

All-Polymer Solar Cells with Perylenediimide Polymer Acceptors*

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Abstract Four polymers based on perylenediimide co-polymerized with thiophene, bithiophene, selenophene and thieno[3,2-*b*]thiophene were investigated as the acceptor materials in all-polymer solar cells. Two different donor polymers, poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*;4,5-*b'*]dithiophene-2,6-diyl-*alt*-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene)-2-carboxylate-2,6-diyl] (PTB7-Th) and poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-*alt*-(3,3''-di(2-dodecyltetradecyl)-2,2';5',2'';5'',2'''-quaterthiophen-5,5'''-diyl)] (PffBT4T-2DT), with suitably complementary absorption spectra and energy levels were applied and examined. Among all different donor-acceptor pairs studied here, the combination of PTB7-Th:poly[*N,N'*-bis(1-hexylheptyl)-3,4,9,10-perylenediimide-1,6/1,7-diyl-*alt*-2,5-thiophene] (PDI-Th) exhibited the best power conversion efficiency (PCE) of 5.13%, with open-circuit voltage (V_{oc}) = 0.79 V, short-circuit current density (J_{sc}) = 12.35 mA·cm⁻² and fill-factor (FF) = 0.52. The polymer of PDI-Th acceptor used here had a regio-irregular backbone, conveniently prepared from a mixture of 1,6- and 1,7-dibromo-PDI. It is also noteworthy that neither additive nor post-treatment is required for obtaining such a cell performance.

Keywords All-polymer solar cells; Polymer acceptor; Perylenediimides; Donor-acceptor pair

INTRODUCTION

In the past few years, polymer solar cells (PSCs) have attracted intensive research efforts, because of their appealing properties including low cost, mechanical flexibility and light weight^[1–4]. To date, the bulk-heterojunction (BHJ) PSCs based on a polymeric electron-donating material with a fullerene derivative acceptor have been widely studied and shown state-of-the-art power conversion efficiencies (PCEs) of over 10%^[5–10]. However, the fullerene acceptors suffer from several drawbacks^[11, 12], such as the high production cost, low visible-light absorption coefficient, and limited photochemical and morphological stability in the active layer of PSCs.

Recently, all-polymer solar cells (all-PSCs) using polymeric acceptors as alternatives to fullerene derivatives have received increasing attention^[13]. Compared to the fullerene derivatives, the *n*-type polymeric materials boast distinct advantages including the lower production cost, higher extinction ability of the visible light, better chemo-stability, higher suitability for large-area processing and device fabrication, *etc*^[14–23]. Moreover, the absorption spectra and frontier orbital levels of the polymer acceptors can be easily fine-tuned

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through rational designs and structure modifications to better complement the polymer donors. Such properties imply great opportunities for further enhancement of the device performance^[24–27]. Recent studies have also shown that all-PSCs exhibit perceptibly improved mechanical properties compared with the fullerene-based PSCs, thus showing better suitability for flexible device fabrications^[28]. Upon all the research efforts invested in molecule designs and device optimizations, the PCEs of all-PSCs have been raised to over 8%^[29]. However, currently the PCEs of all-PSCs are still lower than those based on the fullerene derivatives and organic small molecule acceptors^[30, 31].

In the past few years, we have been focusing on designing new polymer acceptors using perylenediimides (PDIs) as the main building block. Compared to naphthalenediimides (NDIs)-based polymers, PDI-based polymeric acceptors usually do not require special processing conditions such as hot processing^[32] or spin-coating using low-boiling point solvents^[25, 29]. Previously, we developed a set of polymeric acceptors comprising PDI and thiophene units, among which polymer PDI-Th offered the best performance, with a high PCE of 4.4%^[33, 34]. In this contribution, we present further studies on four different PDI-based polymers, prepared from PDI and various co-monomers comprising thiophene (Th), bithiophene (diTh), selenophene (Se) or thieno[3,2-*b*]thiophene (TT) units. To match these acceptors, polymers PTB7-Th^[35] and PffBT4T-2DT^[36] are selected as the donor materials. By changing the partner units in the acceptor backbone, the absorption spectra, frontier orbital energy levels and crystallinity of these PDI acceptor materials can be modified and tuned. As a result, the cell parameters including PCE are found to fluctuate substantially^[37]. Under the optimized cell fabrication conditions, PTB7-Th:PDI-Th showed the best PCE of 5.13% among all different donor-acceptor pairs. This result was obtained with *gio*-irregular PDI-Th. Namely, the polymer backbone comprised randomly distributed 1,6- and 1,7-PDI repeat units. The facile preparation of the polymer, from regio-isomer mixture of 1,6- and 1,7-dibromopDI, warrants the large-scale production of the materials and thus feasibility of its application in industrial processing of relevant cells^[34]. It is also noteworthy that neither additives nor post-treatments were required in the device fabrication. Additionally, it was also observed that PDI-Se exhibited better donor compatibility, offering PCEs of > 3% with both examined donors, whereas the other three polymers all showed greatly disparate performance in the presence of different donors. This may be useful information for the future development of more versatile acceptor materials.

