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# New alternating copolymers of fluorene and triphenylamine bearing terthiophene and acceptor groups in the side chains: Synthesis and photovoltaic properties

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## A R T I C L E I N F O

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# ABSTRACT

A series of conjugated copolymers (**P1** and **P2-CN**–**P4-CN**) were prepared, in which two kinds of side chains were designed: one was the repeating units similar to that of P3HT, with the aim to increase the compatible with  $PC_{61}BM$  and the hole mobility; another one was the acceptor groups connected with the electron-rich backbone through the conjugated 3,4-ethylenedioxythiophene bridge, in order to broaden the absorption and lower the LUMO level. By controlling the ratios of these two kinds of side chains, the absorption band of the resultant conjugated polymers could be fine-tuned, while their energy levels nearly remained unchanged. As the result, the performance of the corresponding devices increased first, then decreased, indicating that there would be a balance between the different function of these two side chains.

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# 1. Introduction

To resolve the problem of the exhausting of fossil energy sources, such as petroleum and coal, different strategies are attempted to develop new renewable energy sources, or convert one kind of energy to another convenient style, among which, the solar energy is, perhaps, the most promising one [1,2]. Polymer solar cells (PSCs), commonly composed of a blend film of conjugated polymer donor and fullerene derivative (such as [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM)) acceptor sandwiched between an ITO positive electrode and a low workfunction metal negative electrode [3–5], have attracted increasing attention as the good candidate to transform the sunlight to electric energy, due to their unique advantages including light weight, mechanical flexibility, low-cost fabrication of large-area devices [6-12], and easy tunability of chemical structure of the conjugated polymers and the fullerene derivatives [13–22]. Thanks to the enthusiastic efforts of polymer chemists, lots of conjugated polymers in different kinds were designed and prepared. As a typical example, poly(3hexylthiophene) (P3HT) was extensively investigated and demonstrated a PCE value as high as 4–5% [23]. In addition to the high charge mobility, the main reason should be ascribed to the good compatible of P3HT with  $PC_{61}BM$ , which contributed much to the high quality of their blend film in the PSC device, directly leading to the high performance.

Despite the above-mentioned lots of advantages, generally, to realize the practical application of PSCs, the lower power conversion efficiency (PCE) rather than commercial inorganic solar cells, still needs to be improved. To achieve the high PCEs, for chemists, some strategies have been utilized: first, the control of the band gap of the conjugated polymers lower than 2.0 eV to match the terrestrial solar radiation as well as possible; second, to lower the high highest occupied molecular orbital (HOMO) level of the polymers by structural modification, to boost the magnitude of the open-circuit voltage ( $V_{oc}$ ). However, it is still a big challenge to obtain low-band gap conjugated polymers exhibiting both strong and broad absorption with large short-circuit current density  $(I_{sc})$  and satisfied energy levels for the high  $V_{oc}$ . Some recent reports proposed one good approach to broaden the absorption and tune the energy level of the conjugated polymers, that is, to design and synthesize two-dimensional conjugated copolymers [24–26], in which the construction blocks in the main chain act as the donor moieties to mainly determine the HOMO level, while some acceptors could be introduced at the ends of the side chain to adjust the LUMO level and broaden the absorption [27]. Thus, by choosing different main chain and acceptors, the



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band gap and HOMO level could be conveniently modified at a large degree, providing more freedom for the polymer chemists to do the molecular design and achieve possibly high PSC performance.

Considering all the above points, mainly the construction block of P3HT, the HOMO and LUMO levels according to the electronic properties of main chain and the acceptor moieties in the side chains, we designed a new series of conjugated copolymers (Chart 1). In these polymers, two kinds of side chains were designed: one was the repeating units similar to that of P3HT, with the aim to increase the compatible with PC<sub>61</sub>BM and the hole mobility; another one was the acceptor groups connected with the electron-rich backbone through the conjugated 3,4-ethylenedioxythiophene bridge, in order to broaden the absorption and lower the LUMO level. By controlling the ratios of these two kinds of side chains, the absorption band of the resultant conjugated polymers could be finetuned, while their energy levels nearly remained unchanged. For comparison, the polymer, P1, only bearing the terthiophene groups as the side chains was prepared. The obtained results realized our thought, giving some interesting rules for the further rational design of this kind of conjugated polymers. Herein, we would like to present the syntheses, UV-vis absorption, energy levels, and photovoltaic performances of these four copolymers in detail.

# 2. Experimental

# 2.1. Materials and instruments

Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. *N*,*N*-Dimethylformamide (DMF) was dried over and distilled from CaH<sub>2</sub>. All other reagents were used as purchased. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2dioxaborolane-2-yl)-9,9-dihexyl- fluorine [29], **1** [30], **2** [31], and **4** [32], were synthesized according to the literature procedures. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on Varian Mercury300 spectrometer using tetramethylsilane (TMS;  $\delta = 0$  ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000–400 cm<sup>-1</sup> on NaCl pellets. UV–visible spectra were obtained using a Shimadzu UV-2550 spectrometer. The thermal properties of the polymers were measured on a Netzsch STA449C thermal analyzer at a heating rate of 10 °C/min in nitrogen at a flow rate of 30 cm<sup>3</sup>/min. Electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with a Pt disk, a Pt plate, and a Ag/Ag<sup>+</sup> electrode as the working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) acetonitrile solution. Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. GPC analysis was performed on an Agilent 1100 series HPLC system and a G1362A refractive index detector. Polystyrene standards were used as calibration standards for GPC. THF was used as an eluent and the flow rate was 1.0 mL/min. Elemental analyses were performed by a CARLOERBA-1106 micro-elemental analyzer. Matrix-assisted laser desorption ionization time-of-flight mass spectra were measured on a Voyager-DE-STR MALDI-TOF mass spectrometer (MALDI-TOF MS; ABI, American) equipped with a 337 nm nitrogen laser and a 1.2 m linear flight path in positive ion mode.

