Molecular Design of Photovoltaic Materials for Polymer Solar Cells: Toward Suitable Electronic Energy Levels and Broad Absorption

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CONSPECTUS

Bulk heterojunction (BHJ) polymer solar cells (PSCs) sandwich a blend layer of conjugated polymer donor and fullerene derivative acceptor between a transparent ITO positive electrode and a low work function metal negative electrode. In comparison with traditional inorganic semiconductor solar cells, PSCs offer a simpler device structure, easier fabrication, lower cost, and lighter weight, and these structures can be fabricated into flexible devices. But currently the power conversion efficiency (PCE) of the PSCs is not sufficient for future commercialization. The polymer donors and fullerene derivative acceptors are the key photovoltaic materials that will need to be optimized for high-performance PSCs.

In this Account, I discuss the basic requirements and scientific issues in the molecular design of high efficiency photovoltaic molecules. I also summarize recent progress in electronic energy level engineering and absorption spectral broadening of the donor and acceptor photovoltaic materials by my research group and others. For high-efficiency conjugated polymer donors, key requirements are a narrower energy bandgap (E_g) and broad absorption, relatively lower-lying HOMO (the highest occupied molecular orbital) level, and higher hole mobility. There are three strategies to meet these requirements: D−A copolymerization for narrower E_g and lower-lying HOMO, substitution with electron-withdrawing groups for lower-lying HOMO, and two-dimensional conjugation for broad absorption and higher hole mobility. Moreover, better main chain planarity and less side chain steric hindrance could strengthen $\pi-\pi$ stacking and increase hole mobility. Furthermore, the molecular weight of the polymers also influences their photovoltaic performance. To produce high efficiency photovoltaic polymers, researchers should attempt to increase molecular weight while maintaining solubility. High-efficiency D−A copolymers have been obtained by using benzodithiophene (BDT), dithienosilole (DTS), or indacenodithiophene (IDT) donor unit and benzothiadiazole (BT), thienopyrrole-dione (TPD), or thiazolothiazole (TTz) acceptor units. The BDT unit with two thienyl conjugated side chains is a highly promising unit in constructing high-efficiency copolymer donor materials. The electron-withdrawing groups of ester, ketone, fluorine, or sulfonyl can effectively tune the HOMO energy levels downward.

To improve the performance of fullerene derivative acceptors, researchers will need to strengthen absorption in the visible spectrum, upshift the LUMO (the lowest unoccupied molecular orbital) energy level, and increase the electron mobility. [6,6]-Phenyl-C_{71}-butyric acid methyl ester ($PC_{70}BM$) is superior to [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) because C_{70} absorbs visible light more efficiently. Indene-C_{60} bisadduct (ICBA) and Indene-C_{70} bisadduct ($IC_{70}BA$) show 0.17 and 0.19 eV higher LUMO energy levels, respectively, than PCBM, due to the electron-rich character of indene and the effect of bisadduct. ICBA and $IC_{70}BA$ are excellent acceptors for the P3HT-based PSCs.
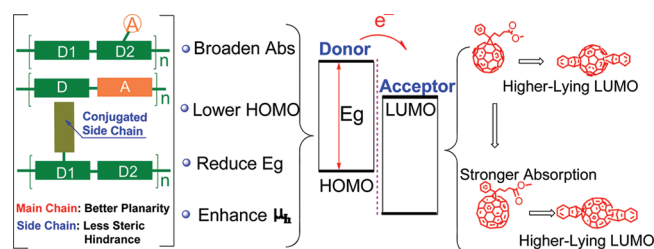
1. Introduction

Bulk heterojunction polymer solar cells (PSCs),[1] which are based on solution-processable conjugated polymer donor and fullerene derivative acceptor materials, have attracted much attention in recent years, due to their advantages of easy fabrication, simple device structure, low cost, light weight, and capability to be fabricated into flexible devices. The maximum power conversion efficiency (PCE)
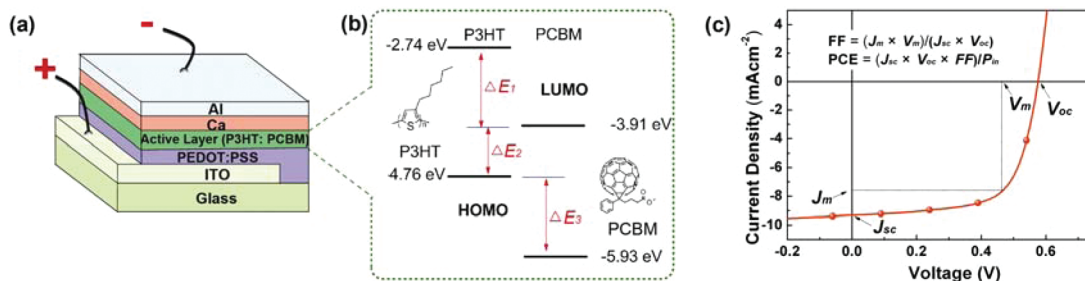
FIGURE 1. (a) Schematic diagram of PSC devices; (b) electronic energy levels of P3HT[7] and PCBM;[6] (c) typical $J-V$ curve of the PSC devices indicating the meaning of J_{sc}, V_{oc}, FF, and PCE.

of the PSCs has increased quickly to over 8% recently.[2] But the efficiency still needs to be improved for the demand of commercialization. Therefore, present studies of the PSCs are mainly focused on increasing PCE of the devices, and the key point to increase the PCE is the design and synthesis of high-efficiency conjugated polymer donor[3−5] and fullerene derivative acceptor[6] photovoltaic materials.

PSCs are commonly composed of a blend layer (active layer) of a conjugated polymer (such as P3HT) donor and a fullerene derivative (such as PCBM) acceptor sandwiched between a PEDOT/PSS-modified ITO positive electrode and a low work function metal negative electrode, as shown in Figure 1a. Figure 1b displays electronic energy levels of the most representative donor poly(3-hexylthiophene) (P3HT) and the most important acceptor [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) in the active layer. When a light irradiates the photoactive layer through the ITO electrode, the conjugated polymer will absorb photons with wavelength in its absorption band to produce excitons (bound electron−hole pairs). The excitons will diffuse toward the donor/acceptor (D/A) interface where the electrons of the excitons will transfer from the LUMO of the donor to the LUMO of the acceptor, so that the charge separation is realized. In the meantime, the acceptor PCBM can also absorb photons to produce excitons, and the holes of the excitons can transfer from the HOMO of PCBM to the HOMO of the donor at the D/A interface to realize the charge separation. The driving force for the exciton dissociation is the energy level offset of LUMO (ΔE_1 in Figure 1b) and HOMO (ΔE_3) between the donor and acceptor materials to overcome the binding energy of the excitons. The separated electrons and holes will transport along PCBM and conjugated polymer interpenetrating network toward the metal cathode and ITO anode, respectively, and be collected by the electrodes to form photocurrent and photovoltage.

Figure 1c shows a typical current density (J)−voltage (V) curve of a PSC device based on P3HT/PCBM under the illumination of AM1.5G, 100 mW/cm². The short circuit current density (J_{sc}), open circuit voltage (V_{oc}), and fill factor (FF) of the devices are also indicated in the figure. J_m and V_m used in the calculation of FF are the current density and voltage values with the maximum $J \times V$ on the $J-V$ curve. The photovoltaic power conversion efficiency (PCE) of the PSCs is proportional to J_{sc}, V_{oc}, and FF. The J_{sc} depends on the efficiencies of the light absorption of the active layer, exciton diffusion to and dissociation at the D/A interface, charge transportation in the active layer, and charge collection on the electrodes. V_{oc} is mainly proportional to the energy level difference (ΔE_2 in Figure 1b) between the LUMO of the acceptor and the HOMO of the donor.[8] FF is related to the series and parallel resistances of the devices; lower series resistance and higher parallel resistance result in higher FF values. Therefore, the following five requirements should be kept in mind in the molecular design of the high efficiency photovoltaic materials:

(1) Broad and strong absorption band in visible and near-infrared region to match the solar spectrum for increasing J_{sc}, that is, we need smaller E_g.

