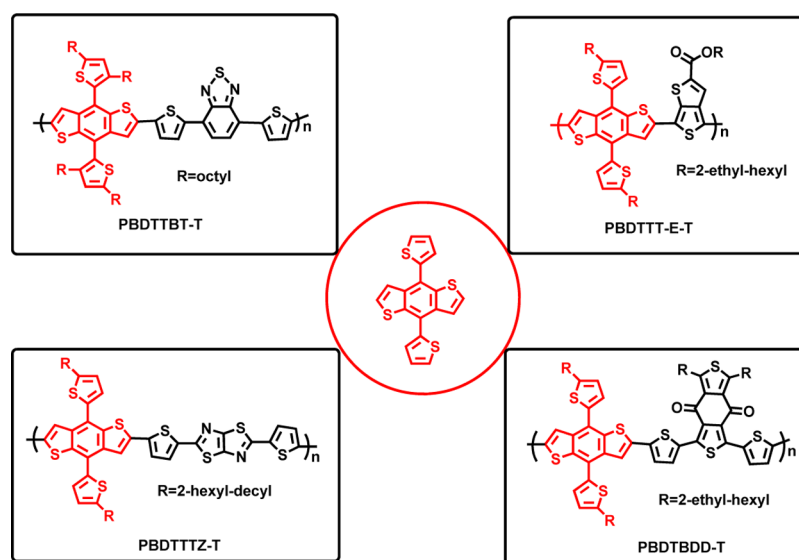


Figure 9. Two groups of 2D-conjugated BDT-based polymers with different chain conformations in their backbones.

grazing incidence X-ray diffraction (GIXRD) analysis, it shows very weak reflection at 1.62 \AA^{-1} , corresponding to the π - π stacking with *d*-spacing of 3.88 Å. When thiophene units were inserted in between the BDT and TT units of its backbone, more straight backbone can be obtained, and as a result, the target polymer PBDDTTT-S-T showed enhanced (010) π - π stacking diffraction peaks at 1.79 \AA^{-1} , corresponding to a *d*-spacing of 3.51 Å.⁴⁴ Moreover, linear backbone structure can also be formed by the replacement of the BDT with dithienobenzodithiophene (DTBDT).⁴⁵ It should be noted that both two polymers with straight backbones, PBDDTTT-S-T and PDBDTTTT-S-T, have similar π - π stacking distance of 3.5–3.6 Å. These values are much smaller than those of the zigzagged analogue polymers and also among the smallest values for conjugated polymers. From the point of view of photovoltaic performance, the PBDDTTT-S-T based PSC showed a PCE of 5.93%, while the PCE of the PSC based on PBDDTTT-S-T and PDBDTTTT-S-T reached 7.81% and

Table 3. Molecular and Photovoltaic Properties of Two Groups of 2D-Conjugated BDT-Based Polymers with Different Chain Conformations in Their Backbones

material	E_g^{opt} [eV]	HOMO [eV]	distance [Å]		V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]	μ_{h} [cm ² /(V s)]	ref
			lamellar	π - π						
PBDPP-O	1.45	-5.29	17.2	3.67	0.69	6.50	63	2.83	4.48×10^{-2}	35
PBDPP-T	1.45	-5.29			0.73	8.42	68	4.23	2.35×10^{-2}	35
PBTDDPP-T	1.43	-5.05	20.0	3.60	0.63	16.25	60	6.18	1.16×10^{-1}	35
PBDTTT-S-T	1.61	-5.29		3.88	0.78	12.27	61.98	5.93		45
PBDTDTT-S-T	1.59	-5.04	24.2	3.51	0.69	17.07	66.3	7.81	2.76×10^{-3}	44
PDTBDTT-S-T	1.59	-5.21	19.6	3.67	0.73	16.63	64.13	7.79		45
PBDTDTBT-T	1.79	-5.27			0.96	9.10	51.8	4.9	1.95×10^{-3}	42
PBDTDTBT-T	1.73	-5.09	18.4	3.61	0.80	11.83	66.6	6.3	5.63×10^{-3}	42
PBDTBT-T	1.63	-5.14	24.1		0.82	5.78	49.5	2.34	1.58×10^{-5}	43
PBDTBT-T	1.65	-5.11	22.9		0.78	12.46	62.0	6.03	1.97×10^{-3}	43

**Figure 10.** High performance photovoltaic polymers based on 2D-conjugated BDT units.

7.79%, respectively. Overall, the results discussed above indicate that morphological properties of the 2D-conjugated BDT-based polymers can be tuned by different methods.

