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ARTICLE

Engineering the band gap and energy level of conjugated polymers using a second acceptor unit

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Three novel isoindigo based donor-acceptor (D-A) conjugated polymers **P1-3** have been synthesized by Suzuki polycondensation and utilized as donor materials for polymer solar cells (PSCs).These three polymers are of the same backbone, but different substituents. All these polymers exhibit high thermal stability and broad absorption in the range of 300 to 770 nm. Hole mobilities of polymer films spin coated from 1,2-dichlorobenzene (DCB) solutions are 7.00×10^{-4}, 2.37×10^{-3} and 2.90×10^{-4} $cm^2V^{-1}s^{-1}$ for **P1**, **P2** and **P3**, respectively. PSCs based on **P2**:$PC_{71}BM$ (1:2 by weight) with a 2% DIO additive displayed power conversion efficiency (PCE) of 3.41% with a short-circuit current density (J_{sc}) of 7.57 mA/cm^2, an open-circuit voltage (V_{oc}) of 0.85 V, and a fill factor (FF) of 53%, under the illumination of AM1.5G (100 mW cm^{-2}). XRD diffraction measurements have shown that these polymers are of short π-π stacking distance in the solid state. The results demonstrate that these conjugated polymers could be promising donor materials in the application of polymer solar cells.

Introduction

Polymer solar cells have experienced two rapid development periods after the appearance of bulk heterojunction concept of active layer and the use of donor-acceptor (D-A) conjugated polymers as the donor materials.[1] The innovations of material and device structure have boosted the power conversion efficiency (PCE) of PSCs to higher than 10%.[2,3] The active layer of bulk heterojunction polymer solar cell is a blend of donor and acceptor, which form an interpenetrated network for highly efficient exciton diffusion and dissociation and the transportation of the formed free charges.[4,5] To achieve high efficiency polymer solar cells, some design criteria of p-type polymer donors are (i) low lying HOMO energy level to increase the open circuit voltage (V_{oc}); (ii) narrow band gap to broaden the absorption range to achieve higher short-circuit current (J_{sc}); (iii) high hole mobility for charge transport. Alternating D-A approach, which involves the copolymerization of an electron rich monomer with an electron deficient monomer, is the most attractive and successful strategy for controlling energy level and the optical band gap of copolymers through the intramolecular charge transfer from donor to acceptor unit.[6-9] On the basis of this concept, a large number of novel D-A type low band gap polymers have been synthesized and used in PSCs.[7] Carbazole,[10-13] fluorene,[14-16] silafluorene,[17,18] thieno[3,4-b]thiophene,[19] and benzo[1,2-b:4,5-b]dithiophene (BDT)[20-22] are commonly used electron-rich donor units; whereas quinoxaline,[23-25] diketopyrrolopyrrole,[26,27] thienopyrazine,[28,29] benzothiadiazole (BT),[30,31] isoindigo,[32-34] and thieno[3,4-c]pyrrole-4,6-dione[35,36] are commonly used electron-deficient acceptor units.

Isoindigo, which is an easily synthesized strong electron withdrawing unit, constitutes a planar moiety capable of forming strong π-π stacks in the solid state. Many isoindigo based D-A alternating conjugated polymers have been synthesized and used for PSC and field effect transistor (FET) applications. The hole and electron mobilities of isoindigo based D-A conjugated polymers have reached 0.81 and 0.66 $cm^2\ V^{-1}s^{-1}$, respectively.[37] PSCs based on isoindigo containing D-A conjugated polymers furnished PCE up to 6.2%.[38]

Among the commonly used acceptor units, BT, which is a widely used planar acceptor unit, can be facilely modified by substitution at the 5- and 6-positions. Many D-A alternating conjugated polymers containing BT have been synthesized and used for PSCs. Especially, D-A alternating conjugated polymers with BT as the acceptor unit, carbazole or fluorene as the donor unit, and thiophene as the spacer have furnished with good PSC device performance.[10,39,40] Although the polymer solar cells gave high open circuit voltage (V_{oc}), the short circuit current (J_{sc}) is still low due to the narrower absorption. To broaden the absorption, BT has been used to polymerize with strong electron donor such as dithienosilole to achieve D-A type conjugated polymers with broad absorption.[41,42] Conjugated polymers based on strong electron donor unit and BT are usually of higher HOMO energy level, which are prone to result in lower V_{oc}.[2,3,43-50] To achieve conjugated polymer with broad absorption and deeper HOMO energy level, we designed and synthesized a series of conjugated polymers containing BT as the acceptor unit, isoindigo as the second acceptor unit, and thiophene as the spacer. As expected, these polymers as thin films exhibit intense and broad absorption and deep HOMO energy level (< 5.44 eV) with a band gap in the range of 1.60-1.63eV. The highest FET hole mobility can be up to 2.37×10^{-3} $cm^2V^{-1}s^{-1}$. PSCs have been fabricated with the polymer as donor and $PC_{71}BM$ as acceptor. Among these three copolymers, the PSC based on **P2**:$PC_{71}BM$ (1:2 by weight) with diiodooctane (DIO) (2% by volume) as the additive showed the best performance with a PCE of 3.41% and a V_{oc} of 0.85 V under an illumination of AM1.5G (100 $mWcm^{-2}$).