#### 2.2. Solar cell device fabrication and characterization

ITO-coated glass substrates were cleaned by sonication in detergent, deionized water, acetone, and isopropyl alcohol, and dried in a nitrogen stream, followed by an oxygen plasma treatment. To fabricate photovoltaic devices, a hole transport thin layer (ca. 40 nm) of PEDOT:PSS (BaytronPVPAI 4083, filtered at 0.45 µm) was spin-coated on the pre-cleaned ITO-coated glass substrates at 3000 rpm and baked at 140 °C for 10 min under ambient conditions. The substrates were then transferred into an argon-filled glovebox. Subsequently, the polymer: PC<sub>61</sub>BM active layer was spin-coated on the PEDOT:PSS layer at 1000 rpm from a homogeneous blend solution. The solution was prepared by dissolving the polymers (0.01 g/mL) and PC<sub>61</sub>BM (0.02 g/mL) in chlorobenzene solvent and filtered with a 0.2 µm PTFE filter. The substrates were annealed at 150 °C for 10 min prior to electrode deposition. To complete device fabrication, the substrates were pumped down to a high vacuum ( $1 \times 10^{-6}$  Torr), calcium (5 nm) and then aluminum (100 nm) were thermally evaporated onto the active layer through shadow masks. The effective devices area was measured to be 0.15 cm<sup>2</sup>. The current density–voltage (I-V) characteristics were recorded with a Keithley 236 source meter. The spectral response was measured with a commercial photomodulation spectroscopic setup (Oriel). A calibrated Si photodiode was used to determine the photosensitivity.



Chart 1.

# 2.3. Monomer synthesis

# 2.3.1. General procedure for synthesis of compounds 3 and 5

Under an atmosphere of dry nitrogen, Compound **2** or **4** (1.0 equiv) and Compound **1** (1.5 equiv) were dissolved in anhydrous THF in an ice bath, and the sodium hydride (5.0 equiv) was added in portion. The reaction mixture was stirred at that temperature for half an hour, then slowly warmed to room temperature, stirred overnight. The reaction was quenched with water and the water phase was extracted twice with dichloromethane. The combined organic extracts were washed with water, dried over magnesium sulfate, evaporated, and purified with column chromatography.

2.3.1.1. 5-Hexyl-5-[2-[4-[N,N-di(4-bromophenyl)amino]phenyl]ethenyl]-2,2; 5,2-terthiophene(**3**). Compound **2** (0.14 g, 0.37 mmol), **1** (0.31 g, 0.55 mmol), sodium hydride (0.045 g, 1.85 mmol), THF (20 mL). Using petroleum ether/chloroform (1:4, v/v) as eluent to obtain **3** as orange powder (0.19 g, 60%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.35–7.37 (m, 6H), 7.05–7.11 (m, 12H), 7.11–6.79 (m, 2H), 6.68 (d, 1H), 2.77–2.82 (br, 2H), 1.33 (br, 6H), 0.90 (br, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 145.14; 144.72; 140.86; 135.92; 134.76; 134.48; 133.37; 131.40; 131.11; 128.42; 126.35; 125.95; 124.68; 123.82; 123.18; 123.04; 122.83; 122.58; 122.39; 119.63; 114.84; 30.53; 29.18; 27.72; 21.53; 13.04. Anal. calcd for: C<sub>38</sub>H<sub>33</sub>Br<sub>2</sub>N<sub>3</sub>: C, 60.08; H, 4.38; N, 1.84. Found: C, 59.19; H, 4.31; N, 1.61. MALDI-TOF MS Calcd for C<sub>38</sub>H<sub>33</sub>Br<sub>2</sub>N<sub>3</sub>, 759.68; found: 759.86.

2.3.1.2. 2-[2-[4-[N,N-Di(4-bromophenyl)amino]phenyl]ethenyl]3,4ethylenedioxythiophene(**5**). Compound **4** (0.65 g, 3.84 mmol), **1** (2.91 g, 5.76 mmol), sodium hydride (0.37 g, 15.37 mmol), THF (30 mL). Using petroleum ether/CHCl<sub>3</sub> (1:1, v/v) as eluent to obtain **5** as yellow powder (1.05 g, 46%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.36–7.26 (m, 6H), 7.07–6.82 (m, 8H), 6.21 (s, 1H), 4.27–4.20 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 146.28; 145.84; 142.00; 139.05; 132.89; 132.36; 127.15; 125.56; 125.35; 124.24; 117.40; 117.19; 115.66; 99.62; 97.50; 64.80; 64.66.

