Polym. Bull. (2011) 67:843–857
DOI 10.1007/s00289-011-0471-6

ORIGINAL PAPER

Synthesis and characterization of n-type conjugated copolymers bearing perylene diimide moieties

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Received: 17 November 2010 / Revised: 6 March 2011 / Accepted: 13 March 2011 /

Abstract Three electron-deficient conjugated polymers based on perylene diimide (PDI) units, namely, poly[(*N*,*N*′-didodecyl-3,4,9,10-perylene diimide-1,7-diyl)-alt-(9,9-dihexylfluorene-2,7-diyl)] (PPDIF), poly{(*N*,*N*′-didodecyl-3,4,9,10-perylene diimide-1,7-diyl)-alt-[*N*-(2-ethylhexyl) carbazole-3, 6-diyl]} (PPDIC) and poly{(*N*,*N*′-didodecyl-3,4,9,10-perylene diimide-1,7-diyl)-co-[*N*-(2-ethylhexyl) carbazole-3,6-diyl]-co-(9,9-dihexylfluorene-2,7-diyl)} (PPDICF) have been synthesized via Suzuki coupling reaction, and their chemical structures are confirmed by ^{1}H NMR, ^{13}C NMR and FT-IR. All these polymers show broad absorption bands in 250–700 nm, and their optical band gaps are calculated to be $\sim$1.7 eV. Cyclic voltammetry results confirm that the objective macromolecules possess high electron affinity of $\sim$3.9 eV. By employing poly-3-hexylthiophene (P3HT) as electron donor and PPDIC as electron acceptor, all polymer solar cells (aPSCs) with bulky heterojunction structure have been fabricated, preliminary results indicate they have

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one of the most highest open-circuit voltage (V_{oc}) (0.86 V) reported so far in aPSCs with PDI-based polymers as electron acceptor.

Keywords Perylene diimide · Conjugated polymer · Carbazole · Fluorene · *n*-Type solar cells materials

Introduction

Polymeric solar cells (PSCs) have attracted considerable attention in recent years, because of their potential for applications in low-cost, lightweight and flexible large-area panel photovoltaic devices by facile printing technologies [1–3], and the record power conversion efficiency (PCE) for PSCs has reached 7.73% [4]. However, PSCs reported with relative high efficiencies generally employ a bulky heterojunction (BHJ) structure with fullerene derivatives, e.g., [6]-phenyl C_{61} or C_{71} butyric acid methyl esters (PCBM) as the electron acceptors [5–7], while they have almost no absorption in the visible-near-infrared region [8–10] despite of their high doping ratio of 80% in the device, and the penalty comes in the term of their little contribution to the light harvesting in the photovoltaic conversion. Therefore, the construction of all polymer solar cells (aPSCs) that based on n-type polymers rather than fullerene derivatives, has drawn much attention recently [11, 12] for the reason that it is more facile to tune both the components of n-type and p-type polymers individually on their optical absorption band and charge transfer, as well as energy level matching. Nevertheless, the PCEs of aPSCs are much inferior to those of fullerene-PSCs, and the record PCE is only 2.32% [13]. Thus, the key challenge for the improvement of PCE lies in exploiting of suitable n-type polymers with high electron affinity, high electron mobility and matchable optical absorption with solar spectrum.

In comparison with well-developed p-type electron-donating conjugated polymers, excellent n-type ones are much less in quantity. Many delicate works have been done to develop cyano or benzothiadiazole modified conjugated polymers as electron-accepting materials, like cyano substituted poly(phenylene vinylene)derivatives (MEH-CN-PPV) [11], poly(1,4-dioctyloxyl-*p*-2,5-dicyanophenyl-enevinylene) (DOCN-PPV) [14] and poly(9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole] (F8TBT) [15]. Recently, another interesting segment, perylene diimide (PDI), has been demonstrated to be a key construction unit as n-type polymer with high electron affinities (E_a) and intense absorption in the visible region with large molar absorption coefficients [16–18], and most of the chemical tailors for PDI-copolymers are focused on the incorporation of electron-donating thiophene segments into their mainchain [19]. As fluorene and carbazole have emerged as the most exceptional components in the development of organic electroluminescent and photovoltaic materials due to their good charge mobility, thermal stability, and photochemical stability [20–24], herein, we report the incorporation of fluorene and carbazole units with PDI to construct three new n-type alternative copolymers.

