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Publisher Citation

Ding, P., Zou, Y., Chu, C., Xiao, D., Hsu, C. (2012). "Effects of Thiophene Units on Substituted Benzothiadiazole and Benzodithiophene Copolymers for Photovoltaic Applications", *J. Appl. Polym. Sci.* 125(5), 2012, 3936-3945. doi: 10.1002/app.36541/

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Effects of thiophene unit on substituted benzothiadiazole and benzodithiophene copolymers for photovoltaic applications

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Abstract: Two conjugated copolymers, **P1** and **P2**, comprising of benzodithiophene and 5, 6-dioctyloxy-benzothiadiazole (DOBT) derivatives with/without thiophene unit, were synthesized via Stille cross-coupling polymerization reaction. These copolymers are promising for the applications in BHJ solar cells due to their good solubilities, proper thermal stability and moderate hole mobility as well as low bandgap. The photovoltaic properties of the copolymers were investigated based on the blend of the different polymer/PC₇₁BM weight ratio under AM1.5G illumination, 100 mW/cm². The device with ITO/PEDOT:PSS/**P2**: PC₇₁BM (1:2, w/w)/Ca/Al gave relatively better photovoltaic performance, with a power conversion efficiency of 1.55%.

INTRODUCTION

In the past two decades, polymer solar cells (PSCs) have attracted broad interests due to their flexibility and low cost of processing.¹⁻³ Conjugated polymers with low bandgaps are emerging as competitive candidates for developing PSCs into practical applications due to the improved absorption of the solar photon flux in order to generate higher photocurrent.⁴ Recent years, bulk heterojunction (BHJ) PSCs has made great progress.⁵⁻⁷ In this type of device, a blend of an electron-donating material (p-type conjugated polymers) and an electron-accepting material (n-type fullerene derivatives) is used as the active layer. One representative BHJ PSCs is the device based on a blend of benzodithiophene (BDT) based conjugated polymers as electron donors and a soluble C₇₀ derivative, [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as an electron acceptor.^{8, 9} In 2009, Hou *et al* reported a power conversion efficiency (PCE) of the PSCs based on FPBDTTT–CF reached up to 7.7%.¹⁰ Last year, Leclerc *et al* synthesized a new BDT-based polymer (PBDTTPD) using thienopyrrodione as the new electron accepting unit, with low bandgap and preferred energy level, exhibiting high PCE up to 5.5 % using a large active area of 1 cm².¹¹ Therefore, alternating donor (D)-acceptor (A) poly(2,6-benzodithiophene) derivatives with a suite of electron-accepting moieties are particularly interesting for the development of PSCs.

As electron donor materials, conjugated polymers are usually required to carry flexible side chains to ensure the polymers with good solubility in organic solvents. The lengths and positions of alkyl or alkoxy chains play an important role in

solubility, molecular weights, energy levels of conjugated polymers, morphologies of blend films, and therefore the photovoltaic performance of devices.^{12,13} Our group recently synthesized a copolymer, namely poly(2-(5-(5,6-bis(octyloxy)-4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)-4,8-di(2-ethylhexyloxy)benzo[1,2-b:3,4-b]dithiophene) (**PBDT-DODTBT**), with two octyloxy chains on benzothiadiazole moiety, which demonstrated that a planar structure was formed due to the low steric hinderance of octyloxy chain, and a PCE of 4 % was achieved.¹⁴ The results indicate 5,6-dioctyloxy-benzothiadiazole (DOBT) is a good electron accepting building block to construct highly soluble polymer photovoltaic materials.

As well known, polythiophene and its derivatives have been investigated as active materials for the wide applications in polymer light-emitting diodes, polymer field-effect transistors and PSCs due to relative higher hole mobility in comparison with other conjugated polymers.¹⁵⁻¹⁷ Obviously, thiophene unit was very important in tuning optoelectronic properties of the polymers. Moreover, to the best of our knowledge, there was no report about incorporating one thiophene unit into DOBT moiety to construct the polymers for the photovoltaic applications or investigating the effect of changing the numbers of thiophene unit on the thermal, optical, electrochemical and photovoltaic properties of DOBT based polymers. Based on the above considerations and our previous work, we have synthesized two conjugated polymers as shown in Scheme 1, **P1** without thiophene unit and **P2** with one thiophene unit in the repeating unit, which both used DOBT as an electron-deficient

moiety and BDT as an electron-rich moiety. A similar polymer, **PBDT-DODTBT** is also listed for comparison.¹⁴ In this work, from **P1** to **PBDT-DODTBT**, hole mobilities and PCEs from polymer/PC₇₁BM blends gradually increased with the increasing introduction of thiophene unit. Furthermore, the relationship between the structure and the optoelectronic properties was also investigated and discussed in detail.

Scheme 1 The chemical structures of low bandgap polymers.

EXPERIMENTAL PART

Materials

Pd(PPh₃)₄, 2-thiophene boronic acid and catechol were obtained from Alfa Asia Chemical Co and Pacific Chem Source, and they were used as received. Toluene was dried over Na/benzophenone ketyl and freshly distilled prior to use. Other reagents and solvents were purchased commercially as analytical-grade quality and used without further purification. Column chromatography was carried out on silica gel (size: 200-300 mesh). 2, 6-Bis(trimethyltin)-4, 8-di(2-ethylhexyloxy)benzo[1, 2-b:3, 4-b]dithiophene (**4**) was prepared according to the literature.^{18,19}

Characterization

¹H NMR spectra were recorded using a Bruker AV-400 spectrometer in deuterated chloroform solution at 298 K, unless specified otherwise. Chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane (TMS) standard.