General procedure for the synthesis of conjugated polymers (P1, P2, and P3)

A mixture of isoindigo based diboronic acid pinacol ester monomer **M4** (0.11 mmol), dibromo monomer **M1-3** (0.11 mmol), toluene, H_2O, and $NaHCO_3$ was carefully degassed before and after $Pd(PPh_3)_4$ was added. The mixture was stirred and refluxed with different reaction time under nitrogen atmosphere. Phenylboronic acid and $Pd(PPh_3)_4$ were added and refluxed for 4 h; after that bromobenzene was added, and the mixture was refluxed overnight to complete the end-capping reaction. After being cooled to room temperature, water and chlorobenzene were added, and the organic layer was separated and washed three times with water. And then, the solution was heated to 100 °C to dissolve the polymers and filtered. After the removal of most solvent, the residue was poured into a large amount of acetone, and the resulting precipitates were collected by filtration and washed with acetone. The crude product was redissolved in a minimum amount of chlorobenzene and precipitated into a large amount of acetone. The formed precipitates were collected by filtration and dried under high vacuum.

Synthesis of polymer (P1)

M4 (100 mg, 0.11 mmol), **M1** (84 mg, 0.11 mmol), toluene (20 mL), H_2O (2 mL), $NaHCO_3$ (0.2 g, 3.1 mmol), and $Pd(PPh_3)_4$ (1.3 mg, 1.2 μmol) were used for Suzuki polycondensation. Phenylboronic acid (10mg, 0.08 mmol), $Pd(PPh_3)_4$ (1.3 mg, 1.2 μmol), and bromobenzene (100 μL, 9.55 mmol) were used for the end-capping reaction. **P1** was obtained as a dark blue solid in a yield of 49% (80 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 9.17-9.13 (2H, br), 8.54-8.53 (2H, br), 7.57-7.35 (2H, br), 7.03-6.92 (4H, br), 4.14 (4H, br), 3.78 (4H, br), 1.51-1.18 (64H, br), 0.80-0.79 (12H, br). Anal. Calcd for $C_{70}H_{96}N_4O_4S_3$: C 72.87, H 8.39, N 4.86. Found: C 72.16, H 8.41, N 4.87 GPC (PS standards): M_w = 17.9 kg/mol, M_n = 16.1 kg/mol, PDI = 1.11.

Synthesis of polymer (P2)

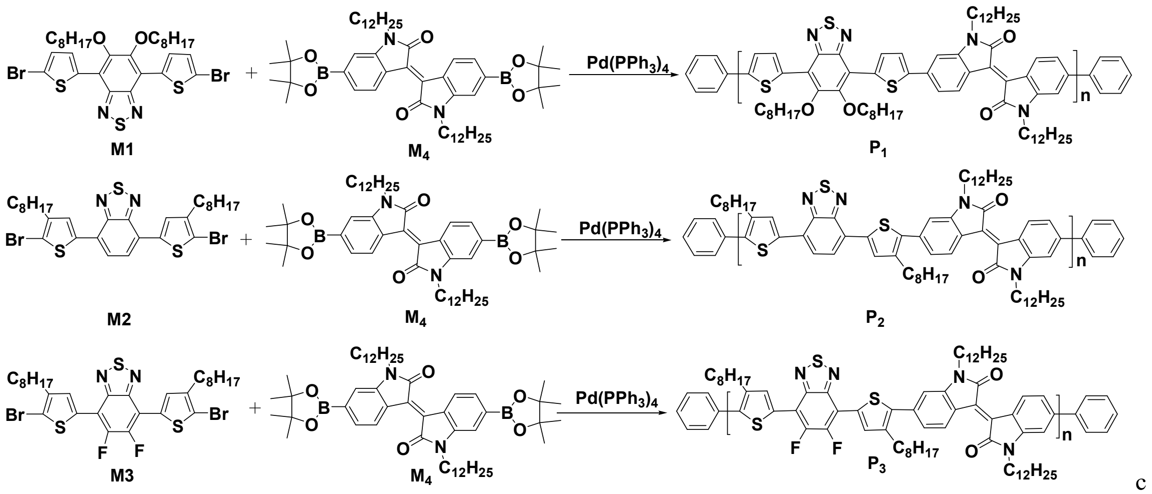
M4 (100 mg, 0.11 mmol), **M2** (80 mg, 0.11 mmol), toluene (20 mL), H_2O (2 mL), $NaHCO_3$ (0.2 g, 3.1 mmol), and $Pd(PPh_3)_4$ (1.3 mg, 1.2 μmol) were used for Suzuki polycondensation. Phenylboronic acid (10 mg, 0.08 mmol), $Pd(PPh_3)_4$ (1.3 mg, 1.2 μmol), and bromobenzene (100 μL, 9.55 mmol) were used for the end-capping reaction. **P2** was obtained as a dark blue solid in a yield of 68% (90 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 9.20-9.18 (2H, br), 8.01-7.93 (2H, br), 7.83-7.81 (2H, br), 6.92-6.90 (4H, br), 3.78-377 (4H, br), 2.77-2.61 (8H, br), 1.68-1.45 (24H, br), 1.20-1.16 (36H, br), 0.80-0.78 (12H, br). Anal. Calcd for $C_{70}H_{96}N_4O_2S_3$: C 74.95, H 8.63, N 4.99. Found: C 74.81, H 8.68, N 4.95. GPC (PS standards): M_w = 13.2 kg/mol, M_n = 12.5 kg/mol, PDI = 1.06.

