Manipulating backbone structure with various conjugated spacers to enhance photovoltaic performance of D–A-type two-dimensional copolymers

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Abstract

A class of low band-gap two-dimensional conjugated polymers of PBDTT-FQ, PBDTT-TQ, PBDTT-BTQ and PBDTT-TTQ was designed and synthesized, which contains the same di(alkylthiophene)-substituted benzo[1,2-b:4,5-b]dithiophene (BDTT) and 6,7-difluoro-quinoxaline (Q) units, as well as various conjugated spacers of furan, thiophene, bithiophene and thieno[3,2-b]thiophene in the main chain. Significant effect of the varied spacers between the BDTT and Q units on the thermal, optical, electrochemical and photovoltaic properties was investigated and observed for these two-dimensional copolymers in the polymer solar cells. The maximum power conversion efficiency of 5.9% with a short circuit current of 13.7 mA/cm² and a fill factor of 0.56 was obtained for the PBDTT-TQ with thiophene spacer in the bulk hetero-junction PSCs using [6,6]-phenyl-C71-butyric acid methyl ester as acceptor.

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1. Introduction

Bulk hetero-junction (BHJ) based polymer solar cells (PSCs), utilizing conjugated polymers and soluble fullerene derivatives [1], have attracted much attention due to their advantages of low cost, light weight, and potential flexibility in large area applications [2–4]. By development of novel low band-gap polymers and optimization of device fabrication, significant progress has been made with power conversion efficiency (PCE) up to 9% in the single BHJ-based device [5]. To improve the photovoltaic performance of PSCs, in general, four key factors have been considered for developing novel polymeric donor materials: (1) broad and strong absorption in visible and near-infrared region to absorb more photons energy and obtain high short circuit current (Jsc), (2) matched energy levels with those of acceptor materials in photoactive layer to ensure efficient exciton dissociation at the donor/acceptor interface and obtain high open circuit voltage (Voc), (3) high charge carrier mobility to facilitate exciton diffusion and separation, (4) sufficient solubility to guarantee solution processability and appropriate compatibility with acceptor of fullerene derivatives forming the nanoscale bi-continuous interpenetrating network in photo-active layer [6,7]. Currently, a general strategy to satisfy these requirements mentioned above is to construct the D–A-type polymers with alternating electron-rich donor moiety (D) and electron-deficient

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acceptor moiety (A), which can narrow the polymeric band-gap by the intra-molecular charge transfer (ICT) [8]. In order to further fine-tune the energy levels and obtain better photovoltaic performance for these D–A polymers, some conjugated groups, such as furan, thiophene, bithiophene and thiieno[3,2-b]thiophene, were employed as spacers to insert into the D and A units [9–14]. For instance, Wang et al. reported a series of D–A polymers with benz[1,2-b:4,5-b]dithiophene (BDT) and isoindigo units [15]. By bearing various numbers of thiophene rings in the backbone, it was found that the PDDBT-BTI polymer with a bithiophene spacer exhibited the maximum PCE of 7.3% in PSCs.

Based on their own unique advantages, the rigid and planar BDT units [16–23] as well as the widely used electron-withdrawing quinoxaline [24–31] were often employed to construct the low band-gap D–A copolymers. By fluoration of quinoxaline, it is possible to reduce the HOMO energy levels of its polymers due to the additional electron-withdrawing effect of fluorine [32–39]. The decreased HOMO energy level is suggested to be available to increase $V_{oc}$ and probably lead to a higher PCE. Therefore, Gedeffaw et al. developed some one-dimensional (1-D) conjugated D–A copolymers based on the BDT and quinoxaline units with different spacers. The different influence of various spacers on the photovoltaic properties was demonstrated for these 1-D conjugated polymers in PSCs. Therein, the PDFTDFQ-TT polymer with thiieno[3,2-b]thiophene (TT) spacer displayed an enhanced PCE of 5.6% [14].