Elemental analysis was performed on a Flash EA 1112 analyzer. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene as the standard (Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4) using THF (HPLC grade) as eluent at a flow rate of 1.0 mL/min at 35 °C. Thermogravimetric analysis (TGA) was conducted on a Shimadzu DTG-60 thermogravimetric analyzer with a heating rate of 20 °C/min under a nitrogen atmosphere. The temperature of degradation (T_d) corresponds to a 5% weight loss. The UV-Vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. For solid state measurements, polymer solution in chloroform was drop-cast on quartz plates. Optical bandgap was calculated from the onset of the absorption spectra. X-ray diffraction (XRD) measurements of the polymer thin films were carried out with a 2-kW Rigaku X-ray diffraction system. XRD patterns were obtained using Bragg-Brentano Geometry (θ - 2θ) with Cu $K\alpha$ radiation as an X-ray source in the reflection mode at 45 kV and 300 mA. The cyclic voltammogram was recorded with a Zahner IM6e electrochemical workstation (Germany) using polymer film on platinum disk as the working electrode, platinum wire as the counter electrode and Ag/Ag⁺ (0.1 M) as the reference electrode in a nitrogen-saturated acetonitrile (CH₃CN) solution containing 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆). Hole mobility of the polymer was measured by the space-charge-limited current (SCLC) method with a device structure of ITO/PEDOT:PSS/polymer/Au. The morphology of the polymer/PCBM blend films was investigated by a SPI 3800N

atomic force microscope (AFM) in contacting mode with a 1 μm scanner.

Fabrication and characterization of photovoltaic cells

The PSCs were fabricated in the configuration of the common sandwich structure with an indium tin oxide (ITO) glass anode and a calcium/aluminum cathode. Patterned ITO glass with a sheet resistance of 15-20 Ω/\square was purchased from CSG HOLDING Co., LTD. (China). Each ITO substrate was patterned using photolithography techniques. Prior to use, the substrates were cleaned with detergent and deionized water. Then, they were ultrasonicated in acetone and isopropanol for 15 minutes, respectively. The ITO substrates were subjected to UV ozone cleaning for 15 minutes. ITO substrates were spin-coated (3500rpm, 60 s) with a thin film (25 nm) of (PEDOT: PSS, Al4083, H. C. Stark) and dried at 150 $^{\circ}\text{C}$ for 30 min in a glove box. A blend of [6,6]-phenyl- C_{71} butyric acid methyl ester (C_{70} -PCBM) (Nano-C, USA) and polymer was solubilized in *o*-dichlorobenzene (ODCB) overnight, filtered through a 0.45 μm poly(tetrafluoroethylene) (PTFE) filter, and then spin-coated at 2000 rpm for 60 s onto the PEDOT: PSS layer. Sequentially, the devices were completed by deposition of a 10 nm Ca and 100 nm Al layer. This layer was thermally evaporated at a pressure of 6×10^{-1} Torr at room temperature. Solar cells were fabricated with an effective area of 0.12 cm^2 . Current versus potential curves (I - V characteristics) were measured with a Keithley 2400 Digital Source Meter under a collimated beam. Illumination of the cells was done through the ITO side using light from 300 W San-Ei Solar Simulator (XES-301S + EL-100) to provide an intensity of 100 mWcm^{-2} . All fabrications after cleaning of ITO substrates and characterizations were performed

in a glove box.

Synthesis of monomers and polymers

Synthetic routes of the monomers and polymers are shown in Scheme 2. The dibromonated monomer **1** was synthesized according to our recent publication.¹⁴ All of the other compounds were synthesized as the following procedures.

Scheme 2 Synthetic routes of the monomer and the corresponding polymers.

4-bromo-5,6-bis(octyloxy)-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (2)

Compound **1** (4.13 g, 7.5 mmol), 2-thiophene boronic acid (2.50 g, 19.5 mmol), 1M NaHCO₃ (75 mL) and CH₃OCH₂CH₂OCH₃ (75 mL) were carefully degassed and then Pd(PPh₃)₄ (0.1156 g, 0.1 mmol) was added. The reaction mixture was stirred at 90 °C under nitrogen atmosphere for 12 hours. After the completion of the reaction, the reaction mixture was poured into ice-water and the water phase was extracted with dichloromethane three times. The combined organic phase was washed with NaOH (aq) and the solvents are evaporated under reduced pressure. The crude product was purified on silica gel column eluting with CH₂Cl₂/hexanes (1:10, v/v). Yellow green oil was obtained. Yield: 2.65 g (64%). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 8.48–8.47 (d, 1H), 7.52–7.51 (d, 1H), 7.24–7.23 (t, 1H), 4.09–4.12 (t, 4H), 1.88–1.96 (m, 4H), 1.41–1.29(m, 20H), 0.91–0.88 (t, 6H). Anal. Calcd. for C₂₆H₃₇BrN₂O₂S₂: C, 56.41; H, 6.74; N, 5.06. Found: C, 56.42; H, 6.76; N, 5.02.

4-bromo-5,6-bis(octyloxy)-7-(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (3)

A mixture of **2** (2.76 g, 5 mmol), *N*-bromosuccimide (NBS) (1.96 g, 11 mmol), glacial acetic acid (100 mL) and chloroform (100 mL) was stirred at room temperature in dark for 24 hours. The solvent was removed under reduced pressure and the residue was chromatographically purified on silica gel column eluting with CH₂Cl₂/hexanes (1:10, *v/v*) to afford **3** as a yellow crystal (2.56 g, 81%). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 8.35–8.34 (d, 1H), 7.17–7.16 (d, 1H), 4.17–4.12 (t, 4H), 1.93–1.91 (m, 4H), 1.37–1.30 (m, 20 H), 0.91–0.88 (t, 6H). Anal. Calcd. for C₂₆H₃₆Br₂N₂O₂S₂: C, 49.37; H, 5.34; N, 4.43. Found: C, 49.40; H, 5.37; N, 4.48.

*Poly(4,7-(5,6-bis(octyloxy))benzo[*c*][1,2,5]thiadiazole-alt-4,8-di(2-ethylhexyloxy)benzo[1,2-*b*:3,4-*b*]dithiophene)(PI)*

4,7-Dibromo-5,6-bis(octyloxy)benzo[*c*][1,2,5]thiadiazole (**1**) (110.0 mg, 0.2 mmol) and 2,6-bis(trimethyltin)-4,8-di(2-ethylhexyloxy)benzo[1,2-*b*:3,4-*b*]dithiophene (**4**) (154.4 mg, 0.2 mmol) were dissolved in toluene (6 mL). The solution was flushed with argon for 10 min, and then Pd(PPh₃)₄ (20 mg, 0.016 mmol) was added into the flask. The flask was purged three times with successive vacuum and argon filling cycles. The polymerization reaction was heated to 100 °C, and the mixture was stirred for 48 h under argon atmosphere. The mixture was cooled to room temperature and poured slowly in methanol (100 mL), the resulting precipitate was collected by filtration. The crude polymer was washed with methanol and hexane in a soxhlet apparatus to remove the oligomers and catalyst residue. Finally the polymer was extracted with chloroform. The polymer solution was condensed to about 20 mL and slowly poured in methanol (200 mL). The precipitate was collected by filtration and

dried under high vacuum to afford **P1** as a purple solid (0.145 g, 84%). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 8.32–8.25(br, 2H), 4.21–3.96(br, 8H), 2.23–1.05(br, 42H), 0.92–0.89(br, 18H). Anal. Calcd. for $(\text{C}_{48}\text{H}_{70}\text{S}_3\text{N}_2\text{O}_4)_n$: C, 69.02; H, 8.45; N, 3.35. Found: C, 69.04; H, 8.42; N, 3.35. M_n = 23115; M_w = 39015; PDI = 1.69.