EXPERIMENTAL

General Procedures

UV-Vis absorption spectra were acquired on a Hitachi U-4100 spectrophotometer. Cyclic voltammetry was performed with a Gamry Interface 1000 electrochemical workstation with three electrodes configuration, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. Polymer thin film was dropped on the working electrode and tetrabutylammonium hexafluorophosphate (0.1 mol·L⁻¹) was dissolved in acetonitrile as the electrolyte. Potentials were referenced to the ferrocenium/ferrocene couple using ferrocene as the external standards in acetonitrile solutions. The scan rate is 100 mV·s⁻¹. AFM measurements were performed using a Bruker's Dimension icon in tapping mode. All film samples were spin-cast on ITO/ZnO substrates. The mobilities were measured using the SCLC method, employing a device architecture of ITO/ZnO/polymer/Ca/Al for electron mobility. The mobility values were obtained by fitting current-voltage curves to a space charge limited form. The SCLC is described by:

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

where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material (assumed to be 3), μ is the electron mobility and L is the thickness of the film. From the plots of $J^{1/2}$ versus V , electron mobilities can be deduced.

Materials

N,N'-bis(1-hexylheptyl)-1,7/1,6-dibromo-3,4,9,10-perylene-diimide^[34] and PffBT4T-2DT^[36] were synthesized using the previously report methods. Monomers 2,5-bis(trimethylstannyl)thiophene, 2,5-bis(trimethylstannyl)selenophene, 5,5'-bis(trimethylstannyl)-2,2'-bithiophene and 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene were purchased from Allmers. PTB7-Th was purchased from 1-Material, and Pd₂(dba)₃ and P(*o*-tol)₃ were purchased from J&K.

Polymer Preparations

PDI-Th: A Schlenk tube containing *N,N'*-bis(1-hexylheptyl)-1,7/1,6-dibromo-3,4,9,10-perylene-diimide (150 mg, 0.16 mmol), 2,5-bis(trimethylstannyl)thiophene (67 mg, 0.16 mmol), Pd₂(dba)₃ (8 mg, 0.009 mmol) and P(*o*-tol)₃ (11 mg, 0.035 mmol) was evacuated and refilled with nitrogen three times, and then toluene (3 mL) was added using a syringe under nitrogen atmosphere. The reaction mixture was sealed under nitrogen atmosphere and stirred at 110 °C for 96 h. Upon cooling to room temperature, an aqueous solution of potassium fluoride (1 g in 3 mL water) was added. This mixture was stirred at room temperature for 6 h before it was extracted with chloroform (20 mL × 3). Organic layers were combined, washed with water (30 mL × 3), dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator. The residue was taken with a small amount of chloroform and precipitated in acetone. The obtained deep purple solid was eluted through a size exclusion chromatography column filled with Bio-Beads S-X1 Beads, and then concentrated on a rotary evaporator. The solid residue was re-dissolved in chloroform (2 mL) and dispersed slowly in methanol (50 mL). The precipitates were collected by filtration, washed with methanol, and dried in vacuum, offering a deep purple solid (88 mg, yield 64%). ¹H-NMR (400 MHz, CDCl₃, δ): 8.77–8.71 (m, 2H), 8.51–8.39 (m, 4H), 7.42–7.30 (m, 2H), 5.16 (m, 2H), 2.23 (m, 4H), 1.84 (m, 4H), 1.33–1.25 (m, 32H), 0.84 (m, 12H). GPC: *M*_n = 11.8 kDa, *M*_w = 23.4 kDa, PDI = 1.98. Elemental Anal., Calcd. For (C₅₄H₆₂N₂O₄S)_n: C, 77.66; H, 7.48; N, 3.35; Found: C, 77.48; H, 7.51; N, 3.36.

The other three polymers were synthesized using similar procedures.

PDI-diTh: The polymer (96 mg, yield 58%) was obtained from a reaction mixture of *N,N'*-bis(1-hexylheptyl)-1,7/1,6-dibromo-3,4,9,10-perylenediimide (165 mg, 0.18 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (89 mg, 0.18 mmol), Pd₂(dba)₃ (9 mg, 0.010 mmol) and P(*o*-tol)₃ (12 mg, 0.039 mmol). ¹H-NMR (400 MHz, CDCl₃, δ): 8.75–8.71 (m, 2H), 8.42–8.34 (m, 4H), 7.32–7.26 (m, 4H), 5.17 (m, 2H), 2.24 (m, 4H), 1.85 (m, 4H), 1.33–1.25 (m, 32H), 0.84 (m, 12H). GPC: *M*_n = 10.4 kDa, *M*_w = 21.5 kDa, PDI = 2.07. Elemental Anal.: Calcd. For (C₅₈H₆₄N₂O₄S₂)_n: C, 75.95; H, 7.03; N, 3.05; Found: C, 75.44; H, 7.01; N, 3.04.