Although the critical effect of the spacer groups on the photovoltaic properties has been reported for 1-D conjugated polymers, there is still lack of systematic study and rational design of spacer groups for copolymers, especially for the two-dimensional (2-D) conjugated polymers. Considering that appending alkylthiophene units instead of alkyl onto BDT units can further lower the HOMO energy levels [21–23], in this work, alkylthiophene-substituted benz[1,2-b:4,5-b]dithiophene (BDTT) and 5,6-difluorothiophene (Q) were selected as D and A building blocks to construct a type of low band-gap 2-D conjugated polymers, named PDDBT-FQ, PDDBT-TQ, PDDBT-TTQ and PDDBT-BTQ, with altered spacer groups in the main chain, including furan, thiophene, thiieno[3,2-b]thiophene and bithiophene, respectively. It is found that these spacers have significant influence on photovoltaic performances of their 2-D conjugated polymers. Among these four copolymers, the PDDBT-TQ polymer with a thiophene spacer here exhibited the highest PCE of 5.8% with a $J_{sc}$ of 13.7 mA/cm$^2$, a $V_{oc}$ of 0.77 V and a fill factor (FF) of 0.56 in the single BHJ PSCs.

2. Experimental section

2.1. Instrumentations and characterization

All $^1$H NMR spectra were recorded on a Bruker AV-400 using CDCl$_3$ as solvent. MALDI-TOF mass spectrometric measurements were performed on Bruker Biflex III MALDI TOF. UV–Vis spectra were measured on a Perkin–Elmer Lamada 25 spectro-meter. Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 analyzer and differential scanning calorimeter (DSC) was measured on a TA Q200 instrument under nitrogen atmosphere at a heating rate of 10°C min$^{-1}$. Surface morphologies were recorded by atomic force microscopy (AFM) on a Veeco-DI multimode NS-3D apparatus in a tapping mode under normal air condition at room temperature. Cyclic voltammograms (CV) were performed with a three electrode electrochemical cell in a 0.1 M tetra(n-butyl)ammonium hexafluorophosphate ([TBAPF$_6$]) solution with a scan rate of 100 mV s$^{-1}$ at room temperature under argon atmosphere. A platinum wire was used as counter electrode and Ag/Ag$^+$ (0.1 M) was adopted as a reference electrode, which was calibrated against the redox potential of ferrocene/ferrocnium (Fc/Fc$^+$). The thin film on the Pt disk, formed by drop-casting polymer solution in o-dichlorobenzene (ODCB) (analytical reagent, 10 mg/mL), was used as the working electrode.

2.2. Fabrication and characterization of polymer solar cells

The photovoltaic cells were made with a traditional sandwich structure through the following steps. The indium tin oxide (ITO)-coated glass substrates were cleaned by a series of ultrasonic treatments each for 10 min in acetone, following by deionized water, then 2-propanol. The substrates were dried under a nitrogen stream and subjected to treatment of Ar/O$_2$ plasma for 5 min. A filtered aqueous solution of poly(3,4-ethylenedioxy-thiophene)-poly(styrenesulfonate) (PEDOT:PSS; Bayer AG) was spun-cast onto the ITO surface at 2000 rpm for 30 s and baked at 150°C for 30 min to form a PEDOT:PSS thin film with a thickness of 30 nm. A blend of polymer and [6,6]-phenyl-C-71-butyric acid methyl ester (PC$_{71}$BM) was dissolved in ODCB, filtered through a 0.45 μm poly(tetrafluoroethylene) filter and spun-cast at 3000 rpm for 30 s onto the PEDOT:PSS layer with a thickness of 100 nm. The substrates were dried under N$_2$ at room temperature and annealed at 150°C for 15 min in a nitrogen-filled glovebox. The devices were completed after thermal deposition of 10 nm calcium and 100 nm aluminum films as the cathode at a pressure of 6 × 10$^{-4}$ Pa. The active area was 0.1 cm$^2$ for each cell. The thicknesses of the spin-cast films were recorded by a profilometer (Alpha-Step 200; Tencor Instruments).

