

Triphenylamine–thiazolothiazole–benzodithiophene based conjugated copolymers for polymer solar cells

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Abstract Two novel conjugated copolymers (P1 and P2) with donor–acceptor architecture, based on triphenylamine, benzodithiophene and thiazolothiazole (TTz), have been prepared by the Stille coupling reaction. Compared with alternative copolymer P1 with the single electron-withdrawing unit TTz, random copolymer P2 introduced another stronger electron-withdrawing unit benzothiadiazole intramolecularly. Incorporation of two different electron-withdrawing units on the backbone was proved to have a significant influence on the optical and electrical properties. Compared with P1, copolymer P2 has the wider absorption spectrum, lower bandgap, and therefore the better device performances.

1 Introduction

Rapid and drastic advances in the performance of polymer based bulk-heterojunction (BHJ) solar cells have brightened the vision of organic photovoltaics for light-weight,

low cost, and large-area flexible fabrication in electronic devices processing [1–7]. Nowadays, the power conversion efficiencies (PCEs) of single-junction BHJ solar cells based on polymer donors and fullerene acceptors have exceeded 10 % [8, 9]. Considering the outstanding performance of fullerene acceptors in organic solar cells (OSCs), research activities have been almost exclusively focused on developing low bandgap polymers via donor (D)–acceptor (A) approach on account of the hybridization of the energy levels of D/A units so as to have a broad light absorption range to harvest more sunlight [10, 11]. In the past decades, a variety of low bandgap polymers have been created for OSCs by incorporating different donor and acceptor blocks. Benzodithiophene (BDT) and triphenylamine (TPA) unit have been widely utilized as the donor building blocks due to its electron-donating capability and good hole-transporting ability while thiazole[5,4-d]thiazole (TTz) and 2,1,3-benzothiadiazole (BT) are used as acceptor moieties in consequence of its electron-withdrawing nitrogen of imine (C=N) [7, 12–22].

Herein, we report the synthesis and characterization of two novel D–A–D type copolymers P1 and P2. Alternating copolymer P1 was synthesized via Stille coupling reaction with TTz as electron-defect unit while BDT and TPA as the electron-donating units. The random copolymer P2 was prepared by analogy with that used for P1 except for the introduction of second electron-deficient unit BT. Owing to stronger electron-withdrawing ability of BT than TTz, P2 has stronger intramolecular charge transfer. Accordingly, copolymer P2 has a wider absorption spectrum and narrower bandgap than copolymer P1. The OSCs based on blends of copolymer P2: [6]-phenyl C₇₁ butyric acid methyl ester (PC₇₁BM) show better device performances than that of copolymer P1: PC₇₁BM.

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2 Experimental

2.1 Materials and measurement

All reagents and chemicals were purchased from chemical supplier (J&K Scientific Ltd., Energy Chemical) and used without further purification except that toluene and tetrahydrofuran (THF) were dried and purified by fractional distillation over sodium/benzophenone and handled in a moisture-free atmosphere.

^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400 (Varian, USA) system with TMS as the internal standard at 298 K. Number-average (M_n) and weight-average (M_w) molecular weights were determined by a Waters GPC 2410 (Waters Co., USA) system in THF using a calibration curve of polystyrene standards. Cyclic voltammetry (CV) measurements were recorded with a CHI610D electrochemical workstation (Chenhua Instrument Co., China) in a tetrabutylammonium perchlorate (TBAP, 0.1 mol L $^{-1}$)/acetonitrile electrolyte at the scan rate of 50 mV s $^{-1}$ at room temperature. A Pt electrode, a platinum wire, and a standard calomel electrode (SCE) were used as the working electrode, the counter electrode, and the reference electrode respectively. The deposition of copolymers on the electrode was done through the evaporation of a dilute chloroform solution. UV–visible absorption spectra were obtained on a UV-2550 spectrophotometer (Shimadzu Co., Japan) at room temperature. Thermogravimetric (TG) curves were recorded in air at a 10 °C min $^{-1}$ scan rate on a Netzschsta 409P (NETZSCH-Gerätebau GmbH, Germany).

