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HOMO Energy Level Regulation of Novel Conjugated Copolymers for Polymer Solar Cells

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Three novel donor-acceptor (D-A) conjugated copolymers for polymer solar cells (PSC) were presented in this work. By Stille coupling polymerization, indacenodithiophene (IDT) as an electron-rich unit was conjugated with an electron-deficient unit of isoindigo (IID), which led to a novel alternative copolymer IDT-IID (**P1**). Two electron-deficient units, 2,1,3-benzooxadiazole (BO) and diketopyrrolopyrrole (DPP), were respectively introduced in the polymerization of **P1**, and two novel IDT-based D-A_1-D-A_2 random copolymers IDT-IID-IDT-BO (**P2**) and IDT-IID-IDT-DPP (**P3**) were obtained. Thermal properties test indicates that these molecules possess relative stability and are suitable for solar cell applications. Optical and electrochemical measurements revealed that the HOMO energy levels of the three copolymers were -5.46 eV, -5.34 eV, and -5.23 eV respectively while the LUMO levels almost keep stable around -3.56 eV, and the low bandgap levels lead to a complete absorption in visible region from 300 to 800 nm. The PSCs based on these copolymers were fabricated with the structure of ITO/PEDOT:PSS/polymer: $PC_{71}BM$/Ca/Al, and the photovoltaic properties disclosed the relatively high values of open circuit voltage (V_{oc}) due to low-lying HOMO energy levels of each copolymer. Hole mobility and atomic force microscope (AFM) study were applied to improve the PSCs performance. Our work provide an efficient method to regulate the HOMO energy levels which will be benefit for PSCs by synthesizing different conjugated copolymers.

Introduction

In the past decades, extraordinary efforts have been made in the development of polymer solar cell (PSC) to strive for large area, solution processed, and highly efficient solar cells.[1] Recently, PSCs based on conjugated polymers as electron donor materials blended with [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) as an electron acceptor material have been achieved surpassing 10% of the power conversion efficiency (PCE) by bulk-heterojunction (BHJ) configuration.[2] Recently, Cao and other groups have successively achieved for high PCEs of 10.61% and 10.8% for PSCs.[3] Nevertheless, more efforts are still required to achieve the PCE of 15% for the photovoltaic technology to reach for large scale applications.[4]
PSCs research has focused on the design and synthesis of high performance polymer materials to improve open-circuit voltage (Voc), short-circuit current density (J_{SC}) and fill factor (FF). Voc is typically linearly proportional to the difference in energy between the highest occupied molecular orbital (HOMO) of the polymer and the lowest unoccupied molecular orbital(LUMO) of the fullerene. Actually, the HOMO level can be decreased by introducing the "strong acceptor" to increase the V_{OC}.[5] On the other hand, J_{SC} is mainly determined by the amount of absorbed light and the width of the absorption in the spectrum of sunlight, while FF value can be increased through a number of factors concerning both materials and processing conditions. So it is well known that the development of novel materials is the key solution to achieve high efficiency PSCs. Unfortunately, up to now, many PSCs conjugated polymers only absorb in a limited region of the solar spectrum and do not exhibit satisfying PCE. To solve this problem, two effective approaches have been adopted, where one is to fabricate tandem devices, and the other is to synthesize a random polymer with one donor in conjugation with two acceptors.[6] Tandem solar devices consist of several single cells, which result combined absorption covers a broader region of the solar spectrum. But the fabrication process is too complicated for practical operation. As for the second approach, the polymer with different monomers with a complementary absorption range could show the broadening of the absorption spectrum. As we know, the molecular structures result inconsistent values of Voc for the photovoltaic devices because their HOMO and LUMO energy levels are largely localized on the donor and acceptor units, respectively.[7] Therefore, random polymer has great potential for improving the performance of PSCs.
In this work, we report synthesis of a D-A copolymer IDT-IID (**P1**) in which indacenodithiophene (IDT) is used as donor and isoindigo (IID) as acceptor for PSCs, as shown in Scheme 1. As a strong electron acceptor unit, IID bears two symmetrical oxindole motifs and can be regarded as a compound with