PDI-Se: The polymer (92 mg, yield 65%) was obtained from a reaction mixture of *N,N'*-bis(1-hexylheptyl)-1,7/1,6-dibromo-3,4,9,10-perylenediimide (147 mg, 0.16 mmol), 2,5-bis(trimethylstannyl)selenophene (74 mg, 0.16 mmol), Pd₂(dba)₃ (8 mg, 0.009 mmol) and P(*o*-tol)₃ (11 mg, 0.035 mmol). ¹H-NMR (400 MHz, CDCl₃, δ): 8.76–8.70 (m, 4H), 8.45–8.41 (m, 2H), 7.58–7.50 (m, 2H), 5.16 (m, 2H), 2.23 (m, 4H), 1.84 (m, 4H), 1.33–1.25 (m, 32H), 0.84 (m, 12H). GPC: *M*_n = 12.0 kDa, *M*_w = 23.5 kDa, PDI = 1.97. Elemental Anal., Calcd. For (C₅₄H₆₂N₂O₄Se)_n: C, 73.53; H, 7.09; N, 3.18; Found: C, 73.49; H, 7.12; N, 3.21.

PDI-TT: The polymer (87 mg, yield 58 %) was obtained from a reaction mixture of *N,N'*-bis(1-hexylheptyl)-1,7/1,6-dibromo-3,4,9,10-perylenediimide (157 mg, 0.17 mmol), 2,5-bis(trimethylstannyl)-thieno[3,2-*b*]thiophene (80 mg, 0.17 mmol), Pd₂(dba)₃ (9 mg, 0.010 mmol) and P(*o*-tol)₃ (12 mg, 0.039 mmol). ¹H-NMR (400 MHz, CDCl₃, δ): 8.85–8.81 (m, 2H), 8.43–8.38 (m, 4H), 7.67–7.58 (m, 2H), 5.16 (m, 2H), 2.23 (m, 4H), 1.84 (m, 4H), 1.33–1.25 (m, 32H), 0.84 (m, 12H). GPC: *M*_n = 13.6 kDa, *M*_w = 30.1 kDa, PDI = 2.27. Elemental Anal., Calcd. For (C₅₆H₆₂N₂O₄S₂)_n: C, 75.47; H, 7.01; N, 3.14; Found: C, 75.27; H, 7.03; N, 3.24.

Device Fabrication and Characterization

Pre-patterned ITO-coated glass with a sheet resistance of ~15 Ω per square was used as the substrate. It was cleaned by sequential cycles of sonication in soap water, deionized water, acetone, and isopropanol for 15 min at each step. After UV/ozone treatment for 60 min, a ZnO electron transport layer was prepared by spin-coating at 5000 r·min⁻¹ from a ZnO precursor solution (diethyl zinc). Active layer solutions (D/A ratio 1:1) were prepared

in CB (polymer concentration at $9 \text{ mg}\cdot\text{mL}^{-1}$). To completely dissolve the polymer, the solution should be stirred on a hot-plate at 110°C for at least 3 h. Active layers were spin-coated from the cooled polymer solution on substrate in a N_2 glove-box at $1700 \text{ r}\cdot\text{min}^{-1}$ to obtain a thickness of $\sim 120 \text{ nm}$. The blend films were then transferred to the vacuum chamber of a thermal evaporator inside the same glove-box. At a vacuum level of $4 \times 10^{-10} \text{ Pa}$, a thin layer (20 nm) of V_2O_5 was deposited as the anode interlayer, followed by deposition of 100 nm of Al as the top electrode. All cells were encapsulated using epoxy inside the glove-box. Device J - V characteristics was measured under AM1.5G ($100 \text{ mW}\cdot\text{cm}^{-2}$) using a Newport solar simulator. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement) to bring spectral mismatch to unity. J - V characteristics were recorded using a Keithley 2400 source meter unit. Typical cells have devices area of 5.9 mm^2 , which is defined by a metal mask with an aperture aligned with the device area. EQEs were characterized using a Newport EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300 W lamp source.

RESULTS AND DISCUSSION

Syntheses and Characterizations of the Polymeric Acceptors

As shown in Fig. 1, the polymeric acceptors were all synthesized *via* the Stille reactions between dibromoperylenediimide (PDI-Br₂) and corresponding organo-tin reagents, using $\text{Pd}_2(\text{dba})_3/\text{P}(o\text{-tol})_3$ as the catalyst. A regio-isomer mixture of 1,6- and 1,7-dibromo-PDI (at a molar ratio of *ca.* 1:4 according to the ^1H -NMR spectrum)^[38] obtained from bromination of PDI was used for the polymerization reactions without isomer separation. More polymer synthesis details can be found in the experimental section. As shown in Table 1, similar number-average molecular weight (M_n) and polydispersity index (M_w/M_n) are shown by all four polymeric acceptors, on the basis of the high-temperature gel permeation chromatography (GPC), which excluded drastic property disparity caused by significantly varied molecular weight. By virtue of the branched alkyl side chains, all the polymers exhibit good solubility in common organic solvents, such as *o*-dichlorobenzene (DCB), chlorobenzene (CB) and chloroform.