Device characterization was characterized under an AM 1.5 G irradiation with an intensity of 100 mW cm$^{-2}$ (Oriel 91160, 300 W). Current density–voltage (J–V) characteristics were measured with a computer-controlled Keithley 2602 source measurement unit in the dark. PCE was detected under a monochromatic illumination (Oriel Cornerstone 260 1/4 m monochrometer equipped with Oriel 70613NS QTH lamp) and the calibration of the incident light was performed with a monocrystalline silicon diode. The external quantum efficiency (EQE) was measured with a source meter, silicon photodiode and a computer-controlled light source-monochrometer-lock-in system. All device fabrication procedures and measurements were carried out in air at room temperature. The resulting photovoltaic data for the PSCs here are reproducible champion values rather than the average values.
2.3. Materials

Monomer 2,5-bis(trimethyltin)-7,8-bis-(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene and 2,5-bis(trimethyltin)-7,8-bis-(4,5-dihexyl-thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene were purchased directly from the Solarmer Materials (Bei-jing) Inc. and SunaTech Inc., respectively. The other reagents and chemicals were purchased from commercial sources (Aldrich, Acros, TCI) and used without further purification unless stated otherwise. Tetrahydofuran (THF) was distilled over sodium and benzophenone under an inert nitrogen atmosphere. 5,8-Dibromo-6,7-difluoro-2,3-bis(3-octyl-oxyphenyl)quinoxaline (1) was prepared according to literatures procedures [40]. The detailed syntheses of monomers were presented in Supporting Information.

2.4. Synthesis of polymers

2.4.1. Synthesis of polymer PBDTT-FQ

In a dry 25 mL flask, tris(dibenzylideneacetone)dipalladium(0) [Pd(dba)3] (5.0 mg) and tri(o-tolyl)phosphine [P(o-Tol)3] (10.0 mg) were added to a solution of 2,5-bis(trimethyltin)-7,8-bis-(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene (190 mg, 0.21 mmol) and M1 (182 mg, 0.21 mmol) in 6 mL degassed toluene under nitrogen and stirred vigorously at 100 °C for 27 h. After cooled to room temperature, the mixture was poured into acetone and the precipitation was occurred. It was collected by filtration and successively extracted in Soxhlet apparatus with diethyl ether and chloroform, respectively. The collected chloroform solution was concentrated and precipitated with ether and chloroform, respectively. The collected solution was then washed with diethyl ether followed by drying over anhydrous sodium sulfate. The dry polymer was recovered by filtration, dissolved in THF and precipitated with methanol. The collected polymer was purified by repeated precipitation with diethyl ether and chloroform. The polymer was collected as a dark red solid (185 mg, 71.1%).

2.4.2. Synthesis of polymer PBDTT-TQ

PBDDT-TQ was prepared according to the synthetic procedure of PBDTT-FQ by the reaction among 2,5-bis(trimethyltin)-7,8-bis-(4,5-dihexyl-thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene and tri(o-tolyl)phosphine [P(o-Tol)3] (10.0 mg) in dry toluene (8 mL). The reaction was stirred for 0.5 h and the polymer was collected as a dark solid (230 mg, 95.8%). 1H NMR (400 MHz, CDCl3) δ (ppm), 8.27–7.88 (br, 2H), 7.85–7.38 (br, 6H), 7.35–7.01 (m, 8H), 7.04–6.71 (br, 4H), 6.11–3.55 (br, 4H), 3.18–2.58 (m, 4H), 2.57–2.38 (m, 4H), 2.35–1.75 (br, 12H), 1.45–1.02 (br, 60H), 1.05–0.56 (br, 18H).

2.4.3. Synthesis of polymer PBDTT-TTQ

PBDDT-TTQ was prepared according to the synthetic procedure of PBDTT-FQ by the reaction among 2,5-bis(trimethyltin)-7,8-bis-(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene and tri(o-tolyl)phosphine [P(o-Tol)3] (10.0 mg) in dry toluene (7 mL). The reaction was stirred for 0.5 h and the polymer was collected as a dark solid (198 mg, 73.6%). 1H NMR (400 MHz, CDCl3) δ (ppm), 8.04–7.82 (br, 1H), 7.80–7.55 (br, 2H), 7.54–7.32 (br, 2H), 7.30–7.09 (m, 6H), 7.08–6.51 (m, 7H), 4.00–3.60 (m, 4H), 3.25–2.58 (m, 4H), 1.95–1.53 (br, 6H), 1.50–1.12 (br, 36H), 1.09–0.77 (m, 18H).