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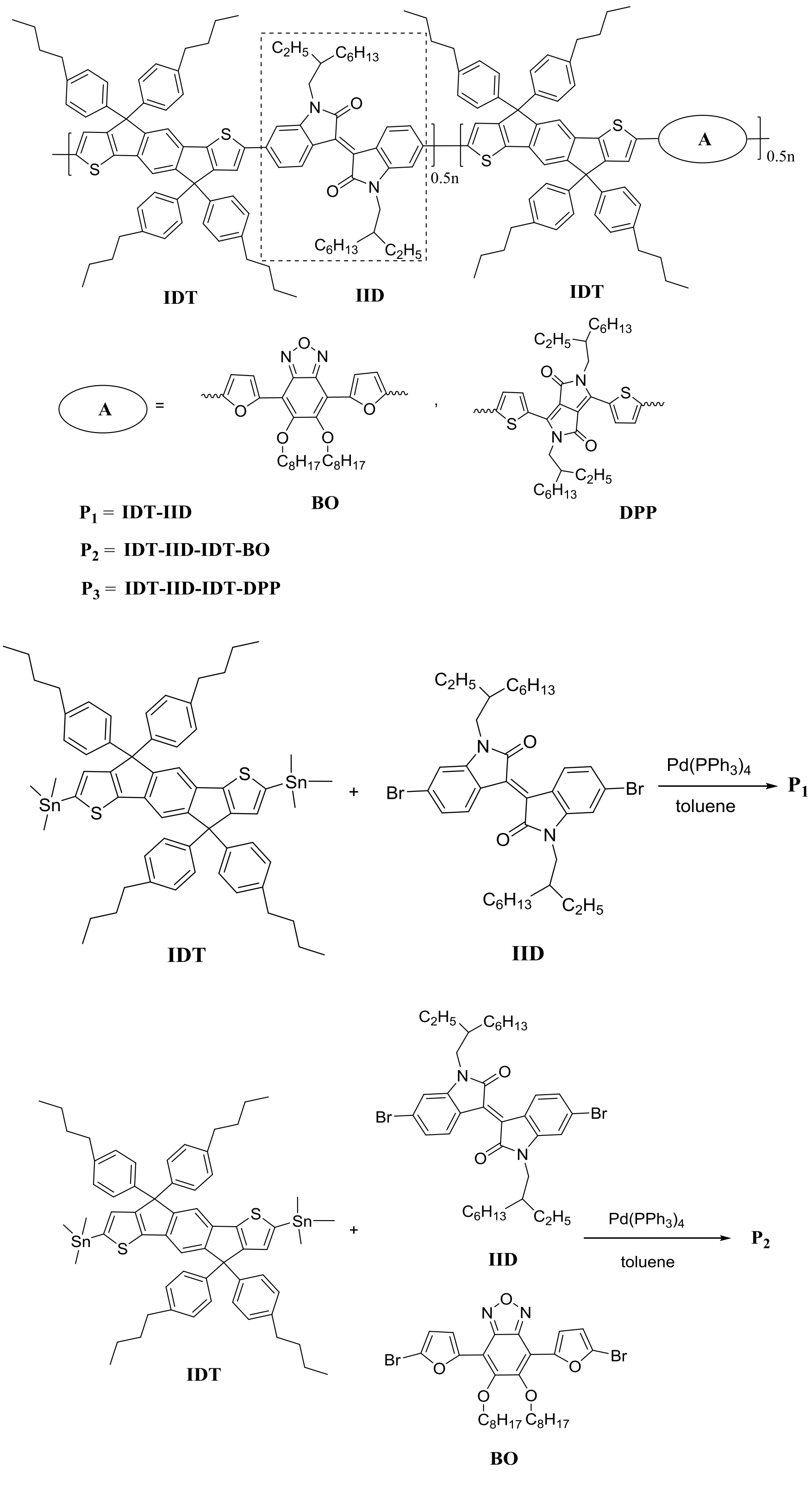
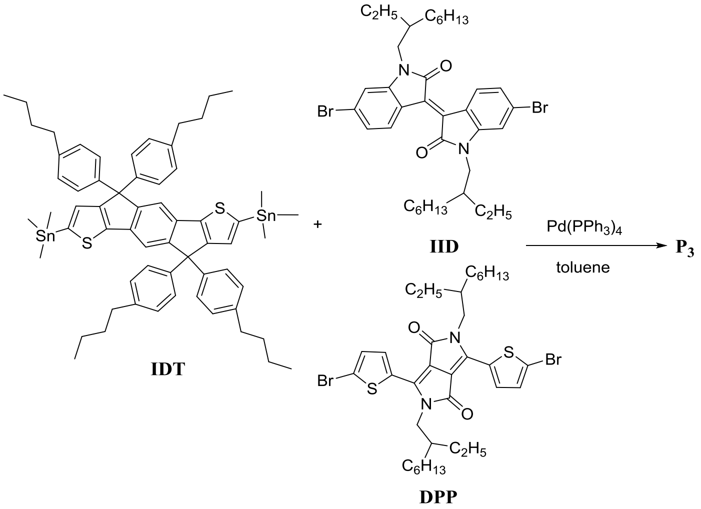
trans-stilbene hydrocarbon backbone linked by two lactam rings. The two lactam rings affiliated to adjacent aryl rings in IID ensure its planar molecular structure.[8] The representative IID-based polymers absorb photons near 750 nm in wavelength with a low-lying HOMO level of around -5.9 eV.[6] For comparison, other two electron-deficient units, BO and DPP, were respectively introduced in the polymerization of **P1**, and two novel D-A$_1$-D-A$_2$ conjugated random copolymers IDT-