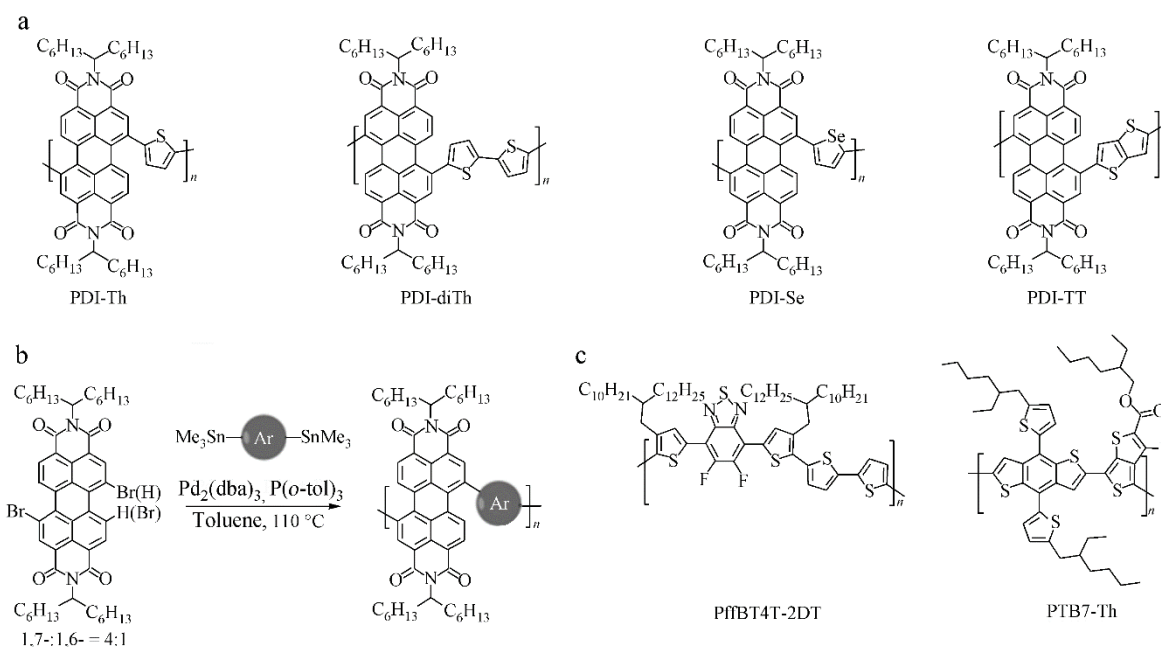


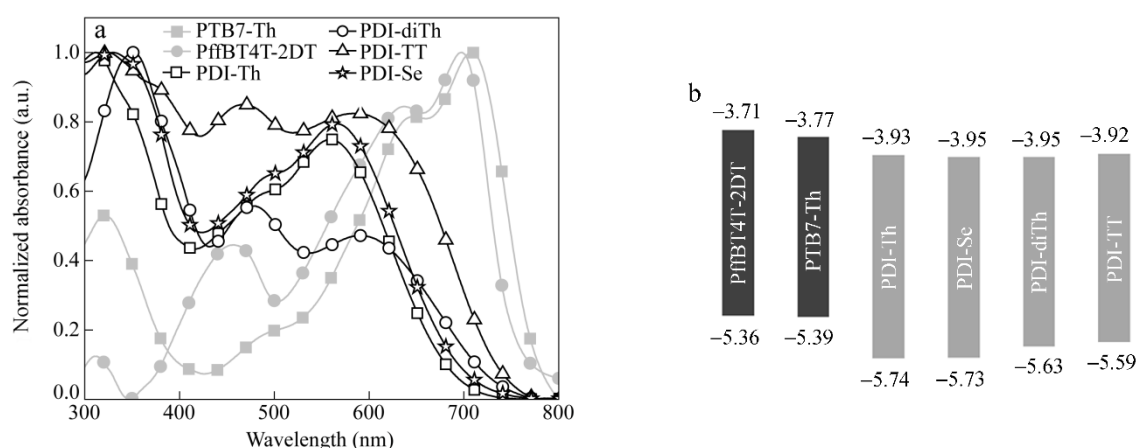
Fig. 1 (a) Chemical structures and (b) general synthetic route of polymeric acceptors; (c) chemical structures of the donor materials