4. APPLICATIONS OF 2D-CONJUGATED BDT IN EFFICIENT PHOTOVOLTAIC POLYMERS AND DEVICES

2D-conjugated BDT units have been broadly used in constructing highly efficient polymer photovoltaic materials in our group. Besides the above-mentioned polymers, other high performance polymers based on 2D-conjugated BDT units will be briefly introduced in this section (see Figure 10) and their corresponding photovoltaic results are collected in Table 4. In 2011, our group synthesized a broad band gap polymer

Table 4. Photovoltaic Results of Efficient PSCs Employing 2D-Conjugated BDT Based-Polymers

material	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]	μ_{h} [cm ² /(Vs)]	ref
PBDTTBT-T	0.92	10.70	57.5	5.66		32
PBDTTT-E-T	0.68	14.59	62.6	6.21	6.74×10^{-3}	33
PBDTTT-T	0.85	10.4	59.0	5.22	1.67×10^{-5}	46
PBDTBDD-T	0.86	10.68	72.27	6.67		47

PBDTTT-T based on alkylthienyl-substituted BDT and thiazolo[5,4-*d*]thiazole (TTZ) ($E_g^{\text{opt}} = 2.0$ eV) and achieved a desirable PCE of 5.21%.⁴⁶ Considering that the absorption of the PBDTTT-T is mainly at the range from 350 to 620 nm, PBDTTT-T should be a potential candidate material for semitransparent PSCs and PSCs with tandem structures. Recently, our group reported a wide band gap polymer named as PBDTBDD-T,⁴⁷ which exhibited stronger aggregation in solution state, and a high FF up to 72% was observed by manipulating the processing temperature. A PCE over 6.6% was obtained from the PBDTBDD-T/PC₆₁BM based PSC, which was also a remarkable result for the PSCs employing PC₆₁BM as electron acceptor.

The superior properties of 2D-conjugated BDT-based polymers make them promising candidates for highly efficient PSC devices with varied architectures. For instance, by replacing the PEDOT:PSS buffer layer with solution processed rhenium oxide, a high PCE of 8.30% was realized in the PBDTTT-C-T-based PSCs with conventional device structure.²⁷ Choy et al. incorporated the dual plasmonic metallic nanostructures into the PBDTTT-C-T-based PSCs with inverted structure, which led to significant improvement in J_{sc} and thus an enhanced PCE of 8.79%.²⁴ Tandem PSCs based on 2D-conjugated BDT-based polymers also exhibited great potentials with PCE up to 9.5%.²⁹ Recently, we and our

collaborators fabricated a series of efficient PSCs employing the 2D-conjugated BDT-based polymers as donor materials and various nonfullerene molecules as acceptor materials, which produced several impressive results.^{48,49} In addition, it should be mentioned that the 2D-conjugated BDT units have also been successfully employed as the promising building blocks in small molecule donors, which were well reviewed by Chen et al.⁵⁰

5. SUMMARY AND PERSPECTIVES

Photovoltaic properties such as energy levels, absorption spectra, crystallinities, and morphologies of BDT-based polymers can be effectively optimized by manipulating the 2D-conjugated structures of BDT. The feasible synthesis route and tunable properties of 2D-conjugated BDT-based polymers make them promising materials for applications in PSCs. The molecular structure evolutions from BDT to 2D-conjugated BDT can be seen as excellent references for the design of organic electronic materials. The excellent results indicate that 2D-conjugated BDT is a very useful building block for the design of high performance photovoltaic polymers.

AUTHOR INFORMATION

Corresponding Author

*E-mail: hjhzl@iccas.ac.cn.

Notes

The authors declare no competing financial interest.

Biographies

Long Ye is a Ph.D. candidate in polymer physics and chemistry at Institute of Chemistry, Chinese Academy of Sciences (ICCAS) under the supervision of Prof. Jianhui Hou since 2010. His current research focuses on the molecular design of conjugated polymers and device engineering of organic photovoltaic devices.

Shaoqing Zhang is a doctoral student at ICCAS under the supervision of Prof. Jianhui Hou since 2012. Her current research interests are the molecular design and synthesis of highly efficient photovoltaic polymers.

Lijun Huo is an Associate Professor in Prof. Jianhui Hou's group at ICCAS. His current research interest is the molecular design of novel photovoltaic polymers.