(2) Suitable LUMO and HOMO energy levels not only for facilitating the exciton dissociation at the donor/acceptor interface but also for getting higher V_{oc} of the PSC devices. This means that we need ΔE_1 and ΔE_3 large enough for efficient exciton dissociation and also small enough to get large ΔE_2 for high V_{oc}.

(3) High charge carrier mobility (high hole mobility for the donors and high electron mobility for the acceptors) to enhance the charge transport efficiency (to increase J_{sc}) and to increase FF of the devices.

(4) High solubility for solution processing in fabrication of the bulk heterojunction PSCs.

(5) Optimal morphology and nanoscaled phase separation of the interpenetrating network of the donor/acceptor blend active layer, which influence the J_{sc}, V_{oc}, and FF of the PSCs significantly.
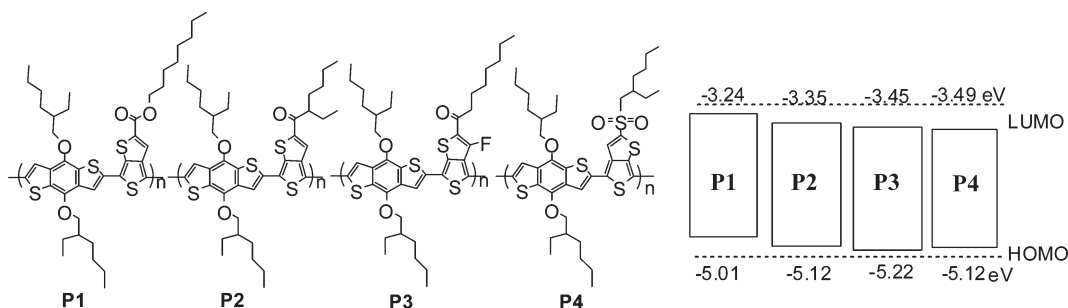
FIGURE 2. Molecular structures and electronic energy levels of the PBDTTT copolymers.

The five requirements are not independent of each other. For example, tuning the LUMO and HOMO energy levels will change the energy bandgap so that influences the absorption, improving solubility of the molecules by attaching alkyl side chains will influence their charge carrier mobility and morphology. Therefore, we need to make balance among the five issues to optimize the molecular structure for high photovoltaic performance.

In this Account, I will focus my attention mainly on tuning the electronic energy levels and absorption spectra of the photovoltaic materials for achieving high-efficiency PSCs and start from analyzing the electronic energy levels of P3HT and PCBM as shown in Figure 1b. As mentioned above, ΔE_1 and ΔE_3 should be greater than the exciton binding energy (0.3–0.5 eV) for efficient exciton dissociation, and the V_{oc} of the PSCs is proportional to ΔE_2. Obviously, ΔE_1 and ΔE_3 (greater than 1 eV) in the P3HT/PCBM system are too big, which results in lower ΔE_2 leading to lower V_{oc} (ca. 0.6 V) of the PSCs. In addition, the absorption properties of the photovoltaic materials depend on their bandgap (E_g, the difference of its LUMO and HOMO). Therefore, tuning the electronic energy levels of the donor and acceptor materials is crucial for improving their photovoltaic properties. Based on the electronic energy levels in Figure 1b, we need to decrease the HOMO level of the donor or to raise the LUMO level of the acceptor to enlarge ΔE_2 for increasing the V_{oc} of the devices, and we need to reduce the E_g of the donor for enhancing sunlight harvest. In the following, I will give examples in the molecular design and summarize the recent progress of the high-efficiency photovoltaic materials.

2. Conjugated Polymers with Electron-Withdrawing Side Groups

In comparison with inorganic semiconductors, a unique advantage of the conjugated polymer photovoltaic materials is that their physicochemical properties can be easily tuned by attaching functional substituents on the polymer main chains. For example, the solubility of the conjugated polymers can be improved by attaching flexible side chains such as alkyl and alkoxy groups, and the electronic energy levels of the polymers can be tuned by using the substituents of electron-donating or electron-withdrawing functional groups. Bredas and Heeger[9] studied the effect of the functional substituents on the electronic energy levels of poly(*p*-phenylene vinylene) (PPV). They found that both the electron-donating groups and the electron-withdrawing groups reduce the bandgap of the conjugated polymers to some extent. The electron-donating groups shift the energy levels upward with the HOMO level up-shifted more than the LUMO level, while the electron-withdrawing groups shift the energy levels downward with the LUMO level down-shifted more than the HOMO level. Obviously, we can select suitable electron-withdrawing substituents to down-shift the HOMO level of the polymer donor or electron-donating substituents to upshift the LUMO level of the fullerene acceptor for obtaining higher V_{oc} of the PSCs. For example, the HOMO level of the polythiophene derivative was down-shifted significantly from −4.76 eV for P3HT[7] to ca. −5.10 eV for the polythiophene derivative with electron-withdrawing ester subsituents, which leads to a larger ΔE_2 and an increase of V_{oc} from ca. 0.6 V to ca. 0.8 V.[10]

Hou et al. tuned the HOMO level of the narrow bandgap copolymers of benzodithiophene (BDT) and thieno[3,4-*b*]-thiophene (TT), PBDTTTs, (see Figure 2).[11] By change of the ester group on the TT unit in **P1** to a more strongly electron-withdrawing ketone group in **P2**, the LUMO and HOMO levels of the polymer dropped by 0.11 eV. By further attachment of a strong electron-withdrawing F atom on the TT unit of **P2** to get **P3**, the HOMO level was shifted downward further by 0.1 eV. The decrease of the HOMO level with keeping the same E_g of the polymers leads to higher V_{oc} and high PCE of the PSC devices. The PSC based on **P3** showed PCE over 7% with a high V_{oc} of 0.76 V.[11]
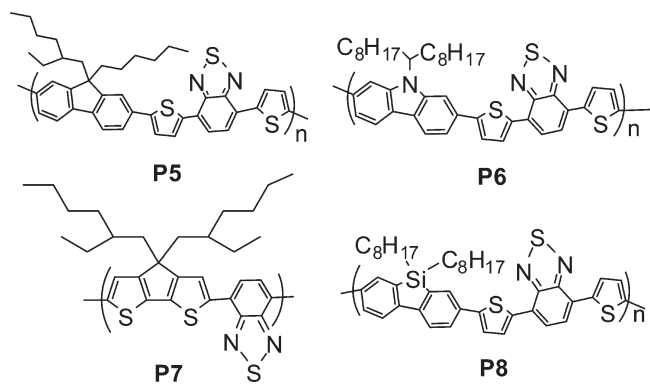
FIGURE 3. D−A copolymers based on fluorene or fluorene-like donor unit and BT acceptor unit.

Recently, Hou et al. put a strong electron-withdrawing sulfonyl group on the TT unit to obtain a new copolymer **P4**[12] (Figure 2). The **P4** film also shows a narrow bandgap of 1.65 eV and lower HOMO energy levels at −5.12 eV. The PSC based on **P4**/PC$_{70}$BM demonstrated a PCE of 6.22% with a high V_{oc} of 0.76 V.[12] Obviously, sulfonyl is another efficient electron-withdrawing group for downward shifting the HOMO level and improving the photovoltaic properties of the high-efficiency polymer PBDTTTs.