Scheme 1 Chemical structures and synthesis of the conjugated copolymers.

IID-IDT-BO (**P2**) and IDT-IID-IDT-DPP (**P3**) were obtained (Scheme 1). Unit BO, 2,1,3-benzooxadiazole, a typically used monomer in a quinoid structure, is also a strongly electron-accepting moiety that has been used in conjugated polymers for PSCs with strong absorption peak near 600 nm and with a low-lying HOMO level of around -5.4 eV.[7] Meanwhile, unit DPP, diketopyrrolopyrrole, possesses a lactam structure and planar, well-conjugated skeletons that give rise to strong π-π interactions and result in absorptions in the near-infrared (NIR) region.[9] The DPP-based polymers show NIR absorption over 900 nm with a high lying HOMO level around -5.2 eV.[6] So it is expected that random copolymerization of the three units can regulate the HOMO energy level as well as the absorption range of the resulting polymers.

Experimental

Materials

All commercially obtained reagents were used without further purification. (4,4,9,9-Tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis (trimethyl-stannane) (IDT) and 6,6'-dibromo-1,1'-bis(2-ethylhexyl)- [3,3'-biindolinylidene]-2,2'-dione (IID) were purchased from SunaTech Inc. and used without further purification. 4,7-Bis(5-bromofuran-2-yl)-5,6-bis(octyloxy) benzo[c][1,2,5]-oxadiazole (DFBO)[10] and 2,5-diethylhexyl-3,6-bis(5- bromothiophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione (DPP)[11] were synthesized according to the reported methods. All the solvents for reactions and photophysical measurements were distilled after dehydration according to conventional methods.

Measurement and characterization

^{1}H NMR spectra were recorded with a Bruker DMX-400 spectrometer. Thermogravimetric analysis (TGA) was performed by a PerkinElmer Pyris. UV-visible absorption spectra were recorded on a Perkin Elmer Lambda 950. Cyclic voltammetry (CV) of the polymer film was measured on a CHI650B potentiostat. Surface images were obtained on a Veeco Dimension 3100 V atomic force microscope (AFM).

Synthesis of polymers

Polymers of **P1**, **P2**, and **P3** were synthesized by Stille coupling polymerization in basically identical process. Briefly, polymers were synthesized as following:

Synthesis of **P1**. A mixture of IDT (200 mg, 0.178 mmol) and IID (124 mg, 0.178 mmol) was dissolved in 4 mL of anhydrous toluene. The solution was flushed with argon for 10 min, and then 5 mg of $Pd(PPh_3)_4$ was added into the flask. The flask was degassed and filled argon cycles three times. The reaction mixture was stirred at 120 °C for 36 h under argon atmosphere. Then, the mixture was cooled to room temperature and poured slowly into 200 mL of methanol. The precipitates were filtered and washed with methanol, acetone, and hexane in a Soxhlet apparatus to remove the oligomers and catalyst residues. Finally, the polymer was extracted with chloroform. The solution was condensed by evaporation and precipitated into methanol. The precipitates were collected and dried under vacuum to give polymer **P1** (147 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.47−7.22 (br, 16H), 7.13−6.95 (br, 10H), 2.59 (br, 6H), 1.61 (br, 8H), 1.31 (br, 40H), 0.97−0.89 (br, 24H).

Synthesis of **P2**. A similar treatment of IDT (200 mg, 0.178 mmol), DFBO (59 mg, 0.089 mmol) and IID (62 mg, 0.089 mmol) obtained 152 mg of polymer **P2** (65% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.47−7.23 (br, 30H), 7.12−6.96 (br, 20H), 2.59 (br, 18H), 1.61 (br, 14H), 1.31 (br, 74H), 0.97−0.89 (br, 42H).