Experimental

Materials and measurements

All the materials and reagents were purchased from commercial suppliers and used without further purification unless otherwise stated. MEH-PPV and poly-3-hexylthiophene (P3HT) used here have a weight-average $M_{\mathrm{w}} > 400{,}000$ g mol^{-1} (Aldrich co.) Toluene and tetrahydrofuran (THF) were dried from sodium/benzophenone ketyl and freshly distilled prior to use. $[\mathrm{Pd(PPh_3)_4}]$ [25], 1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid dianhydride [26], 2,7-dibromofluorene, 2,7-dibromo-9,9-dihexylfluorene, 9,9-dihexylfluorene-2,7-bis(trimethylene borate) [27], 3,6-dibromocarbazole, 3,6-dibromo-*N*-(2-ethylhexyl)carbazole, and 3,6-bis(5,5-dimethyl-1,3,2-dioxaborolan-2-yl)-*N*-(2-ethylhexyl)carbazole [28] were synthesized according to literature procedures.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV II-400 MHz spectrometer operating at 400 MHz for ^{1}H NMR and at 100 MHz for ^{13}C NMR in deuterated chloroform solutions at 298 K, using tetramethylsilane as an internal standard. FT-IR measurement was performed on a Perkin-Elmer 2000 infrared spectrometer with KBr pellets. UV–Vis absorption spectra of the polymers in 10^{-6} mol L^{-1} chloroform solutions and thin films casted from chlorobenzene solution at 2,000 rpm on quartz substrates were recorded on a Shimadzu UV2100 UV–Vis scanning spectrophotometer. PL spectra of the thin films of polymers blend spin-coated from 1 mg/mL chlorobenzene solution at 2,000 rpm on quartz substrates were measured on an F-7000 fluorescence spectrophotometer. Number-average (M_{n}) and weight-average (M_{w}) molecular weights and polydispersity indices (PDI) of the polymers were determined on a PL-GPC model 210 chromatograph at 25 °C at a flow rate of 1 mL min^{-1}, and the calibration was based on polystyrene standards. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 under nitrogen atmosphere at a heating rate of 10 °C/min. Cyclic voltammetry (CV) was performed on a PARSTAT 2273 electrochemical workstation at a scan rate of 50 mV s^{-1} using tetrabutylammonium perchlorate (0.1 mol L^{-1}) as supporting electrolyte in acetoneitrile. A typical three-electrode cell was used with a Pt disk coated with copolymer films as working electrode, Pt wire as counter electrode, and Ag/Ag^{+} (0.1 mol L^{-1}) as reference electrode [referenced against ferrocene/ferrocenium (Fc/Fc^{+})].

The OPV devices with structure ITO/PEDOT-PSS/P3HT:PPDIC/Al were prepared according to the following procedure: the indium tin oxide (ITO) coated glass substrate, and it was coated with a film of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) PEDOT-PSS in aqueous solution using spin casting technology. After the PEDOT film had dried overnight, the photoactive layer was casted on the top of the PEDOT layer. The aluminum (Al) top electrode was deposited by means of thermal evaporation in vacuum better than 10^{-5} mbar onto the photoactive layer. The photoactive layer was deposited by spin coating at 2,000 rpm from a solution of 10 mg mL^{-1} polymer blend in chlorobenzene.

Synthesis of monomers

*N,N'-didodecyl-1,7-dibromo-3,4,9,10-perylene diimide (**2**) [8]*

Deep red solid. Yield: 75%. ^{1}H NMR(400 MHz, $CDCl_3$) δ (ppm): 9.48(d, $J = 8.4$ Hz, 2H), 8.92(s, 2H), 8.70(d, $J = 8.4$ Hz, 2H), 4.22(t, 4H), 1.77(m, 4H), 1.46–1.28(m, 36H), 0.90(t, 6H). ^{13}C NMR(100 MHz, $CDCl_3$): δ162.63, 162.12, 137.91, 137.83, 132.57, 132.45, 129.79, 128.91, 128.26, 126.70, 123.04, 122.59, 120.73, 40.95, 40.83, 31.93, 29.66, 29.64, 29.57, 29.36, 28.06, 27.12, 22.69, 14.13.

*3,6-Bis(5,5-dimethyl-1,3,2-dioxaborolan-2-yl)-N-(2-ethylhexyl)carbazole (**3**)*

White solid. Yield: 80.6%. Mp: 148–150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.65(s, 2H), 7.88(dd, 2H), 7.35(d, $J = 8.4$ Hz, 2H), 4.16(m, 2H), 3.82(s, 8H), 2.05 (t, 2H), 1.36(m, 8H), 1.06(s, 12H), 0.86(m, 6H).

*9,9-Dihexylfluorene-2,7-bis(trimethylene borate) (**4**)*

White soli. Yield: 83.6%. Mp: 122–123 °C. ^{1}H NMR(400 MHz, $CDCl_3$) δ(ppm): 7.75(d, $J = 6.8$ Hz, 2H), 7.72(s, 2H), 7.69–7.68(d, $J = 7.2$ Hz, 2H), 4.20(t, 8H), 2.09(t, 4H), 1.98(m, 4H), 1.08–0.98 (m, 12H), 0.74(t, 6H), 0.56(m, 4H).