3. Donor−Acceptor Copolymers

Donor−acceptor (D−A) copolymerization is one of the most important strategies to broaden the absorption and tune the electronic energy levels of the conjugated polymers. Usually, the D−A copolymers possess an intramolecular charge transfer absorption band at longer wavelength direction, so that the absorption of the copolymers is broadened. Moreover, the HOMO level of the copolymers mainly depends on the donor unit, and their LUMO level is mainly related to the acceptor unit, so the electronic energy levels of the copolymers can be easily tuned by selecting suitable donor and acceptor units. Often, a π-bridge (such as thiophene) is inserted between the donor and acceptor units to reduce the steric hindrance between the donor and acceptor units and to improve the planarity of the copolymers.

In 2003, Andersson et al. reported the photovoltaic properties of a D−A copolymer **P5** containing a fluorene donor unit and a benzothiadiazole (BT) acceptor unit with a thiophene π-bridge (Figure 3); the PCE of the PSC based on **P5**/PCBM reached 2.2%.[13] After that, a variety of D−A copolymers based on BT acceptor unit and fluorene-like donor units were synthesized and used in PSCs, such as **P6**,[14] **P7**,[15] and **P8**[16] (Figure 3). In the following, I will mainly focus on recent progress of high efficiency D−A copolymers from my group and others.

3.1. Dithienosilole-Based D−A Copolymers. In 2008, Hou et al.[17] reported a narrow bandgap D−A copolymer based on dithienosilole (DTS) donor unit and BT acceptor unit, **P9** (Figure 4). The **P9** film shows broad absorption with absorption edge at 850 nm. The PSC based on **P9**/PC$_{70}$BM exhibited a PCE of 5.1%.[17] Recently, Chu et al. synthesized a D−A copolymer of DTS and thienopyrrole-dione (TPD), **P10**. The PSC based on **P10** demonstrated a high PCE of 7.3%.[18]

We recently synthesized a series of DTS-containing D−A copolymers, including **P11**,[19] **P12**,[20] **P13**,[21] **P14**,[22] **P15**,[22] and **P16**[23] (Figure 4) with the acceptor units of bithiazole (BTz), thiazolothiazole (TTz), benzotriazole (BTA), and naphthathiophene-dione (NTDO). Table 1 lists the physicochemical and photovoltaic properties of the D−A copolymers. Among the polymers, **P16** shows the lowest HOMO level at −5.42 eV. Obviously, the two electron-withdrawing ketone groups in the acceptor unit of NTDO played an important role in lowering the HOMO level. The PSC based on **P16** showed a higher PCE of 5.21% with a high V_{oc} of 0.88 V,[23] which benefitted from the lower HOMO level of the polymer. **P12** possesses a high hole mobility of 3.56×10^{-3} cm^2/(V s), which is 1 order of magnitude higher than that of **P11**, due to better planar structure of TTz in **P12** than that of BTz in **P11**. Interestingly, the position of the hexyl side chain on thiophene units in the polymers influenced the photovoltaic properties obviously. By moving the hexyl side chain from the 3-position in **P12** to 4-position of the thiophene units in **P13**, the hole mobility was further enhanced to 7.8×10^{-2} cm^2/(V s) and the absorption was red-shifted due to less steric hindrance in **P13**. The PSC based on **P13** exhibited a higher PCE of 5.88% with a high FF of 71.6%.[21] Jenekhe et al. synthesized a copolymer **P17**, and the polymer also shows high hole mobility of 0.03 cm^2/(V s).[24] The results reveal that BT, TPD, NTDO, and TTz are suitable acceptor units in constructing high photovoltaic performance D−A copolymers based on DTS donor unit.

3.2. Benzodithiophene-Based D−A Copolymers. Benzodithiophene (BDT) is another well used donor unit in high-performance polymer donor materials at present, because it possesses a planar structure and BDT-containing copolymers have high hole mobility and suitable electronic energy levels. Hou et al. first used the BDT donor unit in D−A copolymer photovoltaic materials and studied the effect of different copolymerization units on the photovoltaic properties.[25] Liang et al. combined the BDT unit into the copolymers with TT and synthesized the high-efficiency copolymer PBDTTT.[26] Since then, the BDT-based copolymers
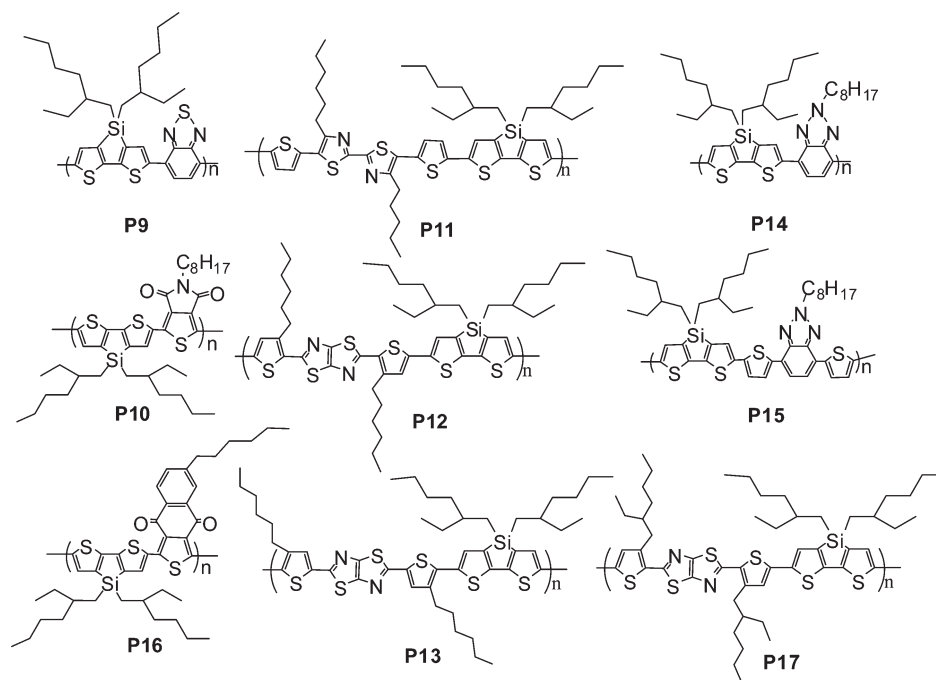
FIGURE 4. Molecular structures of the DTS-containing D–A copolymers.

