Synthesis and Photovoltaic Properties of Two-Dimensional D-A Copolymers with Conjugated Side Chains

DUGANG CHEN,¹ YANG YANG,² CHENG ZHONG,¹ ZHENGRAN YI,¹ FEI WU,¹ LI QU,¹ YU LI,¹ YONGFANG LI,² JINGUI QIN¹

¹Department of Chemistry and Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Wuhan University, Wuhan 430072, China

²Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT: Four novel two-dimensional (2D) donor-acceptor (D-A) type copolymers with different conjugated side chains, **P1**, **P2**, **P3**, and **P4** (see Fig. 1), are designed and synthesized for the application as donor materials in polymer solar cells (PSCs). To the best of our knowledge, there were few reports to systematically study such 2D polymers with D-A type main chains in this area. The optical energy band gaps are about 2.0 eV for **P1–P3** and 1.67 eV for **P4**. PSC devices using **P1–P4** as donor and [6,6]-phenyl-C₆₁-butyric acid methyl ester as acceptor in a weight ratio of 1:3 were fabricated and characterized to investigate the photovoltaic properties of the polymers.

Under AM 1.5 G, 100 mA/cm² illumination, a high open-circuit voltage (V_{oc}) of 0.9 V was recorded for **P3**-based device due to its low HOMO level, and moderate fill factor was obtained with the best value of 58.6% for **P4**-based device, which may mainly be the result of the high hole mobility of the polymers (up to $1.82 \times 10^{-3} \text{ cm}^2/\text{V}$ s). © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3852–3862, 2011

KEYWORDS: atomic force microscopy (AFM); electrochemistry; hole mobility; polymer solar cells; synthesis; two-dimensional conjugated polymers

INTRODUCTION Polymer solar cells (PSCs) have attracted considerable attention as one of the next-generation solar cells because of their advantages of low cost, light weight, and their ability to form large and flexible devices.¹⁻⁴ Solution-processed bulk heterojunction (BHJ) PSCs have been proved to be the most successful device structure, which typically use a two-component active layer consisting of an electron-donating conjugated polymer and an electronaccepting fullerene structured in a disordered bicontinuous interpenetrating network.^{5–8} Ever since the BHJ photovoltaic cells were first reported in 1995,⁹ the overall power conversion efficiency (PCE) has steadily been improved from an initial 1% in the poly(phenylene vinylene) system,⁹ to 4-5% in the poly(3-hexylthiphene) (P3HT) system,^{10,11} and to over 7% in copolymer with donor-acceptor (D-A) structure, as reported recently.^{12,13} However, it is still necessary to increase PCE for large-scale commercialization.

Nowadays, conjugated copolymers with alternating electronrich (donor) and electron-deficient (acceptor) moieties along their backbone have been extensively studied.^{14–21} Their absorption spectra, band gaps, and molecular energy levels can be readily tuned by controlling the intramolecular charge transfer (ICT) from the donor units to the acceptor units. In fact, several D-A type conjugated polymers with PCE as high as $3\sim7\%$ have been realized when they were blended with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) or [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) in BHJ devices.¹⁴⁻²¹

Meanwhile, some two-dimensional (2D) polymers have also been studied in PSCs,^{22–26} because it is well known that extension of conjugation degree leads to enhancement and red-shift of the absorption spectra of conjugated polymers. As reported in literatures,^{22–26} the main chains of the 2D polymers were all constructed by D-D type moieties, and D-D or D-A type conjugated side chains were connected to the backbone to form a much larger conjugated system. These 2D polymers could make some advantages in light absorption and the probability for π - π stacking. As a result, good photovoltaic properties may be obtained.

Since the linear D-A type copolymers showed the highest PCE until now,¹² and introduction of conjugated side chains could increase charge transport ability or extend the absorption range,²²⁻²⁶ we have planned to combine the advantages of these two kinds of structure, namely, to design and to synthesize novel 2D polymers with D-A type main chains and various pendent conjugated side chains for application in

Additional Supporting Information may be found in the online version of this article. Correspondence to: Y. Li (E-mail: liyf@iccas.ac.cn) or J. Qin (E-mail: jgqin@whu.edu.cn)

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FIGURE 1 Chemical Structure of the Polymers P1–P4.

PSCs. As a result, four new 2D polymers were designed (their structures are shown in Fig. 1). This article will report the synthesis, thermal, optical, electrical, and photovoltaic properties of the polymers. The relationship between the structure and the properties will also be discussed. To the best of our knowledge, there were few reports to systematically study such 2D polymers with D-A type main chains and various pendent-conjugated side chains for application in PSCs. Our interest is to explore a possibility of finding a new approach for molecular design and better materials for PSCs.