*Poly(2,5-(4-(thiophen-2-yl)-5,6-bis(octyloxy))benzo[*c*][1,2,5]thiadiazole-*alt*-4,8-di(2-ethylhexyloxy)benzo[1,2-*b*:3,4-*b'*]dithiophene)(P2)*

P2 was synthesized with a similar procedure to **P1** from monomer **3** (126.4 mg, 0.2 mmol) and monomer **4** (154.4 mg 0.2 mmol), giving a dark purple solid of 154 mg. Yield: 78%. ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 8.36–8.17(br, 3H), 7.25–7.21(br, 1H), 4.20–3.97(br, 8H), 2.21–1.06(br, 42H), 0.92–0.90(br, 18H). Anal. Calcd. for $(\text{C}_{52}\text{H}_{72}\text{S}_4\text{N}_2\text{O}_4)_n$: C, 68.08; H, 7.91; N, 3.05. Found: C, 68.09; H, 7.93; N, 3.08. M_n = 6473; M_w = 15098; PDI = 2.33.

RESULTS AND DISCUSSION

Synthesis and characterization

Two benzodithiophene–benzothiadiazole copolymers with the different number of thiophene units were synthesized via the Stille polymerization reaction. The structures and the synthetic route to the polymers are outlined in Scheme 2. The polymers were purified by sequential Soxhlet extraction with methanol, hexanes and CHCl_3 . The CHCl_3 fraction was then reduced in volume, precipitated into methanol, and collected by filtration, yielding a purple (**P1**) or dark purple (**P2**) solid. It is worthy to note that **P1** is an alternating polymer, **P2** is a random polymer in that this polymerization will result in both head-head and head-tail connection regarding the asymmetric monomer

unit in the main chain. The structure and preliminary photovoltaic properties of **PBDT-DODTBT** have been previously published in the literature.¹⁴ The chemical structures of the comonomers and the polymers were verified by ¹H NMR and elemental analysis. The molecular weight of the polymer was determined by GPC in tetrahydrofuran (THF) solution relative to polystyrene standards. The M_n of **P1** and **P2** is 23.1 and 6.5 kg/mol, with a PDI of 1.69, and 2.33, respectively. The relatively low number weight for polymer **P2** and **PBDT-DODTBT** is probably due to the relatively poor solubility in the organic solvents used in the polycondensation reaction. They were precipitated from the reaction mixture during the polycondensation process. The precipitated polymers are readily soluble in the common solvents such as chloroform and 1, 2-dichlorobenzene (DCB), *etc.* Thermal stability of the polymers were investigated with thermogravimetric analysis (TGA) as shown in Figure 1. The TGA analysis revealed that the 5% weight loss temperatures (T_d) of **P1** and **P2** were 302 °C and 271 °C, respectively. This indicates that the thermal stability of the copolymers is good for the optoelectronic applications.

Figure 1 TGA curves of **P1** and **P2** at a scan rate of 20 °C/min under nitrogen atmosphere.

Optical Properties

Normalized absorption spectra of polymers **P1**, **P2** and **PBDT-DODTBT** in CHCl₃ solutions and films are shown in Figure 2(a) and (b), respectively. The related optical

data are summarized in Table I. The polymers generally show two absorption peaks both in chloroform solution and in thin film, which is in accordance with other D-A copolymers.²⁰ The absorption maxima of **P1** in chloroform solution was ca. 570 nm, which is red-shifted in comparison with other two polymers (the absorption peaks of **P2** and **PBDT-DODTBT** solutions are located at 553 nm and 548 nm, respectively). This is mainly caused by the factor that the electron rich thiophene unit weakens the intramolecular charge transfer (ICT) on the conjugated polymer backbone. As shown in Figure 2, the absorption spectra of the polymers **P1**, **P2** and **PBDT-DODTBT** in thin films were broadened and red-shifted in comparison with those of the solution. The broader and better absorption is originated from stronger electronic interaction between the individual polymer chains in the film states. The absorption onset wavelengths of **P1**, **P2** and **PBDT-DODTBT** were 732, 746 and 758 nm, which correspond to the optical bandgaps of 1.69, 1.66 and 1.64 eV, respectively. The optical bandgaps of the polymers were summarized in Table 1. The results show that the number of thiophene unit does not affect the optical bandgap of this kind of polymers.

Figure 2 Normalized absorption spectra of **P1**, **P2** and **PBDT-DODTBT** (a) in CHCl₃ and (b) in thin films.

Electrochemical Properties

Cyclic voltammetry was usually applied to estimate the HOMO and LUMO levels

of the conjugated polymers. The onset oxidation and reduction potentials obtained from the cyclic voltammograms correspond to the HOMO and LUMO energy levels, respectively. The electrochemical properties of the two copolymers were investigated by cyclic voltammetry as shown in Figure.3. All of the potentials are reported using Ag/Ag^+ as the reference with the ferrocene/ferrocenium couple as an internal standard, and the correlation can be expressed as follows:²¹ $HOMO = -e(E_{on}^{ox} + 4.71)$ (eV); $LUMO = -e(E_{on}^{red} + 4.71)$ (eV).