Maojie Zhang is an Associate Professor in Prof. Jianhui Hou's group at ICCAS. His current research focuses on the molecular design of highly efficient photovoltaic polymers.

Jianhui Hou received his Ph.D. degree in chemistry from ICCAS in 2006 (Advisor: Prof. Yongfang Li). Then he joined Prof. Yang Yang's Group at UCLA as a postdoctoral researcher. In 2008, he joined Solarmer Energy Inc. (USA), where he was appointed as Director of Research. Since 2010, he became a Professor at ICCAS, where he led a group of polymer solar cell materials and devices. His research interests include design, synthesis, and application of organic/polymer optoelectronic materials, particularly for photovoltaic applications.

ACKNOWLEDGMENTS

This work has been financed by National High Technology Research and Development Program 863 (2011AA050523), National Basic Research Program 973 (2014CB643500), International S&T Cooperation Program of China (2011DFG63460), Ministry of Science and Technology of China, NSFC (Nos. 51173189, 21325419, 91333204), Chinese

Academy of Sciences (KJZD-EW-J01). J.H. would like to thank the collaborators including Prof. Yongfang Li, Prof. Thomas P. Russell, Prof. Harald Ade, Prof. Wallace Choy, Prof. Zhan'ao Tan, Prof. Chuanlang Zhan, Prof. Zhaohui Wang, and the graduate students for their contributions.

REFERENCES

- (1) Li, G.; Zhu, R.; Yang, Y. Polymer solar cells. *Nat. Photonics* **2012**, *6*, 153–161.
- (2) You, J.; Dou, L.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, C.-C.; Gao, J.; Li, G.; Yang, Y. A polymer tandem solar cell with 10.6% power conversion efficiency. *Nat. Commun.* **2013**, *4*, 1446.
- (3) Li, Y. F. Molecular Design of Photovoltaic Materials for Polymer Solar Cells: Toward Suitable Electronic Energy Levels and Broad Absorption. *Acc. Chem. Res.* **2012**, *45*, 723–733.
- (4) Henson, Z. B.; Mullen, K.; Bazan, G. C. Design strategies for organic semiconductors beyond the molecular formula. *Nat. Chem.* **2012**, *4*, 699–704.
- (5) Guo, X.; Baumgarten, M.; Mullen, K. Designing pi-conjugated polymers for organic electronics. *Prog. Polym. Sci.* **2013**, *38*, 1832–1908.
- (6) Duan, C.; Huang, F.; Cao, Y. Recent development of push-pull conjugated polymers for bulk-heterojunction photovoltaics: rational design and fine tailoring of molecular structures. *J. Mater. Chem.* **2012**, *22*, 10416–10434.
- (7) Scharber, M. C.; Wühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. L. Design rules for donors in bulk-heterojunction solar cells - Towards 10% energy-conversion efficiency. *Adv. Mater.* **2006**, *18*, 789–794.
- (8) Heeger, A. J. 25th Anniversary Article: Bulk Heterojunction Solar Cells: Understanding the Mechanism of Operation. *Adv. Mater.* **2014**, *26*, 10–28.
- (9) Clarke, T. M.; Durrant, J. R. Charge Photogeneration in Organic Solar Cells. *Chem. Rev.* **2010**, *110* (11), 6736–6767.
- (10) Liu, F.; Gu, Y.; Shen, X.; Ferdous, S.; Wang, H.-W.; Russell, T. P. Characterization of the morphology of solution-processed bulk heterojunction organic photovoltaics. *Prog. Polym. Sci.* **2013**, *38*, 1990–2052.
- (11) Ye, L.; Zhang, S.; Ma, W.; Fan, B.; Guo, X.; Huang, Y.; Ade, H.; Hou, J. From Binary to Ternary Solvent: Morphology Fine-tuning of D/A Blends in PDPP3T-based Polymer Solar Cells. *Adv. Mater.* **2012**, *24*, 6335–6341.
- (12) Ye, L.; Jing, Y.; Guo, X.; Sun, H.; Zhang, S.; Zhang, M.; Huo, L.; Hou, J. Remove the Residual Additives toward Enhanced Efficiency with Higher Reproducibility in Polymer Solar Cells. *J. Phys. Chem. C* **2013**, *117*, 14920–14928.
- (13) Huang, F.; Chen, K.-S.; Yip, H.-L.; Hau, S. K.; Acton, O.; Zhang, Y.; Luo, J.; Jen, A. K. Y. Development of New Conjugated Polymers with Donor- π -Bridge-Acceptor Side Chains for High Performance Solar Cells. *J. Am. Chem. Soc.* **2009**, *131*, 13886–13887.
- (14) Dou, L. T.; Gao, J.; Richard, E.; You, J. B.; Chen, C. C.; Cha, K. C.; He, Y. J.; Li, G.; Yang, Y. Systematic Investigation of Benzodithiophene- and Diketopyrrolopyrrole-Based Low-Bandgap Polymers Designed for Single Junction and Tandem Polymer Solar Cells. *J. Am. Chem. Soc.* **2012**, *134*, 10071–10079.
- (15) He, Z. C.; Zhong, C. M.; Su, S. J.; Xu, M.; Wu, H. B.; Cao, Y. Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure. *Nat. Photonics* **2012**, *6*, 591–595.
- (16) Hou, J. H.; Park, M. H.; Zhang, S. Q.; Yao, Y.; Chen, L. M.; Li, J. H.; Yang, Y. Bandgap and molecular energy level control of conjugated polymer photovoltaic materials based on benzo[1,2-b:4,5-b']-dithiophene. *Macromolecules* **2008**, *41*, 6012–6018.
- (17) Huo, L. J.; Hou, J. H. Benzo[1,2-b:4,5-b']dithiophene-based conjugated polymers: band gap and energy level control and their application in polymer solar cells. *Polym. Chem.* **2011**, *2*, 2453–2461.
- (18) Wang, M.; Hu, X. W.; Liu, P.; Li, W.; Gong, X.; Huang, F.; Cao, Y. Donor Acceptor Conjugated Polymer Based on Naphtho[1,2-c:5,6-