EXPERIMENTAL

General

¹H NMR and ¹³C NMR spectra were measured on a MER-CURY-VX300 spectrometer. Elemental analysis of carbon, hydrogen, and nitrogen was performed on a Vario EL III microanalyzer. EI-MS spectra were recorded with a VJ-ZAB-3F-Mass spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Gel permeation chromatography (GPC) analysis was performed on an Agilent 1100 series HPLC system equipped with a G1326A refractive index detector, in which polystyrene standards were used as calibration standards and THF was used as an eluent, and the flow rate was 1.0 mL/min. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 °C min⁻¹ from 30 to 500 °C. Cyclic voltammetry (CV) was carried out in nitrogen-purged anhydrous CH3CN solution at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF₆; 0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consisted of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocenium-ferrocene (Fc⁺/Fc) as the internal standard. Cyclic voltammograms were obtained at a scan rate of 100 mV s⁻¹. Formal potentials were calculated as the average of cyclic voltammetric anodic and cathodic peaks. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram.

Device Fabrication and Characterization of PSCs

PSCs were fabricated with ITO glass as a positive electrode, Al as a negative electrode and the blend film of the polymer/PCBM between them as a photosensitive layer. The ITO glass was precleaned and modified by a thin layer of PEDOT:PSS, which was spin-coated from a PEDOT:PSS aqueous solution (Clevious P VP AI 4083 H. C. Stark, Germany) on the ITO substrate, and the thickness of the PEDOT:PSS layer is about 60 nm. The photosensitive layer was prepared by spin-coating a blend solution of polymers and PCBM in chlorobenzene on the ITO/PEDOT:PSS electrode. Then, the Al cathode was deposited on the polymer layer by vacuum evaporation under 3×10^{-4} Pa. The thickness of the photosensitive layer is about 80 nm, measured on an Ambios Tech. XP-2 profilometer. The effective area of one cell is 4 mm^2 . The current-voltage (*J*-*V*) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. A xenon lamp with AM 1.5 filter was used as the white light source, and the optical power at the sample was around 100 mW/cm².

Materials

Toluene was dried over and distilled from K-Na alloy under an atmosphere of argon. Compound **9** was purchased from Sigma-Aldrich and used without further purification. The starting materials and some intermediates (Compounds $1,^{27}$ $2,^{28}$ $4,^{29}$ $6,^{30}$ $7,^{31}$ $8,^{32}$ M5,³³ and M6²¹) were synthesized according to the literature procedures. Other reagents were obtained from Sinopharm Chemical Reagent (Shanghai, China).

Monomer Synthesis 4,7-Bis(4-dodecylthiophen-2-yl)benzo[c][1,2,5] thiadiazole (3)

A mixture of 2-(4-dodecylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1**; 3 g, 7.9 mmol), 4,7-dibromobenzo[c][1,2,5]thiadiazole (**2**; 1 g, 3.4 mmol), Pd (PPh₃)₄ (2% mmol, 0.18 g), and K_2CO_3 (4.14 g, 30 mmol) in 40 mL of toluene and 15 mL of distilled water was refluxed under argon for 48 h. After the reaction, the resulting mixture was cooled to room temperature and then poured into water and extracted with ethylether. The organic extracts were collected and dried with anhydrous Na₂SO₄. After removal of the solvent, the crude product was purified by column chromatography on silica gel using 30/1 (v/v) petroleum ether/ dichloromethane as eluent. Pure compound was obtained as a yellow powder (1.8 g, 83%).

¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.98 (s, 2H), 7.83 (s, 2H), 7.04 (s, 2H), 2.69 (t, J = 7.5 Hz, 4H), 1.72–1.68 (m, 4H),

1.36–1.26 (m, 36H), 0.88 (t, J = 6.0 Hz, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 152.73, 144.43, 139.09, 129.08, 126.12, 125.60, 121.60, 32.00, 30.73, 30.58, 29.75, 29.57, 29.45, 22.76, 14.18. Anal. Calcd for C₃₈H₅₆N₂S₃ (%): C, 71.64; H, 8.86; N, 4.40. Found: C, 71.36; H, 8.68; N, 4.52.

4,7-Bis(5-bromo-4-dodecylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (M1)

Compound **3** (1.8 g, 2.83 mmol) was dissolved in a mixture of chloroform (80 mL) and glacial acetic acid (80 mL). NBS (1.06 g, 5.96 mmol) was then added to the solution and stirred for 12 h in the dark. Much precipitate appeared during the reaction. After the reaction, the mixture was poured into water and extracted with chloroform. The organic extracts were collected and dried with anhydrous Na_2SO_4 . After removal of the solvent, the crude product was purified by column chromatography on silica gel using 1/1 (v/v) petroleum ether/dichloromethane as eluent. Pure compound as a deep red powder was obtained by recrystallization from *n*-hexane.