TABLE 1. HOMO Energy Levels, Bandgaps and Photovoltaic Properties of the D–A Copolymers under the Illumination of AM1.5, 100 mW/cm^2

polymers (weight ratio of polymer/PC$_{70}$BM)	E_g (eV)	HOMO (eV)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	ref
P9 (1:1)	1.46	−5.05	0.68	12.7	55	5.1	17
P10 (1:2)	1.73	−5.57[a]	0.88	12.2	68	7.3	18
P11 (1:1)	1.85	−5.18	0.68	7.85	53.5	2.86	19
P12 (1:1)	1.81	−5.05	0.77	11.9	61.0	5.58	20
P13 (1:1.3)	1.76	−5.04	0.73	11.25	71.6	5.88	21
P15 (1:1)	1.78	−5.05	0.63	9.52	63.3	3.80	22
P17 (1:2)	1.82	−5.1	0.65	12.6	61	5.0	24
P16 (1:2)	1.65	−5.21	0.88	9.24	64	5.21	23
P18 (1:2)	1.8	−5.26[a]	0.85	9.81	66	5.5	27
P19 (1:1,PCBM)	1.7	−5.40	0.87	10.03	57.3	5.0	28
P20 (1:1,PCBM)	1.7	−5.54	0.91	12.91	61.2	7.2	28
P21 (1:2,PCBM)	1.98	−5.29	0.70	11.14	55.2	4.30	29
P22 (1:2,PCBM)	2.00	−5.36	0.79	11.83	72.9	6.81	29
P23 (1:1,PCBM)	1.74	−5.27	0.86	10.4	66.4	5.7	30
P24 (1:1)	1.97	−5.15	0.86	7.84	57	3.82	31
P25 (1:1)	1.96	−5.12	0.82	9.01	60.3	4.46	32

[a]Recalculated based on the vacuum level of Fc/Fc$^+$ at −4.8 eV for comparison with other polymers.

have attracted much attention in the field of conjugated polymer photovoltaic materials.

Figure 5 shows the molecular structures of some recently reported BDT-based D–A copolymers, including **P18**,[27] **P19** and **P20**,[28] **P21** and **P22**,[29] **P23**,[30] **P24**,[31] and **P25**.[32] The photovoltaic properties of the polymers are also listed in Table 1 for clear comparison. All the polymers show lower HOMO energy levels in the range of −5.1 to −5.5 eV. The lower HOMO level results in larger ΔE_2 (see Figure 1b), which leads to higher V_{oc} of 0.7−0.9 V for the PSCs based on the polymers. In comparison of **P20** with **P19** (and **P22** with **P21**), the electron-withdrawing fluorine substitution on the

acceptor units of the polymers results in lower HOMO level of the polymers, higher V_{oc}, and higher PCE of the PSCs. Obviously, the fluorine substitution on BT or BTA acceptor units is an effective way to further down-shift the HOMO level and improve the photovoltaic performance of the polymers.

We synthesized the BDT-based D–A copolymers containing simple structured BTz acceptor unit, **P24**[31] and **P25**.[32] We found that the length of the π-bridge between the donor and acceptor units also influenced the hole mobility and photovoltaic performance of the D–A copolymers. Polymer **P25** with a bithiophene π-bridge showed a higher hole mobility of 1.77×10^{-3} cm^2/(V s) than that of **P24**
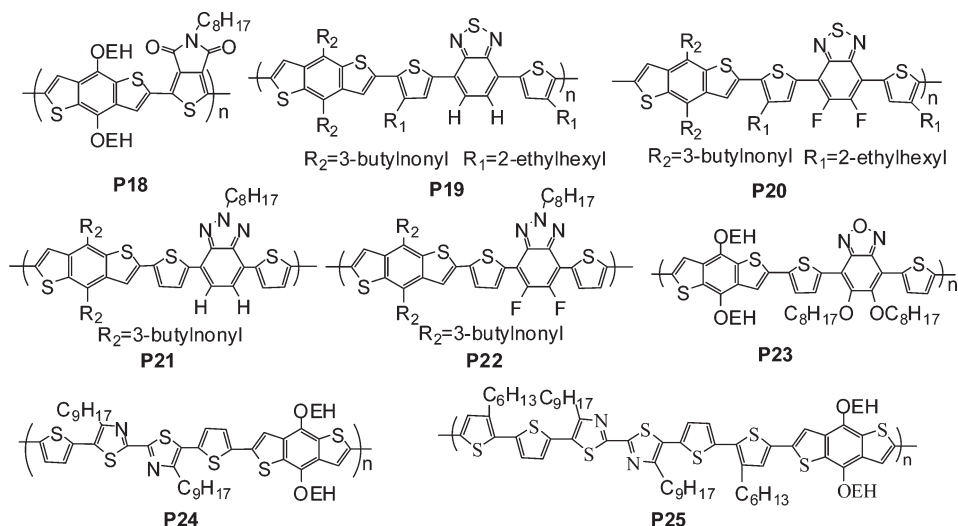
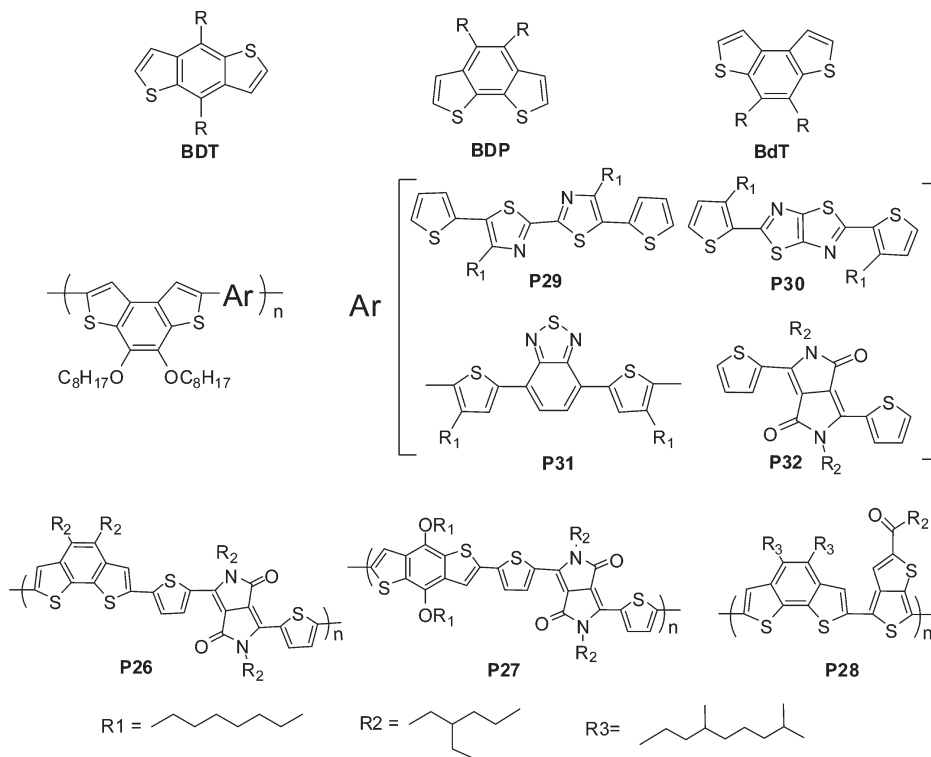**FIGURE 5.** Molecular structures of the D−A copolymers based on BDT donor unit.

FIGURE 6. Molecular structures of the D−A copolymers based on BDT isomers.

$(6.84 \times 10^{-4}$ cm^2/(V s)) with a thiophene π-bridge and exhibited a higher photovoltaic performance (PCE = 4.46% for **P25** versus 3.86% for **P24**).