c]bis[1,2,5]thiadiazole for High-Performance Polymer Solar Cells. *J. Am. Chem. Soc.* **2011**, *133*, 9638–9641.

(19) Price, S. C.; Stuart, A. C.; Yang, L.; Zhou, H.; You, W. Fluorine Substituted Conjugated Polymer of Medium Band Gap Yields 7% Efficiency in Polymer–Fullerene Solar Cells. *J. Am. Chem. Soc.* **2011**, *133*, 4625–4631.

(20) Li, K.; Li, Z.; Feng, K.; Xu, X.; Wang, L.; Peng, Q. Development of Large Band-Gap Conjugated Copolymers for Efficient Regular Single and Tandem Organic Solar Cells. *J. Am. Chem. Soc.* **2013**, *135*, 13549–13557.

(21) Yang, T. B.; Wang, M.; Duan, C. H.; Hu, X. W.; Huang, L.; Peng, J. B.; Huang, F.; Gong, X. Inverted polymer solar cells with 8.4% efficiency by conjugated polyelectrolyte. *Energy Environ. Sci.* **2012**, *5*, 8208–8214.

(22) Zhang, M.; Guo, X.; Zhang, S.; Hou, J. Synergistic Effect of Fluorination on Molecular Energy Level Modulation in Highly Efficient Photovoltaic Polymers. *Adv. Mater.* **2014**, *26*, 1118–1123.

(23) Cui, C.; Wong, W.-Y.; Li, Y. Improvement of Open-Circuit Voltage and Photovoltaic Properties of 2D-Conjugated Polymers by Alkylthio Substitution. *Energy Environ. Sci.* **2014**, DOI: 10.1039/C4EE00446A.

(24) Li, X. H.; Choy, W. C. H.; Huo, L. J.; Xie, F. X.; Sha, W. E. I.; Ding, B. F.; Guo, X.; Li, Y. F.; Hou, J. H.; You, J. B.; Yang, Y. Dual Plasmonic Nanostructures for High Performance Inverted Organic Solar Cells. *Adv. Mater.* **2012**, *24*, 3046–3052.

(25) Liu, S.; Zhang, K.; Lu, J.; Zhang, J.; Yip, H.-L.; Huang, F.; Cao, Y. High-Efficiency Polymer Solar Cells via the Incorporation of an Amino-Functionalized Conjugated Metallopolymer as a Cathode Interlayer. *J. Am. Chem. Soc.* **2013**, *135*, 15326–15329.

(26) Liao, S.-H.; Jhuo, H.-J.; Cheng, Y.-S.; Chen, S.-A. Fullerene Derivative-Doped Zinc Oxide Nanofilm as the Cathode of Inverted Polymer Solar Cells with Low-Bandgap Polymer (PTB7-Th) for High Performance. *Adv. Mater.* **2013**, *25*, 4766–4771.