Table 1 Molecular weights, energy levels and SCLC mobilities of polymers

Polymer	M_n (kDa)	M_w/M_n	$E_g^{opt\ a}$ (eV)	E_{LUMO}^b (eV)	E_{HOMO}^c (eV)	e-mobility ^d ($cm^2 \cdot V^{-1} \cdot s^{-1}$)
PDI-Th	11.8	1.98	1.81	-3.93	-5.74	1.1×10^{-3}
PDI-diTh	10.4	2.07	1.68	-3.95	-5.63	1.2×10^{-3}
PDI-Se	12.0	1.97	1.78	-3.95	-5.73	0.9×10^{-3}
PDI-TT	13.6	2.27	1.67	-3.92	-5.59	1.7×10^{-3}

^a Data obtained from the thin-film state; ^b Measured from the CV; ^c Estimated from ($E_{LUMO} - E_g$); ^d Measured with the SCLC method

The optical properties of these polymeric acceptors were examined by the UV-Vis absorption spectroscopy in the thin-film state. As shown in Fig. 2(a), PDI-Se exhibits a slightly red-shifted absorption band and narrower band-gap compared to PDI-Th, consistent with the analogous NDI-based polymers^[39]. When the thiophene unit was changed into stronger donors, the intramolecular charge transfer (ICT) absorption peaks of PDI-diTh (591 nm) and PDI-TT (586 nm) show about 30 nm redshift compared to that of PDI-Th (559 nm), while the bandgaps are narrowed by about 0.1 eV. Generally, the spectra of all four polymeric acceptors cover from about 300 nm to 650 nm, very well complementing those of the donor polymers which absorb around 600 nm to 750 nm. The fact that the combined absorptions of acceptor and donor can cover the entire visible range is a good indication of adequate solar-energy harvesting capacity. The lowest unoccupied molecular orbital (LUMO) levels of the four polymeric acceptors are determined based on the reduction potentials measured with the cyclic voltammetry (CV). As shown in Fig. 2(b), very similar LUMO levels around -3.93 eV are found for all four polymer acceptors. The highest occupied molecular orbital (HOMO) levels of PDI-diTh and PDI-TT are higher than those of PDI-Th and PDI-Se, corresponding to their narrower bandgaps. The charge transport properties of the neat polymers were measured by the space-charge limited current (SCLC) method. Using a device structure of ITO/ZnO/polymeric acceptor/Ca/Al, the electron mobility of all four polymeric acceptors are estimated to be around $1 \times 10^{-3} cm^2 \cdot V^{-1} \cdot s^{-1}$, which is comparable to the fullerene derivatives. The sufficient electron mobility of these polymers ensures good charge transport properties in the active layer of all-PSCs.

**Fig. 2** UV-Vis absorption spectra (a) and energy levels (b) of polymer thin films

Device Performance

To evaluate the acceptor properties of these polymer materials, two polymers with suitable absorption spectra, energy levels and showing optimal performance in non-fullerene PSCs, PTB7-Th and PffBT4T-2DT, were chosen as the donor materials. The BHJ all-PSCs were fabricated with an inverted device structure of ITO/ZnO/active layer/ V_2O_5 /Al. The active layers were spin-casted from a solution of CB with a D/A weight ratio of 1:1. The device performance was tested under an illumination of AM 1.5 simulated solar light at $100 mW \cdot cm^{-2}$. The $J-V$ curves are shown in Fig. 3(a) and the corresponding parameters are summarized in

Table 2. The data indicate that those all-PSCs based on PTB7-Th donor typically offer higher PCEs than the corresponding devices comprising PffBT4T-2DT, which can mainly be attributed to the higher J_{sc} of the former set of devices. Among the devices incorporating PTB7-Th, the V_{oc} of PDI-Th, PDI-Se and PDI-TT are in good agreement to the LUMO levels of these three polymeric acceptors. However, the V_{oc} obtained from PTB7-Th:PDI-diTh is surprisingly high compared to the other three systems. While relevant evidence is yet to be collected, the minimal energy loss of this system is presumably due to a special charge transfer (CT) state of this blend system. Besides, the PCEs are also in good accordance to the values of J_{sc} and FF. Among all the devices, PTB7-Th:PDI-Th showed a best PCE of 5.13%, with $V_{oc} = 0.79$ V, $J_{sc} = 12.35$ mA·cm⁻² and FF = 0.52. Notably, the regio-irregular polymer, prepared from an isomer mixture of 1,6- and 1,7-dibromo-PDI directly obtained from the bromination reaction of precursor PDI without separation, was used for the current device studies. Furthermore, no additives or post-treatments were necessary during the device fabrication. All these features represent great advantages for large-scale productions.