There are three isomers for the BDT unit, BDT, BDP and BdT as shown in Figure 6. BDP and BdT also possess planar structure and similar electron-donating properties. The D−A copolymer **P26**[33] of BDP with dithienyl-pyrrolopyrrole-dione (DPP) acceptor unit exhibits a lower-lying HOMO level in comparison with its corresponding BDT-containing copolymer **P27**. A copolymer of BDP and TT, **P28**, also shows deeper HOMO level at −5.35 eV and narrow band-gap of 1.55 eV. The PSC based on **P28** demonstrated a PCE of 5.21% with a higher V_{oc} of 0.82 V.[34]

Recently, we synthesized a series of BdT-based D−A copolymers with different acceptor units including BTz, TTz, DTBT, and DPP, **P29**, **P30**, **P31**, and **P32** (Figure 6), and compared their physicochemical and photovoltaic properties.[35] Bandgaps and HOMO energy levels of the
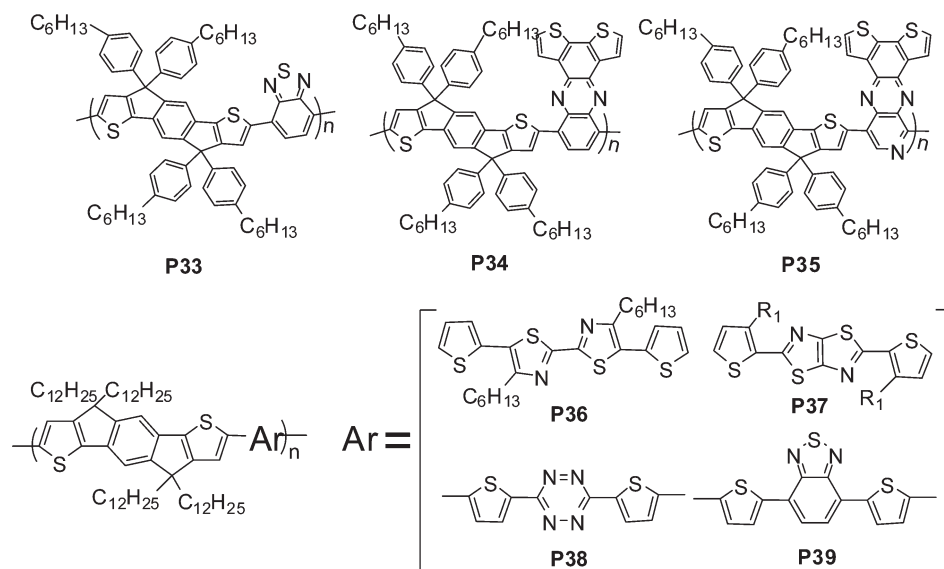
FIGURE 7. Molecular structures of the D−A copolymers based on IDT donor units.

copolymers were tuned effectively by using different acceptor units. Among the polymers, **P30** exhibits a relatively lower HOMO at −5.19 eV. The PSCs based on **P30** showed a PCE of 3.40% with a high V_{oc} of 0.90 V.[35]

The above results indicate that the copolymers based on the two isomers of BDP and BdT show deeper HOMO energy levels and higher V_{oc} when the polymers were used as donor in PSCs, in comparison with the copolymers based on BDT. BDP and BdT are also the promising donor units for constructing high-efficiency D−A copolymer photovoltaic materials.

3.3. Indacenodithiophene-Based D−A Copolymers. Indacenodithiophene (IDT) has also attracted attention as a donor unit in the D−A copolymer photovoltaic materials in recent years,[36,37] because the coplanarity of the IDT unit could enhance interchain interaction of the polymers and lead to higher hole mobility. Chen et al.[36] and Jen and co-workers[37] synthesized a series of copolymers based on IDT with aryl substituents, such as **P33**, **P34**, and **P35** (Figure 7). Polymer **P33** possesses lower-lying HOMO energy levels at −5.36 eV and exhibited a PCE of 6.1% in PSCs.[36] The polymers **P34** and **P35** have low bandgaps of 1.61 and 1.48 eV and higher hole mobilities of 5.6×10^{-2} and 1.5×10^{-2} cm^2 V^{-1} s^{-1}, respectively. The PCE of the PSC based on **P34** reached 6.06%.[37]

We synthesized four D−A copolymers of alkyl-substituted IDT donor units with different acceptor units including BTz, TTz, bis(thiophen-2-yl)-tetrazine (TZ), and DTBT, **P36**, **P37**, **P38**, and **P39**[38] (Figure 7). The copolymers possess good solubility benefitted from the four alkyl side chains on the IDT unit, deeper HOMO levels at −5.2 eV and tunable bandgap depending on the acceptor units. Among the copolymers, **P37** has the highest hole mobility (μ_h) of 4.99×10^{-3} cm^2/(V s). The PCE of the PSC based on **P37** reached 5.79%. The **P39** film has the smallest bandgap of 1.68 eV and exhibited a higher PCE of 6.17% with a large J_{sc} of 13.27 mA/cm^2 and a high V_{oc} of 0.82 V in PSCs.[38]

4. Two-Dimensional Conjugated Polymers

4.1. Polythiophenes with Conjugated Side Chains. For broadening the absorption spectra of the polythiophene (PT) derivatives, we proposed a two-dimensional conjugated (2-D conjugated) concept by attaching a conjugated side chain on PT main chains and synthesized a series of 2-D conjugated PT derivatives,[5,7,39−41] as shown in Figure 8. Among the polymers, PT8 with bi(thienylenevinylene) conjugated side chains showed a broad absorption plateau in the visible region from 350 to 650 nm.[7] In addition, the HOMO energy level of PT8 dropped by ca. 0.2 eV in comparison with P3HT, which is beneficial to higher V_{oc} of the PSCs. The PSC device based on PT8/PCBM demonstrated a PCE of 3.18% with a higher V_{oc} of 0.72 V.[7] In contrast, the PSC based on P3HT displayed PCE of 2.55% and V_{oc} of 0.60 V under the same experimental conditions. Recently, we synthesized a new 2-D conjugated polymer **PT10**[42] based on a side-chain isolated concept. **PT10** exhibited better main chain planarity, less side chain steric hindrance, stronger visible $\pi−\pi^*$ transition absorption, and deeper HOMO level, in comparison with other 2-D conjugated PTs. The PSC based on **PT10** as donor and indene-C$_{60}$ bisadduct (ICBA) as acceptor demonstrated a PCE of 3.6% with a high V_{oc} of 0.94 V.[42]
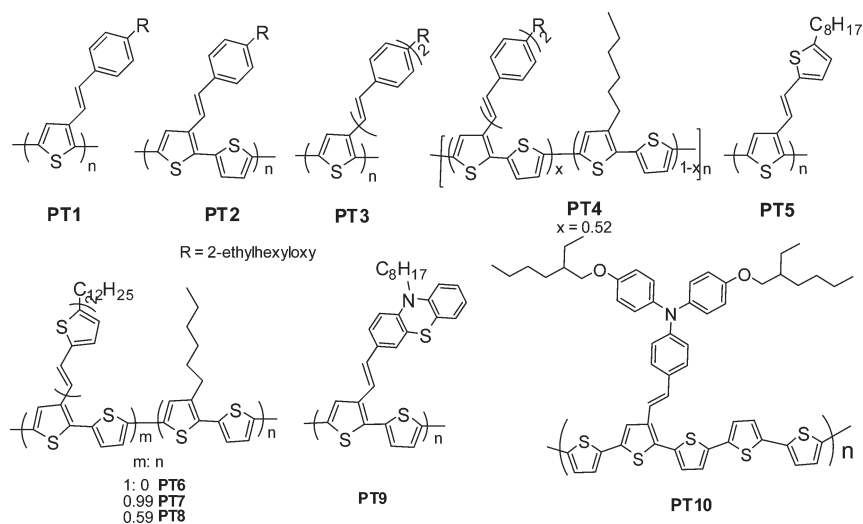
FIGURE 8. Molecular structures of the 2-D conjugated polythiophene derivatives.
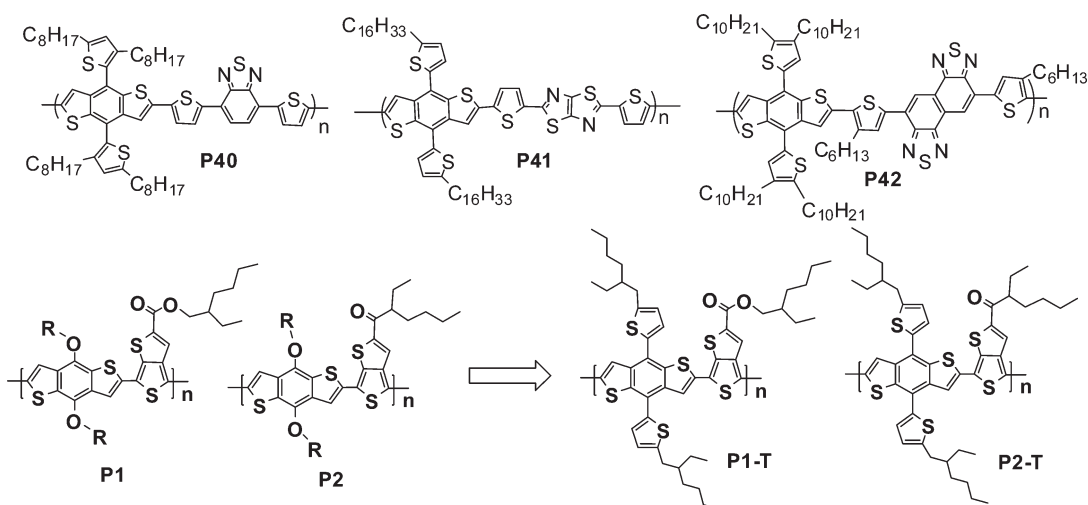