2.4.4. Synthesis of polymer PBDTT-BTQ

PBDDT-BTQ was prepared according to the synthetic procedure of PBDTT-FQ by the reaction among 2,5-bis(trimethyltin)-7,8-bis-(4,5-dihexyl-thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene (144 mg, 0.14 mmol), M3 (150.1 mg, 0.14 mmol), Pd(dba)3 (5.0 mg) and P(o-Tol)3 (10.0 mg) in dry toluene (8 mL). The reaction was stirred for 0.5 h and the polymer was collected as a dark solid (203 mg, 95.8%). 1H NMR (400 MHz, CDCl3) δ (ppm), 8.27–7.88 (br, 2H), 7.85–7.38 (br, 6H), 7.35–7.01 (m, 8H), 7.04–6.71 (br, 4H), 4.11–3.55 (br, 4H), 3.18–2.68 (br, 4H), 2.57–2.38 (m, 4H), 2.35–1.75 (br, 12H), 1.45–1.02 (br, 60H), 1.05–0.56 (br, 18H).

3. Results and discussion

3.1. Synthesis and thermal properties

The synthetic routes of four copolymers of PBDTT-FQ, PBDTT-TQ, PBDTT-TTQ and PBDDT-BTQ are outlined in Scheme 1. All the polymers were synthesized by the palladium-catalyzed Stille-coupling polymerization with moderate yield. In order to increase the solubility, 4,5-dihexyl-thiophen-2-yl was attached on BDT units instead of 5-(2-ethylhexyl)thiophen-2-yl for polymer PBDDT-BTQ. The molecular weights of these polymers were determined by GPC relative to polystyrene standards and the corresponding data are listed in Table 1. The maximum and minimum number molecular weights (Mn) are observed to be 58 kDa for PBDDT-TQ and 35 kDa for PBDDT-FQ, respectively.

The recorded TGA and DSC curves of these copolymers are depicted in Fig. S1 (see Supporting Information). The thermal decomposition temperatures of 410–420 °C are observed at 5% weight loss (Fig. S1a), which are higher than those of the analogic 1-D copolymers [14]. No thermal transition point is observed from 40 °C to 300 °C in the DSC curve (Fig. S1 b), indicating that these 2-D copolymers have amorphous characteristics.

3.2. Optical properties

The normalized UV–Vis absorption spectra of these 2-D copolymers in ODCB solution and the solid state are shown in Fig. 1. Two typical absorption bands are observed for these four polymers. The high-lying absorption band from 350 to 450 nm is assigned to the π–π transition, the other low-lying absorption band from 500 to 700 nm is attributed to the strong intra-molecular charge transfer. Interestingly, three polymers without furan spacer show similar absorption profiles with little shift. The polymer PBDDT-FQ with furan spacer displays an obvious blue-shift absorption profile compared with other three polymers. This blue-shift phenomenon was caused by the weakest electron-donating properties of the furan unit among these
Furthermore, PBDTT-FQ exhibits the largest red-shift absorption spectrum by about 30 nm, while the other three polymers display a slight absorption profile variation about 15 nm from solution to the solid state. It indicates that PBDTT-FQ has the strongest inter-molecular packing potential in the solid state. The optical data were summarized in Table 2.

### 3.3. Electrochemical properties

As polymeric energy levels are highly important in determining their photovoltaic performance, cyclic voltammetry (CV) was performed to investigate polymeric electro-chemical properties and energy levels. Fig. 2 shows the recorded CV curves of four copolymers. The observed onset oxidation and reduction potentials ($E_{\text{onset}}/E_{\text{red}}$) for PBDTT-FQ, PBDTT-TQ, PBDTT-TTQ and PBDTT-BTQ are 0.61 V/1.65 V, 0.35 V/1.54 V, 0.30 V/1.60 V and 0.23 V/1.72 V against the redox potential of ferrocene/ferrocenium (Fc/Fc$^+$), respectively. According to the equations, the HOMO and LUMO energy levels ($E_{\text{HOMO}}/E_{\text{LUMO}}$) of polymers can be calculated from the onsets of oxidation and reduction potentials, respectively [41]:

$$E_{\text{HOMO}} (\text{eV}) = -(E_{\text{onset, ox vs Fc}}/\text{Fc}^+ + 5.1)$$  \hspace{1cm} (1)  

$$E_{\text{LUMO}} (\text{eV}) = -(E_{\text{onset, red vs Fc}}/\text{Fc}^+ + 5.1)$$  \hspace{1cm} (2)