2.3.1.3. 2-[2-[4-[N,N-Di(4-bromophenyl]amino]phenyl]ethenyl]3,4ethylenedioxythiophen-5-al (6). To a solution of 5 (1.14 g 2.00 mmol) and anhydrous DMF (1 mL, 13 mmol) in anhydrous 1,2-dichloroethane (50 mL) at 0 °C under a N<sub>2</sub> atmosphere was added POCl<sub>3</sub> (0.76 g 5.00 mmol) dropwise, and the mixture was refluxed for 12 h. After being cooled to room temperature, the mixture was poured into an aqueous solution of sodium acetate and then stirred for 2 h. The organic phase was separated by decantation and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phases was collected, dried over MgSO<sub>4</sub> and evaporated under vacuum, and purified by column chromatography (silica gel, petroleum ether/CHCl<sub>3</sub>, 1:1, as eluent) to obtain **6** as pink powder (1.00 g, 83.7%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.89 (s, 1H, -CHO), 7.38-7.35 (m, 8H, Ar-H), 7.05-7.01 (m, 2H, -CH= CH-), 6.98-6.95 (m, 4H, Ar-H), 4.38-4.37 (m, 4H, -CH<sub>2</sub>-CH<sub>2</sub>-). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, *δ*): 179.47; 148.95; 147.32; 146.19; 138.71; 132.74; 131.41; 131.02; 128.60; 128.19; 126.21; 123.75; 116.46; 116.32; 1115.48; 65.62; 64.81. Anal. calcd for: C<sub>27</sub>H<sub>19</sub>Br<sub>2</sub>NO<sub>3</sub>S: C, 54.29; H, 3.21; N, 2.34; found: C, 54.88; H, 2.93; N, 2.39.

#### 2.3.2. General procedure for the synthesis of P1-P4

A total of 0.3 mmol of the mixture of Compound 6 (*x* mmol) and 3 ((0.3 - x) mmol) was put into a three-neck flask. The content of each component in the mixture was controlled with different ratios for the preparation of different polymers. Then THF (14 mL), potassium carbonate (2.0 M in water, 2.5 mL) and Pd(PPh<sub>3</sub>)<sub>4</sub> (3% mol) were carefully degassed and charged with nitrogen. The reaction mixture was stirred at 60 °C for 3 days. After the solution

was cooled to ambient temperature, it was dropped into methanol to remove monomers. The obtained solid was dissolved in THF, and the insoluble solid was filtered out. The filtrate was concentrated, precipitated into methanol, and the obtained solid was then washed with a lot of acetone. The solid was dried under vacuum for 1 day to give the product. The yield, <sup>1</sup>H NMR, and molecular weight of the four polymers are as follows.

**P1:** Yield: 50%.  $M_n = 11000$ ; PDI = 1.48. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.70 (br, 2H), 7.53 (br, 8H), 7.32 (br, 3H), 7.19–6.77 (br, 12H), 6.62 (br, 1H), 2.72 (br, 2H), 1.98 (br, 2H), 1.61 (br,2H), 1.20–1.01 (br, 22H), 0.70 (br, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 151.93; 147.31; 146.72; 145.97; 140.07; 135.83; 134.67; 132.58; 128.19; 127.58; 125.93; 125.09; 124.94; 124.41; 124.12; 123.85; 123.66; 121.22; 120.67; 120.23; 55.49; 40.73; 31.78; 30.42; 29.94; 28.99; 24.05; 22.81; 14.23; 1.25. UV–vis (CH<sub>3</sub>Cl, 1 × 10<sup>-5</sup> mol/L):  $\lambda_{max} = 388, 444$  nm.

**P2:** Yield: 61%.  $M_n$  = 6800; PDI = 1.76. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 9.89 (s, -CHO),7.79 (br, Ar–H), 7.67–7.49 (br, Ar–H), 7.41 (br, Ar–H), 7.29 (br, Ar–H), 7.19 (br, Ar–H), 7.08–6.90 (br, Ar–H), 6.69 (br, Ar–H), 4.39 (br,  $-OCH_2-CH_2O_-$ ), 2.80 (br,  $-CH_2-$ ), 2.04 (br,  $-CH_2-$ ), 1.63 (br,  $-CH_2-$ ), 1.31 (br,  $-CH_2-$ ), 1.07 (br,  $-CH_2-$ ), 0.76 (br,  $-CH_3$ ). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ): 178.22; 150.68; 149.83; 147.72; 146.86; 146.48; 145.26; 144.90; 139.71; 139.21; 138.88; 138.19; 137.38; 137.29; 135.68; 131.40; 130.20; 130.00; 129.79; 128.43; 127.77; 127.57; 126.99; 126.90; 125.98; 125.77; 124.96; 124.63; 124.51; 123.95; 123.09; 122.36; 122.19; 121.98; 121.84; 119.92; 118.93; 118.66; 114.81; 114.52; 114.17; 64.36; 63.55; 54.24; 54.10; 39.40; 30.45; 28.68; 22.74; 22.36; 21.54; 12.99.

**P3:** Yield: 50%.  $M_n = 3100$ ; polydispersity = 1.70. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 9.89 (s, -CHO), 7.79–7.60 (br, Ar–H), 7.62–7.58 (br, Ar–H), 7.40–7.38 (br, Ar–H), 7.29 (br, Ar–H), 7.18 (br, Ar–H), 7.10–6.84 (br, Ar–H), 6.69 (br, Ar–H), 4.39–4.37 (br, -OCH<sub>2</sub>–CH<sub>2</sub>O–), 2.82–2.77 (br, -CH<sub>2</sub>–), 2.05 (br, -CH<sub>2</sub>–), 1.60 (br, -CH<sub>2</sub>–), 1.33 (br, -CH<sub>2</sub>–), 1.08 (br, -CH<sub>2</sub>–), 0.76 (br, -CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ):178.14; 157.49; 157.39; 150.71; 147.65; 146.92; 146.55; 145.29; 144.95; 144.72; 138.92; 138.27; 137.38; 137.30; 135.71; 134.61; 133.44; 131.37; 130.25; 130.05; 129.53; 127.73; 126.94; 126.18; 124.98; 124.68; 123.97; 122.87; 122.60; 122.41; 120.49; 119.96; 118.99; 114.90; 114.62; 114.21; 64.37; 63.57; 54.28; 39.47; 30.44; 29.17; 28.68; 27.73; 22.82; 21.51; 12.99; 12.92.