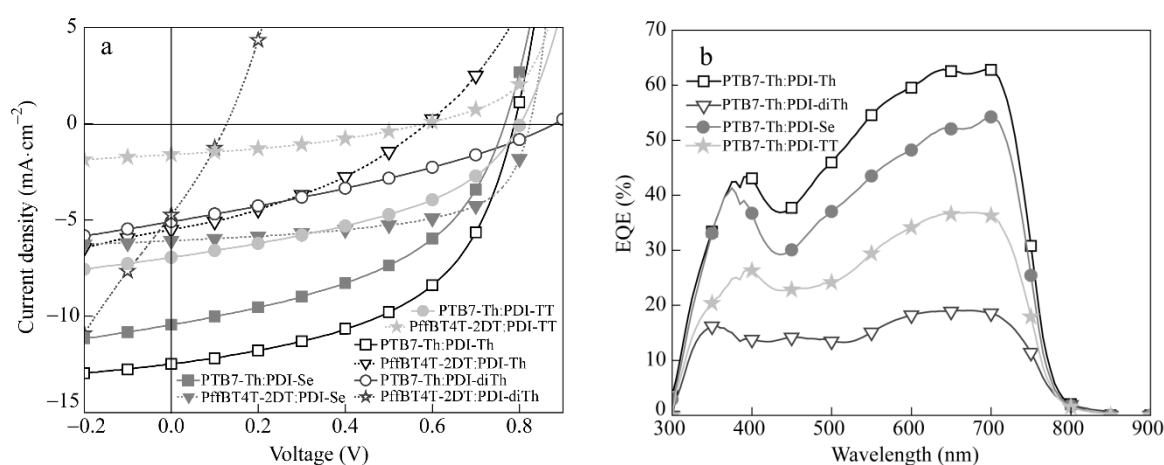


Fig. 3 (a) J - V curves and (b) EQE spectrums of all-PSCs with D/A weight ratio of 1:1 under the illumination of AM1.5G, 100 mW·cm⁻²

Table 2 The photovoltaic parameters of inverted all-PSCs processed with D/A weight ratio of 1:1 under the illumination of AM1.5G, 100 mW·cm⁻²

Acceptors	Donors	V_{oc} (V)	J_{sc} (mA·cm ⁻²)	FF	PCE _{avg} ^a (%)	PCE _{max} (%)
PDI-Th	PTB7-Th	0.79	12.35	0.52	5.08 ± 0.10	5.13
	PffBT4T-2DT	0.53	5.51	0.35	1.00 ± 0.11	1.15
PDI-diTh	PTB7-Th	0.88	4.90	0.32	1.36 ± 0.10	1.42
	PffBT4T-2DT	0.05	4.11	0.25	0.06 ± 0.06	0.17
PDI-Se	PTB7-Th	0.77	10.28	0.46	3.66 ± 0.11	3.72
	PffBT4T-2DT	0.82	5.62	0.60	2.77 ± 0.24	3.02
PDI-TT	PTB7-Th	0.80	7.07	0.43	2.45 ± 0.15	2.50
	PffBT4T-2DT	0.53	1.64	0.35	0.33 ± 0.12	0.53

^a Averaged data over 10 cells

Photo-response Properties of the Blend Films

The external quantum efficiency (EQE) was measured to determine the spectral response of the all-PSCs. As shown in Fig. 2(b), all four PTB7-Th-based devices showed reasonable photo-response in the entire visible region, in good agreement with the combined absorptions of the donor and acceptor. It is also shown that both photo-induced electron and hole transfers are effectively contributing to the charge photo-generation, indicating that PTB7-Th is a suitable choice as the polymer donor, well matching with the polymeric acceptors in the all-PSCs. The J_{sc} values calculated from the integration of EQEs roughly agree with the J_{sc} values obtained from the J - V curves. Among all the devices, PTB7-Th:PDI-Th showed a high EQE of over 60% from 650 nm to 750 nm, illustrating the remarkable photo-response properties of this system, thus offering the best J_{sc} . The similar EQE

ranges of all four systems also suggest that the disparate J_{sc} values were not related to the different absorption properties of the four polymeric acceptors.

Morphology Characterizations

Atomic force microscopy (AFM) was used to investigate the morphology of the PTB7-Th:acceptor (Fig. 4) and PffBT4T-2DT:acceptor blends (shown in Fig. 5). From the data, all blend films comprising PffBT4T-2DT show a rough surface and poor phase separation compared to the corresponding blend films containing PTB7-Th. These results may explain the lower J_{sc} of the devices based on PffBT4T-2DT compared to PTB7-Th-based devices. For the PTB7-Th-blend films, AFM images are also well correlated to the J_{sc} and FF of all-PSCs. Among them, PTB7-Th:PDI-Th showed the most smooth and uniform surface with a root-mean-square (RMS) roughness of 0.88 nm. The phase images of this blend film also indicate that the domain size is about 10–20 nm, which is similar to that of high-performance BHJ blends. Therefore, PTB7-Th:PDI-Th showed the best device performance among all the combinations. Other devices all showed relatively rough surface or coarse phase separation compared to PTB7-Th:PDI-Th, thus lower J_{sc} and FF.