Synthesis of **P3**. A mixture of IDT (200 mg, 0.178 mmol), DPP (66 mg, 0.089 mmol) and IID (62 mg, 0.089 mmol) was polymerized to get 159 mg of polymer **P3** (67% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.47−7.23 (br, 30H), 7.12−6.96 (br, 20H), 2.59 (br, 16H), 1.61 (br, 12H), 1.31 (br, 78H), 0.97−0.89 (br, 48H).

Device fabrication

All organic photovoltaic devices were fabricated with the conventional architecture of ITO/PEDOT:PSS/polymer: $PC_{71}BM$/Ca/Al. ITO coated glass substrates were cleaned ultrasonically in detergent, water, acetone, and iso-propanol (IPA) sequentially, followed by treating in an ultraviolet ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 min. The cleaned substrates were covered with PEDOT:PSS (Baytron PV PAI 4083, Germany) by spin coating. After annealing in a glovebox at 140 °C for 20 min, the samples were cooled to room temperature. Polymers were dissolved in dichlorobenzene (DCB) mixed with 3% (v/v) 1-chloronaphthalene (CN), and then $PC_{71}BM$ was added. The solution was heated at 60 °C and stirred overnight. Then the solution of polymer:$PC_{71}BM$ was spin-coated onto the PEDOT:PSS coated ITO to form the active layer. The devices were completed after the deposition of Ca/Al as the cathode through a shadow mask under high vacuum ($<10^{-6}$ Torr). Typical devices were thermally annealed at 120 °C after putting the top contact. The effective area of the device was measured to be 0.1257 cm^2. The current-voltage (I-V) characteristics of all the photovoltaic cells were measured in the Argon atmosphere under the simulated solar light (100 mW cm^{-2}; AM 1.5 G) provided by a Newport-Oriel® Sol3A 450 W solar simulator without encapsulation. Electrical data were recorded using a Keithley 2440 source meter, and the intensity of the simulated solar light was calibrated by a standard Si photodiode detector (PV measurements Inc.), which was calibrated at National Renewable Energy Laboratory of the United States.

Results and discussion

Thermal properties

The thermal properties of the copolymers were determined by thermogravimetric analysis (TGA) under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The synthesized copolymers **P1**, **P2**, and **P3** all showed good thermal stability with onset decomposition temperatures (T_d) corresponding to a 5% weight loss at 426 °C, 349 °C and 419 °C, respectively (Table 1 and Fig. 1). Such high T_d values indicate that these molecules possess relative stability, and may be suitable for solar cell applications.

Table 1 Molecular weights and thermal properties of the copolymers.

copolymers	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI	T_d (°C)
P1	23.5	51.7	2.2	426
P2	31.2	59.2	1.9	349
P3	27.6	71.7	2.6	419

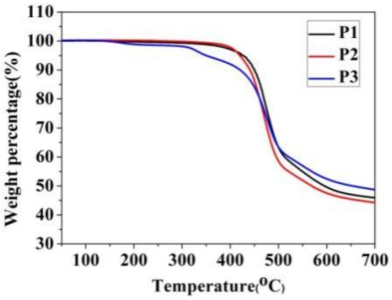


Fig. 1 TGA curves of copolymers at scan rate of 10 °C min^{-1}.

Optical properties

Fig. 2 shows the absorption spectra of the synthesized polymers **P1**, **P2**, and **P3** in chloroform solution and in the solid state, respectively. Optical data including the absorption peak wavelengths ($\lambda_{max, abs}$), absorption edge wavelengths ($\lambda_{edge, abs}$), and optical band gaps (E_g^{opt}) are summarized in Table 2.

It can be seen that the relative position and intensity of the absorption peaks of the conjugated copolymers can be effectively tuned by importing BO or DPP unit. In chloroform solution, the maximum absorption peaks (λ_{max}) of **P1**, **P2**, and **P3** are located at 694 nm, 623 nm and 714 nm, respectively, whereas they are correspondingly located at 676 nm, 619 nm and 683 nm in the solid state. The main absorption peak in the solution for the **P2** was shifted to 623 nm, which shows an obvious shorter wavelength upon introducing themonomer of BO unit compared to **P1** at 694 nm. On the other hand, the main absorption peak for **P3** was red-shifted to 714 nm by the presence of DPP unit. These results indicate that the absorption spectra of the polymers can be readily changed by BO units and DPP unit. The absorption spectra of the three polymers in the solid state are similar to their corresponding solution spectra. The film absorption spectrum of each of these three copolymers features two absorption bands: one at 300-500 nm, which we assign to the localized π-π* transitions,[12] and the other, broader band in the long wavelength region, from 500 to 800 nm, which can be ascribed