Synthesis of polymer (P3)

M4 (100 mg, 0.11 mmol), **M3** (85 mg, 0.11 mmol), toluene (20 mL), H_2O (2 mL), and $NaHCO_3$ (0.2 g, 3.1 mmol), and $Pd(PPh_3)_4$(1.3 mg, 1.2 μmol) were used for Suzuki polycondensation. Phenylboronic acid (10 mg, 0.08 mmol), $Pd(PPh_3)_4$ (1.3 mg, 1.2 μmol), and bromobenzene (100 μL, 9.55 mmol) were used for the end-capping reaction. **P3** was obtained as a dark blue solid in a yield of 42% (60 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 9.20-9.18 (2H, br), 8.14-8.13 (2H, br), 7.32-7.31 (2H, br), 6.92-6.90 (2H, br), 3.78-3.72 (8H, br), 2.79-2.78 (8H, br), 1.68-1.49 (8H, br), 1.21-1.16 (48H, br), 0.80-0.76 (12H, br). Anal. Calcd for $C_{70}H_{94}F_2N_4O_2S_3$: C 72.62, H 8.18, N 4.84. Found: C 72.54, H 8.23, N 4.81. GPC (PS standards): M_w = 37.5 kg/mol, M_n = 21.2 kg/mol, PDI = 1.77.

RESULTS AND DISCUSSION

Monomers **M1**,[10] **M2**,[39] **M3**,[51] and **M4**[52] were synthesized according to the literature procedures and their structure and purity were confirmed by ^1H and ^{13}C NMR spectroscopy and elemental analysis. As outlined in Scheme 1, polymers **P1-3** were synthesized by Suzuki polycondensation of **M1**, **M2**, and **M3** with **M4**, respectively. The polycondensations were conducted in a biphasic mixture of toluene and aqueous $NaHCO_3$ with freshly prepared $Pd(PPh_3)_4$ as the catalyst precursor under nitrogen atmosphere. After the polymerization, phenylboronic acid and then bromobenzene were successively added at a time interval of 4 h to cap the bromo and boronic acid end groups. After standard workup, **P1**, **P2** and **P3** were obtained in yields of 49%, 68%, and 42%, respectively. **P1** and **P2** showed good solubility in common organic solvents such as $CHCl_3$, chlorobenzene (CB), DCB, and THF. **P3** was only partially soluble in DCB at room temperature, but could be fully dissolved in DCB at elevated temperature. As summarized in Table 1, number average molecular weights (M_n) of the polymers are 16.2 kg/mol for **P1**, 12.5 kg/mol for **P2**, and 21.2 kg/mol for **P3**, with polydispersity indexes (PDIs) of 1.11, 1.06 and 1.77, respectively, measured by gel permeation chromatography (GPC) at room temperature with THF as an eluent and polystyrene as calibration standards.



Scheme 1. The synthesis of **P1-3**: Reagents and conditions: Pd(PPh$_3$)$_4$, toluene, H$_2$O, NaHCO$_3$, 100 ^{o}C, 24-72 h.

Thermal properties

Thermal properties of **P1-3** were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) at a scanning speed of 10 °C/min under nitrogen atmosphere. A 5% mass loss is defined as the thermolysis threshold. As shown in Figure 1a, **P1-3** exhibited good thermal stability and the thermolysis onsets of **P1**, **P2**, and **P3** are located at 316, 438, and 399 °C, respectively. The data are also summarized in table 1. As shown in Figure S1 (see Supporting Information), for all polymers, no noticeable thermal transition was observed from 25 to 300 °C by DSC measurements, which is probably attributed to the stiff backbone that limits the chain motion.

X-ray studies

The packing of polymer chains in the solid state plays a pivotal role in determining the hole mobility of polymer films and the power conversion efficiency of PSCs. Therefore, X-ray diffractions (XRD) of **P1−3** powdery samples were performed to investigate the packing of polymer chains in solid state and the diffraction patterns are shown in Figure S2. **P1** and **P3** exhibited five sharp diffraction peaks; whereas the diffraction peaks for **P2** became weaker and broader. The first peak (d$_1$), usually denoted as (100) reflection,[53] at the small angle region can be attributed to the distance of conjugated polymer chains separated by the two extended alkyl chains. The interchain separation distances are 20.45, 20.75, and 20.11 Å for **P1**, **P2**, and **P3**, respectively. The last diffraction peak (d$_2$), usually denoted as (010) diffraction,[53] at wide angle region probably corresponds to the π-π stacking distance between polymer backbones. The π-π stacking distances are 3.49, 3.61, and 3.47 Å for **P1**, **P2**, and **P3**, respectively. These results indicated that **P1** and **P3** formed more ordered and closer packing in solid state than **P2**. The close packing of **P1** and **P3** polymer chains in solid state is probably due to the following two reasons. For **P1**, the existence of intramolecular S-O interaction endows the polymer backbone with a more planar conformation;[54,55] whereas for **P3**, the existence of fluorine atoms in the polymer backbone usually enhance the interchain interactions and makes the polymer chains packing more closer.[56-58]

Table 1. Molecular Weights and Thermal Properties of the Polymers

Polymers	M$_n$^{a} (kDa)	M$_w$^{a} (kDa)	PDI	T$_d$^{b} (^{o}C)	Yield (%)
P1	16.2	17.9	1.11	316	49
P2	12.5	13.2	1.06	438	68
P3	21.2	37.5	1.77	399	42

[a] Determined by GPC using polystyrene standards with THF as the eluent.
[b] The 5% weight-loss temperatures under nitrogen atmosphere.