As observed from the cyclic voltammograms in Figure.3, the two copolymers exhibited partial reversible oxidation and irreversible reduction processes. The onset potentials for oxidation (E_{ox}) were observed to be 0.46 and 0.47 V for **P1** and **P2**, respectively. In addition, the onset potentials from the reduction (E_{red}) part were found to be -1.22 and -1.14 V, respectively. From the values of E_{ox} and E_{red} , the HOMO, LUMO energy levels and electrochemical bandgaps (E_g) of the copolymers were calculated, and the results were shown in Table I, the corresponding electrochemical bandgaps are similar to the optical bandgaps within the experimental error. We found the oxidation onset potentials of **P1**, **P2** and **PBDT-DODTBT** were similar, which indicated that the HOMO levels of the three polymers are mainly determined by the BDT segments. Compared with **P1**, **P2** by the incorporation of one thiophene unit and **PBDT-DODTBT** by the incorporation of two thiophene units were found to possess the higher reduction onset potential.

Table I The optical and electrochemical properties of the polymers.

Figure 3 Cyclic voltammograms of the copolymers films on platinum electrode in 0.1 mol/L Bu_4NPF_6 , CH_3CN solution.

Theoretical Calculations

The optimal geometries and electronic state wavefunction distribution of HOMO and LUMO of the D-A model compound were obtained at the DFT B3LYP/6-31G* level using the Gaussian 03 program suit²³ (Figure 4). To simplify the calculations, all of the alkyl chains were replaced by $-\text{CH}_3$ groups. DFT/B3LYP/ 6-31G* has been found to be an accurate method for calculating the optimal geometry and electronic structures of many molecular systems without considerations of solvent effect and interactions between polymer chains. *Ab initio* calculations on the model compound **1** for **P1** and the model compound **2** for **P2** show that the two copolymers are planar, which enable the electrons to be delocalized within the entire molecule due to the pi-conjugation. For **P1** and **P2**, the electronic wavefunction of the HOMO was distributed entirely over the conjugated molecules, which is beneficial for obtaining higher hole mobility,²⁴ however, the electron wavefunction of LUMO was mainly localized on the DOBT part. Thus, the incorporation of DOBT segment effectively reduced the bandgap due to the low LUMO energy level of the DOBT unit. From the DFT B3LYP/6-31G* level calculations combined with the equations provided by Leclerc group,²⁵ HOMO and LUMO energy levels of **P1** are -5.21 and -3.45 eV, HOMO and LUMO energy levels of **P2** are -5.22 and -3.53 eV, respectively, which are in good agreement with the experimental values for the energy gap and the

HOMO and LUMO energy levels. Therefore, the DFT calculations performed on the repetitive units can provide good estimations of the HOMO, LUMO, and bandgap energy trends, thus allowing a rapid screening of the promising polymeric structures.

Figure 4 Molecular orbital isosurfaces of HOMO and LUMO of the model compounds from **P1** and **P2**, calculated at the DFT B3LYP/6-31G* level.

Hole Mobility

Hole mobility is another important parameter of the conjugated polymers for the photovoltaic application. We measured the hole mobilities of **P1** and **P2** with the space-charge-limited current (SCLC) model using a device structure of ITO/ PEDOT: PSS/ active layer (170 nm)/Au (100 nm). The results are plotted as $\ln(Jd^3/V^2)$ vs $(V/d)^{0.5}$, as shown in Figure 5. Herein, J stands for current density, d is the thickness of the device, $V = V_{\text{appl}} - V_{\text{bi}}$, V_{appl} is the applied potential, and V_{bi} is the built-in potential.

$$J_{SCLC} = \frac{9}{8} \epsilon_o \epsilon_r \mu_o \frac{(V - V_{bi})^2}{d^3} \exp\left[0.89\gamma \sqrt{\frac{V - V_{bi}}{d}}\right] \quad (1)$$

According to equation 1²⁶ and Figure5, hole mobilities of **P1** and **P2** are evaluated to be $5.96 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $9.67 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The results show that the polymers exhibit good hole mobility, which are suitable as the polymer donor materials in PSCs. In view of the hole mobility of **PBDT-DODTBT** was $7.15 \times 10^{-3} \text{ cm}^2/\text{Vs}$,¹⁴ **P1** displayed the lowest hole mobility among the three copolymers. **P2** exhibit the relatively lower mobility compared to that of **PBDT-DODTBT**, which

may be due to random structure and low regioregularity. The results suggested that incorporation of thiophene units into the D-A conjugated polymer backbone may be a good way to improve the hole mobility, which can lead to an enhanced device performance.

Figure 5 $\ln(Jd^3/V^2)$ vs $(V/d)^{0.5}$ plot of the copolymers for the measurement of hole mobilities by the SCLC method.

X-Ray Analysis

To evaluate the crystallinity of the polymers, X-ray diffraction measurements were taken for the spin coated films on SiO₂ substrate. Figure 6 shows the XRD spectra of the thin film of **P1** and **P2** at room temperature. It is clear that **P1** and **P2** exhibited the broad band centered around 15-40 degrees, which indicates the copolymers are amorphous.

Figure 6 X-ray diffraction patterns of the polymers in solid films.

Photovoltaic Properties

To investigate the photovoltaic properties of the polymers, the photovoltaic devices with **P1**, **P2** or **PBDT-DODTBT** as electron donor and PC₇₁BM as electron acceptor were fabricated. The typical device structure was ITO/PEDOT: PSS/active layer/Ca (10 nm)/ Al (100 nm). The devices were characterized under AM1.5G illumination, 100 mW/cm². The photovoltaic properties of the devices with the

different polymer/PC₇₁BM weight ratio were summarized in Table II. The polymer/PC₇₁BM weight ratio of 1:2 showed the best photovoltaic properties. Figure 7 shows the current density-voltage curves of the devices and corresponding values of open-circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factors (FF), power conversion efficiencies (PCE) were listed in Table II. At 1:2 weight ratio of polymer/PC₇₁BM, the devices with **P1**/PC₇₁BM as active layer (75 nm) gave a V_{oc} value of 0.66 V, a FF of 41.82%, and a J_{sc} value of 1.84 mA/cm², resulting in a PCE value of 0.51%. The devices with **P2**/PC₇₁BM as active layer (70 nm) showed a V_{oc} of 0.74 V, a J_{sc} of 3.94 mA/cm², and a FF of 53.30%, resulting in a PCE of 1.55%. The devices with **PBDT-DODTBT**/PC₇₁BM as active layer (80 nm) exhibited a V_{oc} of 0.76 V, a J_{sc} of 8.84 mA/cm², a FF of 59.59%, and a PCE of 4%.