2.2 Fabrication and characterization of photovoltaic devices

The OSCs were fabricated with the structure of ITO/PEDOT: PSS (40 nm)/copolymer: PC $_{71}$ BM/Al (100 nm). The ITO-coated glass substrates were cleaned with sonication in neutral detergent, distilled water, acetone and 2-propanol. Subsequently, PEDOT: PSS (40 nm) was spin-coated on a cleaned ITO substrate and heated at 120 °C for 15 min under vacuum before the active layer was spin-coated on top of the PEDOT:PSS layer. A predissolved composite solution in *o*-dichlorobenzene (*o*-DCB) was filtered through a syringe filter and spin-coated on the PEDOT: PSS-coated ITO substrate to form the active layer. Finally, Al (100 nm) was deposited onto the active layer under pressure less than 4×10^{-4} Pa by vacuum evaporation and the active area of the solar cells was 4.5 mm 2 . The current density–voltage (J – V) characteristics were determined through illuminating the cells using simulated solar light (AM1.5G) with an intensity of 100 mW cm $^{-2}$

(solar simulator Model ss-50A, Photo Emission Tech., Camarillo, California). The external quantum efficiency (EQE) spectra were measured using an IQE-200 test system (Oriel Co., USA) with the solar cells illuminated with chopped monochromatic light through the ITO side.

2.3 Synthesis of the intermediate and copolymers

2.3.1 Synthesis of 2,5-bis(4-bromo-*N,N*-diphenylaniline)-thiazole[5,4-*d*]thiazole (2) [23]

In a round bottom flask, compound 1 (3.5 g, 10 mmol) and dithio oxamide (0.4 g, 3.3 mmol) were dissolved in 50 mL *N,N*-dimethylformamide, stirred at 150 °C for overnight. Then the reaction mixture was cooled to room temperature and extracted by ethyl acetate (50 mL \times 3). The organic layer was combined and dried over anhydrous magnesium sulfate (MgSO $_4$), then filtered off and concentrated. Evaporation of the solvent and purification by chromatography on silica gel [petroleum ether: dichloromethane (3:1, v/v)], a yellow solid 2 was obtained (1.13 g, 29 %). ^1H NMR (CDCl $_3$, 400 MHz, ppm): 7.81–7.79 (m, 4H), 7.38–7.36 (m, 4H), 7.28–7.31 (m, 4H), 7.11–7.13 (m, 6H), 7.05–7.07 (m, 4H), 6.99–7.01 (m, 4H). ^{13}C NMR (CDCl $_3$, 100 MHz, ppm): 168.2, 150.2, 149.5, 146.4, 146.0, 132.5, 129.7, 127.6, 127.4, 125.4, 124.4, 122.3, 116.3. Elem. anal. for C $_{40}$ H $_{26}$ Br $_2$ N $_4$ S $_2$ calc.: C, 61.08; H, 3.33; N, 7.12; S, 8.15. Found: C, 61.02; H, 3.38; N, 7.16; S, 8.12.

2.3.2 Synthesis of copolymer P1

Under nitrogen atmosphere, a mixture of compound 2 (170 mg, 0.216 mmol), compound 3 (161 mg, 0.216 mmol), Pd (PPh $_3$) $_4$ (12.5 mg, 0.01 mmol) and toluene (20 mL) was stirred at 90 °C for 48 h and small amount of tributyl-(4-hexyl-thiophen-2-yl)-stannane and 2-bromothiophene was added to endcap the polymer chain. Undergoing the reaction of another 12 h, the reaction mixture was cooled to room temperature and precipitated in methanol. The raw copolymer was purified by soxhlet extraction for 48 h with acetone and chloroform. After removal of the solvent, the concentrated solution of P1 was precipitated again in methanol to afford a brown short fiber (128 mg, 55 %). ^1H NMR (CDCl $_3$, 400 MHz, ppm): 7.87–7.85 (m, 4H), 7.67–7.65 (m, 4H), 7.37–7.33 (m, 6H), 7.15–7.22 (m, 14H), 4.22–4.20 (m, 2H), 3.70–3.76 (m, 2H), 1.86–1.83 (m, 2H), 1.61 (m, 2H), 1.41 (m, 2H), 1.25 (m, 12H), 1.05–0.92 (m, 12H).

2.3.3 Synthesis of copolymer P2

The synthesis of copolymer P2 was similar with the procedure described for P1. The copolymerization of

compound **2** (157 mg, 0.2 mmol), compound **3** (125 mg, 0.2 mmol), compound **4** (309 mg, 0.4 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol) and toluene (25 mL) gave P2 as a brown powder (189 mg, 47 %). ¹H NMR (CDCl₃, 400 MHz, ppm): 7.81–7.86 (m, 2H), 7.73–7.76 (d, 2H), 7.55–7.65 (m, 6H), 7.33–7.40 (m, 6H), 7.14–7.20 (m, 14H), 7.01–7.06 (m, 2H), 4.21 (s, 4H), 2.96 (s, 4H), 1.44–1.83 (m, 20H), 1.02–1.06 (m, 12H), 0.88–0.97 (m, 18H).