Synthesis of the polymers

Poly{[N,N′-didodecyl-3,4,9,10-perylene diimide-1,7-diyl]-alt-[N-(2-ethylhexyl)carbazole-3,6-diyl]} (PPDIC)

2 (504.4 mg, 0.549 mmol), $Pd(PPh_3)_4$ (15 mg, 13 μmol) and **3** (276.1 mg, 0.549 mmol) were placed in a 50 mL two-neck flask under the protection of argon, followed by addition of deoxygenated toluene (10 mL) and aqueous potassium carbonate (2 mol L^{-1}, 10 mL). The dark red reactant mixture was stirred vigorously at 90 °C for 72 h. After the black sticky solution was cooled to room temperature, 100 mL $CHCl_3$ was added, the organic layer was separated, washed with water (3 × 50 mL), and dried over anhydrous $MgSO_4$. After removal of solvents under vacuum, the resulted sticky residue was poured into methanol (400 mL). The black precipitate was filtered, washed with methanol, and redissolved in $CHCl_3$ (5 mL), followed by precipitation from methanol for three times. The resulted precipitate was collected and dried under vacuum for 24 h. Yield: 92.8%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.79–8.52(br, 4H), 8.07–8.19(br, 4H), 7.84(br, 2H), 7.54(br, 2H), 4.18(br, -N-CH_2-, 6H), 2.19(br, 1H), 1.60(br, 4H), 1.22(br, 40H), 1.03(br, 4H), 0.86(br, 12H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 163.53, 142.84, 141.38, 135.60, 132.82, 129.70, 127.64, 126.99, 124.48, 122.24, 121.79, 111.09, 48.02, 40.59, 39.56, 31.87, 31.16, 29.68, 29.58, 29.30, 28.78, 28.15, 27.14, 24.63, 23.18, 23.01, 22.63, 14.04, 11.09, 10.97. FT-IR (KBr pellet) $\nu = 1697.4$, 1658.2 cm^{-1} (C=O); $\nu = 1326.7$ cm^{-1} (C–N).

Poly{[N,N′-didodecyl-3,4,9,10-perylene diimide-1,7-diyl]-alt-[9,9-dihexylfluorene-2,7-diyl]} (PPDIF)

PPDIF was obtained as a black solid with a yield of 95.6% from the reaction of **2** with **4** according to the procedure described for the synthesis of polymer PPDIC. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.65(br, 2H), 7.85–8.14(br, 6H), 7.40(br, 4H), 4.12(br, $-N-CH_2-$, 4H), 1.56(br, 8H), 1.17(br, 52H), 0.80(br, 12H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 163.63, 163.05, 153.18, 142.50, 141.72, 140.89, 134.47, 133.20, 132.66, 129.37, 129.46, 127.70, 122.23, 55.95, 40.54, 31.89, 31.46, 29.67, 29.61, 29.41, 29.32, 28.18, 27.16, 24.05, 22.64, 14.05, 13.94. FT-IR (KBr pellet) $v = 1699.5, 1658.7\ \mathrm{cm}^{-1}$ (C=O); $v = 1328.0\ \mathrm{cm}^{-1}$ (C–N).

Poly{(N,N′-didodecyl-3,4,9,10-perylenediimide-1,7-diyl)-co-[N-(2-ethylhexyl) carbazole-3,6-diyl]-co-(9,9-dihexylfluorene-2,7-diyl)} (PPDICF)

A procedure similar to the synthesis of PPDIC was used, starting with monomer **2** (0.6439 g, 0.7 mmol), monomer **3** (0.5035 g, 1 mmol), 2,7-dibromo-9,9-dihexylfluorene (0.1477 g, 0.3 mol), dry toluene (20 mL) and $Pd(PPh_3)_4$ (30 mg). PPDICF was obtained as a black solid with a yield of 93.7%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.72(br, 1.5H), 8.13–8.63(br, 2.8H), 7.97(br, 1.5H), 7.52(br, 2H), 7.48(br, 4H), 4.17(br, $-N-CH_2-$, 4.2H), 3.82(br, $-N-CH_2-$, 0.6H), 2.13(br, 1.6H), 1.68(br, 3.6H), 1.24(br, 38H), 0.85(br, 12H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 162.52, 151.57, 140.36, 138.06, 134.93, 134.40, 131.90, 129.14, 128.60, 127.44, 126.52, 125.89, 125.19, 123.36, 121.16, 120.45, 120.09, 119.92, 109.58, 54.68, 46.72, 39.59, 39.15, 38.55, 36.09, 31.75, 30.88, 30.42, 30.11, 29.02, 28.68, 28.59, 28.31, 27.78, 27.15, 26.15, 23.78, 23.61, 22.63, 22.03, 21.64, 21.53, 20.91, 18.72, 13.05, 9.95. FT-IR (KBr pellet) $v = 1696.5, 1658.2\ \mathrm{cm}^{-1}$ (C=O); $v = 1332.8\ \mathrm{cm}^{-1}$ (C–N) (Table 1).