From the photovoltaic device results of **P1**, **P2** and **PBDT-DODTBT**, we observed that V_{oc} was almost the same with the different polymer/PC₇₁BM, but J_{sc} exhibited significant difference. The phenomenon confirmed V_{oc} of PSCs is directly related to the difference of the LUMO of the electron acceptor and the HOMO of the electron donor.²⁷ In comparison with **P1**, **P2** and **PBDT-DODTBT** exhibited relatively better photovoltaic performances. This may be explained that the incorporation of thiophene units into the conjugated polymer backbone favored the light harvesting and enhanced hole mobilities, and then gave relatively higher J_{sc} . Furthermore, the lower LUMO energy level of **P2** and **PBDT-DODTBT** is favorable to decrease energy level difference between the LUMO energy levels of the donor and PCBM, which can decrease the energy loss upon exciton splitting.²⁸ **P2** shows lower

J_{sc} and FF compared to those of **PBDT-DODTBT**, which may result from lower mobility and chain packing.

Table II Photovoltaic properties of the PSC devices.

Figure 7 J - V curves of the photovoltaic cells based on the polymer: PC₇₁BM (1:2, w/w) under the illumination of AM 1.5, 100 mW/cm².

Morphology

Morphology is very important in determining photovoltaic properties in PSCs. The morphologies of the blend films with the polymers: PC₇₁BM blend of 1:2 were investigated by atomic force microscopy (AFM). As shown in Figure 8, all of the blend films show smooth surface with root-mean-square roughness (R_{rms}) of 1.06 nm for **P1**: PC₇₁BM blend, 0.61 nm for **P2**: PC₇₁BM blend, indicating good miscibility between the copolymers and PC₇₁BM. In addition, the image mean roughness (R_a) of **P1**: PC₇₁BM film and **P2**: PC₇₁BM film are 0.91 nm and 0.38 nm, respectively. From the phase images, the polymer and fullerene domains are homogeneously distributed throughout the blend film, in other words, the nanometer-scale interpenetrating network can be formed in this blend, which can benefit not only the charge separation but also the charge transport, therefore, leading to a good FF of the PSCs.

Figure 8 AFM ($5 \times 5 \mu\text{m}$) topography (a), (c) and phase images (b), (d) for polymer: PC₇₁BM blend films (1:2, w/w): (a), (b) **P1**: PC₇₁BM blend; (c), (d) **P2**: PC₇₁BM blend.

CONCLUSION

In summary, two copolymers from substituted benzothiadiazole derivatives and benzodithiophene have been synthesized by a Stille cross-coupling reaction, for comparison, the polymer **PBDT-DODTBT** is also introduced in this work. Incorporation of thiophene units showed some influences on hole mobilities, morphologies and photovoltaic properties on the DOBT based copolymers. Preliminary investigations on PSCs with ITO/PEDOT:PSS/polymer: PC₇₁BM/Ca/Al were done. The polymer/PC₇₁BM weight ratio of 1:2 showed the best photovoltaic properties and PCE of the device based on **P2**/PC₇₁BM with the weight ratio of 1:2 reached 1.55%, which indicated that **P2** was a promising candidate for PSCs. Optimizations of structures with high regioregularity, molecular weights of DOBT based polymers and morphologies of blends can be believed to further enhance photovoltaic performance of this kind of polymers.

Acknowledgements: The authors acknowledge *Bo Liu, Bo Peng* for the synthesis of the intermediates and some characterizations of polymers and helpful discussions from Prof. *Yongfang Li*. This work was supported by *Lieying* Project, the Fundamental Research Funds for the Central Universities (2010QZZD0112), Doctoral Fund of Ministry of Education of China (20100162120033) and the Opening Fund of *State Key Laboratory of Powder Metallurgy*.

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Figure and Scheme caption:

Chart 1 The chemical structures of low bandgap polymers.

Scheme 1 Synthetic routes of the monomer and the corresponding polymers.

Figure 1 TGA curves of **P1** and **P2** at a scan rate of 20 °C/min under nitrogen atmosphere.

Figure 2 Normalized absorption spectra of **P1**, **P2** and **PBDT-DODTBT** (a) in CHCl₃ and (b) in thin films.

Figure 3 Cyclic voltammograms of the copolymers films on platinum electrode in 0.1 mol/L Bu₄NPF₆, CH₃CN solution.

Figure 4 Molecular orbital isosurfaces of HOMO and LUMO of the model compounds from **P1** and **P2**, calculated at the DFT B3LYP/6-31G* level.

Figure 5 $\ln(Jd^3/V^2)$ vs $(V/d)^{0.5}$ plot of the copolymers for the measurement of hole mobilities by the SCLC method.

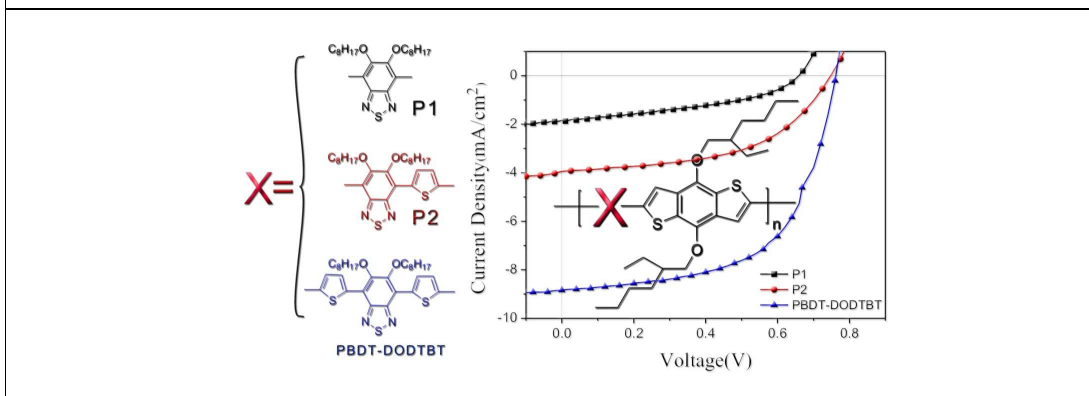
Figure 6 X-ray diffraction patterns of the polymers in solid films.