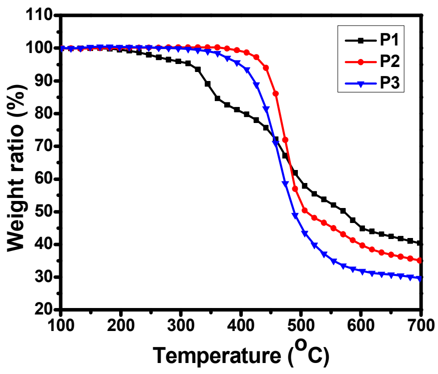


Figure1. (a) TGA plots of **P1-3** at a heating rate of 10 °C/min under nitrogen atmosphere;

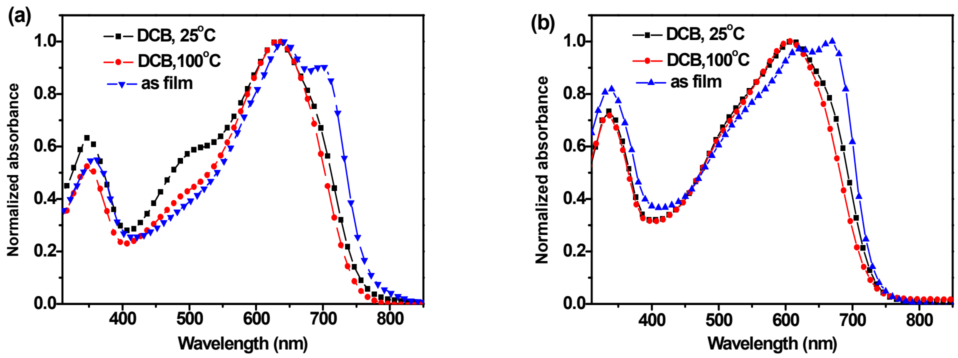
Optical properties

To access a good deal of information about the electronic structure of polymers, photophysical properties of **P1-3** were investigated by UV-vis-NIR absorption spectroscopy. The absorption spectra of **P1-3** in 1,2-dichlorobenzene (DCB) solutions at room temperature and elevated temperature and as thin films are shown in Figure 2. As shown in Figure 2a, **P1** in DCB solution at room temperature exhibited a broad absorption in the visible region with one weak absorption peak located at 347, one intense absorption peak located at 633 nm, and one shoulder at 496 nm. **P1** in DCB solution at elevated temperature showed almost the same absorption spectrum, only the intensity of shoulder absorption at 496 nm decreased. Compared with solution absorption spectra, the absorption spectrum of **P1** as thin films became broader and red-shifted. A new absorption peak at 700 nm appeared, which can be ascribed to the aggregation of polymer chains in the solid state. The absorption spectra of **P2** in DCB solutions at room temperature and elevated temperature are almost the same; whereas the absorption spectrum of **P2** as thin films is broadening and red-shifted with two absorption bands in the long wave length region peaked at 621 and 668 nm, respectively, indicating the aggregation of polymer chains in the solid state. **P3** in DCB solution at room temperature displayed a broad absorption in the visible region with two peaks at 331 and 608 nm and a shoulder at 497 nm. At elevated temperature, the absorption spectrum of **P3** in DCB solution is blue shifted and the two peaks are located at 328 and 575 nm, respectively. As thin films, the absorption spectrum of **P3** is markedly red shifted and broadening and exhibited two absorption peaks located at 627 and 684 nm, respectively, in the long wave length region. These results indicated that **P1** and **P2** formed real solutions in DCB at room temperature and elevated temperature; whereas **P3** formed aggregation in DCB solution at room temperature, which can be dissociated at elevated temperature. The high energy band is attributed to the π-π* transition and the low energy band originates from the intramolecular charge transfer (ICT) from the donor unit to the acceptor one. Optical band gaps (E_g^{opt}) of **P1**, **P2**, and **P3** films estimated from absorption edges of film spectra are 1.60, 1.63, and 1.62 eV, respectively. The narrower band gap of **P1** than that of **P2** and **P3** is probably due to the incorporation of electron donating alkoxy side groups on the benzothiadiazole moiety of the **P1**, which elevates the HOMO energy level and decreases the band gap. The broad absorption and small optical band gap make these polymers promising materials for PSCs. The photophysical parameters are also tabulated in Table 2.

Table 2 Optical and electrochemical properties of three isoindigo-based conjugated polymers

	Solution λ (nm)[a]	Film λ (nm)[b]			oxidation (V, vs Ag/Ag$^+$ in CH_3CN)	
Polymer	λ_{max}^{abs}	λ_{max}^{abs}	λ_{onset}^{abs}	E_g^{opt} (eV)[c]	HOMO (eV)	LUMO (eV)
P1	633, 347	644,358	775	1.60	-5.44	-3.84
P2	608, 336	668,338	761	1.63	-5.49	-3.86
P3	575, 328	627,353	765	1.62	-5.52	-3.90

[a] Measured in dichlorobenzene solution. [b] Thin film spin-coated from chlorobenzene solution. [c] Calculated from the UV absorption band edge of the copolymers film by the equation, $E_g^{opt} = 1240/\lambda_{edge}$



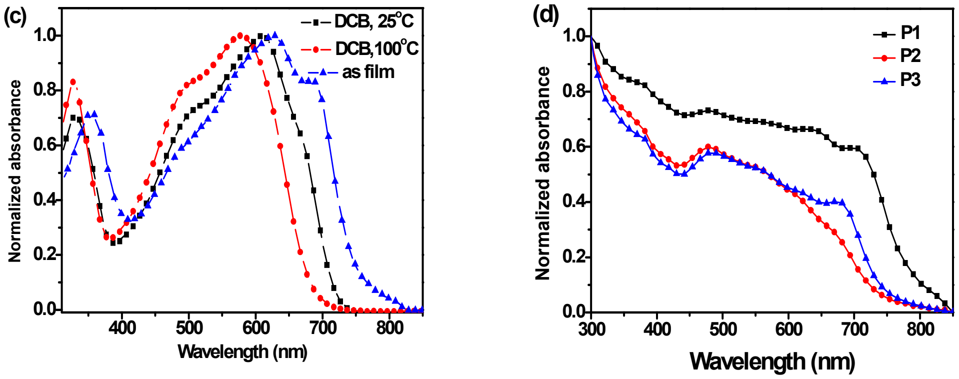


Figure 2. Normalized UV–vis absorption spectra of **P1**(a),**P2**(b),and **P3** (c)in dichlorobenzene solutions at 25 °C, 100 °C, and as films, respectively, and (d) in the blend films with the ratio of polymer to $PC_{71}BM$ of 1:2.