Results and discussion

Synthesis and characterization

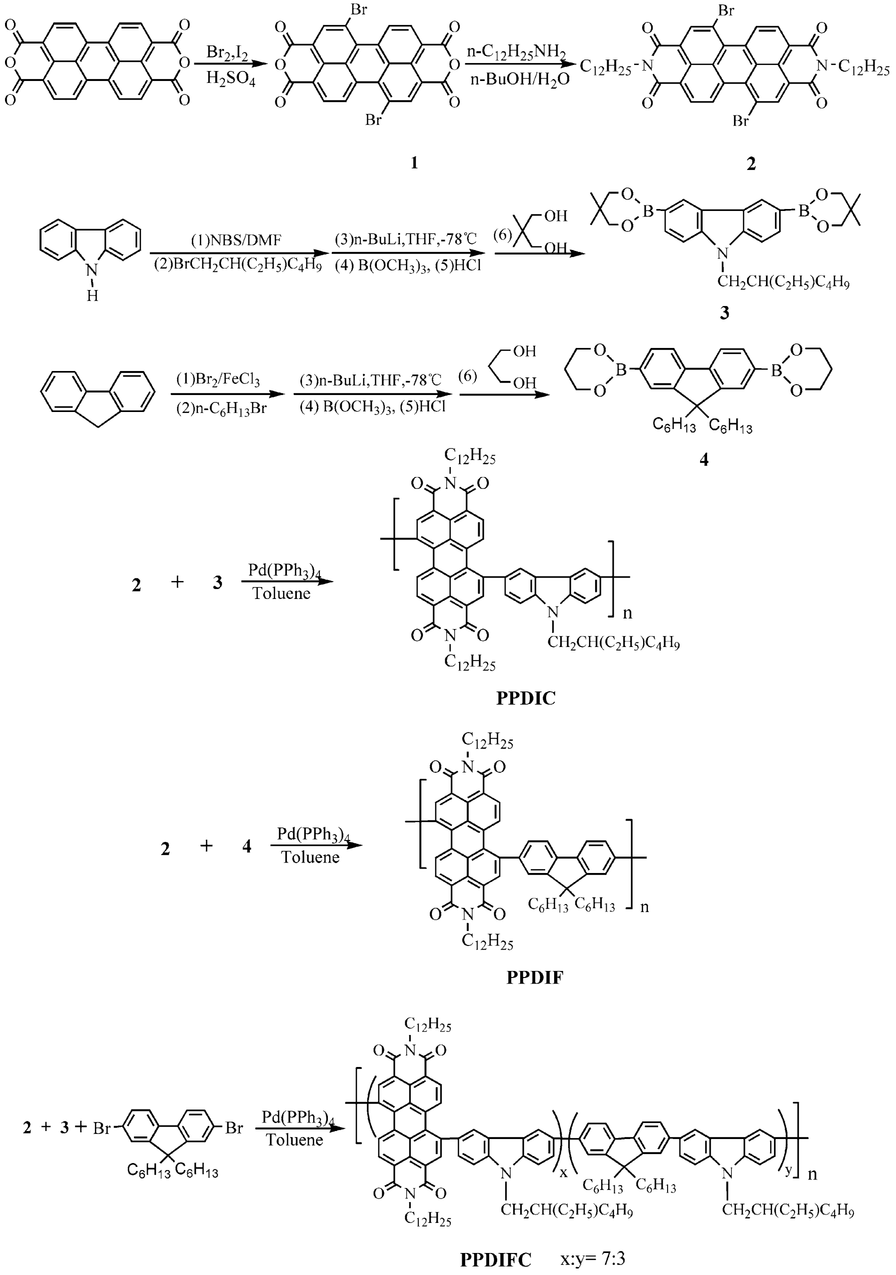
The synthetic route to the intermediates and objective polymers is shown in Scheme 1. The three target copolymers have been synthesized via Suzuki coupling

Table 1 Molecular weights and thermal decomposition temperature of the polymers PPDIF, PPDIC and PPDICF

Polymers	M_w	M_n	PDI (M_w/M_n)	T_d (°C)
PPDIF[a]	34,941	22,475	1.55	343
PPDIC[a]	35,787	20,880	1.71	434
PPDIFC[b]	18,805	10,998	1.70	300

[a] GPC in $CHCl_3$ using polystyrene standards

[b] GPC in THF using polystyrene standards



Scheme 1 The chemical structures of the intermediates and target polymers, and synthetic route to them

reaction in the presence of $Pd(PPh_3)_4$ as catalyst. In order to optimize the reaction condition, two kinds of solvents, i.e., THF at 65 °C and toluene at 90 °C, have been employed. The results indicated that when using THF as solvent, the reaction has to