Yield: 1.91 g, 85%. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.77-7.76 (m, 4H), 2.64 (t, J = 7.5Hz, 4H), 1.68-1.64 (m, 4H), 1.36-1.26 (m, 36H), 0.88 (t, J = 5.7 Hz, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 152.28, 143.25, 138.67, 128.20, 125.34, 124.89, 111.85, 32.19, 29.94, 29.73, 29.64, 22.97, 14.41. Anal. Calcd for C₃₈H₅₄Br₂N₂S₃ (%): C, 57.42; H, 6.85; N, 3.52. Found: C, 57.52; H, 6.76; N, 3.57.

Diethyl 4-(benzo[d]thiazol-2-yl)benzylphosphonate (5)

A mixture of 2-(4-(bromomethyl)phenyl)benzo[d]thiazole (4; 1 g, 3.29 mmol) and 5 mL of triethyl phosphite were heated at 120 °C for 16 h. Excess triethyl phosphite was removed by vacuum distillation. The crude product was purified by column chromatography (CHCl₃) to give compound **5** as white solid.

Yield: 1 g, 85%. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 8.09– 8.04 (m, 3H), 7.92 (d, J = 8.1 Hz, 1H), 7.53–7.35 (m, 4H), 4.10–4.00 (m, 4H), 3.23 (d, J = 22 Hz, 2H), 1.27 (t, J = 6.9Hz, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 168.26, 153.28, 135.78, 134.69, 131.82, 130.72, 128.07, 126.83, 125.69, 123.14, 121.82, 62.48, 34.61, 33.68, 16.57. Anal. Calcd for C₁₈H₂₀NO₃PS (%): C, 59.82; H, 5.58; N, 3.88. Found: C, 59.89; H, 5.42; N, 3.87. EI-MS: m/z 361.0 (Calcd: 361.1).

(E)-4-(4-(benzo[d]thiazol-2-yl)styryl)-N,N-bis(4-bromophenyl)aniline (M2)

Compound **5** (0.5 g, 1.39 mmol) and compound **6** (0.66 g, 1.53 mmol) were dissolved in 20 mL of anhydrous DMF under nitrogen. To this solution was added NaH (0.15 g, 6.25 mmol) in an ice-water bath. Then the reaction was stirred for 5 h at room temperature under nitrogen. After the reaction, the mixture was poured into water. The precipitate was filtered and washed with water and methanol. The crude product was purified by column chromatography (PE/CHCl₃, 2:1) to give 0.62 g of **M2**.

16.2 Hz, 1H), 7.08–6.97 (m, 7H). ¹³C NMR (CDCl₃, 150 MHz) δ (ppm): 167.86, 154.45, 146.93, 146.37, 140.35, 135.23, 132.71, 132.65, 132.28, 129.75, 128.13, 128.07, 127.07, 126.87, 126.59, 126.05, 125.39, 124.13, 123.37, 121.83, 116.23. Anal. Calcd for C₃₃H₂₂Br₂N₂S (%): C, 62.08; H, 3.47; N, 4.39. Found: C, 61.65; H, 3.28; N, 4.27. EI-MS: *m/z* 638.0 (Calcd: 638.0).

(E)-2-(4-(2-(2,5-dibromothiophen-3-yl)vinyl)phenyl) benzo[d]thiazole (M3)

M3 was obtained with a procedure similar to that for M2, excepted with the use of 2,5-dibromothiophene-3-carbalde-hyde (7; 0.38 g, 1.39 mmol) as one reactant. The crude product was purified by column chromatography (PE/CHCl₃, 1:1) to give 0.5 g of **M3**.

Yield: 75% ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 8.10–8.07 (m, 3H), 7.92 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.26 (d, J = 3.3 Hz, 1H), 7.11 (d, J = 16.2 Hz, 1H), 6.94 (d, J = 16.2 Hz, 1H). ¹³C NMR (CDCl₃, 150 MHz) δ (ppm): 139.79, 131.72, 131.46, 131.14, 131.09, 128.68, 128.44, 128.07, 127.80, 127.65, 126.31, 125.72, 125.44, 125.37, 125.26, 125.09, 123.80, 122.97, 122.89, 112.26, 110.66. Anal. Calcd for C₁₉H₁₁Br₂NS₂ (%): C, 47.82; H, 2.32; N, 2.93. Found: C, 48.09; H, 2.23; N, 3.04. EI-MS: *m/z* 477.0 (Calcd: 476.9).