As a result, the corresponding HOMO and LUMO energy levels are $-5.71 \text{ eV} / -3.45 \text{ eV}$, $-5.45 \text{ eV} / -3.56 \text{ eV}$, $-5.40 \text{ eV} / -3.50 \text{ eV}$ and $-5.33 \text{ eV} / -3.38 \text{ eV}$ for PBDTT-FQ, PBDTT-TQ, PBDTT-TTQ and PBDTT-BTQ, respectively. The correlate data are summarized in Table 2. Significant influence of the spacers on the energy levels is observed. Polymer PBDTT-FQ with furan spacer exhibits a deeper HOMO level than the other three polymers. On the other hand, the

<table>
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<tr>
<th>Polymers</th>
<th>$M_n$ (kDa)</th>
<th>$M_w$ (kDa)</th>
<th>PDI</th>
<th>$T_d$ (°C)</th>
</tr>
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<tbody>
<tr>
<td>PBDTT-FQ</td>
<td>35</td>
<td>109</td>
<td>3.08</td>
<td>426</td>
</tr>
<tr>
<td>PBDTT-TQ</td>
<td>58</td>
<td>116</td>
<td>2.01</td>
<td>411</td>
</tr>
<tr>
<td>PBDTT-TTQ</td>
<td>54</td>
<td>116</td>
<td>2.12</td>
<td>413</td>
</tr>
<tr>
<td>PBDTT-BTQ</td>
<td>49</td>
<td>130</td>
<td>2.65</td>
<td>431</td>
</tr>
</tbody>
</table>

**Scheme 1.** Synthetic routes of 2-D copolymers.
LUMO energy levels of these copolymers are located within a suitable range from $C0^{3.38}$ to $C0^{3.56}$ eV, which are higher than that of PC71BM. Therefore, efficient charge transfer and separation could be expected to occur in their corresponding devices.

### 3.4. Photovoltaic properties

To investigate the effect of the conjugated spacers on the photovoltaic properties, polymer solar cells with a structure of ITO/PEDOT:PSS/polymer:PC71BM/Ca/Al were fabricated. Fig. S2 depicts the current density–voltage ($J$–$V$) characteristics of these copolymers-based devices under different blending ratios of copolymers to PC71BM and the corresponding photovoltaic data are summarized in Table S1 (see Supporting Information). The optimized blending weight ratios to PC71BM are 1:1 for PBDTT-FQ and PBDTT-TQ, whereas 1:2 for PBDTT-TTQ and PBDTT-BTQ. Under these optimized blending ratios and annealing conditions (90–100°C), the $J$–$V$ characteristics of these copolymers-based devices are measured and shown in Fig. 3.

![Normalized UV–Vis absorption spectra of 2-D copolymers in solution (a) and film state (b).](image)

**Fig. 1.** Normalized UV–Vis absorption spectra of 2-D copolymers in solution (a) and film state (b).

**Table 2**

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Optical properties</th>
<th>Electrochemical properties</th>
<th>Packing properties</th>
</tr>
</thead>
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<tr>
<td></td>
<td>$\lambda_{abs}^a$ (nm)</td>
<td>$\lambda_{abs}^b$ (nm)</td>
<td>$\lambda_{onset}^b$ (nm)</td>
</tr>
<tr>
<td>------------</td>
<td>-------------------</td>
<td>---------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>PBDTT-BTQ</td>
<td>360, 460, 616, 620</td>
<td>360,462, 602,635</td>
<td>718</td>
</tr>
</tbody>
</table>

* Measured in ODCB solution.