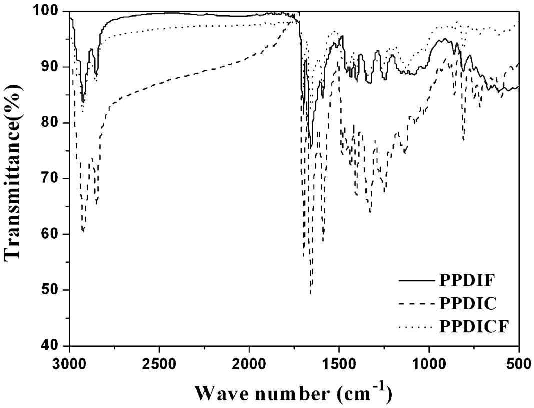


Fig. 1 FT-IR spectra of the polymers PPDIF, PPDIC and PPDICF

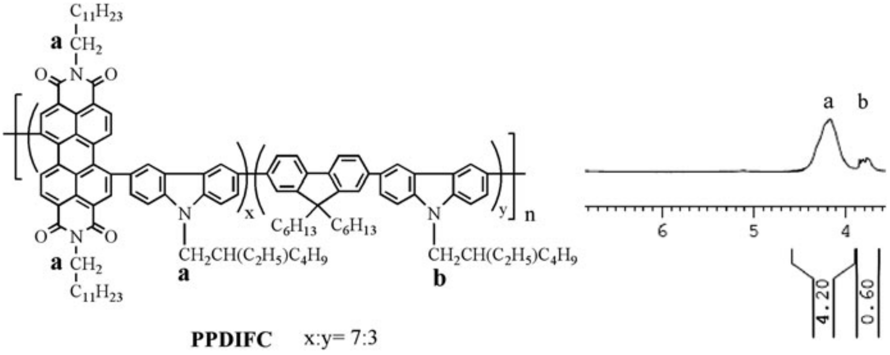
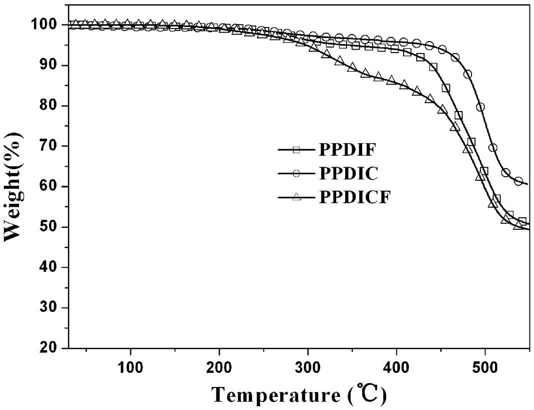


Fig. 2 ^{1}H NMR spectra of PPDICF for the determination of composition

be carried at ≤65 °C, thus the resulting polymers have much lower M_w. For example, the M_w of PPDIF and PPDIC are 6,500 g mol^{-1}. Nevertheless, when the reaction is carried out in toluene at 90 °C for 72 h, the corresponding polymers have much higher $M_w > 35{,}000$ g mol^{-1}, $M_n > 20{,}000$ g mol^{-1}, due to the better solubility.

The intense absorption peaks at 1,658–1,699 cm^{-1} in FT-IR spectra of the polymers (Fig. 1), witness the existence of C=O stretching vibrations, hence validate the presence of perylene diimide moiety in the polymer. The ^{1}H NMR spectra of the polymers show broad upfield signal at 8.1–8.7 ppm which can be assigned to the perylene protons for PPDIF, PPDIC, and PPDICF; while those observed at 7.5–7.9 ppm for PPDIF, 7.5–8.1 ppm for PPDIC, 7.4–7.5 and 7.8–7.9 ppm for PPDICF can be assigned to the protons originated from fluorene or (and) carbazole segments, respectively. The signal at $\delta = 4.1$ ppm can be attributed to the characteristic methylene group (N–CH_2–) of the polymers. Moreover, the component ratio of F:C (x:y) in the random copolymers PPDICF is determined as 7:3 from its ^{1}H NMR spectrum (Fig. 2), because the peak at $\delta = 4.1$ and 3.8 ppm can be attributed to the hydrogen at position atoms at position *a* and position *b* on the side chain of polymer PPDICF, respectively. This *x:y* value just

Fig. 3 TGA thermogram of the polymers PPDIF, PPDIC and PPDICF



resembles to the feeding ratio for compound 2 and 2,7-dibromo-9,9-dihexylfluorene (7:3).

Thermal analysis

The thermal stability of the three polymers is evaluated by TGA (shown in Fig. 3), and the high onset decomposition temperatures (T_d) (5% weight loss) in the range of 300–434 °C for these polymers suggest that they exhibit excellent thermal stability. DSC results reveal that all these macromolecules show no obvious glass transition temperature (T_g) below 250 °C.

Optical properties

The polymers are readily soluble in common organic solvents such as chloroform, methylene dichloride, chlorobenzene and 1,2-dichlorobenzene, thus uniform thin films can be prepared from these solutions. The UV–vis absorption spectra of the monomers and polymers in $CHCl_3$ are shown in Fig. 4, and the corresponding data

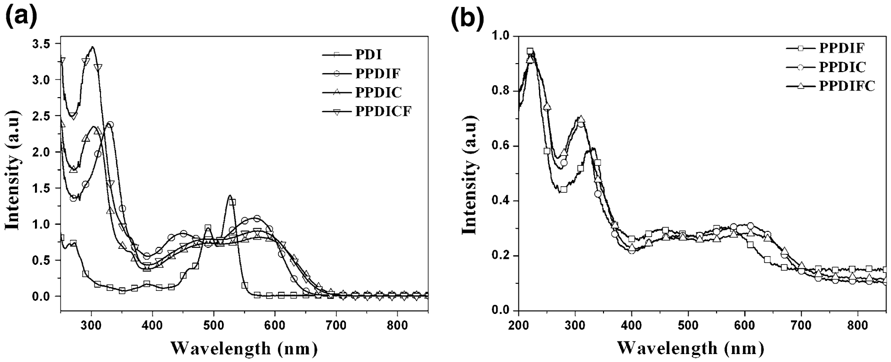


Fig. 4 UV–Vis absorption spectra of PDI, PPDIF, PPDIC and PPDICF in $CHCl_3$ (**a**) and thin films (**b**)