(E)-2,5-dibromo-3-(2-(pyren-1-yl)vinyl)thiophene (M4)

M4 was obtained with a procedure similar to that for M2, excepted with the use of diethyl(2,5-dibromothiophen-3-yl)methylphosphonate (**8**; 1 g, 2.55 mmol) and pyrene-1-car-baldehyde (**9**; 0.6 g, 2.61 mmol) as the reactant. The crude product was purified by column chromatography (PE/CHCl₃, 10:1) to give 0.83 g of **M4**.

Yield: 70%. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 8.41 (d, J = 9.3 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H), 8.21–8.12 (m, 4H), 8.07–7.97 (m, 4H), 7.44 (s, 1H), 7.23 (d, J = 15.6Hz, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 139.79, 131.72, 131.46, 131.14, 131.09, 128.68, 128.44, 128.07, 127.80, 127.65, 126.31, 125.72, 125.44, 125.37, 125.26, 125.09, 123.80, 122.97, 122.89, 112.26, 110.66. Anal. Calcd for C₂₂H₁₂Br₂S (%): C, 56.44; H, 2.58. Found: C, 56.31; H, 2.63. EI-MS: m/z 468.0 (Calcd: 467.9).

Polymer Synthesis

Synthesis of P1

M5 (0.192 g, 0.328 mmol), **M1** (0.130 g, 0.164 mmol), **M2** (0.104 g, 0.163 mmol), and Pd (PPh₃)₄ (2% mmol, 8 mg) were dissolved in toluene (12 mL). A total of 6 mL aqueous solution of Bu_4NOH (10%) was then added to the reaction mixture. The polymerization was carried out at 90 °C for 3 days under argon. After the reaction was completed, the mixture was cooled to room temperature, and the polymer was precipitated by slowly adding the mixture into CH₃OH (200 mL). The precipitated material was collected by filtration through a funnel. Then, the crude product was washed via a Soxhlet apparatus with methanol, acetone, hexane, and finally extracted with chloroform. Only the chloroform-solu-

ble portion was collected, concentrated, and precipitated from methanol to yield **P1** as a red solid.

Yield: 80%. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 8.12–8.08 (m, 5H), 7.91 (br, 3H), 7.78 (br, 4H), 7.65–7.60 (m, 9H), 7.51–7.48 (m, 8H), 7.42–7.37 (m, 2H), 7.31–7.20 (m, 6H), 7.11–7.05 (m, 1H), 2.81 (br, 4H), 2.06 (br, 8H), 1.77 (br, 8H), 1.26 (br, 28H), 1.10 (br, 28H), 0.88–0.85 (m, 6H), 0.79–0.77 (m, 20H).

Synthesis of P2

P2 was obtained with a procedure similar to that for P1, except with the use of M3 (0.078 g, 0.164 mmol) instead of M2.

Yield: 85%. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 8.08 (br, 5H), 7.91–7.70 (m, 9H), 7.60–7.54 (m, 9H), 7.40 (br, 2H), 7.26 (m, 2H), 2.82 (br, 4H), 2.09 (br, 8H), 1.76 (br, 4H), 1.26–1.13 (m, 60H), 0.88–0.80 (m, 26H).

Synthesis of P3

P3 was obtained with a procedure similar to that for P1, except with the use of M4 (0.077 g, 0.164 mmol) instead of M2.

Yield: 81%. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 8.61 (br, 1H), 8.22 (br, 5H), 8.06–7.97 (m, 7H), 7.91–7.82 (m, 7H), 7.65–7.54 (m, 8H), 2.82 (br, 4H), 2.07 (br, 8H), 1.76 (br, 4H), 1.26–1.12 (m, 60H), 0.88–0.80 (m, 26H).

Synthesis of P4

M6 (0.216 g, 0.244 mmol), **M1** (0.098 g, 0.123mmol), **M4** (0.057g, 0.122mmol), and Pd (PPh₃)₄ (2% mmol, 6 mg) were dissolved in toluene (10 mL). The polymerization was carried out at 110 °C for 3 days under argon. After the reaction was completed, the mixture was cooled to room temperature, and the polymer was precipitated by slowly adding the mixture into CH₃OH (200 mL). The precipitated material was collected by filtration through a funnel. Then, the crude product was washed via a Soxhlet apparatus with methanol, acetone, hexane, and finally extracted with chloroform. Only the chloroform-soluble portion was collected, concentrated, and precipitated from methanol to yield **P4** as a black solid.

Yield: 85%. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 8.00–7.26 (m, 20H), 4.31 (br, 8H), 2.95–0.87 (m, 142H).