3 Results and discussion

3.1 Synthesis and thermal properties

The synthetic routes of the monomer and copolymers are shown in Scheme 1. Monomer **2** was obtained by the reaction of compound **1** and dithiooxamide. Then monomer **2** was copolymerized with monomer **3** by Stille reaction to afford the alternative copolymer P1. An equimolar amount of monomers **2** and **4** was copolymerized with monomer **3** by Stille reaction to afford the random copolymer P2. At the end of polymerization, 4-(hexyl-2-thienyl)stannane and

2-bromothiophene were added to remove the bromine and tributylstannane end groups, respectively. The copolymers have good solubility in common organic solvents. The number average molecular weights are 19,000 and 14,400 for P1 and P2, respectively. The molecular weight of the copolymers is relatively low because of the poor solubility of monomer **2** (Table 1).

The thermal properties of the copolymers were described by thermal gravimetric analysis (TGA) as shown in Fig. 1 and listed in Table 1. The degradation temperature (*T_d*) of 5 % weight loss for P1 is 355 °C and for P2 is 362 °C, indicating that the copolymers have excellent thermal stability.

3.2 Photophysical and electrochemical properties

The UV–Vis absorption spectra of copolymers P1 and P2 in the diluted CHCl₃ solution (concentration of 1×10^{-5} mol L⁻¹) and in the thin films are shown in Fig. 2a, b respectively and the corresponding data are summarized in Table 1. As shown in Fig. 2a, the copolymer P1 shows two absorption bands in the range of 280–500 nm in