Table 2 Optoelectronic and electrochemical properties of objective polymers

Polymers	Solution		Films		CV				
	λ_{max} (nm)	ε_{max} [10^5 L/(mol cm)]	λ_{max} (nm)	E_g^{opt} (eV)	E_{ox}^{nset} (V)[a]	E_{red}^{onset} (V)[a]	HOMO (eV)	LUMO (eV)	E_g^{ec} (eV)
PPDIF	328	8.8	570	1.81	1.00	−0.89	−5.83	−3.94	1.89
	567	4.2							
PPDIC	304	8.9	611	1.74	0.82	−0.90	−5.65	−3.93	1.72
	581	3.1							
PPDICF	301	13.2	609	1.76	0.80	−0.92	−5.63	−3.91	1.72
	572	3.4							

[a] Versus Ag/Ag$^+$

absorption of maxima (λ_{max}) and molar absorption coefficients (ε_{max}) are summarized in Table 2. The λ_{max} of PPDIF, PPDIC, and PPDICF are observed at 567, 581, and 572 nm with ε_{max} of $>10^5$ L/(mol cm), respectively; while those of thin films are observed at 570, 611, and 609 nm. In comparison with the absorption spectra of the monomer PDI, the absorption spectra of the polymers in solution are broadened and bathochromic shifted obviously, suggesting there exists more extended conjugated length system in the polymers. The two distinguishable absorption bands at 290–400 and 400–700 nm, the longer wavelength band which is most important for the coverage with solar spectrum should be ascribed to the charge transfer transition state in the donor–acceptor–donor (D–A–D) segment. Their spectra in the thin films (depicted in Fig. 4) are similar with the spectra in solution, yet are broadened and red-shifted to some extent compared with PPDIF, The absorption peaks and absorption band-edge of PPDIC and PPDICF are both bathochromicly shifted for about 40 nm, which may be due to the stronger electron-donating ability of the carbazole relative to that of fluorene [29]. The optical bandgaps (E_g^{opt}) of the copolymers calculated from the absorption onset [30] are 1.81 eV for PPDIF, 1.74 eV for PPDIC, and 1.76 eV for PPDICF, which are lower than those of DOCN-PPV(2.1 eV) [14] and F8TBT(2.2 eV) [15], hence have more coverage with the solar spectrum, and consequently contribute more for light harvesting.

Electrochemical properties

The cyclic voltammogram curves of the objective copolymers are shown in Fig. 5. All of them show one-electron quasireversible reduction wave at lower potentials, which imply that they can accept electron easily and are relative stable in the redox cycles. The onset reduction potential (E_{red}^{onset}) for the three macromolecules are nearly identical at −0.90 V, suggest that the E_{red}^{onset} is determined by their electron-deficient perylene diimide segments. However, the onset oxidation potential (E_{ox}^{onset}) of PPDIF is 1.00 V, and those of PPDIC and PPDICF are 0.82 and 0.80 V, respectively. The different E_{ox}^{onset} may arise from the difference of electron-donating capability of carbazole and fluorene. The HOMO and LUMO energy levels and the

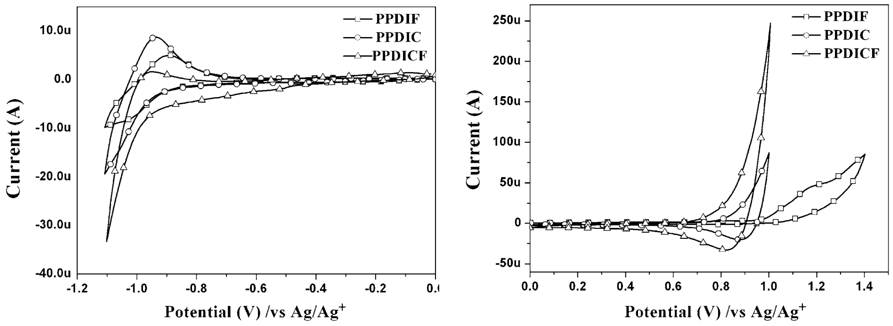


Fig. 5 Cyclic voltammogram of PPDIF, PPDIC and PPDICF films on a platinum electrode

E_g^{ec} of the copolymers can be deduced from the E_{ox}^{onset} and E_{red}^{onset} according to the equation HOMO/LUMO = $-e[E^{onset} - (-0.03\ \text{V})] - 4.8$ eV [31] and $E_g^{ec} = E_{ox}^{onset} - E_{red}^{onset}$, where the value −0.03 V is for Fc/Fc$^+$ vs. Ag/Ag$^+$, and the E_g^{ec} is estimated to be 1.89 eV for PPDIF, and 1.72 eV for both PPDIC and PPDICF, which is quite close to those derived from the optical method. The LUMO energy levels of the three polymers are determined as −3.91 to −3.94 eV for PPDICF, which is nearly similar to that of PCBM (−4.1 eV), but much lower than F8TBT (−3.2 eV) (shown in Fig. 8), indicating that the objective copolymers are potential n-type polymer materials for fabrication of aPSCs.