RESULTS AND DISCUSSION

Synthesis

Monomer Synthesis

A long alkyl chain (dodecyl-) was added to the thiophene in Compound **1** to keep good solubility of **M1**. As shown in Scheme 1, Compound **3** was synthesized by Suzuki coupling reaction in toluene and water using $Pd(PPh_3)_4$ as catalyst and K_2CO_3 as base at 90 °C for 48 h. **M1** was obtained by bromination of Compound **3** via NBS. Compound **5** was synthesized by refluxing of the blend solution of Compound **4** and triethyl phosphite at 120 °C for about 16 h. **M2**, **M3**, and **M4** were synthesize by Wittig-Hornor reaction using NaH as base in DMF at room temperature overnight, and these monomers were all trans-configuration verified by ¹H



SCHEME 1 Synthetic Routes of Monomers **M1–M4**. Conditions: (a) $Pd(PPh_3)_4$, K_2CO_3 , toluene/ H_2O , 90 °C, 48 h; (b) NBS, $CHCl_3/CH_3COOH$, rt, 12 h; (c) $P(OEt)_3$, 120 °C, 16 h; (d) NaH, DMF, rt, 12 h.

NMR with a split number of about 16 Hz of the hydrogen in double bond. $^{\rm 34}$

Polymer Synthesis

As shown in Scheme 2, Polymers **P1**, **P2**, and **P3** were synthesized by Suzuki coupling reaction, and **P4** was prepared by Stille coupling reaction. After the reaction was completed, the crude polymers were precipitated from methanol and

washed via a Soxhlet apparatus with methanol, acetone, hexane, and finally chloroform. Only the chloroform-soluble portion was collected to obtain a pure, high molecular weight, solution processable polymer. The real segment ratios were estimated from the ¹H NMR spectra of the polymers and were found to be agreed with the designed ratio very well (Supporting Information, Fig. S1). All the polymers have good solubility in common organic solvents such as toluene,



SCHEME 2 Synthetic Routs of Polymers **P1–P4**. Conditions: (a) Pd (PPh₃)₄, Bu₄NOH (10%, aqueous), toluene, 90 °C, 72 h; (b) Pd(PPh₃)₄, toluene, 110 °C, 72 h.

chloroform, THF, and chlorobenzene. A noticeable amount of residue remained in the extraction thimble when **P4** was purified. This insoluble fraction maybe caused by the poorer solubility of **M6** compared with **M5**, which has a branched alkyl chain. As a result, **P4** has a relatively lower molecular weight than the other copolymers. Molecular weights and polydispersity indices (PDIs) of polymers, as shown in Table 1, are determined by gel permeation chromatography (GPC) analysis in THF with a polystyrene standard calibration.

Thermal Stability

Thermal stability of the polymers was investigated with TGA, as shown in Figure 2. The TGA plots reveals that there were two degradation stages for **P1** and **P2**, one around 190 °C where the polymers began to lose weight and one around 400 °C where the weight-loss reached 5%. It may be more appropriate to denote the first temperature as the decomposition temperature (T_d) of **P1** and **P2**, and the T_d of **P3** and **P4** were 418 and 448 °C, respectively, which were the onset temperatures of 5% weight-loss. All the decomposition temperatures are high enough for device fabrication process.

TABLE 1 Molecular Weights and Thermal Property of the

 Polymers

Polymers	<i>M</i> _n ^a	<i>M</i> _w ^a	$PDI^{a} (M_{w}/M_{n})$	<i>T</i> _d (°C)
P1	21.8K	55.4K	2.5	190 ^b
P2	37.8K	89.6K	2.4	190 ^b
P3	29.0K	68.9K	2.4	418 ^c
P4	9 76K	29 7K	30	448 ^c

 $^{\rm a}$ $M_{\rm n},$ $M_{\rm w},$ and PDI of the polymers were determined by GPC using polystyrene standards in THF.

^b Temperatures at which the polymers began to lose weight.

 $^{\rm c}$ The 5% weight-loss temperatures under N_2 atmosphere.



FIGURE 2 TGA plots of the copolymers with a heating rate of 10 °C/min under inert atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Optical Properties

Figure 3 shows the normalized UV-vis absorption spectra of the polymers in chloroform and in the solid films spincoated on quartz substrates. All the polymers showed two main peaks: one at around 400 nm originating from the



FIGURE 3 UV-vis spectra of all polymers: (a) in chloroform solution and (b) in solid film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 4 Cyclic voltammograms of **P1–P4** films on a platinum electrode measured in 0.1 mol/L Bu_4NPF_6 acetonitrile solutions at a scan rate of 100 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