FIGURE 9. Molecular structures of the copolymers based on BDT units with or without bithienyl conjugated side chains.

The results indicate that the strategy for broadening absorption by attaching conjugated side chains is efficient for improving the PCE of the PSCs.

4.2. Copolymers Containing a Thienyl-Substituted BDT Unit. As mentioned above, BDT is a famous structural unit for constructing high-efficiency copolymer donor materials. Two alkoxy or alkyl side chains are usually used on the BDT unit for improving the solubility of the polymers. Huo et al. applied the 2-D conjugation concept to the BDT-containing polymers and synthesized a copolymer **P40** (Figure 9) based on the BDT unit with two thienyl conjugated side chains (BDT-T).[43] The 2-D conjugated **P40** shows a broad absorption band, a lower HOMO level at −5.31 eV, and a higher PCE of 5.66% with a high V_{oc} of 0.92 V in PSCs.[43] Recently, new BDT-T-based copolymers **P41**[44] and **P42**[45] were reported. Polymer **P41** also possesses a deeper HOMO level at −5.3 eV

and showed a PCE of 5.22%.[44] Polymer **P42** possesses a higher hole mobility and broader absorption. The PSC based on **P42** demonstrated a higher PCE of 6.0%.[45]

In considering the high photovoltaic performance of the PBDTTT copolymers and the BDT-T-based D−A copolymers, Huo et al.[46] recently synthesized two BDT-T-based PBDTTT derivatives, **P1-T** and **P2-T** (Figure 9). The 2-D conjugated **P1-T** and **P2-T** exhibit better thermal stabilities, red-shifted absorption spectra, lower HOMO levels, significantly higher hole mobility, and greatly improved photovoltaic properties, in comparison with the two corresponding alkoxy substituted copolymers **P1** and **P2**. The PCE of the PSC based on **P2-T** reached 7.59% in comparison with 6.43% for the device based on **P2**.[46] The results reveal that the 2-D conjugated BDT-T will be a highly promising unit for the design of high-performance photovoltaic copolymers.
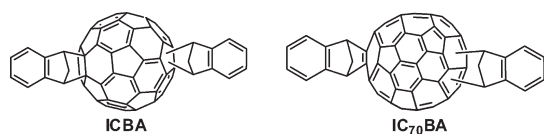
FIGURE 10. Molecular structures of indene adducts of fullerene derivatives.

5. Indene−Fullerene Bisadduct Acceptors

As mentioned in the Introduction, upshift of the LUMO level of the fullerene acceptors is preferred for enlarging ΔE_2 and increasing V_{oc} of the P3HT-based PSCs. For example, PCBM bisadduct (bisPCBM) shows ca. 0.1 eV higher LUMO energy level than PCBM, and the PCE of the PSC based on P3HT/bisPCBM reached 4.5% with a higher V_{oc} of 0.73 V benefitting from the higher LUMO level of the acceptor.[47]

Considering the electron-donating nature of indene and the effect of bisadduct on the upshift of the LUMO energy level of PCBM, we synthesized indene-C_{60} bisadduct (ICBA, see Figure 10) for up-shifting its LUMO level. As we expected, ICBA shows a LUMO level up-shifted by 0.17 eV in comparison with PCBM.[48] The PSC based on P3HT as donor and ICBA as acceptor reached a PCE of 6.48% with a high V_{oc} of 0.84 V and a high FF of 72.7%.[49] In comparison, the PSC with PCBM as acceptor only showed a PCE of 3.84% and a V_{oc} of 0.58 V under the same experimental conditions. ICBA has also been successfully used in high-efficiency inverted structure PSCs[50] and tandem structure PSCs[51] recently. The high photovoltaic performance of ICBA in the P3HT-based PSCs is mainly derived from its higher LUMO level, which results in high V_{oc}.

Based on the success of ICBA, we further synthesized indene-C_{70} bisadduct (IC$_{70}$BA).[52] IC$_{70}$BA exhibits stronger visible absorption from C_{70} and 0.19 eV upshift of its LUMO energy level than PCBM. The PSC based on P3HT as donor and IC$_{70}$BA as acceptor demonstrated a PCE of 6.69% with a high V_{oc} of 0.86 V and a high FF of 72%.[53]

6. Summary and Outlook

Absorption, electronic energy level, charge carrier mobility, solubility, and aggregation properties are the key factors that we should consider in the molecular design of the photovoltaic materials for PSCs. For high-efficiency conjugated polymer donor materials, narrower E_g and broad absorption, relatively lower-lying HOMO level, and higher hole mobility are of most importance. Three strategies have been proven to be effective to meet the requirements, including D−A copolymerization for narrower E_g and

lower-lying HOMO, substitution with electron-withdrawing groups for lower-lying HOMO, and two-dimensional conjugation for broad absorption and higher hole mobility. High-efficiency D−A copolymers have been obtained by using BDT, DTS, or IDT donor unit and BT, TPD, or TTz acceptor units. The electron-withdrawing groups of ester, ketone, fluorine, or sulfonyl are effective in downward tuning the HOMO energy level of the high efficiency PBDTTT polymers. The BDT-T unit with two thienyl conjugated side chains is a highly promising unit in high efficiency D−A copolymers and 2-D conjugated PBDTTT polymers, which possess the preferred broad absorption, lower-lying HOMO level, and higher hole mobility. For the fullerene derivative acceptors, PC$_{70}$BM is superior to PCBM because of the stronger visible absorption of C_{70}. ICBA and IC$_{70}$BA show 0.17 and 0.19 eV higher LUMO energy level, respectively, than PCBM, due to the electron-rich character of indene and the effect of bisadduct. ICBA and IC$_{70}$BA are excellent acceptors for the P3HT-based PSCs.

Bulk heterojunction PSCs and related photovoltaic materials have been developed into a hot research field in recent years. The PCE of the PSCs has been steadily increased from ca. 1% in 1995[1] to over 8% recently,[2] by the research progress on both the new photovoltaic materials and new device structures. It can be expected that the PCE will exceed 10% in a few years, and the molecular design of the photovoltaic materials will play a key role in promoting the commercial application of the PSCs.