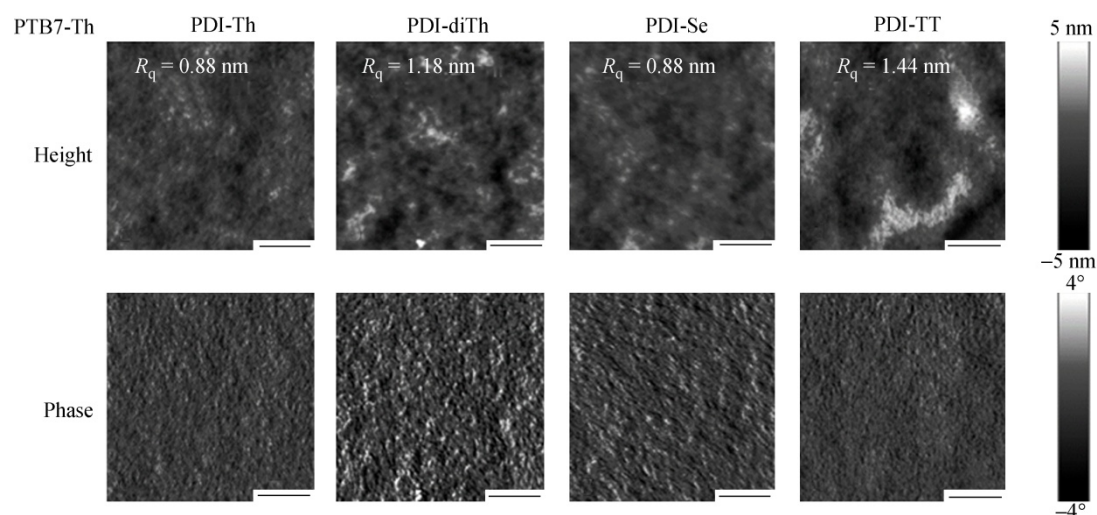


Fig. 4 AFM height and phase images ($1 \mu\text{m} \times 1 \mu\text{m}$) of PTB7-Th:acceptor blend films (The scale bars are 250 nm.)

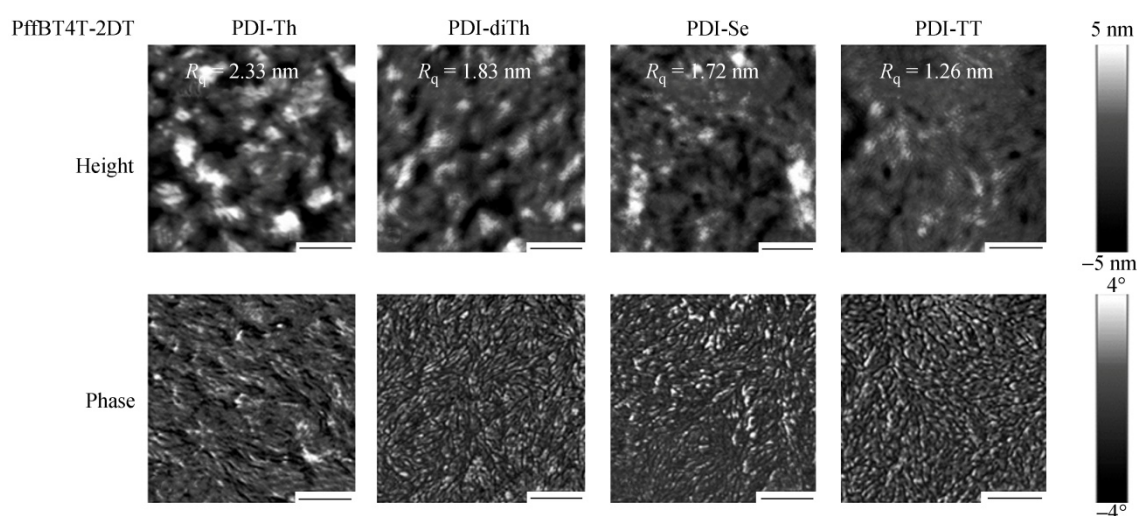


Fig. 5 AFM height and phase images ($1 \mu\text{m} \times 1 \mu\text{m}$) of PffBT4T-2DT:acceptor blend films (The scale bars are 250 nm.)