Scheme 1 Synthetic routes of monomer and copolymers

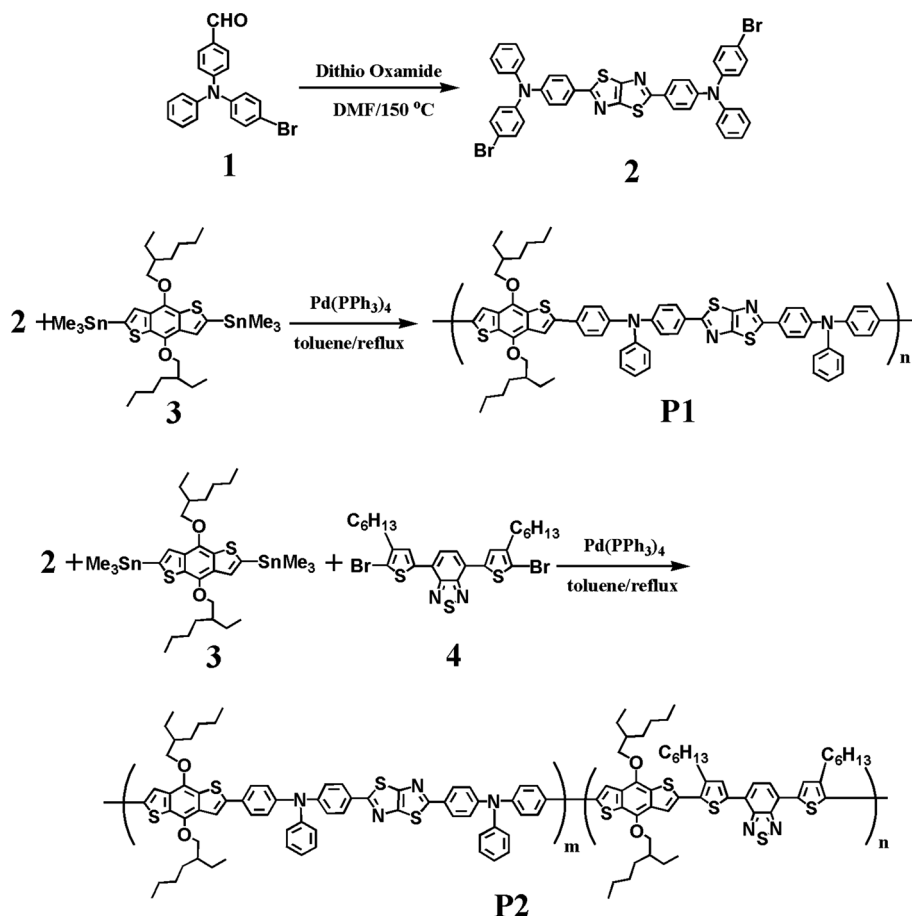


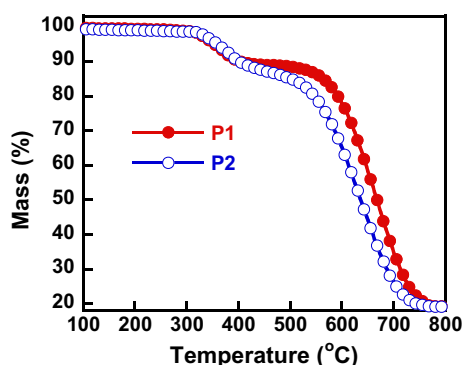
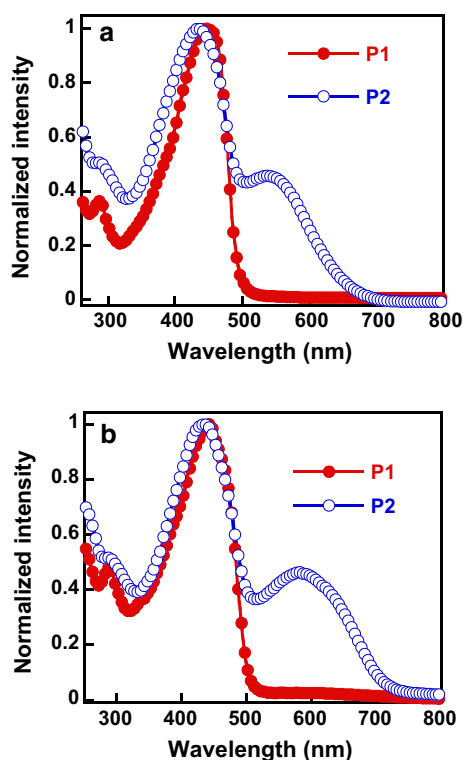
Table 1 Molecular weights, thermal, optical and electrochemical properties of the copolymers

Copolymer	T_d (5 % loss)/°C	$M_n \times 10^3$	PDI	$\lambda_{max,s}/nm$	$\lambda_{max,f}/nm$	E_g^{opt}/eV^a	E_{ox}^{onset}/V	E_{HOMO}^c/eV^b	E_{LUMO}^c/eV
P1	355	19.0	2.6	446	442	2.40	0.86	−5.26	−2.86
P2	362	14.4	1.3	434,538	434,582	1.71	0.83	−5.23	−3.52

^a Optical band gaps determined from the onset of absorption spectra of the polymer films [$E_g^{opt} = 1240/\lambda_{edge}$ (nm)]

^b Calculated from the E_{ox}^{onset}

^c Estimated from the E_g^{opt} and the HOMO energy levels

**Fig. 1** TG curves of copolymers at scan rate of 20 °C min^{−1} in air atmosphere**Fig. 2** UV–Vis absorption spectra of the copolymers in chloroform solutions (a) and thin film (b)

the solution. The first absorption band at the short wavelength is ascribed to the localized aromatic π – π^* transition. The second strong absorption band at the long wavelength with the absorption maxima (λ_{max}) at 446 nm is attributed to the ICT from the electron-donating units to the electron-deficient TTz unit. Compared with copolymer P1, copolymer P2 has another absorption peak at 538 nm which is ascribed to the ICT from the electron-donating units to the electron-deficient BT unit. The absorption spectra of the copolymers in the film are slightly red-shifted compared to those in chloroform solution, which indicates the existence of aggregation or π – π^* stacking in the film. The optical band gaps (E_g^{opt}) are estimated as 2.40 eV for P1 and 1.71 eV for P2 from the absorption onsets in their thin films, indicating that the optical band gap of P2 reduces 0.69 eV compared with P1, which is due to the introduction of the second acceptor unit BT.

The electrochemical properties were measured by the cyclic voltammetry (CV) to calculate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the copolymers. The detailed data are shown in Table 1. The onset oxidation potentials (E_{ox}) are observed to be 0.86 V (vs. SCE) for P1 and 0.83 V (vs. SCE) for P2. The HOMO and LUMO levels were calculated according to the empirical formula [$E_{HOMO} = -(E_{ox} + 4.4)$ eV] [24]. The HOMO energy levels are calculated as −5.26 eV for P1 and −5.23 eV for P2, which are beneficial for obtaining high V_{oc} . From the HOMO energy level and E_g^{opt} using the equation $E_{LUMO} = E_{HOMO} - E_g^{opt}$, the LUMO energy levels are calculated as −2.86 and −3.52 eV for P1 and P2, respectively. Compared with P1, the lower LUMO of P2 could be the introduction the second acceptor unit BT, which leads to the extension of π -electron delocalization in the polymer backbone.