Photoluminescence (PL) quenching experiment

In order to validate the possible application of the target macromolecules as electron acceptor materials, PL spectra of the blend of our objective polymers with MEH-PPV at different doping ratio are recorded and shown in Figs. 6a (PPDIF), 6b (PPDIC), and 7 (PPDICF), respectively. The results indicate that the addition of the PPDIF, PPDIC, or PPDICF into MEH-PPV would lead to the PL quenching of MEH-PPV obviously, even under a low doping ratio of 10 wt%, while higher doping ratio of 1:1 (wt) would lead to completely quenching of emission from MEH-PPV. These results indicate that there should exist efficient electron transfer from MEH-PPV to the objective copolymers. These results convince that the energy level diagram of MEH-PPV and objective copolymers should match perfectly (shown in Fig. 8), and BHJ may be formed when doping them with appropriately p-type polymers.

Photovoltaic properties of aPSCs

In order to investigate the potentialities of the copolymers as electron acceptor materials for photovoltaic application, PPDIC with both narrower band gap and high electron affinity is selected to act as electron acceptor, and well-known P3HT is chosen as electron donor to fabricate aPSCs with the sample structure of ITO/PEDOT:PSS/P3HT:PPDIC/Al (data summarized in Table 3). Their current density–voltage (I–V) characteristics are shown in Fig. 9 with different blending ratio of

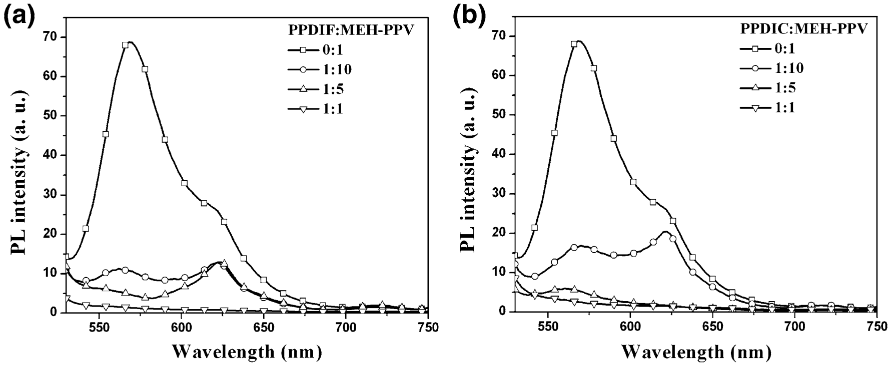


Fig. 6 PL spectra of the blend films of MEH-PPV and PPDIF (**a**) or PPDIC (**b**) with different weight ratios

Fig. 7 PL spectra of the blend films of MEH-PPV and PPDICF with different weight ratios

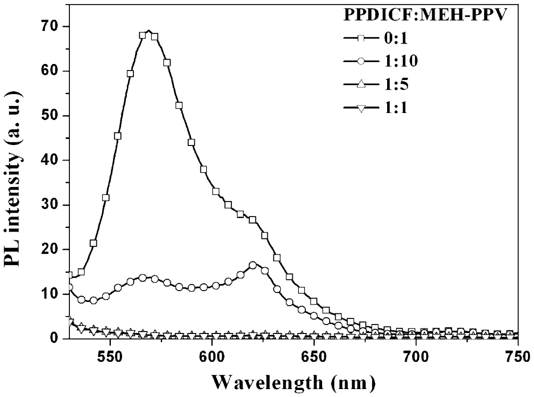
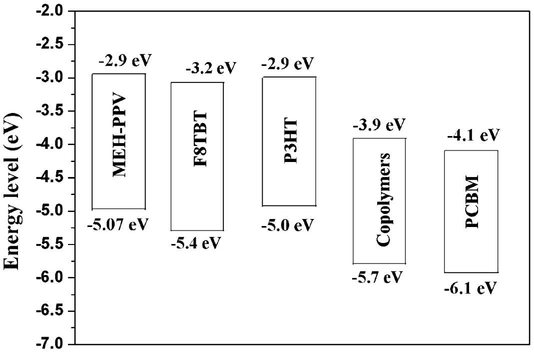


Fig. 8 Energy level of copolymers and PCBM



PPDIC and P3HT and it can be observed that the device doping ratio of 1:1 is the best performance. Under the AM 1.5 simulated solar illumination (100 mW/cm^2), this BHJ devices exhibit a high open circuit voltage (V_{oc}) of 0.86 V, a very low short circuit photocurrent (J_{sc}) of 4.8×10^{-3} mA/cm^2. The fill factor (FF) is 19.3%,

Table 3 Photovoltaic parameters of ITO/PEDOT:PSS/P3HT:PPDIC/Al bulk heterojunction solar cells