* Measured in the neat film.

![Cyclic voltammograms of the 2-D copolymer films on Pt electrode in 0.1 mol/L Bu$_4$NPF$_6$, CH$_3$CN solution with a scan rate of 100 mV/s.](image)

**Fig. 2.** Cyclic voltammograms of the 2-D copolymer films on Pt electrode in 0.1 mol/L Bu$_4$NPF$_6$, CH$_3$CN solution with a scan rate of 100 mV/s.

![Normalized Current (a.u.) vs Potential VS. Fc/Fc’ (V)](image)

**Fig. 3.** Current density–voltage characteristics of the 2-D copolymers/PC$_{71}$BM-based PSCs under the illumination of AM 1.5 G, 100 mW/cm$^2$
Fig. 3, as well as the corresponding data are listed in Table 3. The highest $V_{oc}$ of 0.91 V for the PBDTT-FQ-based device and the lowest $V_{oc}$ of 0.66 V for the PBDTT-BTQ-based device are observed, which is coincident with the reported deduction that the $V_{oc}$ is proportional to the difference between the HOMO level of copolymers and the LUMO level of PC$_7$BM. Unfortunately, PBDTT-FQ with furan spacer exhibits the lower $J_{sc}$ value (9.10 mA/cm$^2$) than the other three copolymers with thiophene, thieno[3,2-b]thiophene and bithiophene spacers, respectively. The maximum $J_{sc}$ of 13.7 mA/cm$^2$ and the highest PCE up to 5.9% are obtained in PBDTT-TQ-based device. Significant influence of these spacers on the photovoltaic properties of their copolymers is presented in these BHJ-based PSCs. Here, the thiophene spacer makes the best effect on improving photovoltaic properties of its 2-D copolymer of PBDTT-TQ. Surprisingly, PBDTT-BTQ with bithiophene spacer exhibits the lowest PCE value (3.5%) in the optimized device although it only increases one more thiophene spacer compared to PBDTT-TQ. In order to explain why PBDTT-TQ exhibits the highest PCE and $J_{sc}$ values, the external quantum efficiency ($EQE$) curves of these PSC devices were also measured. As shown in Fig. 4, the PBDTT-TQ/PC$_7$BM device demonstrates the highest $EQE$ value of 72.5% at 400 nm and $EQE$ over 58% covers a broad range from 360 to 680 nm, which is coincident with its absorption spectrum. The relatively higher $EQE$ value is available for PBDTT-TQ to present enhanced $J_{sc}$ and PCE values in PSCs.

3.5. Hole mobility

To further understand the effect of spacers on photovoltaic performance of their copolymers in PSC devices, hole mobilities of these photoactive layers were measured by the space charge limited current (SCLC) method in the hole-only devices with a structure of ITO/PEDOT:PSS/active layer/MoO$_3$/Al at the optimized condition. The SCLC can be approximated by the Mott–Gurney equation: $J = \frac{9}{8}e_0\epsilon_r d^3 (V/d^2)$ [42]. Here $J$ is current density, $\epsilon_r$ is dielectric constant of copolymer, $\epsilon_0$ is free-space permittivity (8.85 × 10$^{-12}$ F/m), $d$ is thickness of the blended film layer, $V = V_{appl} - V_{bi}$. $V_{appl}$ is applied potential, and $V_{bi}$ is built-in potential which results from the work function difference between anode and cathode. Fig. 5 displays the $J^{1/2}$–$V$ curves of these hole-only devices containing copolymers/PC$_7$BM active layers, respectively. As summarized in Table 3, the hole mobilities of 9.0 × 10$^{-5}$–2.2 × 10$^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ are obtained for these copolymers in the hole-only devices. It is unexpected that PBDTT-BTQ with dithiophene spacer presents the highest hole mobility among four copolymers even if this copolymer displays the lowest $V_{oc}$ and $EQE$ values in the PSCs. Therefore, various impact factors besides hole mobility on photovoltaic performance of copolymers need be fully considered in order to improve their photovoltaic performance in PSCs.