(27) Tan, Z. a.; Li, L.; Wang, F.; Xu, Q.; Li, S.; Sun, G.; Tu, X.; Hou, X.; Hou, J.; Li, Y. Solution-Processed Rhenium Oxide: A Versatile Anode Buffer Layer for High Performance Polymer Solar Cells with Enhanced Light Harvest. *Adv. Energy Mater.* **2014**, DOI: 10.1002/aenm.201300884.

(28) Cabanetos, C.; El Labban, A.; Bartelt, J. A.; Douglas, J. D.; Mateker, W. R.; Frechet, J. M. J.; McGehee, M. D.; Beaujuge, P. M. Linear Side Chains in Benzo[1,2-*b*:4,5-*b'*]dithiophene-Thieno[3,4-*c*]pyrrole-4,6-dione Polymers Direct Self-Assembly and Solar Cell Performance. *J. Am. Chem. Soc.* **2013**, *135*, 4656–4659.

(29) Dou, L. T.; Chang, W. H.; Gao, J.; Chen, C. C.; You, J. B.; Yang, Y. A Selenium-Substituted Low-Bandgap Polymer with Versatile Photovoltaic Applications. *Adv. Mater.* **2013**, *25*, 825–831.

(30) Hou, J. H.; Tan, Z. A.; Yan, Y.; He, Y. J.; Yang, C. H.; Li, Y. F. Synthesis and photovoltaic properties of two-dimensional conjugated polythiophenes with bi(thienylenevinylene) side chains. *J. Am. Chem. Soc.* **2006**, *128*, 4911–4916.

(31) Li, Y. F.; Zou, Y. P. Conjugated polymer photovoltaic materials with broad absorption band and high charge carrier mobility. *Adv. Mater.* **2008**, *20*, 2952–2958.

(32) Huo, L. J.; Hou, J. H.; Zhang, S. Q.; Chen, H. Y.; Yang, Y. A Polybenzo[1,2-*b*:4,5-*b'*]dithiophene Derivative with Deep HOMO Level and Its Application in High-Performance Polymer Solar Cells. *Angew. Chem., Int. Ed.* **2010**, *49*, 1500–1503.

(33) Huo, L. J.; Zhang, S. Q.; Guo, X.; Xu, F.; Li, Y. F.; Hou, J. H. Replacing Alkoxy Groups with Alkylthienyl Groups: A Feasible Approach To Improve the Properties of Photovoltaic Polymers. *Angew. Chem., Int. Ed.* **2011**, *50*, 9697–9702.

(34) Duan, R. M.; Ye, L.; Guo, X.; Huang, Y.; Wang, P.; Zhang, S. Q.; Zhang, J. P.; Huo, L. J.; Hou, J. H. Application of Two-Dimensional Conjugated Benzo[1,2-*b*:4,5-*b'*]dithiophene in Quinoxaline-Based Photovoltaic Polymers. *Macromolecules* **2012**, *45*, 3032–3038.

(35) Zhang, S.; Ye, L.; Wang, Q.; Li, Z.; Guo, X.; Huo, L.; Fan, H.; Hou, J. Enhanced Photovoltaic Performance of Diketopyrrolopyrrole (DPP)-Based Polymers with Extended π Conjugation. *J. Phys. Chem. C* **2013**, *117*, 9550–9557.

(36) Huo, L. J.; Hou, J. H.; Chen, H. Y.; Zhang, S. Q.; Jiang, Y.; Chen, T. L.; Yang, Y. Bandgap and Molecular Level Control of the Low-Bandgap Polymers Based on 3,6-Dithiophen-2-yl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione toward Highly Efficient Polymer Solar Cells. *Macromolecules* **2009**, *42*, 6564–6571.

(37) Zhang, M.; Gu, Y.; Guo, X.; Liu, F.; Zhang, S.; Huo, L.; Russell, T. P.; Hou, J. Efficient Polymer Solar Cells Based on Benzothiadiazole and Alkylphenyl Substituted Benzodithiophene with a Power Conversion Efficiency over 8%. *Adv. Mater.* **2013**, *25*, 4944–4949.

(38) Huang, Y.; Liu, F.; Guo, X.; Zhang, W.; Gu, Y.; Zhang, J.; Han, C. C.; Russell, T. P.; Hou, J. Manipulating Backbone Structure to Enhance Low Band Gap Polymer Photovoltaic Performance. *Adv. Energy Mater.* **2013**, *3*, 930–937.