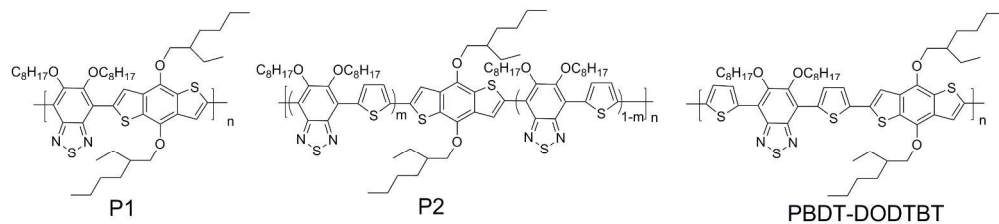
Figure 8 AFM (5 × 5 μ m) topography (a), (c) and phase images (b), (d) for polymer: PC₇₁BM blend films (1:2, w/w): (a), (b) **P1**: PC₇₁BM blend; (c), (d) **P2**: PC₇₁BM blend.

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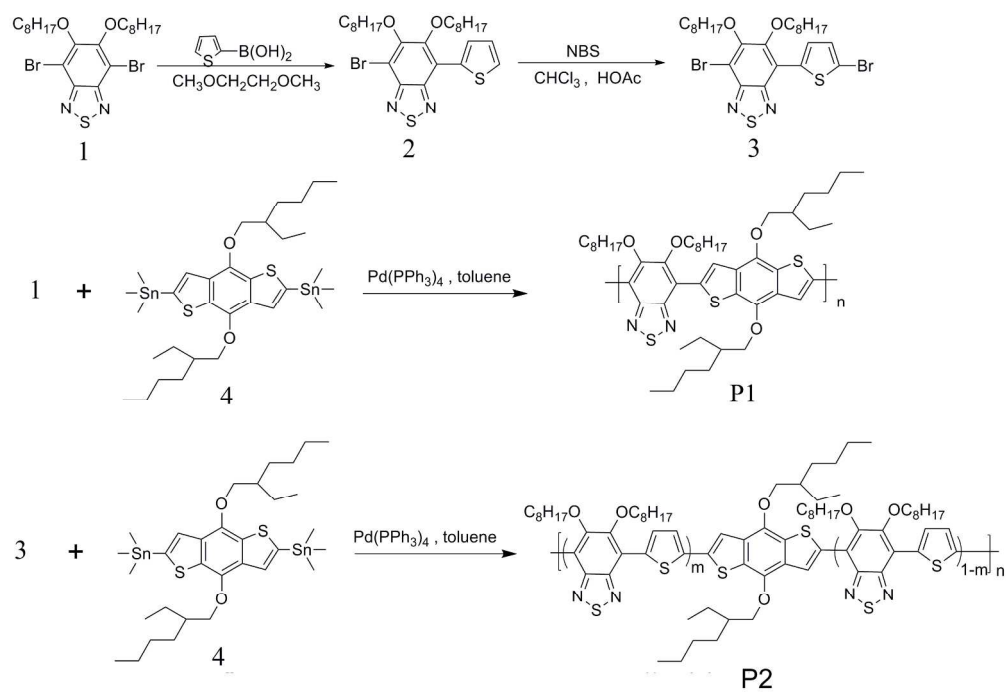
Effects of thiophene unit on substituted benzothiadiazole and benzodithiophene copolymers for photovoltaic applications