 π - π * transition and the absorption of side chain groups, and the longer wavelength absorption should be due to an ICT interaction between the donors and acceptors along the main chain. The ICT interactions in electron rich-poor alternating structures can reduce the band gap of polymers. In the film, the spectra were somewhat broad and slightly redshifted in the longer wavelength region, 13-15 nm for P1-P3, and 21 nm for P4, relative to those in solution. From the relative absorption intensity, we can see that the short wavelength absorption intensity is much stronger than that in the long wavelength for P1-P3, and the absorption spectra are quite similar. It indicates that in our cases the effects of the side chain groups to the UV-vis absorption are almost the same no matter the moieties are electron-deficient benzothiazole unit or electron-rich pyrene unit when the main chains are constructed by the same donor and acceptor, and the connection units also affect little to the absorption spectra, compared P1 with P2, which have triphenylamine and thiophene moiety as the connection site, respectively. P4 exhibited the best absorption spectra among the four polymers with absorption range from 300 nm to about 742 nm in the film, from which an optical energy band gap was calculated to be as low as 1.67 eV, and the absorption intensity in the long wavelength is as strong as that in the short wavelength, indicating that a more effective absorption of sunlight can be realized to compare the other three polymers. On the whole, the introduction of side chains could increase the absorption intensity in the short wavelength range.

Electrochemical Properties

Electrochemical cyclic voltammetry is often used to measure the redox properties of the polymers from which the energy levels of HOMO and LUMO can be estimated. Figure 4 shows the cyclic voltammograms of the four polymer films on Pt disk electrode in 0.1 mol/L Bu₄NPF₆ acetonitrile solution. The HOMO and LUMO energy levels of polymers were calculated from the onset oxidation potentials (E_{onset}^{ox}) and onset reduction potentials (E_{onset}^{red}), respectively, according to eqs 1 and 2.^{35–37} The electrochemically determined band gaps were deduced from the difference between onset potentials from oxidation and reduction of copolymers as depicted in eq 3.^{35–37}

$$HOMO = -e(E_{onset}^{ox} + 4.8)(eV)$$
(1)

$$LUMO = -e(E_{onset}^{red} + 4.8)(eV)$$
(2)

$$E_{g}^{ec} = e(E_{onset}^{ox} - E_{onset}^{red})(eV)$$
(3)

The electrochemical data of all the polymers are summarized in Table 2. The E_{g}^{ec} values of polymers are slightly higher than the corresponding optical band gaps, which is probably due to the exciton binding energy of polymers.³⁸ The electrochemical data shows that there is little influence on the electrochemical properties among **P1**, **P2**, and **P3**, when the side chain groups are altered with the main chain donor–acceptor units unchanged. However, when the donor moiety was changed from fluorene to benzodithiophene (BDT), both the HOMO and LUMO levels were altered. It indicates that the groups along the backbone contribute more to the electrochemical properties of polymers in our cases.

The offsets between the LUMO levels of all polymers and PCBM $(-3.91 \text{ eV})^{39}$ is larger than 0.3 eV, indicating that the charge transfer from the polymers to PCBM would be efficient.⁴⁰ As

TABLE 2 Optical and Electrochemical Data of All Polymers

	UV-Vis Absorption									
	CHCl ₃ Solution ^a			Film ^b				Cyclic Voltammetry		
Polymer	λ _{max}	(nm)	λ _{onset} (nm)	<i>E</i> g (eV) ^c	λ _{max}	(nm)	λ _{onset} (nm)	E _g (eV) ^c	E ^{ox} _{onset} (V)/HOMO (eV)	E ^{red} onset (V)/LUMO (eV)
P1	382	504	589	2.11	386	517	603	2.06	0.66/-5.46	-2.09/-2.71
P2	377	504	589	2.11	374	519	612	2.03	0.62/-5.42	-2.02/-2.78
P3	382	504	591	2.10	388	517	609	2.03	0.64/-5.44	-2.08/-2.72
P4	414	523	723	1.72	422	544	743	1.67	0.35/-5.15	-1.80/-3.00

^a Measured in chloroform solution.

^b Cast from chloroform solution.

 c Band gap estimated from the onset wavelength (λ_{edge}) of the optical absorption: $E_{g}=1240/\lambda_{edge}$



FIGURE 5 HOMO and LUMO wavefunctions of the four oligomer (n = 1) model systems calculated at the B3LYP/6-31g(d) level. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the open-circuit voltage (V_{oc}) of PSCs is related to the difference between the LUMO level of the electron acceptor (PCBM) and the HOMO level of the electron donor (polymer),⁴¹ the previous three polymers (**P1-P3**) would lead to a higher V_{oc} than **P4**, owing to the more electron-rich BDT unit introduced to the backbone of **P4**. Furthermore, the HOMO energy levels of all polymers are well aligned with the workfunction of the PEDOT:PSS (-5.0 eV),¹⁹ indicating that holes can be easily transported from the HOMO of polymers to PEDOT:PSS. Therefore, all the polymers can be used as electron donors with PCBM as an electron acceptor for BHJ devices.