3.3 Photovoltaic properties

In order to investigate the effect of copolymers in solar cells, we fabricated bulk heterojunction photovoltaic cells based on P1 and P2 as donor and PC₇₁BM as acceptor.

Typical device structure is ITO/PEDOT: PSS (40 nm)/copolymer: PC₇₁BM (80 nm) (1:3)/Al (100 nm) under AM 1.5G irradiation (100 mW cm⁻²). The active layers were spin coated from different solvents (*o*DCB and chloroform) using different weight ratio blends of copolymer: PC₇₁BM, respectively. And we found that *o*DCB is better than chloroform and the better weight ratio blends of copolymer: PC₇₁BM is 1:3. The *J*-*V* curves are depicted in Fig. 3 and the corresponding data are shown in Table 2. The PCE of devices based on P1 and P2 is about 0.61 % ($J_{sc} = 3.08 \text{ mA cm}^{-2}$, $V_{oc} = 0.60 \text{ V}$, FF = 0.33) and 1.04 % ($J_{sc} = 4.33 \text{ mA cm}^{-2}$, $V_{oc} = 0.67 \text{ V}$, FF = 0.36), respectively. According to the data, the PCEs of the copolymers are relatively low, which are ascribed to the low current density and low V_{oc} . The lower FF of the devices may result from the relatively low molecular weight of the copolymers. Compared with P1, the J_{sc} of P2 increased by introducing BT units. The strong and wide absorption of P2 results in high J_{sc} values. In order to verify the efficiency of the device, the external quantum efficiency (EQE) spectra of the photovoltaic devices from copolymer: PC₇₁BM blends are illustrated in Fig. 4. Two blends show the broad photo responses within the range from 300 to 700 nm. The EQE spectra of the copolymers show maxima of 21.3 % at 450 nm for P1 and 35.3 % at 450 nm for P2.

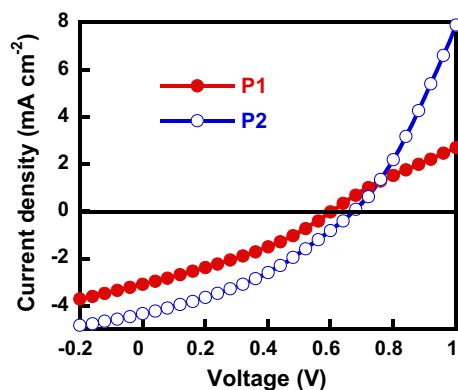


Fig. 3 *J*-*V* characteristics of devices under the illumination of an AM 1.5 G solar simulator (100 mW cm⁻²)

Table 2 Photovoltaic properties of the devices based on the copolymers P1 and P2

Copolymer	$J_{sc}/\text{mA cm}^{-2}$	V_{oc}/V	FF	PCE (%)
P1	3.08	0.60	0.33	0.61
P2	4.33	0.67	0.36	1.04

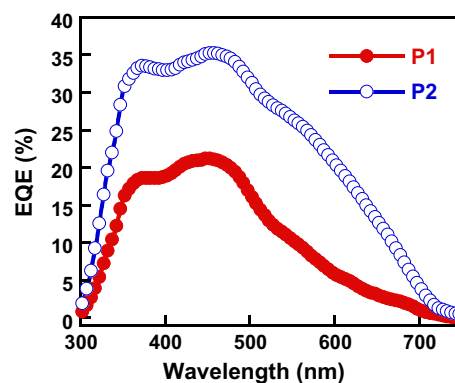


Fig. 4 EQE spectra of the BHJ solar cells under the illumination of an AM 1.5 G solar simulator (100 mW cm⁻²)

4 Conclusions

In summary, we have successfully synthesized two copolymers P1 and P2, via Pd-catalyzed Stille coupling reaction, compared their photophysical and electrochemical properties and investigated them as donor materials along with PC₇₁BM as an acceptor for the fabrication of solution-processed BHJ polymer solar cells. Compared with copolymer P1 with one electron-deficient unit in the main chain, copolymer P2 has wider absorption spectrum and narrower bandgap due to two different electron-deficient units. Therefore, the OSCs based on the blend of copolymer P2 and PC₇₁BM have better device performances. The best devices with P2: PC₇₁BM in *o*-dichlorobenzene show a V_{oc} of 0.67 V, a J_{sc} of 4.33 mA cm⁻², and FF of 0.36, which corresponds to the PCE of 1.04 %.

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