BIOGRAPHICAL INFORMATION

Yongfang Li is a professor in Institute of Chemistry, Chinese Academy of Sciences (ICCAS), since 1993. He obtained his Ph.D. degree in physical chemistry in 1986 from Fudan University and then came to ICCAS as a postdoctoral fellow working on conducting polymers with Prof. Renyuan Qian in 1986−1988. He did visiting research in Prof. Hiroo Inokuchi's laboratory in Institute for Molecular Science from 1988 to 1991 and in Prof. Alan J. Heeger's laboratory in UCSB from 1997 to 1998. His present research interests are polymer solar cells and related photovoltaic materials, including conjugated polymer donor, solution-processable organic molecule donor, and fullerene derivative acceptor materials.

FOOTNOTES

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REFERENCES

1 Yu, G.; Gao, J.; Hummelen, J.; Wudl, F.; Heeger, A. J. Polymer Photovoltaic Cells: Enhanced Efficiency via a Network of Internal Donor-Acceptor Heterojunctions. *Science* **1995**, *270*, 1789–1791.

2 He, Z.; Zhong, C.; Huang, X.; Wong, W.; Wu, H.; Chen, L.; Su, S.; Cao, Y. Simultaneous Enhancement of Open-Circuit Voltage, Short-Circuit Current Density, and Fill Factor in Polymer Solar Cells. *Adv. Mater.* **2011**, *23*, 4636–4643.

3 Cheng, Y.; Yang, S.; Hsu, C. Synthesis of Conjugated Polymers for Organic Solar Cell Applications. *Chem. Rev.* **2009**, *109*, 5868–5923.

4 Inganas, O.; Zhang, F.; Andersson, M. Alternating Polyfluorenes Collect Solar Light in Polymer Photovoltaics. *Acc. Chem. Res.* **2009**, *42*, 1731–1739.

5 Li, Y.; Zou, Y. Conjugated Polymer Photovoltaic Materials with Broad Absorption Band and High Charge Carrier Mobility. *Adv. Mater.* **2008**, *20*, 2952–2958.

6 He, Y.; Li, Y. Fullerene Derivative Acceptors for High Performance Polymer Solar Cells. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1970–1983.

7 Hou, J.; Tan, Z.; Yan, Y.; He, Y.; Yang, C.; Li, Y. Synthesis and Photovoltaic Properties of Two-dimensional Conjugated Polythiophenes with Bi(thienylenevinylene) Side Chains. *J. Am. Chem. Soc.* **2006**, *128*, 4911–4916.

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

9 Bredas, J.; Heeger, A. J. Influence of Donor and Acceptor Substituents on the Electronic Characteristics of Poly(para-phenylene vinylene) and Poly(para-phenylene). *Chem. Phys. Lett.* **1994**, *217*, 507–512.

10 Zhang, M.; Guo, X.; Yang, Y.; Zhang, J.; Zhang, Z.; Li, Y. Downwards Tuning HOMO Level of Polythiophene by Carboxylate Substitution for High Open-Circuit-Voltage Polymer Solar Cells. *Polym. Chem.* **2011**, *2*, 2900–2906.

11 Chen, H.; Hou, J.; Zhang, S.; Liang, Y.; Yang, G.; Yang, Y.; Yu, L. P.; Wu, Y.; Li, G. Polymer Solar Cells with Enhanced Open-Circuit Voltage and Efficiency. *Nat. Photonics* **2009**, *3*, 649–653.

12 Huang, Y.; Huo, L.; Zhang, S.; Guo, X.; Han, C. C.; Li, Y.; Hou, J. Sulfonyl: A New Application of Electron-Withdrawing Substituent in Highly Efficient Photovoltaic Polymer. *Chem. Commun.* **2011**, *47*, 8904–8906.

13 Svensson, M.; Zhang, F.; Veenstra, S.; Verhees, W.; Hummelen, J.; Kroon, J.; Inganas, O.; Andersson, M. High-Performance Polymer Solar Cells of an Alternating Polyfluorene Copolymer and a Fullerene Derivative. *Adv. Mater.* **2003**, *15*, 988–991.

14 Blouin, N.; Michaud, A.; Leclerc, M. A Low-Bandgap Poly(2,7-Carbazole) Derivative for Use in High-Performance Solar Cells. *Adv. Mater.* **2007**, *19*, 2295–2300.

15 Peet, J.; Kim, J.; Coates, N.; Ma, W.; Moses, D.; Heeger, A. J.; Bazan, G. Efficiency Enhancement in Low-Bandgap Polymer Solar Cells by Processing with Alkane Dithiols. *Nat. Mater.* **2007**, *6*, 497–500.

16 Wang, E.; Wang, L.; Lan, L.; Luo, C.; Zhuang, W.; Peng, J.; Cao, Y. High-Performance Polymer Heterojunction Solar Cells of a Polysilafluorene Derivative. *Appl. Phys. Lett.* **2008**, *92*, No. 033307.

17 Hou, J.; Chen, H.; Zhang, S.; Li, G.; Yang, Y. Synthesis, Characterization, and Photovoltaic Properties of a Low Band Gap Polymer Based on Silole-Containing Polythiophenes and 2,1,3-Benzothiadiazole. *J. Am. Chem. Soc.* **2008**, *130*, 16144–16145.

18 Chu, T.; Lu, J.; Beaupre, S.; Zhang, Y.; Pouliot, J.; Wakim, S.; Zhou, J.; Leclerc, M.; Li, Z.; Ding, J.; Tao, Y. Bulk Heterojunction Solar Cells Using Thieno[3,4-c]pyrrole-4,6-dione and Dithieno[3,2-b:20,30-d]silole Copolymer with a Power Conversion Efficiency of 7.3%. *J. Am. Chem. Soc.* **2011**, *133*, 4250–4253.

19 Zhang, M.; Fan, H.; Guo, X.; He, Y.; Zhang, Z.; Min, J.; Zhang, J.; Zhan, X.; Li, Y. Synthesis and Photovoltaic Properties of Bithiazole-Based Donor-Acceptor Copolymers. *Macromolecules* **2010**, *43*, 5706–5712.

20 Zhang, M.; Guo, X.; Li, Y. Synthesis and Characterization of a Copolymer Based on Thiazolothiazole and Dithienosilole for Polymer Solar Cells. *Adv. Energy Mater* **2011**, *1*, 557–560.

21 Zhang, Z.; Min, J.; Zhang, S.; Zhang, J.; Li, Y. Alkyl Chain Engineering on Dithieno[3,2-b:2′,3′-d]silole-alt- dithienylthiazolo[5,4-d]thiazole Copolymer Toward High Performance Bulk Heterojunction Solar Cell. *Chem. Commun.* **2011**, *47*, 9474–9476.

22 Min, J.; Zhang, Z.; Zhang, S.; Zhang, M.; Zhang, J.; Li, Y. Synthesis and Photovoltaic Properties of D-A Copolymers Based on Dithienosilole and Benzotriazole. *Macromolecules* **2011**, *44*, 7632–7638.

23 Cui, C.; Fan, X.; Zhang, M.; Zhang, J.; Min, J.; Li, Y. D-A copolymer of Dithienosilole and a New Acceptor Unit of Naphtho[2,3-c]thiophene-4,9-dione for Efficient Polymer Solar Cells. *Chem. Commun.* **2011**, *47*, 11345–11347.