Molecular Orbital Calculations

The geometries of oligomer structures of the four copolymers were optimized at the density functional theory (DFT) ri-BP86/def2-SVP level, then the electronic properties were calculated at B3LYP/6-31g(d) level.^{42,43} The Frontier energy levels (HOMO and LUMO) were characterized for the neutral electronic states. Note that the calculations were performed on model systems of copolymers where all alkyl chain substituents were replaced with methyl groups (this has only minimal effect on the electronic properties).

TABLE 3 B3LYP/6-31G(d) Gas-Phase HOMO and LUMO Levels of the Oligomer (n = 1) Calculations

Compound HOMO (eV) LUMO (eV) Eg (P1 -5.16 -2.62 2.54 P2 -5.08 -2.64 2.44 P3 -5.02 -2.63 2.39 P4 -4.85 -2.80 2.05				
P1 -5.16 -2.62 2.54 P2 -5.08 -2.64 2.44 P3 -5.02 -2.63 2.39 P4 -4.85 -2.80 2.05	Compound	HOMO (eV)	LUMO (eV)	E _g (eV)
P2 -5.08 -2.64 2.44 P3 -5.02 -2.63 2.39 P4 -4.85 -2.80 2.05	P1	-5.16	-2.62	2.54
P3 -5.02 -2.63 2.39 P4 -4.85 -2.80 2.05	P2	-5.08	-2.64	2.44
P4 -4.85 -2.80 2.05	P3	-5.02	-2.63	2.39
	P4	-4.85	-2.80	2.05



FIGURE 6 J-V characteristics of photovoltaic devices with an active layer of the polymers:PCBM (weight ratio = 1:3) mixture. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As shown in Figure 5, the HOMO energy levels are nearly delocalized over the whole molecules for P3 and P4, but partly delocalized to the side chains for P1 and P2, which are due to the electron deficiency of benzothiazole unit at the end of the side chains. On the other side, the delocalization of HOMO levels demonstrates that the side chain groups are conjugated to the main chains very well and changing the segment ratios will alter the HOMO levels of polymers. The LUMO energy levels are all predominantly localized on the benzothiadiazole (BTZ) units, so the alternation of segment ratios will not affect the LUMO levels a lot. These results implied that the HOMO-LUMO transition for the four polymers is mainly accompanied by charge transfer from the electron-rich segments to BTZ units due to the strong electron deficiency of BTZ units. The HOMO and LUMO levels of the molecules from the calculation are listed in Table 3. When compared with the first three polymers, the LUMO level of P4 is lowered by about 0.17 eV, which shows that the conjugation of P4 is better than the others. When compare with the data from CV measurement, it shows that the tendencies of the data change on HOMO or LUMO level from the calculation are almost the same.

Hole Mobility

Hole mobility is another important parameter for the polymer applied to PSC devices, because high hole mobility is essential for efficient charge extraction and a good fill factor (FF). Here, we measured the hole mobility of the copolymers

TABLE 4 Photovoltaic Performances of the PSCs Based on **P1–P4**:PCBM (1:3 w/w) under the Illumination of AM 1.5, 100 mA/cm²

Active Layer	$V_{\rm oc}$ (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
P1 :PCBM = 1:3	0.62	2.79	32.2	0.56
P2 :PCBM = 1:3	0.75	1.03	33.5	0.26
P3 :PCBM = 1:3	0.90	1.52	31.7	0.43
P4 :PCBM = 1:3	0.79	1.64	58.6	0.76



FIGURE 7 AFM height images for P1–P4:PCBM (1:3 w/w). All images are 1 μ m \times 1 μ m.

by space-charge limit current (SCLC) method using a device structure of ITO/PEDOT:PSS/polymer/Au. For the hole-only devices, SCLC is described by

$$J \cong (9/8) \varepsilon \varepsilon_0 \mu_0 V^2 \exp(0.89\sqrt{V/E_0 L})/L^3$$
(4)

where ε is the dielectric constant of the polymer, ε_0 is the permittivity of the vacuum, μ_0 is the zero-field mobility, E_0 is the characteristic field, *J* is the current density, *L* is the thickness of the blended films layer, $V = V_{\rm appl} - V_{\rm bi}$, $V_{\rm appl}$ is the applied potential, and $V_{\rm bi}$ is the built-in potential, which results from the difference in the work function of the anode and the cathode (in this device structure, $V_{\rm bi} = 0.2$ V). The results are plotted as $\ln(JL^3/V^2)$ versus $(V/L)^{0.5, 44-46}$ According to eq 4, the hole mobility obtained are 5.33 \times 10⁻⁴, 3.23 \times 10⁻⁶, 1.77 \times 10⁻⁴, and 1.82 \times 10⁻³ cm²/V s for **P1-P4**, respectively. Obviously, the hole mobility of P4 is in the same scale as that of P3HT (10^{-3} cm²/V s), and it is fit for the application as photovoltaic donor materials in PSCs. As reported in literature,⁴⁷ the polymers with similar backbone structure compared with P4 (but without a pendent conjugated group), showed the hole mobility in the scale of 10^{-5} cm^2/V s, which is almost two orders of magnitude smaller than that of P4. So, the introduction of a pendent conjugated groups to polymers can increase the hole mobility.