Ping Ding,^a Yingping Zou,^{a*} Cheng-Che Chu,^b Dequan Xiao,^c Chain-Shu Hsu^b

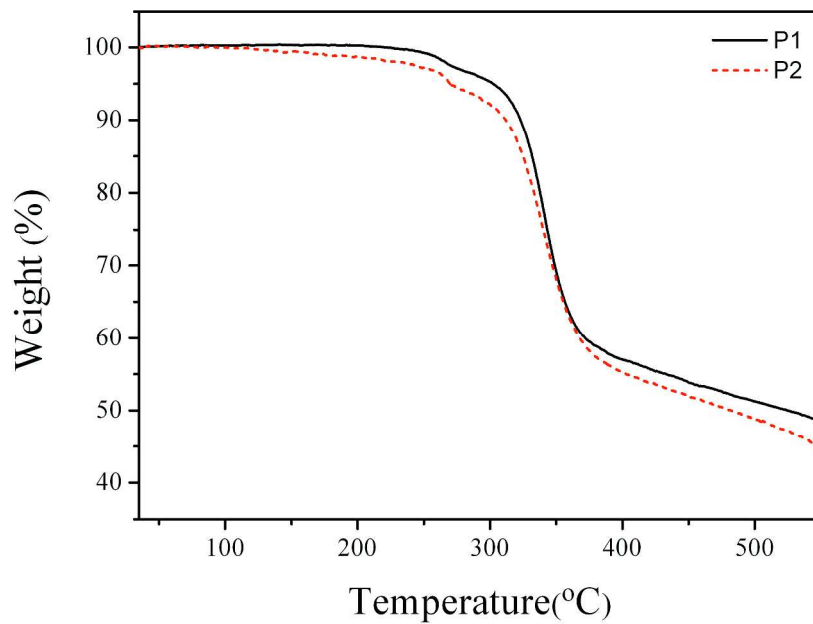




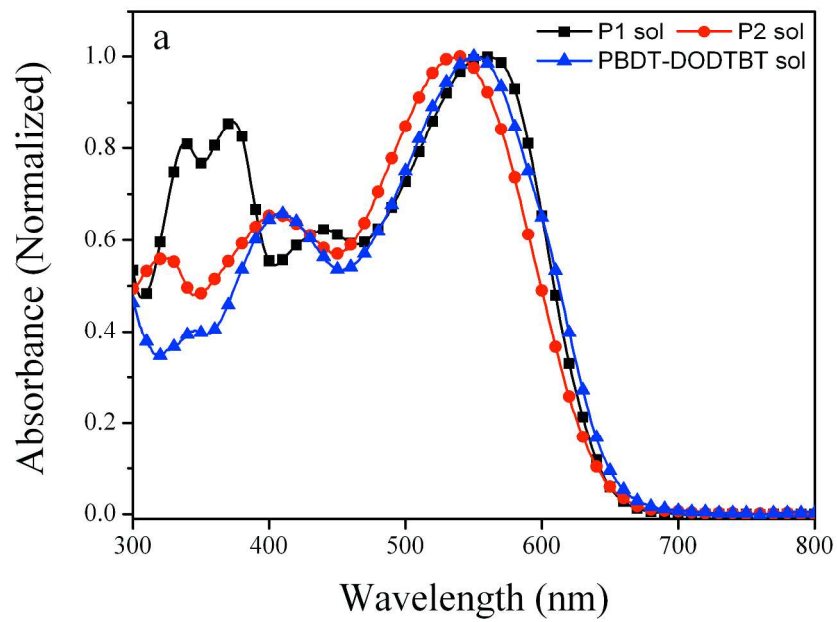
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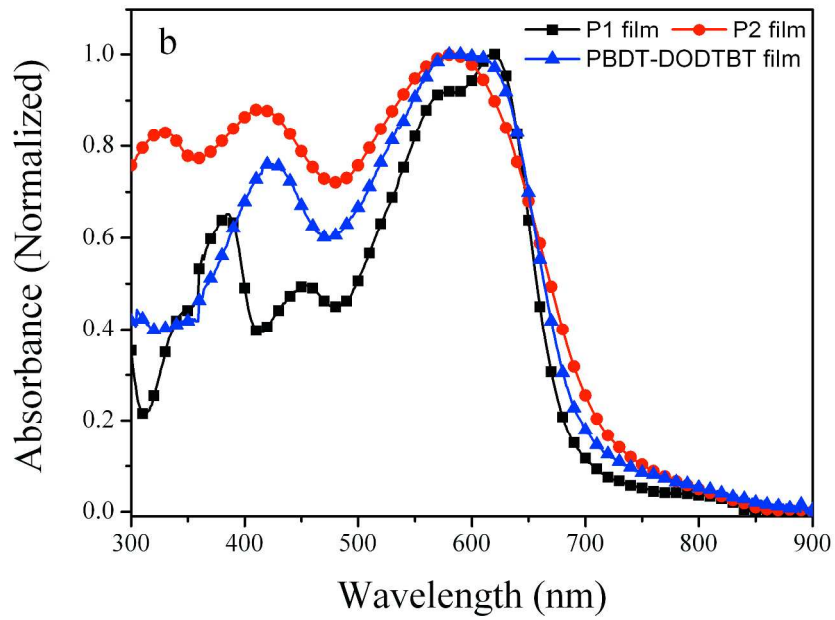
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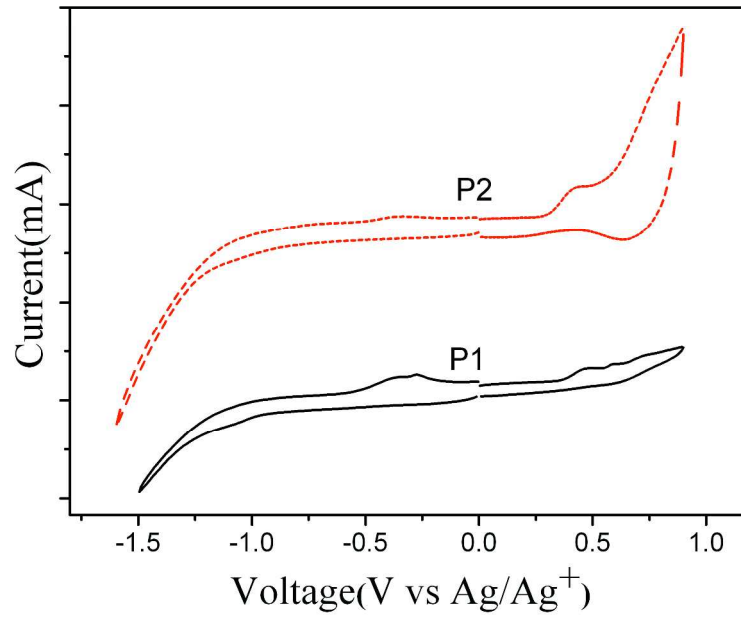
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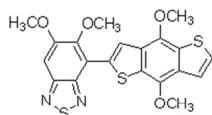
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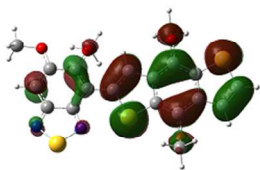
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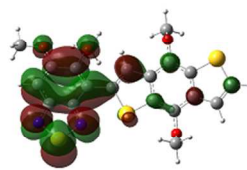
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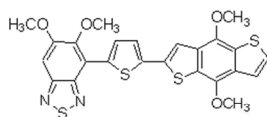
D-A Model compound 1 from P1



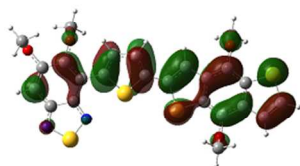
HOMO



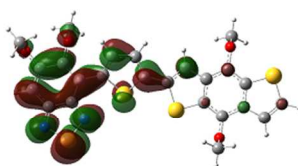
LUMO



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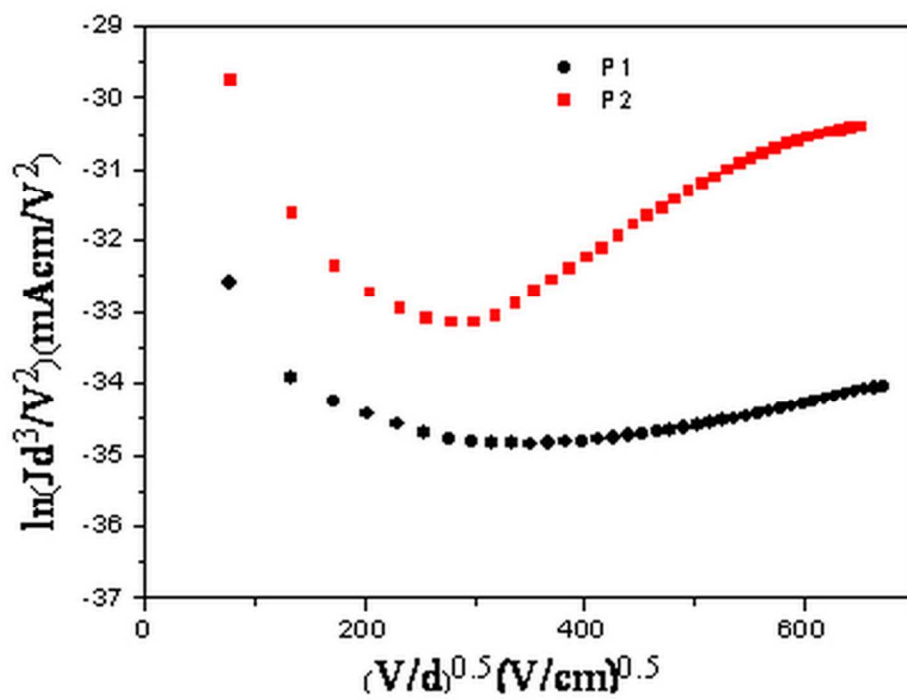