Electrochemical properties

Electrochemical properties of **P1-3** were investigated by cyclic voltammetry (CV) with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) solution in acetonitrile using polymer films on the Pt working electrode with a scanning rate of 50 mVs^{-1} under nitrogen atmosphere at room temperature. CV curves of polymer films are shown in Figure 3, and the electrochemical data are also summarized in Table 2. HOMO energy levels of **P1**, **P2**, and **P3** were calculated to be -5.44, -5.49 and -5.52 eV, respectively, from the onset of oxidative peaks using the equation E_{HOMO}= -e(E_{ox} + 4.71) (eV), where E_{ox} is the onset oxidation potential in volts. Considering that the open circuit voltage (V_{oc}) of PSCs is correlated to the difference of the LUMO energy level of acceptor and the HOMO energy level of donor polymer, the deep HOMO level of **P1-3** is prone to give high V_{oc} PSCs. The two substituents on benzothiadiazole unit can slightly affect the HOMO energy level of copolymers. The HOMO energy level of non-substituted benzothiadiazole based **P2** is -5.49eV. **P1** with two electron donating octyloxy substitutes on the 5,6-positions of benzothiadiazole unit showed the highest HOMO energy level of -5.44 eV within these three polymers. The introduction of two electron withdrawing fluoro substituents on the 5,6-positions of benzothiadiazole unit can lower the HOMO energy level of copolymers. **P3** is of the lowest HOMO energy level of -5.52 eV. Therefore higher V_{oc} is expected for **P3**-based PSCs. According to the equation E_{LUMO} = E_{HOMO} + E_{bandgap}, the LUMO energy levels of **P1**, **P2**, and **P3** are calculated to be −3.84, −3.86, and −3.90eV, respectively.

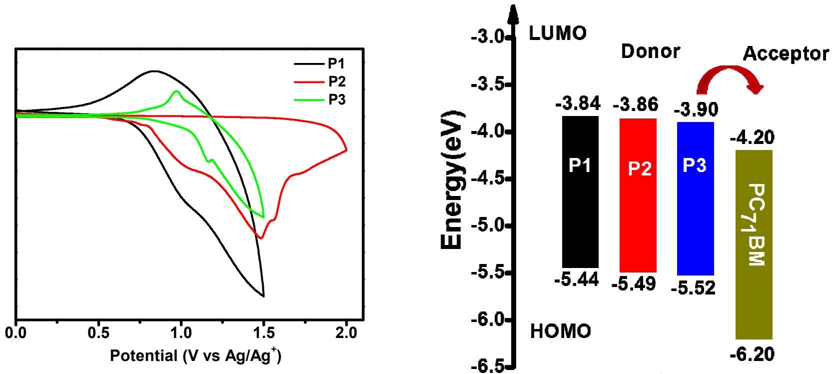


Figure 3 Cyclic voltammograms (left) of **P1-3** films in 0.1 M Bu_4NPF_6/CH_3CN solutions with a scanning rate of 50 mVs^{-1}. Energy level diagrams (right) for **P1**, **P2**, and **P3** as donor and $PC_{71}BM$ as acceptor.

Field-effect transistor fabrication and characterization

High efficiency polymer solar cells require that the donor acceptor blend films are of balanced charge carrier mobility. Carrier transport properties of polymers were therefore investigated by fabrication of bottom-gate/top-contact organic thin film field effect transistors (FETs). Thin film FETs were fabricated by spin coating the polymer solutions in 1,2,4-trichlorobenzene (TCB) on the OTS-modified Si/SiO_2 substrates. The as-prepared spin-coated **P1-3** films did not exhibit observable field effect; therefore polymer films, which were subjected to thermal annealing at 160 °C for 30 min, were used for the FET measurements. The output and transfer characteristic curves of **P1**, **P2**, and **P3** films on OTS-treated Si/SiO_2 substrates are shown in Figure 4. Hole mobilities (μ) of **P1**, **P2**, and **P3** were estimated to be 6.01×10^{-4}, 1.28×10^{-3} and 1.94×10^{-4} $cm^2V^{-1}s^{-1}$, respectively, from the derivative plots of the square root of source-drain current (I_{SD}) versus gate voltage

(V_G) in the saturated regime through equation I_{SD} = $(W/2L)C_i\mu(V_G - V_T)^2$ where W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer (SiO_2, 500 nm, C_i = 7.5 nF/cm^2), and V_T is the threshold voltage. The on/off ratios of **P1**, **P2**, and **P3** based devices are 1.0×10^4, 6.6×10^3, and 6.0×10^3, respectively.