(39) Dong, Y.; Hu, X.; Duan, C.; Liu, P.; Liu, S.; Lan, L.; Chen, D.; Ying, L.; Su, S.; Gong, X.; Huang, F.; Cao, Y. A Series of New Medium-Bandgap Conjugated Polymers Based on Naphtho[1,2-*c*:5,6-*c'*]bis(2-octyl-[1,2,3]triazole) for High-Performance Polymer Solar Cells. *Adv. Mater.* **2013**, *25*, 3683–3688.

(40) Zhang, M.; Guo, X.; Ma, W.; Zhang, S.; Huo, L.; Ade, H.; Hou, J. An Easy and Effective Method to Modulate Molecular Energy Level of the Polymer Based on Benzodithiophene for the Application in Polymer Solar Cells. *Adv. Mater.* **2014**, *26*, 2089–2095.

(41) Huang, Y.; Zhang, M.; Ye, L.; Guo, X.; Han, C. C.; Li, Y.; Hou, J. Molecular energy level modulation by changing the position of electron-donating side groups. *J. Mater. Chem.* **2012**, *22*, 5700–5705.

(42) Zuo, G.; Li, Z.; Zhang, M.; Guo, X.; Wu, Y.; Zhang, S.; Peng, B.; Wei, W.; Hou, J. Influence of the backbone conformation of conjugated polymers on morphology and photovoltaic properties. *Polym. Chem.* **2014**, *5*, 1976–1981.

(43) Guo, X.; Zhang, M.; Huo, L.; Xu, F.; Wu, Y.; Hou, J. Design, synthesis and photovoltaic properties of a new D- π -A polymer with extended π -bridge units. *J. Mater. Chem.* **2012**, *22*, 21024–21031.

(44) Huang, Y.; Guo, X.; Liu, F.; Huo, L. J.; Chen, Y. N.; Russell, T. P.; Han, C. C.; Li, Y. F.; Hou, J. H. Improving the Ordering and Photovoltaic Properties by Extending π -Conjugated Area of Electron-Donating Units in Polymers with D-A Structure. *Adv. Mater.* **2012**, *24*, 3383–3389.

(45) Wu, Y.; Li, Z.; Ma, W.; Huang, Y.; Huo, L.; Guo, X.; Zhang, M.; Ade, H.; Hou, J. PDT-S-T: A New Polymer with Optimized Molecular Conformation for Controlled Aggregation and π - π Stacking and Its Application in Efficient Photovoltaic Devices. *Adv. Mater.* **2013**, *25*, 3449–3455.

(46) Huo, L. J.; Guo, X.; Zhang, S. Q.; Li, Y. F.; Hou, J. H. PBDTTTz: A Broad Band Gap Conjugated Polymer with High Photovoltaic Performance in Polymer Solar Cells. *Macromolecules* **2011**, *44*, 4035–4037.

(47) Qian, D. P.; Ye, L.; Zhang, M. J.; Liang, Y. R.; Li, L. J.; Huang, Y.; Guo, X.; Zhang, S. Q.; Tan, Z. A.; Hou, J. H. Design, Application, and Morphology Study of a New Photovoltaic Polymer with Strong Aggregation in Solution State. *Macromolecules* **2012**, *45*, 9611–9617.

(48) Zhang, X.; Lu, Z.; Ye, L.; Zhan, C.; Hou, J.; Zhang, S.; Jiang, B.; Zhao, Y.; Huang, J.; Zhang, S.; Liu, Y.; Shi, Q.; Liu, Y.; Yao, J. A Potential Perylene Diimide Dimer-Based Acceptor Material for Highly Efficient Solution-Processed Non-Fullerene Organic Solar Cells with 4.03% Efficiency. *Adv. Mater.* **2013**, *25*, 5791–5797.

(49) Jiang, W.; Ye, L.; Li, X.; Xiao, C.; Tan, F.; Zhao, W.; Hou, J.; Wang, Z. Bay-linked perylene bisimides as promising non-fullerene acceptors for organic solar cells. *Chem. Commun.* **2014**, *50*, 1024–1026.

(50) Chen, Y.; Wan, X.; Long, G. High Performance Photovoltaic Applications Using Solution-Processed Small Molecules. *Acc. Chem. Res.* **2013**, *46*, 2645–2655.