**P4:** Yield: 62%.  $M_n$  = 5000; polydispersity = 1.48. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 9.89 (br, 1H), 7.79–7.76 (br, 4H), 7.65–7.58 (br, 6H), 7.41–7.38 (br, 2H), 7.29 (br, 2H), 7.19–7.16 (br, 2H), 7.10–7.08 (br, 2H), 4.38 (br, 4H), 2.05 (br, 4H), 1.58 (br, 4H), 1.07 (br, 12H), 0.76 (br, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ, ppm): 179.51; 151.96; 147.34; 146.76; 146.54; 145.99; 142.44; 140.14; 139.56; 136.63; 135.89; 134.72; 132.61; 131.70; 129.02; 128.20; 127.57; 127.02; 125.91; 125.11; 1224.95; 124.41; 124.14; 123.88; 123.69; 121.26; 120.25; 115.83; 65.65; 64.85; 55.54; 31.78; 30.46; 29.98; 28.99; 24.10; 22.82; 14.24; 1.26.

#### 2.3.3. General procedure for synthesis of P2-CN-P4-CN

To a solution of **P2–P4** and malononitrile in THF (10 mL) was added 0.1 mL of pyridine. The content of malononitrile was controlled with different ratios for the preparation of different polymers. The mixture was stirred at room temperature overnight, then the resultant mixture was poured into methanol, the precipitate was filtered off and washed with water. The obtained polymer was purified by repeated precipitation from its THF solution to methanol. The solid was dried under vacuum for 1 day to yield the product.

**P2-CN: P2** (0.132 g), malononitrile(0.103 g). Dark blue powder (0.120 g, 87.8%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.76 (br, Ar–H), 7.61–7.58(br, Ar–H), 7.41–7.39(br, Ar–H), 7.26(br, Ar–H), 7.17 (br, Ar–H), 7.06 (br, Ar–H), 7.00–6.84 (br, Ar–H), 6.69 (br, Ar–H), 4.40–4.36 (br,  $-\text{OCH}_2-\text{CH}_2\text{O}$ ), 2.79–2.77 (br,  $-\text{CH}_2$ –), 2.05 (br,  $-\text{CH}_2$ –), 1.69–1.66 (br,  $-\text{CH}_2$ –), 1.32 (br,  $-\text{CH}_2$ –), 1.07 (br,  $-\text{CH}_2$ –), 0.76 (br,  $-\text{CH}_3$ ). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm):

151.91; 146.72; 145.93; 142.37; 140.07; 139.53; 136.55; 135.82; 134.68; 128.99; 128.17; 127.53; 125.87; 125.53; 124.90; 124.38; 124.09; 123.84; 123.64; 121.20; 120.20; 68.18; 55.48; 40.74; 31.77; 30.42; 29.95; 28.97; 25.85; 24.03; 22.80; 14.23; 1.24 . GPC: (THF, polystyrene standard)  $M_{\rm n} = 4.54 \, {\rm kg \, mol^{-1}}$ ,  $M_{\rm w} = 5.97 \, {\rm kg \, mol^{-1}}$ , PDI = 1.32. UV-vis (CH<sub>3</sub>Cl, 1 × 10<sup>-5</sup> mol/L):  $\lambda_{\rm max} = 383, 438, 547 \, {\rm nm}$ .

**P3-CN: P3** (0.130 g), malononitrile (0.236 g). Dark blue powder (0.076 g, 61.6%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.81–7.76 (br, Ar–H), 7.63–7.58 (br, Ar–H), 7.42–7.40 (br, Ar–H), 7.26 (br, Ar–H), 7.19–7.17 (br, Ar–H), 7.10–6.85 (br, Ar–H), 6.68 (br, Ar–H), 4.41–4.37 (br,  $-\text{OCH}_2-\text{CH}_2\text{O}-$ ), 2.80–2.77 (br,  $-\text{CH}_2-$ ), 2.06 (br,  $-\text{CH}_2-$ ), 1.66 (br,  $-\text{CH}_2-$ ), 1.32 (br,  $-\text{CH}_2-$ ), 1.07 (br,  $-\text{CH}_2-$ ), 0.76 (br,  $-\text{CH}_3$ ). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 151.99; 146.10; 145.93; 142.37; 140.07; 139.53; 136.55; 135.82; 134.68; 128.99; 128.17; 127.53; 125.87; 125.53; 124.90; 124.38; 124.09; 123.84; 123.64; 121.20; 120.20; 68.18; 55.48; 40.74; 31.77; 30.42; 29.95; 28.97; 25.85; 24.03; 22.80; 14.23; 1.24 . GPC: (THF, polystyrene standard)  $M_n = 6.07$  kg mol<sup>-1</sup>,  $M_w = 7.92$  kg mol<sup>-1</sup>, PDI = 1.28. UV–vis (CH<sub>3</sub>Cl, 1 × 10<sup>-5</sup> mol/L): λ<sub>max</sub> = 383, 438, 547 nm.