Active layer		V_{oc} (V)	I_{sc} (1×10^{-3} mA cm^{-2})	FF (%)	PCE (1×10^{-3}%)
Donor:acceptor	wt/wt				
P3HT:PPDIC	2:1	0.78	9.03	16.8	1.18
	1:1	0.79	9.40	16.6	1.23
	1:2	0.83	4.59	19.2	0.73
	1:4	0.86	4.79	19.3	0.80

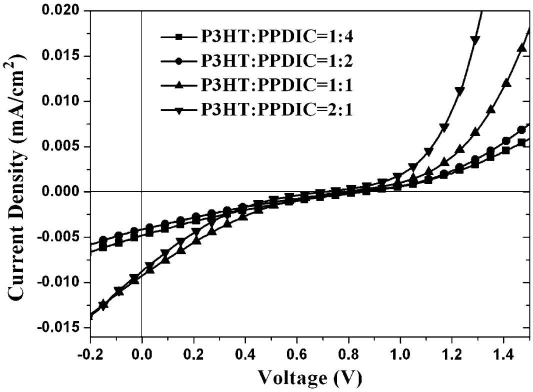


Fig. 9 I–V curves of aPSCs based on P3HT/PPDIC with different weight ratio

and PCE is about 1.23×10^{-3}%. To the best of our knowledge, The V_{oc} of 0.86 V is one of the most highest open-circuit voltage in comparison with reported so far in aPSCs with PDI-based polymers as electron acceptor in the literature [16, 17]. However, the low PCE of the devices reported here are much inferior, due to the much lower J_{sc}. As the J_{sc} of aPSCs is highly dependent on the morphology of blend films, atomic force microscopy (AFM) is used to investigate if BHJ has been formed between PPDIC with P3HT (Fig. 10). The image indicate that the blend film of active layer shows a rough surface without obvious phase separation between PPDIC and P3HT, which may account for the low J_{sc} of this devices. Therefore, P3HT should not be the right candidate to construct BHJ device with PPDIC. This may be further supported by the current reports for PDI-based aPSCs, since most of them are constructed by employing more complicated polythiophene derivatives, such as unavailable commercially poly(3-phenyl hydrazone thiophene) (PHHT) or poly(thienylene vinylene) derivatives with conjugated side chains as electron donor materials [13, 17–19]. Moreover, as the thermo-evaporation of LiF or Ca buffer layer is precluded by our experimental limitations, the poor contact between active layer and Al cathode may also lead to much lower J_{sc} [32]. However, inspired by the high V_{oc} obtained from our preliminary aPSCs, we believe that the PCE would be improved greatly after further optimization of the devices structures of aPSCs, i.e., the usage of more matchable p-type polymers, the employment of more active Ca cathode, or the incorporation of buffer layer with the device.

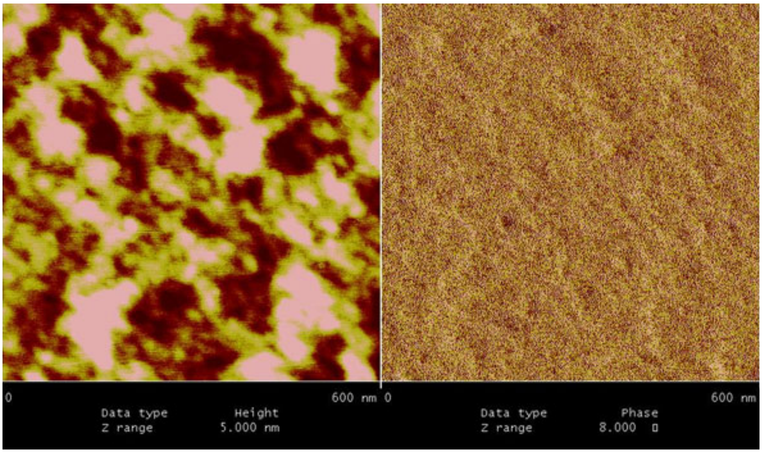


Fig. 10 Trapping mode AFM image of 1:1 weight ratio blend of P3HT with PPDIC

Conclusion

Three PDI-based conjugated copolymers are synthesized in good yield through Suzuki polymerization reaction. The objective polymers are readily soluble in common organic solvents, and uniform thin films can be casted from their solutions. The copolymers have broad and intense absorption through the visible region with narrow band gap of 1.72–1.89 eV, and their E_a values are 3.91–3.94 eV, which are quite close to that of the famous electron-accepting PCBM, suggesting they are promising n-type polymers. Moreover, the PL of MEH-PPV could be completely quenched by these target copolymers, implying that there should exist efficient charge transfer from MEH-PPV to these macromolecules. Despite the low PCEs that the preliminary aPSCs exhibit, $V_{oc} \sim 0.86$ V are higher than those reported PDI-based aPSCs devices. The relative low PCEs are mainly arisen from the poor J_{sc}, which may be ascribed to the unmatchable p-type polymer employed, and the lacking of LiF or Ca buffer layers.

Acknowledgment This study was supported by the National Natural Science Foundation of China (Project grant No. 50803040 and 20872103) and the Open Project Program of Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, China (No. 10HJYH02). We are greatly thank to the analytical & testing center of Sichuan University for providing measurements of NMR, UV–Vis and PL data for the intermediates and objective compounds.

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