3.6. Morphology study

Fig. 6 shows the X-ray diffraction patterns of four copolymers in their thin films. Two typical broad diffraction peaks are observed in all these thin films. The first

<table>
<thead>
<tr>
<th>Polymers</th>
<th>D:A ratio</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Hole mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDTT-FQ</td>
<td>1:1$^a$</td>
<td>9.10</td>
<td>0.91</td>
<td>0.53</td>
<td>4.3</td>
<td>9.0 × 10$^{-5}$</td>
</tr>
<tr>
<td>PBDTT-TQ</td>
<td>1:1$^a$</td>
<td>13.7</td>
<td>0.77</td>
<td>0.56</td>
<td>5.9</td>
<td>1.0 × 10$^{-4}$</td>
</tr>
<tr>
<td>PBDTT-TTQ</td>
<td>1:2$^a$</td>
<td>12.0</td>
<td>0.72</td>
<td>0.52</td>
<td>4.6</td>
<td>1.1 × 10$^{-4}$</td>
</tr>
<tr>
<td>PBDTT-BTQ</td>
<td>1:2$^a$</td>
<td>9.40</td>
<td>0.66</td>
<td>0.56</td>
<td>3.5</td>
<td>2.2 × 10$^{-4}$</td>
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$^a$ Annealing at 100 °C.

$^b$ Annealing at 90 °C.
one located at ca. 2θ = 4.4–5.0° (2θ₁) is the (100) diffraction peak, which corresponds to an inter-chain spacing (d₁) of 19.67, 18.85, 18.61 and 18.46 Å for PBDTT-FQ, PBDTT-TQ, PBDTT-TTQ and PBDTT-BTQ, respectively. The second one located at ca. 2θ = 25° (2θ₂) represents the (010) diffraction peak, which is ascribed to a facial π–π stacking with a stacking distance (d₂) of 3.84, 3.63, 3.68 and 3.58 Å for PBDTT-FQ, PBDTT-TQ, PBDTT-TTQ and PBDTT-BTQ, respectively [43,44]. The shortest inter-chain spacing and stacking distance are found in the PBDTT-BTQ thin film, which is consistent with its highest hole mobility. Obviously, these spacers play an important impact on the inter-chain spacing and facial π–π stacking. The highest PCE and Jsc values from the PBDTT-TQ-based devices indicate that appropriate inter-chain spacing and π–π stacking distance are necessary for 2-D copolymers to get high-performance PCSSs.

To further understand difference of photovoltaic performance for these copolymers in PSCs devices, morphology of four copolymers in PC71BM were also studied by atomic force microscopy (AFM). Fig. 7 depicts AFM height images (3.0 μm × 3.0 μm) of these polymeric blend films with PC71BM. Root mean square (RMS) of 0.43, 0.49, 0.67 and 1.12 nm are observed from the PBDTT-FQ, PBDTT-TQ, PBDTT-TTQ and PBDTT-BTQ blend films with PC71BM, respectively. It indicates that PBDTT-FQ, PBDTT-TQ, PBDTT-TTQ display more smooth morphology than PBDTT-BTQ in the blend films. The roughest morphology for the PBDTT-BTQ blend film probably ultimately result in a decreased Jsc and PCE values for PBDTT-BTQ in PSCs [45].

4. Conclusion

In conclusion, four low band-gap 2-D copolymers of PBDTT-FQ, PBDTT-TQ, PBDTT-TTQ and PBDTT-BTQ were obtained with different conjugated spacers and the same di(alkylthiophene)-substituted benzo[1,2-b:4,5-b’]dithiophene (BDTT) and 6,7-difluoroquinoxaline (Q) units in backbone. Significant effect of conjugated spacers, such as furan, thiophene, thieno[3,2-b]thiophene and bithiophene, on photovoltaic properties of their copolymers was observed in the BHJ PSCs. Due to the enhanced absorption properties, proper energy levels and compatibility with PC71BM, the PBDTT-TQ with thiophene spacer exhibited the best photovoltaic performance with a PCE of 5.9%, Voc of 0.77 V, FF of 0.56 and Jsc of 13.7 mA/cm².
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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2014.08.022.

References