**P4-CN: P4** (0.073 g), malononitrile (0.265 g). Dark blue powder (0.076 g, 60.7%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.81–7.77 (br, 3H), 7.63–7.58 (br, 7H), 7.42 (br, 2H), 7.26 (br, 4H) 7.16–7.10 (br, 4H), 4.42–4.37 (br, 4H), 2.05 (br, 4H), 1.65 (br, 4H), 1.07 (br, 12H), 0.76 (br, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ, ppm): 151.97; 140.19; 128.35; 125.54; 120.29; 107.94; 55.51; 40.78; 31.74; 29.96; 24.06; 22.84; 14.29; 1.27. GPC: (THF, polystyrene standard)  $M_n = 6.18$  kg mol<sup>-1</sup>,  $M_w = 7.92$  kg mol<sup>-1</sup>, PDI = 1.28. UV–vis (CH<sub>3</sub>Cl, 1 × 10<sup>-5</sup> mol/L):  $\lambda_{max} = 379$ , 548 nm.

# 3. Results and discussion

# 3.1. Synthesis

The structures and the synthetic routes to monomers and the two-dimensional conjugated copolymers were shown in Schemes 1 and 2. The double bonds in monomer **3** and Compound **5** were formed by Wittig–Hornor reaction. Then, **5** were subjected to a Vilsmeier reaction in the presence of DMF and POCl<sub>3</sub> in refluxing 1,2-dichloroethane, affording selectively aldehyde **6** in moderate yields. In the Wittig–Hornor reaction, here, sodium hydride was used as the base, instead of the normal *t*-butoxide potassium, to get the satisfactory yields. It was easily known that if some other aldehydes but not **2** and **4** were used in the Wittig–Hornor reaction, as a result, other monomers rather than **3** and **6** could be yielded. For example, other thiophene oligomers bearing aldehyde groups, i.e. quaterthiophene and quinquethiophene, could be treated as the starting material instead of **2**, to adjust the conjugated length of the thiophene-based side chain to possibly modify the quality of the blend films of the polymers and PC<sub>61</sub>BM. Similar, other conjugated blocks could replace the substituted thiophene one in **4** to partially control the intramolecular charge transfer to regulate the absorption band and LUMO level.

The polymers, P1 and three precursor polymers, P2, P3 and P4, were synthesized by Suzuki coupling reaction by adding different ratios of monomer **3** and **6**. The three resultant polymers, **P2-CN**, **P3-CN** and **P4-CN**, were obtained by a Knoevenagel condensation between the aldehyde-functionalized conjugated precursor polymer and malononitrile in the presence of pyridine. Just simply controlling the monomer ratio of **3** and **6** in the polymerization process, the ratio of x in the polymers could be easily modulated. This was another advantage of this kind of copolymers, that was, the concentrations of the different construction blocks in the resultant polymers could be conveniently handled according to the different requirements. Since the aldehyde groups could react with different acceptors, such as 1,3-diethylthiobarbituric acid, rather than malononitrile used in this paper, thus, other conjugated copolymers of this kind could be easily prepared if needed. From this point. P2–P4 could be considered as polymeric reactive intermediates for the synthesis of other functional polymers. Further work was still underway in our lab.

# 3.2. Structural characterization

The monomers and polymers were characterized by spectroscopic methods, and all gave satisfactory spectral data. The monomers **3** and **6** were new compounds, and all the polymers were not reported yet. Fig. 1 showed the IR spectra of all the polymers except **P1**, in which the absorption bands associated with



Monomer Synthesis

Scheme 1. Synthetic routes to monomers.



Scheme 2. Synthetic routes to polymers.

the aldehyde group were at  $1652 \text{ cm}^{-1}$  in **P2–P4**, while that of cvano group at about 2222 cm<sup>-1</sup> in **P2-CN–P4-CN**. It was easily seen that after the conversion to P2-CN, P3-CN, and P4-CN, these characteristic absorptions of aldehyde moieties disappeared, and new absorption peaks at  $2222 \text{ cm}^{-1}$  (corresponding to C=N stretching for the three polymers) emerged, indicating the complete conversion of the aldehyde groups to the cyano ones within the limits of the sensitivity of FT-IR [24]. This case was further confirmed by their <sup>1</sup>H NMR spectra: there were no signals of the aldehyde groups observed at about 9.89 ppm in the spectra of P2-CN, P3-CN, and P4-CN [26,27]. As mentioned above, the ratio of x in the polymers could be modulated by controlling the monomer ratio of **3** and **6**, the actual values of *x* were calculated according to the <sup>1</sup>H NMR spectra of the polymers (see Fig. 2). In the <sup>1</sup>H NMR spectrum of **P1**, there was a peak at  $\delta$  2.80 ppm (peak a), which should be attributed to the hydrogen on the side chain of **P1**; the <sup>1</sup>H NMR spectrum of P4-CN displayed a new peak at 4.37 ppm (peak b), which should be assigned to the hydrogen of 3,4ethylenedioxythiophene. However, P2-CN and P3-CN have both peaks. Thus, the ratio of x in P2-CN and P3-CN could be determined to be 0.33 for P2 and 0.66 for P3, by the ratio of the integral areas of peak a to peak b in Fig. 2, which were close to the feeding ratios of the monomer in the reactions (0.33 for P2-CN and 0.75 for P3-CN).