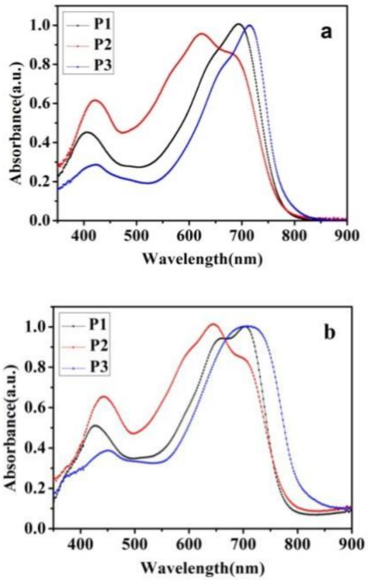


Fig. 2 UV–Vis absorption spectra of three copolymers: (a) in diluted chloroform solution, and (b) in thin film.

Table 2 Optical and electrochemical properties of the copolymers.

copolymers	Solution		Film		E_g^{opt}	HOMO	LUMO	E_g^{ec}
	λ_{max}(nm)	λ_{onset}(nm)	λ_{max}(nm)	λ_{onset}(nm)	(eV)	(eV)	(eV)	(eV)
P1	694/406	788	676/402	759	1.63	-5.46	-3.56	1.90
P2	623/421	789	619/417	772	1.60	-5.34	-3.58	1.76
P3	714/422	811	683/423	802	1.54	-5.23	-3.57	1.66

to the intramolecular charge transfer (ICT) between the acceptor units and the donor units. Therefore, the random copolymers with extended light absorption would provide strong potential for achieving panchromatic PSCs.

Electrochemical properties

The molecular energy levels of the synthesized copolymers **P1**, **P2**, and **P3** were determined by electrochemical cyclic voltammetry (CV). Fig. 3 shows the CV curves of the copolymers films on platinum plate working electrodes in 0.1 mol/L tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6)-acetonitrile solution. Ferrocene was used as the internal standard in each measurement conditions, and it was located at 0.40 eV to the Ag/AgCl electrode.[13] The HOMO and LUMO energy levels were then calculated according to the following equations:[14]

$$HOMO = -e(E_{ox} + 4.4)\ (eV) \quad (1)$$

$$LUMO = -e(E_{red} + 4.4)\ (eV) \quad (2)$$

$$= e(E_{ox} - E_{red})\ (eV) \quad (3)$$

Where E_{ox} is the onset oxidation potential vs Ag/AgCl and E_{red} is the onset reduction potential vs Ag/AgCl.

The LUMO levels of **P1**, **P2**, and **P3** were measured to be −3.56 eV, −3.58 eV, and −3.57 eV whereas their corresponding HOMO levels are −5.46eV, −5.34 eV, and −5.23 eV, respectively (Table 2). The low HOMO energy levels of the random conjugated copolymers are beneficial for their relatively high stability against oxidation and also for a potentially high Voc value for PSCs. Yet the LUMO energy levels of the copolymers are constant (-3.56 eV to -3.58 eV), which were significantly greater than that of $PC_{71}BM$ (ca. 4.1 eV). Thus, we would expect efficient charge transfer/dissociation to occur in their corresponding devices. It can be seen that the HOMO levels of random copolymers have been changed by the introduction of the BO unit and the DPP unit onto their backbones. The electrochemical band gaps (E_g^{ec}) of **P2** and **P3** were 0.11 eV and 0.21 eV smaller than **P1**, respectively. The results clearly indicate that the introduction of new units to the backbones of D-A polymers is an efficient way to decrease their bandgaps by regulating the molecular energy levels. We can predict that the decreased band gaps may lead to a broadened absorption spectral range, which is accordant with the previous optical properties results. In addition, E_g^{ec} of the random copolymers, calculated from the difference between the onset potential for oxidation and reduction, were in the range 1.66-1.87 eV. These values were slightly larger than the corresponding optical band gaps. It is assumed that this difference between the electrochemical and optical band gap resulted from the exciton binding energies of the polymers and the interface barriers for charge injection.[15]