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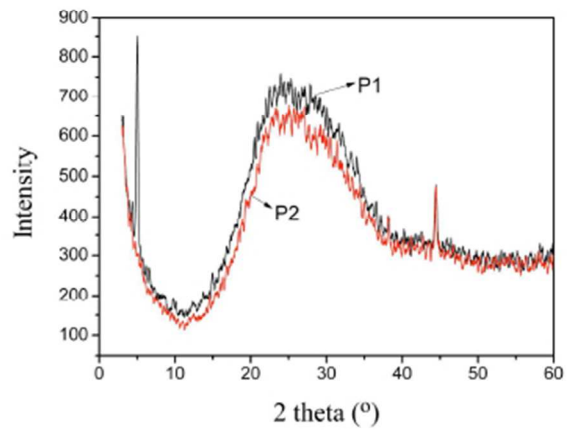


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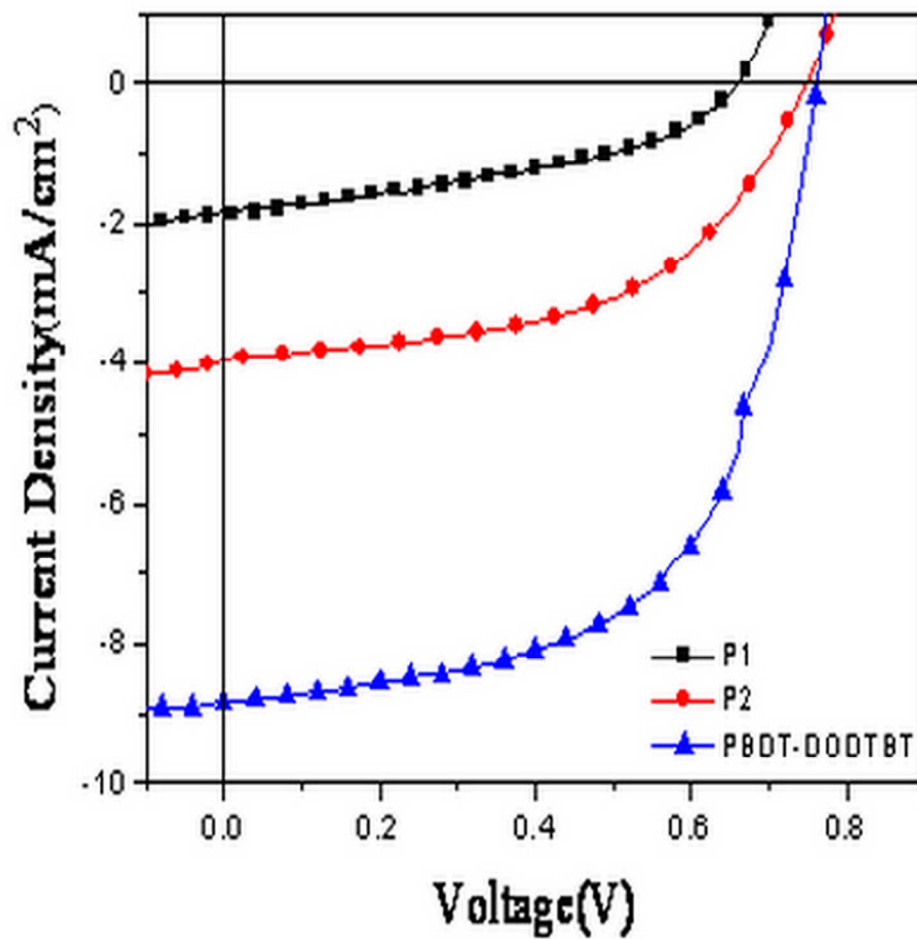
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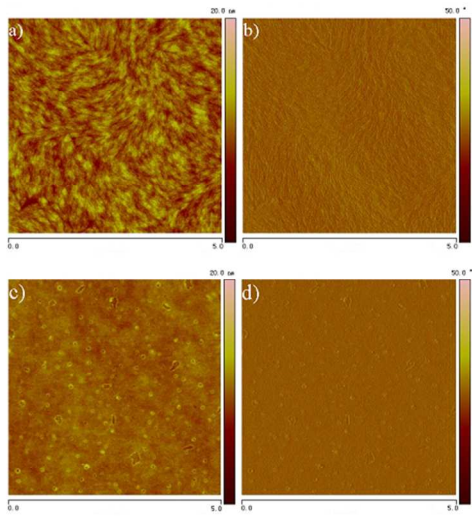
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Table I The optical and electrochemical properties of the polymers.

Polymers	Absorption spectra				Cyclic voltammetry(vs Ag/Ag ⁺)		
	solution ^a		film ^b		<i>p</i> -doping	<i>n</i> -doping	E_g^{EC} (eV)
	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	$E_g^{opt\ c}$ (eV)	E_{on}^{ox} /HOMO (V)/(eV)	E_{on}^{red} /LUMO (V)/(eV)	
P1	570	620	732	1.69	0.46/-5.17	-1.22/-3.49	1.68
P2	553	571	746	1.66	0.47/-5.18	-1.14/-3.57	1.61
PBDT-DODTBT	548	600	758	1.64	0.46/-5.17	-1.10/-3.61	1.56

^aMeasured in chloroform solution. ^bCast from chloroform solution. ^cBandgap estimated from the onset wavelength of the optical absorption.²²

Table II Photovoltaic properties of the PSC devices.

Polymer	Polymer:PC ₇₁ BM (w/w)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
P1	1:1	0.68	0.90	44.18	0.30
	1:2	0.66	1.84	41.82	0.51
P2	1:1	0.72	4.26	39.9	1.22
	1:2	0.74	3.94	53.30	1.55
	1:3	0.74	3.25	49.61	1.19
PBDT-DODTBT	1:1	0.80	5.40	54.40	2.35
	1:2	0.76	8.84	59.59	4.02