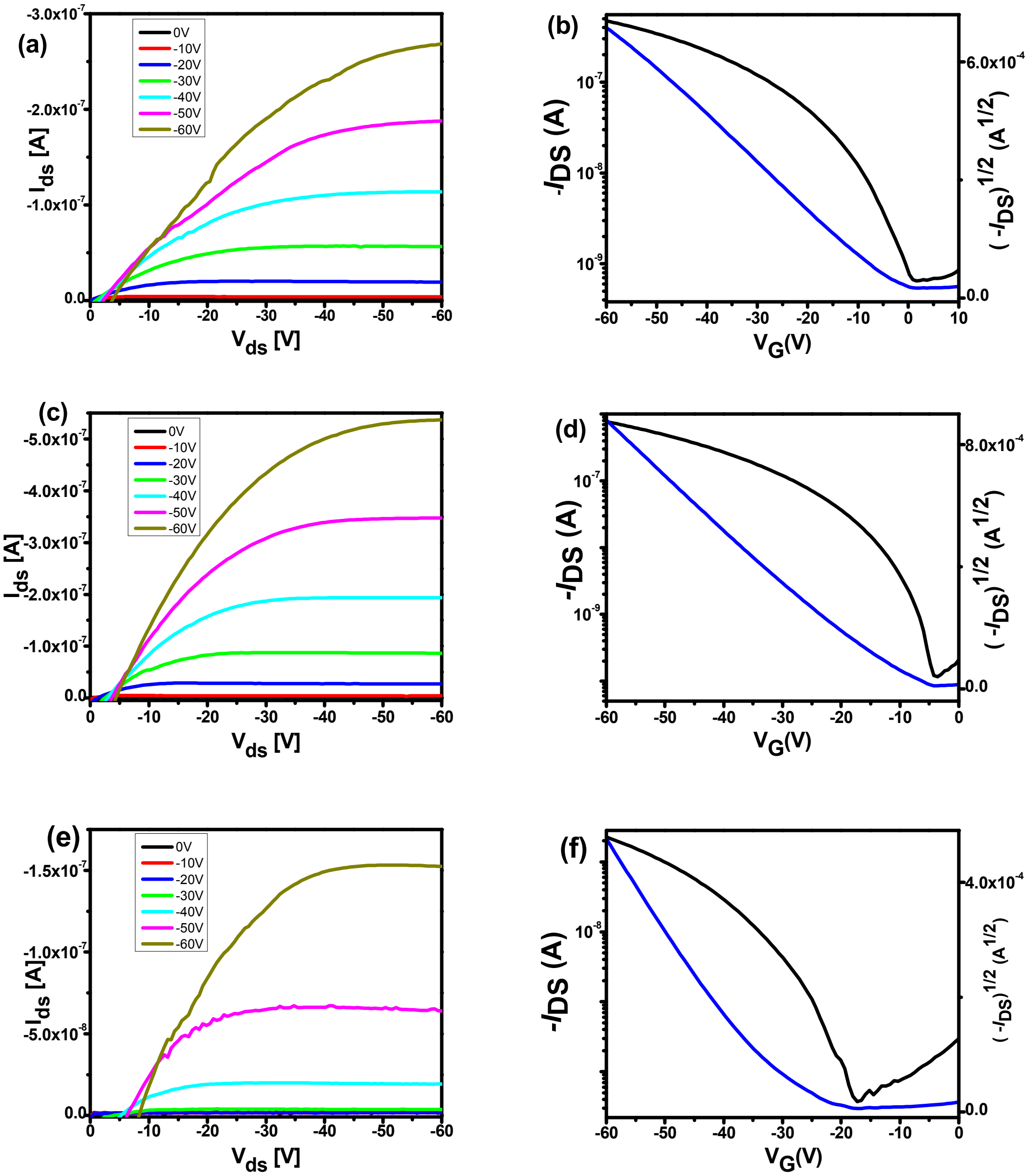


Figure 4. Output and transfer characteristics of (a, b) **P1**, (c, d) **P2**, and (e, f) **P3** devices (spin-coated from TCB solutions, 10 mg/mL) at V_{SD} = −60 V (L = 50 µm, W = 2.5 mm) after thermal annealing at 160 °C for 30 min.

Photovoltaic properties

The broad absorption, narrow band gap, and appropriate HOMO/LUMO energy level make these polymers promising donor materials for BHJ PSCs. Bulk heterojunction solar cells were fabricated with a device structure of glass/ITO/PEDOT:PSS/active layer/LiF/Al. The thicknesses of PEDOT:PSS, LiF, and Al are 40, 0.5, and 100 nm, respectively. Photovoltaic properties of **P1−3** were firstly investigated by blending **P1−3** and $PC_{71}BM$ in DCB in different weight ratios, different concentrations, and different spin-coating speeds. When pure DCB was used as the processing solvent, PSCs with polymer:$PC_{71}BM$ (1:2, by weight) as the active layer gave the best device performance. Namely, **P1** based PSCs showed a V_{oc} of 0.78 V, a short circuit current (J_{sc}) of 7.89 mA/cm^2, a fill factor (*FF*) of 0.45, and a power conversion efficiency (PCE) of 2.75%; **P2** based polymer solar cells showed a V_{oc} of 0.83 V, a J_{sc} of 5.79 mA/cm^2, an *FF* of 0.47, and a PCE of 2.25%; and **P3** based devices showed a V_{oc} of 0.92 V, a J_{sc} of 7.02 mA/cm^2, an *FF* of 0.43, and a PCE of 2.79%. The use of 1,8-diiodooctance