Molecular weights of the polymers were determined by gel permeation chromatography (GPC) in THF, using polystyrene as



Fig. 1. FT-IR spectra of the polymers.

standard, with the results summarized in Table 1. The numberaverage molecular weights ( $M_n$ ) of **P1**, **P2-CN**, **P3-CN**, **P4-CN** were found to be 12.1, 4.54, 6.07 and 6.18 kg mol<sup>-1</sup> respectively, with the corresponding polydispersity indices of 2.13, 1.32, 1.66 and 1.28. All the polymers have excellent solubility in common organic solvents such as THF, chloroform, and chlorobenzene due to its bulky side chain which could be readily cast into uniform thin films, rendering them good candidates for the fabrication of PSCs devices. The thermal property of the copolymers was investigated *via* thermogravimetric analysis (TGA) under an atmosphere of dry nitrogen. As shown in Table 1 and Figure S2 (see Supporting information), the 5% weight loss temperatures for **P1**, **P2-CN**, **P3-CN** and **P4-CN** were in the range of 338–390 °C, which was adequate for the application of the copolymers as active materials in PSCs and other optoelectronic devices [25,26,28].

Fig. 3 showed the absorption spectra of P1, P2-CN, P3-CN and P4-CN, in both chloroform solutions and thin films. In solution, P1 exhibited two distinct absorption peaks: the absorption peak at about 392 nm originated from the  $\pi - \pi^*$  transition of its conjugated main chain [24–26]; while that of  $\sim$ 439 nm corresponded to the  $\pi - \pi^*$  transition of the terthiophene moieties in the side chain [31]. After the introduction of the electronic acceptor of dicyano groups, taking **P4-CN** as an example, a new absorption peak at the longer wavelength of 548 nm appeared, which should be attributed to the strong intramolecular charge transfer (ICT) interaction between the conjugated main chain and the pendant acceptor moieties [24-27] and would capture the sunlight at longer wavelength than that for P3HT to contribute to the performance of the resultant PSC devices. However, it was noted that in the range of 420-480 nm, P4-CN demonstrated very weak or nearly no absorption, which would surely decease the PCE value in some degree. However, in the spectra of copolymers of P2-CN and P3-CN, the absorption peak of the terthiophene moieties remained in some extent, while the peak of ICT interaction at 548 nm appeared, thanks to their special structure. The good absorption of P3HT in the visible region contributed to its good PSC efficiency, and the absorption of the low-band gap conjugated polymers at longer wavelength should be achieved. Thus, by regulating the ratios of the two components as shown in P2-CN and P3-CN, the absorption spectra of the resultant polymers could be easily tuned, to possibly control the



Fig. 2. <sup>1</sup>H NMR spectra of the polymers

performance the corresponding PSC devices. This might be another advantage of this kind of copolymers. Also, by bonding some other more stronger acceptor moieties instead of the dicyano groups used here, the absorption band of ICT interactions could be further redshifted [24–26], and the adjustment of the balance between the absorption of terthiophene moieties and the ICT one should be more important for the PCE values of the PSC devices. The optical band gaps  $(E_{\alpha}^{opt})$  of the four polymers were calculated from the absorption onset in the solutions. Different from the higher one, 2.34 eV, of P1, P2-CN, P3-CN and P4-CN had the similar value of  $\sim$  1.82 eV, which was lower than 2.0 eV, for the possibly good match of the terrestrial solar radiation. By manipulating the different acceptors in the side chains, the photophysical properties of this kind of copolymers could be further adjusted according to the practical requirements. Similar to those reported in the literature, the polymer films spin-coated on glass substrate showed redshifted and broadened absorptions, in comparison with those of their corresponding dilute solutions, due to the enhanced interchain interactions in the solid state and the probably increased polarizability of the film. All the above-related data were also summarized in Table 1.

# 3.3. Electrochemical properties

Cyclic voltametry (CV) was employed to investigate the redox behavior of the chromophores and estimate their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. The CV curves were shown in Fig. 4 and the corresponding data were summarized in Table 1. All reported potentials were calibrated against the ferrocene/ferrocenium  $(Fc/Fc^+)$  couple, which was used as the internal standard. In the anodic scan, the initial onset oxidation potential of the conjugated copolymers were found to occur at 0.93, 0.89, 0.89 and 0.90 V (vs Ag/Ag<sup>+</sup>), respectively, which corresponded to HOMO levels of -5.30, -5.26, -5.26 and -5.27 eV, respectively, according to the empirical equation,  $E_{(HOMO)} = -(E_{ox} + 4.37)$ . Since the cathodic scans for these polymers failed despite many attempts, the LUMO energy levels of these conjugated copolymer were estimated from the optical band gaps and the HOMO energies, based on the relation of  $E_{\rm g} = E_{\rm LUMO} - E_{\rm HOMO}$ , which were calculated to be -2.96, -3.44, -3.44 and -3.45 eV, respectively (Table 1). Due to the same conjugated backbone of these four polymers, their HOMO energy levels were nearly the same, although there were some pendant acceptor groups in the side chains of P2-CN, P3-CN and P4-CN. In accordance with the different structure, the LUMO energy level of P1 (-2.96 eV) was different, while those of P2-CN, **P3-CN** and **P4-CN** were similar ( $\sim$  –3.44 eV), which were decreased after the introduction of the dicyano groups in the conjugated side chains on the thiophene moieties. It was reported that the threshold HOMO level for air stable conjugated polymers was calculated to be about 5.2 eV [33], thus, the little lower HOMO levels of these four polymers should contribute much to their chemical stability in ambient conditions, as confirmed by their relatively good decomposed temperature shown in Table 1. Since  $V_{\rm oc}$  of PSCs was generally proportional to the difference between the LUMO level of the acceptor and the HOMO level of the donor, it was reasonable to expect that the deeper HOMO levels of the polymers would assure the high  $V_{\rm oc}$  values of the corresponding PSCs at a large degree. Also, the big difference (larger than 0.3 eV) between the LUMO levels of the polymers and  $PC_{61}BM$  (-4.3 eV)