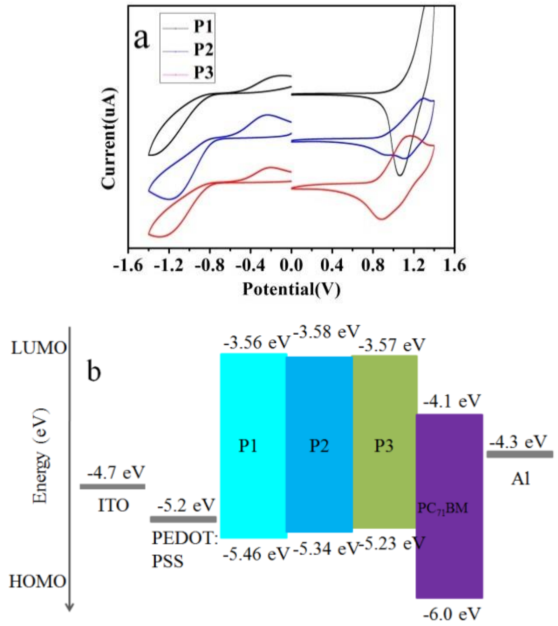


Fig. 3 (a) CV of the copolymers films were casted on platinum wire in 0.1 M Bu_4NPF_6/CH_3CN at a scan rate of 50 mV s^{-1}. (b) Energy level diagram showing the HOMO and LUMO energy levels of all copolymers and $PC_{71}BM$.

Photovoltaic properties

To investigate the photovoltaic properties of the three polymers, we fabricated the PSCs devices with a conventional structure of ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al, where PEDOT:PSS and Ca layers were employed as buffer layers to facilitate hole and electron extractions. The J–V characteristics of the bulk-heterojunction PSCs are shown in Fig. 4. The photovoltaic parameters V_{oc}, J_{sc}, FF, and PCE of the devices were measured under the illumination of AM 1.5G (100

Table 3 J-V parameters for the copolymer/$PC_{71}BM$ PSCs with different treatments.*

Polymer	Ratio (wt%)	treatment	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%) (P_{max})	Hole mobility $cm^2v^{-1}s^{-1}$
P1	1:1	no	0.85	2.66	38.85	0.85 (0.87)	9.81×10^{-7}
	1:1	3%CN	0.83	4.57	36.28	1.34 (1.38)	1.24×10^{-6}
P2	1:2	no	0.80	4.07	35.33	1.13 (1.16)	1.01×10^{-6}
	1:2	3%CN	0.81	5.92	38.78	1.82 (1.87)	1.27×10^{-6}
P3	1:1	no	0.82	4.37	38.00	1.29 (1.36)	1.28×10^{-6}
	1:1	3%CN	0.83	5.28	40.29	1.71 (1.77)	1.71×10^{-6}

*: Averaged from at least 40 devices measurements.

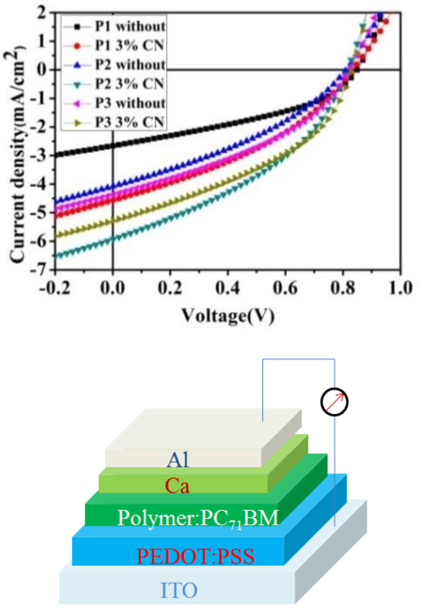


Fig. 4 J-V characteristics of PSCs based on copolymers/$PC_{71}BM$ under the illumination of AM 1.5 G, 100 mW cm^{-2}.

mW/cm^2) and the obtained values are summarized in Table 3.Dichlorobenzene (DCB) was used to prepare the solutions for spin-coating of the active layers, and the concentration of the solutions used was 10 mg/mL. An optimized weight ratio for **P1**:$PC_{71}BM$ and **P3**:$PC_{71}BM$ was found to be 1:1 while **P2**:$PC_{71}BM$ was found to be 1:2. Due to low-lying HOMO energy levels of each copolymer, relatively high values of open circuit voltage (V_{oc}) above 0.80 V were obtained for the devices based on **P1**, **P2**, and **P3** (Table 3). However, the short-circuit current density (J_{sc}) was small for devices based on each polymer and resulted in overall low PCE.