(DIO) as the additive for DCB, the performance of PSCs can be markedly improved for **P2**, but decreased for **P1** and **P3**. PSCs fabricated with the blend of polymer and $PC_{71}BM$ in a weight ratio of 1:2, the blend concentration of 28 mg/mL, DCB containing DIO (2.0%, by volume) as the solvent gave the best performance for **P2**. The highest PCE for **P2** based PSCs reached 3.41% with a J_{sc} of 7.57 mA/cm^2, a V_{oc} of 0.85 V, and an *FF* of 0.53. In contrast to **P2**, PCEs of **P1** and **P3** based PSCs were drastically decreased after the addition of DIO (2.0%, by volume) as an additive. Devices showed a PCE of 1.97% with a J_{sc} of 5.03 mA/cm^2, a V_{oc} of 0.76 V, and an *FF* of 0.51 for **P1** and a PCE of 1.50% with a V_{oc} of 0.78 V, a J_{sc} of 3.58 mA/cm^2 and an *FF* of 0.54 for **P3**. The highest V_{oc} of **P3** based PSCs is ascribed to the deepest HOMO energy level of **P3** among these three polymers, due to the strong electron withdrawing effect of the fluorine atoms. Current density−voltage (*J−V*) curves of the optimized photovoltaic cells are shown in Figure 5. All devices are tested under 1 sun of simulated AM 1.5G solar radiation (100 mW/cm^2) and the data are summarized in Table 3. To evaluate the accuracy of the J_{sc} measurement results, external quantum efficiencies (EQEs) of PSCs were measured under illumination of monochromatic light. As shown in Figure 5b, PSCs based on **P1-3**:$PC_{71}BM$ (1:2, by weight) fabricated without (**P1** and **P3**) and with 2% DIO as additive (**P2**) exhibited a significant broad photoresponse ranging from 400 to 750 nm, which is consistent with the UV-vis absorption spectra of the blend film shown in Figure 2d. All current intensity (J_{sc}) values calculated from integration of the EQEs of the devices with an AM 1.5G reference spectrum agreed well with the J_{sc} values obtained from the J-V measurements.

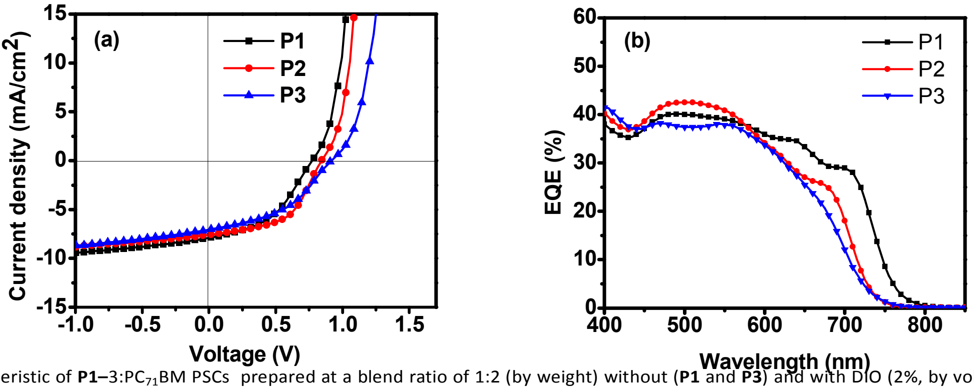


Fig. 5 (a) J–V characteristic of **P1**–3:$PC_{71}BM$ PSCs prepared at a blend ratio of 1:2 (by weight) without (**P1** and **P3**) and with DIO (2%, by volume) (**P2**) as the additive; (b) EQE curves of the optimized **P1–3** devices.

Table 3. Device Performance of polymer (**P1-P3**):$PC_{71}BM$ at a ratio of 1:2 (by weight) Devices [a]

Active layer	Solvent	J_{sc}(mA cm^{-2})	V_{oc} (V)	*FF*	PCE (%)	Thickness (nm)
P1:$PC_{71}BM$	DCB	7.89	0.78	0.45	2.75 (2.66)	113
P1:$PC_{71}BM$	DCB+ 2% DIO	5.03	0.76	0.51	1.97 (1.88)	98
P2:$PC_{71}BM$	DCB	5.79	0.83	0.47	2.25 (2.13)	115
P2:$PC_{71}BM$	DCB+ 2% DIO	7.57	0.85	0.53	3.41 (3.13)	111
P3:$PC_{71}BM$	DCB	7.02	0.92	0.43	2.79 (2.70)	92
P3:$PC_{71}BM$	DCB+ 2% DIO	3.58	0.78	0.54	1.50 (1.40)	109

[a] The average PCE in parentheses were calculated using at least 3 devices for each condition.

Morphology

The morphology of active layer is considered to be a key factor that dictates PCE of PSCs. We used atomic force microscopic (AFM) operating in tapping mode to investigate the surface morphology of the active layer. AFM images of **P1-3**:$PC_{71}BM$ (1:2, by weight) blend films spin coated from DCB solutions without or with DIO (2.0%, by volume) are shown in Figure 6. Without DIO, all the blend films show rather smooth surface morphology with apparent phase separation as shown in Figure

6a-c. The root-mean-square (rms) values are 1.93 nm for **P1**, 1.49 nm for **P2**, and 1.20 nm for **P3**. When 2.0% DIO was used as the additive for DCB, the morphology of **P1:**$PC_{71}BM$ and **P3**:$PC_{71}BM$ blend films became apparently rougher, and the domain size got larger. The rms values were increased to 7.25 and 3.64 nm, for **P1** and **P3** based blend films, respectively. The increase of domain size may be responsible for the decreasing the PCE for **P1** and **P3** based PSCs fabricated with the addition of DIO. For **P2**:$PC_{71}BM$ blend films, the addition of 2% DIO only brought about slight increasing of domain size and rms value (1.99 nm). It is apparent that the appropriate phase separation and the decreasing of domain size are favorable for efficient charge separation and transportation in the active layer. AFM results are consistent with the device performances.