Photoluminescence Quenching Experiments

The photoluminescence (PL) quenching of the blends was measured to determine the percentage of excitons that could reach and dissociate at the donor/acceptor interface. Overall, all the blend films based on PTB7-Th showed higher PL quenching efficiency compared to the corresponding blend films of PffBT4T-2DT, which could explain the higher PCE of the former set of materials (shown in Fig. 6). Blending PTB7-Th with PDI-Th results in fluorescence quenching of over 75%, indicating efficient photo-induced charge transfer between PTB7-Th and PDI-Th in the blend film. PTB7-Th:PDI-Se and PTB7-Th:PDI-TT blends all showed similar quenching efficiencies. However, a surprisingly high quenching efficiency of 98% was observed with PTB7-Th:PDI-diTh blend, which further proved the existence of a special charge separation pathway with a faster charge transfer rate, in line with the unexpectedly high V_{oc} discussed earlier.

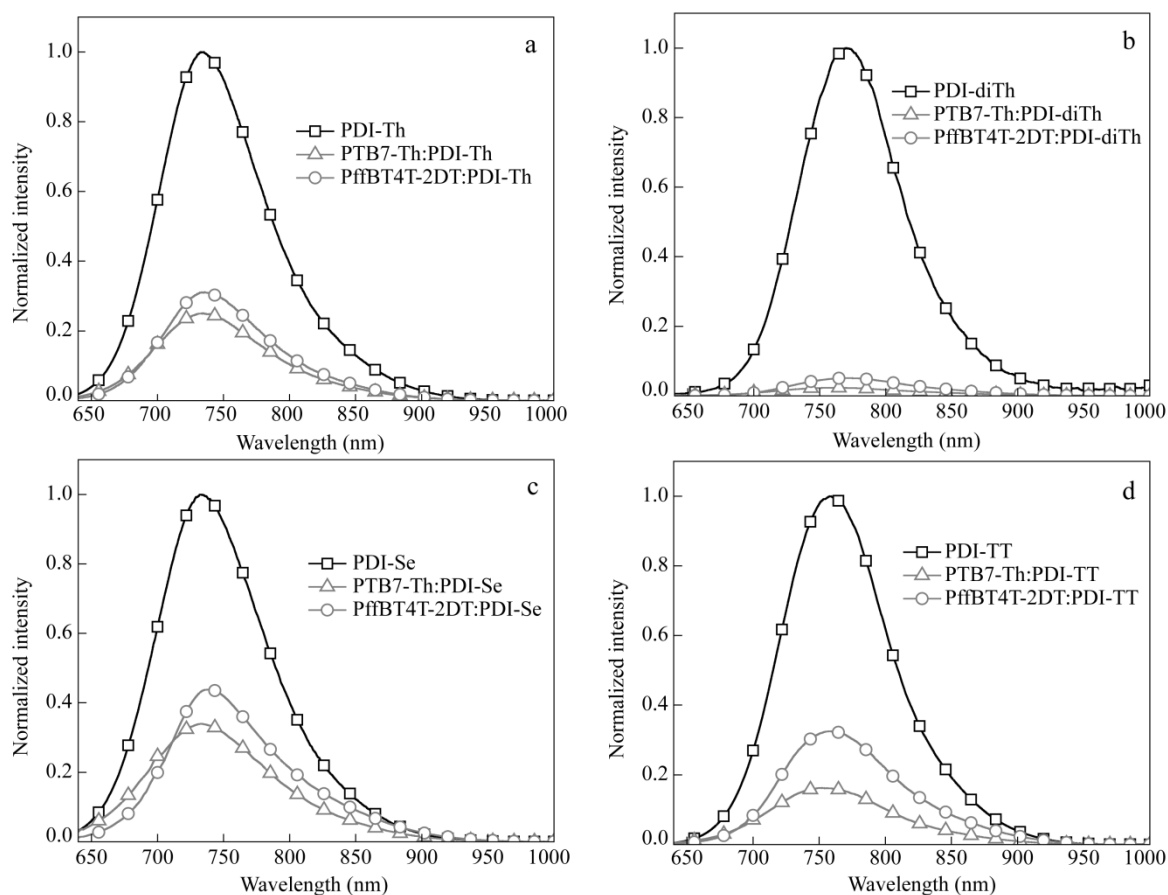


Fig. 6 The photoluminescence spectra of all the blend films compared with those of neat acceptor films (The excitation wavelength was 633 nm.)

CONCLUSIONS

We report the synthesis of a series of polymeric materials based on PDI units and their application as acceptor materials in all-PSCs. Two polymer materials were chosen as the donors considering the absorption spectra and energy levels of these acceptors. Among all the devices, all-PSCs based on PTB7-Th:PDI-Th exhibited the best PCE of 5.13%, with $V_{oc} = 0.79$ V, $J_{sc} = 12.35$ mA·cm⁻² and FF = 0.52. Morphology study showed that desirable surface morphology and appropriate phase separation was the key for such high efficiency. Furthermore, the devices were fabricated using regio-irregular polymers containing a random distribution of 1,6- and 1,7-substituted PDI units, and no additives or post-treatments were required in the device fabrication. These results suggest that the PDI-based polymers present great promise for application in all-PSCs.

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