To improve the PCE of the active layer, we also added a small amount of 1-chloronaphthalene (CN; 3% vol., relative to DCB) to process these blends. CN has been reported as a processing additive to increase the compatibility of the polymers and $PC_{71}BM$ and to decrease the domain size.[16] The performance of the devices is enhanced by the formation of nanoscale phase separation of copolymers.[17] The values of V_{oc} and FF of the devices were not affected by the addition of 3% CN to the solvents for processing the polymer:$PC_{71}BM$ blend. However, the J_{sc} increased slightly from 3.16, 3.23 and 4.19 mA/cm^{-2} to 4.49, 5.92, and 5.28 mA cm^{-2}, respectively, which contributed to an enhancement of overall photovoltaic performance.

Hole mobility

From the above discussion, we know that the J_{sc} values of the synthesized copolymer **P1**, **P2**, and **P3** can be increased by the additive CN. In order to explore the effects of additive on charge transport properties, we investigated the carrier mobility of polymer:$PC_{71}BM$ with the space charge limited current (SCLC) model by using hole-only devices (ITO/PEDOT:PSS/ polymer:$PC_{71}BM$/Au),[18] which can be approximated by modified Mott–Gurney's law:[19]

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu_0\frac{V^2}{L^3}$$

where J is the current density, ε_r is the dielectric constant of the polymer, ε_0 is the free-space permittivity (8.85×10^{-12} F/m), μ_0 is the charge mobility at zero field, L is the thickness of the blended film layer, $V = V_{appl}-V_{bi}$, V_{appl} is the applied potential, and V_{bi} is the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure, V_{bi} = 0.2 V). Fig. 5 shows the $J^{1/2}$-（V_{appl}-V_{bi}） curves of the hole-only devices. According to the above equation, the hole mobility of **P1**, **P2** and **P3** was calculated to be 1.24×10^{-6}, 1.27×10^{-6} and 1.71×10^{-6} cm^2 V^{-1} s^{-1} in the hole-only polymer: $PC_{71}BM$ devices, respectively. These values are nearly 1.26, 1.27 and 1.34 times higher than those of the devices without additives (9.81×10^{-7}, 1.01×10^{-6} and 1.28×10^{-6} cm^2 V^{-1} s^{-1}) (Table 3). From the carrier mobility measurement, we concluded that the introduction of additive is beneficial to improve the charge mobility.

The morphology of the photoactive layer also plays an important role in the photovoltaic performance of the PSCs. In some cases the performance of the devices strongly depends on its morphological features.[20] Nanoscale phase separation is an ideal morphology for the active layer in high-performance PSCs, which enables exciton diffusion with a large interface area, and a continuous percolating path for hole and electron transport to the corresponding electrodes.[21] Therefore, the atomic force microscopy (AFM) was used to investigate the surface morphology of the polymer:$PC_{71}BM$ blend (1:1 or 1:2, w/w) spin-coated from DCB solutions with and without the additive 1-chloronaphthalene(CN). AFM images of the polymer: $PC_{71}BM$ blend films are shown in Fig. 6. Surface RMS (root mean- square) roughness of the polymer:$PC_{71}BM$ films without CN was found to be 0.729 nm, 4.37 nm and 0.622 nm for **P1**, **P2** and **P3**, respectively. In contrast, the blend films with CN, showed a smooth surface with a decrease in roughness from 0.729, 4.37, 0.622 nm to 0.616, 2.76, 0.623 nm, respectively. A smooth surface and a good phase separation induce better contact with the electrode and the bicontinuous phase separation improves better charge transport and excitons dissociation, and this will lead to an increase in the short-circuit current density as well as the device efficiency. So this result indicates that the CN additive can be used to modify the morphology of the active layer to achieve better photovoltaic performance.

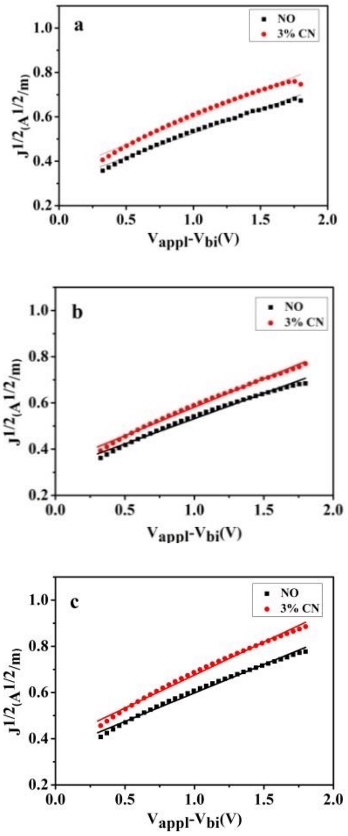


Fig. 5 $J^{1/2}$ versus V_{appl}-V_{bi} plots for the measurement of the hole mobility in polymer:$PC_{71}BM$ blends by the SCLC method. (a) **P1**; (b) **P2**; (c) **P3**.