Table	1
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Molecular weights, thermal properties, electrochemical and optical properties of the polymers.

polymers	<i>M</i> <sub>n</sub> (kg/mol)	M <sub>w</sub> (kg/mol)	PDI $(M_w/M_n)$	$T_{d}^{a}(^{\circ}C)$	$\lambda_{abs} (nm)$ Solution	λ <sub>abs</sub> (nm) Film	$E_{g}^{b}$ (eV)	$E_{\rm HOMO}^{\rm c}({\rm eV})$	$E_{\rm LUMO}^{\rm d} (\rm eV)$
P1	12.1	25.9	2.13	361	392,439	388,444	2.34	-5.30	-2.96
P2-CN	4.54	5.97	1.32	390	383,438 547	391,548	1.82	-5.26	-3.44
P3-CN	6.07	10.1	1.66	349	383,438 547	384,547	1.82	-5.26	-3.44
P4-CN	6.18	7.92	1.28	338	379,548	379,549	1.82	-5.27	-3.45

<sup>a</sup> 5% Weight loss temperature measured by TGA under N<sub>2</sub>.

<sup>b</sup> Band gap estimated from optical absorption band edge of the film.

<sup>c</sup> Calculated from the onset oxidation potentials of the polymers.

<sup>d</sup> Estimated using empirical equations  $E_{LUMO} = E_{HOMO} + E_{g}$ .



Fig. 3. UV-vis absorption spectra of the polymer in the CHCl<sub>3</sub> solutions and films.

would contribute much to the charge transfer from the polymers to PC<sub>61</sub>BM to benefit the device performance.

# 3.4. Theoretical calculations

To get some insight into the fundamentals of molecular architecture, density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d) level using Gaussian 09, Revision A.02 program [34] with a chain length of n = 2 for **P1** and **P4-CN** (while 1 for the repeating unit in **P2-CN** and **P3-CN**) for their good comparison, and the corresponding Kohn–Sham orbitals were obtained at the same level of theory. To simplify the calculating process, aliphatic side chains of the fluorine moieties in the polymers were replaced by methyl groups. This is a reasonable approach since the substituents in the 9-position of the fluorene ring were not in conjugation with the aromatic system and had no



Fig. 4. Cyclic voltammograms of the copolymer thin films on platinum electrode in  $0.1 \text{ mol/L Bu}_4\text{NPF}_6$ , CH<sub>3</sub>CN solution.

noticeable effect on the electronic distribution properties of the polymer systems. The calculated frontier orbitals for the repeating units of these polymers were shown in Figure S3 (see Supporting information). Although there were some discrepancies existed between the calculation and experimental results, we could still obtain some information from Figure S3 (see Supporting information). As shown in Figure S3a (see Supporting information) and 6c, when the chain length of P1 and P4-CN was 2, their HOMOs were located throughout the whole conjugated system, resulting in their similar HOMO values (Table 1). Interestingly, their LUMO values were different at a relatively large degree, no matter the computed LUMOs localized mainly on the side chains. This was reasonable. As mentioned above, the LUMO levels of this kind of copolymers were almost determined by the acceptor moieties in the side chains, thus, after malononitrile was introduced to P4-CN, its LUMO level should surely be lowered. Unlike those of P1 and P4-CN, the electron density distributions at HOMO comprised part of the main chain and the terthiophene group, while those of LUMO were highly localized near the acceptor moieties in the side chains. The well-separated distribution of HOMO and LUMO levels disclosed there was a charge-transfer transition between them, partially indicating the charge separation through sequential transfer for electrons from the conjugated donor to the side chain acceptor groups and then to PC<sub>61</sub>BM in the bulk-heterojunction PSCs. If some other stronger acceptors were used, it was expected that even lower LUMO energy levels could be obtained.

# 3.5. Photovoltaic properties

Bulk-heterojunction PSCs using the prepared four conjugated polymers P1, P2-CN, P3-CN and P4-CN as donor and PC<sub>61</sub>BM as acceptor were investigated with the device configuration of ITO/ PEDOT:PSS/Polymer:PC<sub>61</sub>BM(1:2, w/w)/Ca/Al. Photovoltaic performance characteristics of the PSCs were summarized in Table 2. Fig. 5 showed the current density-voltage (J-V) curves of the PSCs based on the copolymers/PC<sub>61</sub>BM (1:2, w/w), measured under the illumination of simulated AM 1.5 G conditions (900 W/m<sup>2</sup>). All the devices exhibited a high  $V_{oc}$  (in the range of 0.80-0.90 V), due to their relatively low HOMO level, which was mainly determined by their main-chain donor. P3-CN demonstrated better photovoltaic performance than the other three polymers with  $J_{sc}$  of 3.76 mA/cm<sup>2</sup>, FF of 0.36,  $V_{oc}$  of 0.90, corresponding to a PCE of 1.34%.