Photovoltaic Properties

Bulk heterojunction photovoltaic devices were constructed to investigate and compare the photovoltaic properties of the four polymers. To maintain similarly structured devices, all polymers were blended with PCBM at 1:3 weight ratio in chlorobenzene at 30 mg/mL and identical spin rate (3000 rpm) was used. A typical fabricated solar cell has a configuration of ITO/PEDTO:PSS/polymer:PCBM (1:3 w/w)/Al. The current–voltage characteristics of the solar cells based on these four polymers blended with PCBM are shown in Figure 6 under the illumination of AM 1.5, 100 mW/cm². The corresponding open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), FF, and PCE of the devices are summarized in Table 4.

The PSCs based on **P3** shows the highest V_{oc} , benefited from the rather low HOMO energy level. Although the HOMO level of **P1** and **P2** are almost the same as that of **P3**, they show a little lower value of V_{oc} , 0.62 and 0.75 V, respectively. The V_{oc} is proportional to the offset between HOMO level of donor (polymer) and LUMO level of acceptor (i.e., PCBM). However, we are surprised to find that the V_{oc} of the PSC based on **P4** with a higher HOMO level is larger than those of PSCs based on **P1** and **P2**. On the whole, all the devices exhibit relatively high V_{oc} , with a best one as high as 0.9 V. The FF of the PSC based on **P4** is fair enough with a value of 58.6%,



FIGURE 8 IPCE of the PSC based on P4:PCBM (1:3 w/w).

ascribed to the best hole mobility among all the polymers. Also, the FF of the PSCs based on the other three polymers are not bad with the value around 32%. The PCE of the polymers are below 1%, which is mainly due to the low $J_{\rm sc}$ value that depends on many factors such as the morphology of the blend films. Thus, the film morphology of polymer:PCBM blends was studied. As the tapping-mode atomic force microscopy (AFM) images shown in Figure 7, the surface of the active layers of polymers/PCBM is relatively rough, with a root-mean-square roughness (rms) of 3.68, 2.77, 11.9, and 6.33 nm for **P1–P4**, respectively. However, the phase separation between the polymer and PCBM is not clear, and the domain size is relatively large, which may lead to low $J_{\rm sc}$ and PCE.

The incident photon-to-converted current efficiency (IPCE) of the PSC device based on P4/PCBM was further tested in considering the better photovoltaic performance of P4. It is apparent that the device exhibited a broad response range, covering from 300 to 700 nm, as shown in Figure 8. In comparison of the IPCE curve with the absorption spectrum of P4, the photon-to-electron conversion efficiency corresponding to the longer wavelength absorption peak (at ca. 600 nm) of P4 is quite low, indicating that the ICT absorption of the 2D D-A copolymer contributes to the photovoltaic conversion much less than that of the π - π * absorption in the shorter wavelength region of 400~500 nm.

CONCLUSIONS

We have successfully synthesized a series of new 2D conjugated copolymers with donors-acceptors in main chains and pendent electron-rich or -deficient groups. Along the main chains of the polymers, fluorene, triphenylamine, thiophene, and benzodithiophene were designed as donor units with benzothiadiazole as the acceptor unit. They showed good solubility in common organic solvents, good thermal stability, and high molecular weights. Their absorption spectra were tested, and **P4** exhibited the widest absorption range from 300 to 724 nm in chloroform and to 743 nm in solid film. The optical energy band gap of **P4** was estimated to be 1.67 eV, which is an ideal value for donor materials blended with PCBM for application on PSCs. The electrochemical data of P1, P2, and P3 also indicated that these copolymers are suitable as electron donors with PCBM as the acceptor for BHJ PSCs. The hole mobility were measured with SCLC method with high value of 1.82×10^{-3} cm²/V·s for **P4**, and moderate value for P1 and P3, which indicate that 2D conjugated polymers can facilitate the hole transportation. PSC devices based on the polymers blended with PCBM with a ratio of 1:3 in weight showed a high $V_{\rm oc}$ of 0.9 eV for P3 and good FF of 58.6 % for P4. The PCE of all the devices were not very high due to the low J_{sc} , which may owe to the bad film morphology. However, a lot of improvements may be achieved by various approaches, such as changing the ratio of polymers:PCBM and adding some additive to the solvent in film processing to improve the film morphology. In general, 2D conjugated copolymers with different pendent groups can lead to some positive effect on their photovoltaic properties.

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