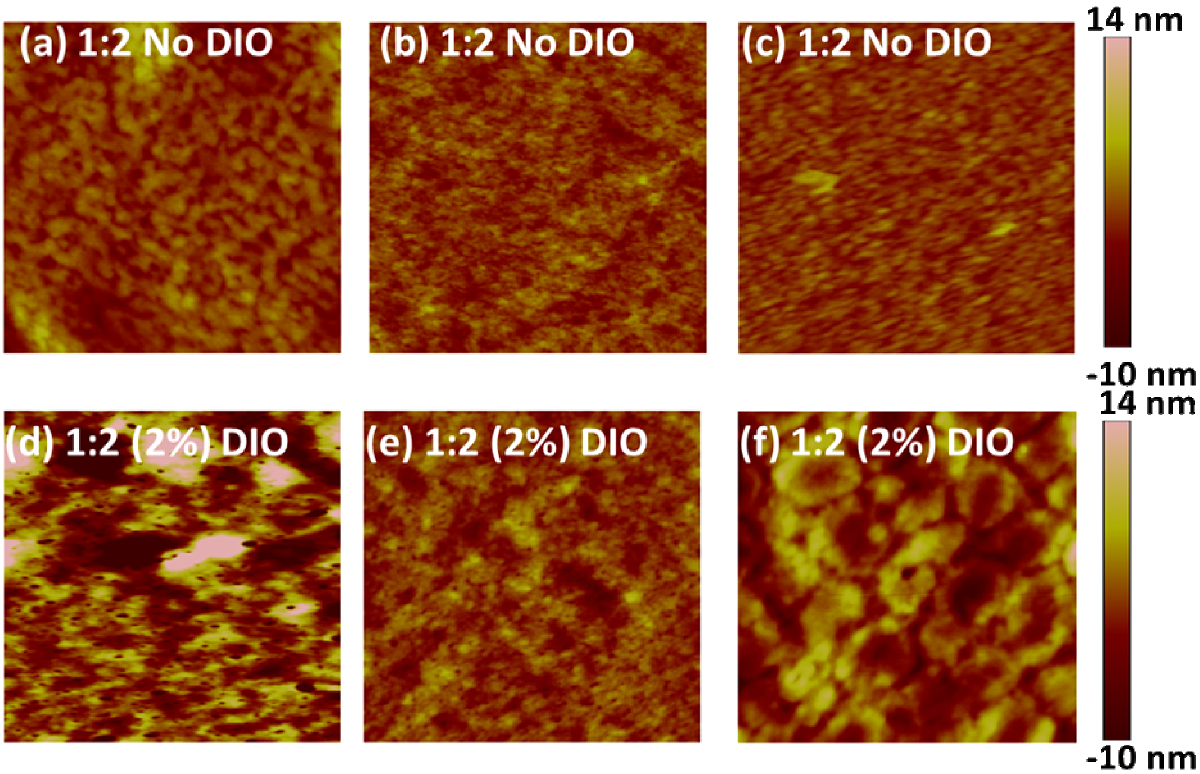


Fig.6 Tapping mode AFM height images (2×2μm) of (a) **P1**:$PC_{71}BM$, (b) **P2**:$PC_{71}BM$, and (c) **P3**:$PC_{71}BM$ in a weight ratio of 1:2 spin coated from DCB solutions; for (d) **P1**:$PC_{71}BM$, (e) **P2**:$PC_{71}BM$, and (f) **P3**:$PC_{71}BM$ with 2% DIO as the additive.

Conclusions

In summary, three new D-A type π-conjugated polymers **P1-3** containing two different acceptor units in the polymer main chain have been synthesized and used as donor materials for PSCs. As films, these polymers are of broad absorption ranging from 300 to 750 nm, narrow band gap around 1.60 eV, and deep HOMO energy level from -5.44 to -5.52 eV. The hole mobilities of **P1-3** films are ranging from 1.94×10^{-4} to 1.28×10^{-3} $cm^2V^{-1}s^{-1}$. Polymer solar cells fabricated with the blends of **P2**:$PC_{71}BM$ as the active layer using DCB as the solvent and 2.0% DIO as the additive gave the maximum PCE of 3.41% with a J_{sc} of 7.57 mA/cm^2, a V_{oc} = 0.85 V, and an *FF* of 0.53. These results demonstrate that two different acceptor units can be used to construct D-A type conjugated polymers to achieve appropriate energy levels for PSC applications.

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Notes and references

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†Electronic Supplementary Information (ESI) available: [XRD patterns, ^1H and ^{13}C NMR spectra, output and transfer characteristic curves of blend films and DSC curves]. See DOI: 10.1039/b000000x/

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Engineering the band gap and energy level of conjugated polymers using a second acceptor unit

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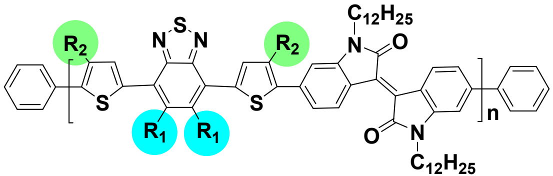
Three conjugated polymers containing two different acceptor units were prepared and used for field effect transistors and polymer solar cells.



P1: $R_1 = OC_8H_{17}$, $R_2 = H$
P2: $R_1 = H$, $R_2 = C_8H_{17}$
P3: $R_1 = F$, $R_2 = C_8H_{17}$