 Table 2

 Photovoltaic properties of the polymer solar cells.

polymers	$V_{\rm oc}\left({\rm V} ight)$	$J_{\rm sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
P1	0.80	1.04	34	0.32
P2-CN	0.85	1.73	37	0.61
P3-CN	0.90	3.76	36	1.34
P4-CN	0.90	2.73	32	0.86

It seemed that there were no rules present in the tested results at the first glance. If analyzing their Jsc values in detail, it was found that from P1 to P2-CN and further to P3-CN, the Jsc values increased from 1.04 to 1.73 then to 3.76 mA/cm<sup>2</sup>. This result should be ascribed to the progressively improved absorption spectra in the long wavelength as the result of the appeared new absorption peak at about 547 nm brought by the enhanced ICT interaction. However, the  $J_{sc}$  value of **P4-CN** decreased to 2.73 mA/cm<sup>2</sup>, no matter its absorption band with the peak centered at about 548 nm further enhanced, due to the increased concentration of the repeating units bearing the acceptors. This was reasonable. Generally, the Isc value was mainly determined by the absorption behavior of the conjugated polymers. As discussed in the part of the absorption behavior of these four conjugated polymers, although P4-CN absorbed very well at the longer wavelength from 480 to 610 nm, it demonstrated very weak or nearly no absorption in the range of 420-480 nm, which would surely decease the PCE value in some degree. However, in the spectra of copolymers of P2-CN and P3-CN, the absorption peak of the terthiophene moieties remained in some extent with the absorption band shorter than about 480 nm, while the peak of ICT interaction at 548 nm appeared, thanks to their special structure. Thus, the remained absorption peak originated from the terthiophene moieties in the range of 420-480 nm, contributed much to the good performance of P3-CN, indicating that the absorption band at the short wavelength could not be ignored in the design of the conjugated polymers. So, considering the results carefully, there would be a balance between the absorptions at short wavelengths and the longer ones.

Fig. 6 demonstrated the comparison of the PCE values of the polymers using **P1** as reference. It was seen that the PCE values increased first, then decreased, accompanying with the increasing concentration of the D $-\pi$ -A ones in the polymers, visually exhibiting the changing trend of these four polymers discussed above. Since we only prepared two polymers. **P2-CN** and **P3-CN**. which contained both the terthiophene moieties and the  $D-\pi-A$ ones, there might be other polymers of this kind with different ratios of these two components exhibiting even better results. However, the preliminary experimental results could give some clues for the design of conjugated copolymers for the PSCs: the prolonging of the absorption band to the long wavelength by the introduction of the D– $\pi$ –A structure, could not be built on the victim of the sharply decreased absorption in the short wavelength. On the other hand, the obtained results indicated the advantage of the structure of P2-CN and P3-CN: the functional units with different absorption behavior could be integrated into the copolymers. It should be pointed out that the PSC devices were not well optimized, thus, better performance might be achieved.

With the aim to know some information about the morphology of copolymer: PC<sub>61</sub>BM blends, AFM was used to characterize their films, with the obtained topography images shown in Fig. 7. It was easily seen that the surface of P1:PC<sub>61</sub>BM and P3-CN:PC<sub>61</sub>BM blend films were quite smooth, with root-mean-square roughness (rms) of 0.474 and 0.324 nm, respectively. Also, the surface of P2-CN:PC<sub>61</sub>BM blend films was still good, with rms of 0.648. This indicated the good miscibility between P1, P2-CN, P3-CN, and PC<sub>61</sub>BM without large phase separation. However, the surface of P4-CN:PC<sub>61</sub>BM were very rough, with rms of 3.735 nm. Comparing their structure carefully, in P4-CN, there was only one kind of side chains with the terminal acceptors, but no side chains of the terthiophene groups. As discussed in the introduction part, the introduction of the terthiophene groups in the side chains, was to increase the compatibility of the resultant polymers with PC<sub>61</sub>BM. Thus, the AFM results confirmed the role of the terthiophene groups, without their presence, the compatibility was much worse.



Fig. 5. J-V characteristics of the devices with the structure of ITO/PEDOT:PSS/Polymer:PC<sub>61</sub>BM (1:2, w/w)/Ca/Al.



Fig. 6. The comparison of the PCE values of the polymers using P1 as reference. Line is included as a guide to the eye.



Fig. 7. AFM images  $(2 \times 2 \mu m^2)$  of the active layers from the four polymers (polymer: PC<sub>61</sub>BM ratio of 1:2)

This indicated that in the design of new polymers with better photovoltaic performance, perhaps, the introduction of some thiophene oligomer blocks could contribute to the compatibility with  $PC_{61}BM$ .

# 4. Conclusions

In summary, a series of conjugated copolymers were successfully prepared, and well characterized, which were soluble in common polar solvents and exhibited good thermal stability. The preliminary study demonstrated the following.

The performance of the copolymers in the PSC devices did not always increase accompanying the increasing concentration of the malononitrile substituted side chain. Thus, there should be a balance between the absorptions at short wavelengths and the longer ones. This might be a new strategy to design conjugated copolymers for PSC applications with adjustable performance, into which the functional units with different absorption behavior could be integrated.

Although not optimized, the photovoltaic devices based on these copolymers with low-band gap still exhibit high  $V_{oc}$ , further confirming the good advantages of this kind of polymers bearing acceptor groups in the side chains. It was believed that by

modifying the structure, other copolymers with better performance should be obtained.

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# Supporting information

Supporting information associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2011.09.022.

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