24 Subramaniyan, S.; Xin, H.; Kim, F. S.; Shoaee, S.; Durrant, J. R.; Jenekhe, S. A. Effects of Side Chains on Thiazolothiazole-Based Copolymer Semiconductors for High Performance Solar Cells. *Adv. Energy Mater.* **2011**, *1*, 854–860.

25 Hou, J.; Park, M.; Zhang, S.; Yao, Y.; Chen, L.; Li, J.; 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.

26 Liang, Y.; Wu, Y.; Feng, D.; Tsai, S.; Son, H.; Li, G.; Yu, L. Development of New Semiconducting Polymers for High Performance Solar Cells. *J. Am. Chem. Soc.* **2009**, *131*, 56–57.

27 Zou, Y.; Najari, A.; Berrouard, P.; Beaupre, S.; Aich, B.; Tao, Y.; Leclerc, M. A Thieno[3,4-c]-pyrrole-4,6-dione-Based Copolymer for Efficient Solar Cells. *J. Am. Chem. Soc.* **2010**, *132*, 5330–5331.

28 Zhou, H.; Yang, L.; Stuart, A.; Price, S.; Liu, S.; You, W. Development of Fluorinated Benzothiadiazole as a Structural Unit for a Polymer Solar Cell of 7% Efficiency. *Angew. Chem., Int. Ed.* **2011**, *50*, 2995–2998.

29 Price, S.; Stuart, A.; 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.

30 Jiang, J.; Yang, P.; Chen, H.; Wei, K. Synthesis, Characterization, and Photovoltaic Properties of a Low-Bandgap Copolymer Based on 2,1,3-benzooxadiazole. *Chem. Commun.* **2011**, *47*, 8877–8879.

31 Zhang, M.; Fan, H.; Guo, X.; He, Y.; Zhang, Z.; Min, J.; Zhang, J.; Zhan, X.; Li, Y. Synthesis and Photovoltaic Properties of a Copolymer of Benzodithiophene and Bithiazole. *Macromolecules* **2010**, *43*, 8714–8717.

32 Zhang, M.; Guo, X.; Li, Y. Photovoltaic Performance Improvement of D-A Copolymers Containing Bithiazole Acceptor Unit by Using Bithiophene Bridges. *Macromolecules* **2011**, *44*, 8798–8804.

33 Huo, L.; Hou, J.; Chen, H.; Zhang, S.; Jiang, Y.; Chen, T.; 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.

34 Huo, L.; Guo, X.; Li, Y.; Hou, J. Synthesis of a Polythieno[3,4-b]thiophene Derivative with Low-Lying HOMO Level and its Application in Polymer Solar Cells. *Chem. Commun.* **2011**, *47*, 8850–8852.

35 Zhang, M.; Sun, Y.; Guo, X.; Cui, C.; He, Y.; Li, Y. Synthesis and Characterization of Dioctyloxybenzo[1,2-b:4,3-b′]dithiophene-Containing Copolymers for Polymer Solar Cells. *Macromolecules* **2011**, *44*, 7625–7631.

36 Chen, Y.; Yu, C.; Fan, Y.; Hung, L.; Chen, C.; Ting, C. Low-Bandgap Conjugated Polymer for High Efficient Photovoltaic Applications. *Chem. Commun.* **2010**, *46*, 6503–6505.

37 Zhang, Y.; Zou, J.; Yip, H.; Chen, K.; Davies, J.; Sun, Y.; Jen, A. Synthesis, Characterization, Charge Transport, and Photovoltaic Properties of Dithienobenzoquinoxaline- and Dithieno-benzopyridopyrazine-Based Conjugated Polymers. *Macromolecules* **2011**, *44*, 4752–4758.

38 Zhang, M.; Guo, X.; Wang, X.; Wang, H.; Li, Y. Synthesis and Photovoltaic Properties of D-A Copolymers Based on Alkyl-Substituted Indacenodithiophene Donor Unit. *Chem. Mater.* **2011**, *23*, 4264–4270.

39 Hou, J.; Huo, L.; He, C.; Yang, C.; Li, Y. Synthesis and Absorption Spectra of Poly-[3-(phenylene-vinyl) thiophene] with Conjugated Side-Chains. *Macromolecules* **2006**, *39*, 594–603.

40 Hou, J.; Yang, C.; He, C.; Li, Y. Poly[3-(5-octyl-thienylene- vinyl)-thiophene]: A Side-Chain Conjugated Polymer with Very Broad Absorption. *Chem. Commun.* **2006**, 871–873.

41 Zou, Y.; Wu, G.; Sang, G.; Yang, Y.; Liu, Y.; Li, Y. Polythiophene Derivative with Phenothiazine-Vinylene Conjugated Side Chain: Synthesis and Its Application in Field-Effect Transistors. *Macromolecules* **2007**, *40*, 7231–7237.

42 Zhang, Z.; Zhang, S.; Min, J.; Chui, C.; Zhang, J.; Li, Y. Conjugated Side-Chain Isolated Polythiophene: Synthesis and Photovoltaic Application. *Macromolecules* **2012**, *45*, 113–118.

43 Huo, L.; Hou, J.; Zhang, S.; Chen, H.; 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.

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

45 Wang, M.; Hu, X.; 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.

46 Huo, L.; Zhang, S.; Guo, X.; Xu, F.; Li, Y.; Hou, J. Replacement of Alkoxy with Alkylthienyl: A Feasible Approach to Improve Photovoltaic Properties of PBDTTT-based Polymers. *Angew. Chem., Int. Ed.* **2011**, *50*, 9697–9702.

47 Lenes, M.; Wetzelaer, G.; Kooist, F.; Veenstra, S.; Hummelen, J.; Blom, P. Fullerene Bisadducts for Enhanced Open-Circuit Voltages and Efficiencies in Polymer Solar Cells. *Adv. Mater.* **2008**, *20*, 2116–2119.

48 He, Y.; Chen, H.; Hou, J.; Li, Y. Indene-C_{60} Bisadduct: A New Acceptor for High Performance Polymer Solar Cells. *J. Am. Chem. Soc.* **2010**, *132*, 1377–1382.

49 Zhao, G.; He, Y.; Li, Y. 6.5% Efficiency of the Polymer Solar Cells Based on Poly(3-hexylthiophene) and Indene-C_{60} Bisadduct by Device Optimization. *Adv. Mater.* **2010**, *22*, 4355–4358.

50 Cheng, Y.; Hsieh, C.; He, Y.; Hsu, C.; Li, Y. Combination of Indene-C_{60} Bis-adduct and Cross-Linked Fullerence Interlayer Leading to Highly Efficient Inverted Polymer Solar Cells. *J. Am. Chem. Soc.* **2010**, *132*, 17381–17383.

51 Yang, J.; Zhu, R.; Hong, Z.; He, Y.; Kumar, A.; Li, Y.; Yang, Y. Achieving High Performance Tandem Polymer Solar Cells. *Adv. Mater.* **2011**, *23*, 3465–3470.

52 He, Y.; Zhao, G.; Peng, B.; Li, Y. High Yield Synthesis, Electrochemical and Photo-voltaic Properties of Indene-C_{70} Bisadduct. *Adv. Funct. Mater.* **2010**, *20*, 3383–3389.

53 Sun, Y.; Cui, C.; Wang, H.; Li, Y. Efficiency Enhancement of Polymer Solar Cells Based on Poly(3-hexylthiophene)/Indene-C_{70} Bisadduct via Methylthiophene Additive. *Adv. Energy Mater.* **2011**, *1*, 1058–1061.