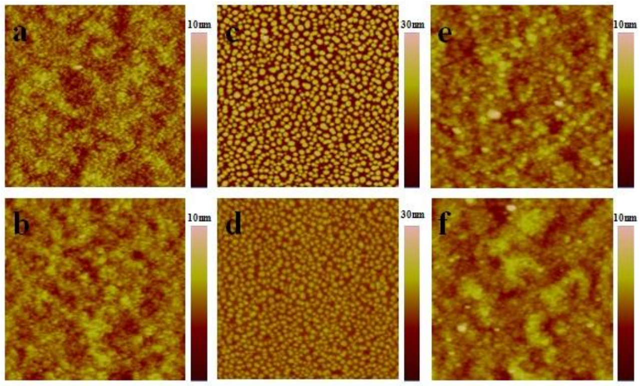


Fig. 6 AFM images of polymer/$PC_{71}BM$ blends (1:1 or 1:2 w/w) cast from dichlorobenzene with or without 3% CN (a) **P1**/$PC_{71}BM$ (1:1) without CN; (b) **P1**/$PC_{71}BM$ (1:1)with 3% CN; (c)**P2**/$PC_{71}BM$ (1:2) without CN; (d)**P2**/$PC_{71}BM$ (1:2) with 3% CN; (e)**P3**/$PC_{71}BM$ (1:1) without CN; (f)**P3**/$PC_{71}BM$ (1:1) with 3% CN.

Conclusions

In summary, a donor (D) unit indacenodithiophene (IDT) and three acceptor (A) units, isoindigo (IID), 2,1,3-benzooxadiazole (BO), and diketopyrrolopyrrole (DPP), were used to synthesize D-A conjugated copolymers by Stille coupling polymerization. A new conjugated alternating copolymer IDT-IID (**P1**) and two new random copolymers IDT-IID-IDT-BO (**P2**) and IDT-IID-IDT-DPP (**P3**) were obtained. By changing the third component in the terpolymers, we have successfully regulated the HOMO energy levels and the optical absorption. The HOMO levels of the three copolymers were measured as -5.46 eV, -5.34 eV, and -5.23 eV respectively and the lower bandgap levels lead to a complete absorption in visible region. These copolymers also possess excellent thermal stability and photovoltaic properties. The PSCs based on these copolymers were fabricated with the structure of ITO/PEDOT:PSS/polymer: $PC_{71}BM$/Ca/Al, and the relatively high values of open circuit voltage (V_{oc}) were obtained due to the low-lying HOMO energy levels of each copolymer.

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Table of Contents

HOMO Energy Level Regulation of Novel Conjugated Copolymers for Polymer Solar Cells

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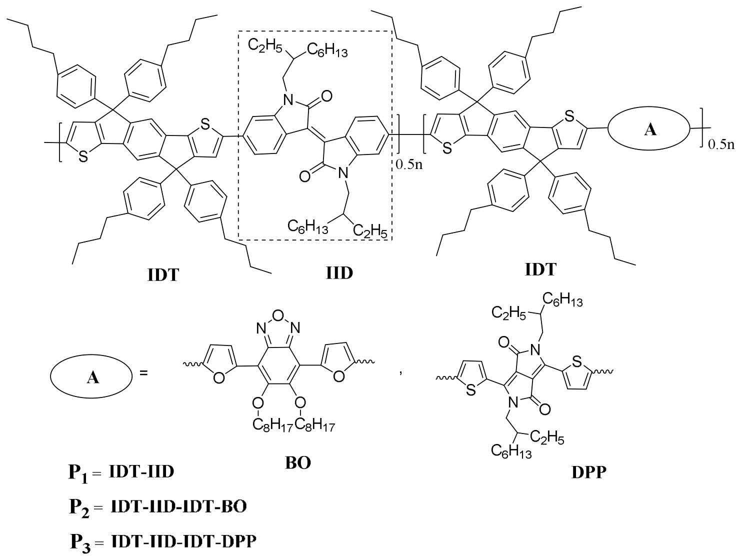

P_1 = IDT-IID

P_2 = IDT-IID-IDT-BO

P_3 = IDT-IID-IDT-DPP

Novel donor-acceptor conjugated copolymers were synthesized, and the HOMOs were regulated to high open circuit voltage and wide spectral absorption.