Low Band Gap Copolymers Consisting of Porphyrins, Thiophenes, and 2,1,3-Benzothiadiazole Moieties for Bulk Heterojunction Solar Cells

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ABSTRACT: Two novel low band gap conjugated copolymers containing porphyrins, thiophenes, and 2,1,3-benzothiadiazole (BTZ) moieties were synthesized and applied in bulk heterojunction solar cells. The thermal, optical, electrochemical, and photovoltaic properties of the two copolymers were examined to investigate the effect of the introduction of BTZ moiety in the backbone of the porphyrin polymers. The copolymers exhibited good thermal stability and film-forming ability. The absorption spectra indicated that the BTZ moiety has significant influence on the UV-visible region spectra of the copolymers: with increasing the molar amount of BTZ moieties in conjugated main chain, the absorption in the range of 450–700 nm is largely broadened and red-shifted compared to the similar polymers without BTZ moiety, and the optical band

INTRODUCTION In the last few decades, solar cells based on conjugated polymeric materials have recently received considerable attention due to their excellent electrical and optical properties comparable with inorganic semiconductors, but also because they can provide devices with flexibility, cost-effectiveness, light weight, and easy processability.^{1,2} To achieve high power conversion efficiency (PCE), bulk heterojunction (BHJ) devices containing polymer donors and fullerene-derived acceptors have been used and represent the most efficient polymer solar cells (PSCs) structure.^{3–5} A PCE of 7.4% has been achieved from BHJ devices of **PTB7**/PC₇₁BM, which is the first polymer solar cell with the PCE over 7% so far.⁶

Conventional wisdom dictates that suitable HOMO and LUMO energy levels, broad and strong absorption, good film-forming property, and high hole mobility in polymer blend are important prerequisites for the conjugated polymers.^{7,8} To broaden light absorption range, many low band gap conjugated polymers have been exploited in the past decade.^{9–18} There are various means to obtain the low band gap conjugated polymers. One effective method is to make the conju

gaps of copolymers were narrowed to ~1.50 eV. The photoluminescence spectra showed that there is effective charge transfer in the whole conjugated main chain. Cyclic voltammetry displayed that the band gaps were reduced effectively by the introduction of the **BTZ** moieties. The bulk heterojunction solar cells were fabricated based on the blend of the copolymers and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) in a 1:2 weight ratio. The maximum power conversion efficiency of 0.91% was obtained by using **P2** as the electron donor under the illumination of AM 1.5, 100 mW/cm². © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 2685–2692, 2011

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gated system more planar to increases the delocalization of the backbone and then the reduction of the band gap.¹⁹ Another successful and flexible strategy to design low band gap polymers involves the alternation of electron-rich unit (donor, e.g., bithiophene, benzodithiophene) and electrondeficient unit (acceptor, e.g., 2,1,3-benzothiadiazole, quinoxaline, dithiopheneylbenzothiadiazole) along the polymer chain.^{20–22} The first breakthrough on the way to developing highly efficient low band gap donor-acceptor (D-A) polymers is **PCPDTBT** investigated by Heeger and coworkers.²⁰

Since 54.3% of the sunlight energy is distributed in the visible region from 380 to 800 nm, an ideal active layer for a polymer solar cell should have a broad and strong absorption spectrum in this range.²³ Porphyrins possess a strong absorption band at around 425 nm, and weak Q-bands at around 600 nm. And investigators have been aiming to redshift the Soret-band and broaden the Q-bands of the spectra of the porphyrins. Bo et al. have investigated a series of soluble conjugated alternating porphyrin-dithienothiophene copolymers (**IIa** and **IIb**) and an achieved power conversion efficiency (PCE) of 0.3% under AM 1.5, 100 mW/cm² for the

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PSC using **IIb**:PCBM (1:3, w/w) as active layer.²⁴ In our previous articles, two star-shaped polymers with the structure of porphyrin as core and four polythiophene derivatives as arms were synthesized and characterized, to obtain a power conversion efficiency of 0.61%.²⁵ In addition, we introduced thiophene derivertives into the meso-positions to synthesis two novel soluble π -conjugated porphyrin polymers **P-PTT** and **P-POT** to obtain the best PCE of 0.32%.²⁶ To further broaden the absorption spectra and enhance the lightharvest ability of porphyrin polymers, in this article, we design and synthesis two copolymers consisting of porphyrins, thiophenes, and 2,1,3-benzothiadiazole (BTZ) moieties in the backbone to obtain low band gap copolymers. With the introduction of BTZ moieties, the energy gap between HOMO and LUMO energy levels was narrowed and the electronic spectra were red-shifted and broadened compared with previous porphyrin polymers (P-PTT and P-POT) without BTZ moieties. Moreover, we introduced octyloxy and hexyl as side chains on polymer backbones to improve the solubility of polymers.

EXPERIMENTAL

Materials and Characterization

All the chemicals were purchased from Alfa Aesar and Shanghai Medical Company (China), THF and toluene were distilled from sodium-benzophenone prior to use. All other reagents were used as received. The ¹H NMR and ¹³C NMR spectra were measured with Bruker AVANCE 400 spectrometer. Element analyses were measured by an Elementar Vario EL III element analyzer.FT-IR spectra were obtained on a Perkin-Elmer spectrometer, using KBr pellets. UV-visible absorption spectra were measured on a Perkin-Elmer Lambda 25 UV/vis/NIR spectrometer. The photoluminescence emission spectra (EL) were recorded with Perkin-Elmer LS-50 luminescence spectrometer. The average molecular weight and polydispersity index (PDI) of the copolymers were determined using Waters1515 gel permeation chromatography (GPC) analysis with THF as eluent and polystyrene as standard. Thermogravimetric analysis (TGA) measurements were conducted with a Netzsch TG 209 analyzer under nitrogen at a scan rate of 20 °C/min. Differential scanning calorimetry (DSC) analysis was made on a TA DSCQ10 instrument at a scan rate of 20 °C/min. Electrochemical measurements were made with EG&G Princeton Applied Research Model 273 Electrochemical Workstation. Redox potentials of the polymers were measured by cyclic voltammetry (CV) in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte, An Pt disk working electrode coated with polymer films, saturated calomel electrode (SCE) reference electrode, and Pt wire counter electrode were employed.

Fabrication and Characterization of PSCs

The PSCs were fabricated in the traditional sandwich structure (denoted as ITO/PEDOT: PSS/copolymer: PC61BM/Al). The fabrication process was as follows: a layer about 30 nm of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) was spin-coated from an aqueous solution (Bayer AG) on a precleaned indium tin oxide (ITO)/glass substrate, and was dried at 150 °C for 30 min. After cooling to room temperature, the solutions containing both copolymer and PC61BM (in chloro-benzene at a concentration of 24 mg/mL) were spin coated onto the ITO/PEDOT:PSS electrode, and then dried at 150 °C for 10 min in a nitrogenfilled glove-box. And the thickness of the active layers of liF0.7 nm. Finally, the aluminium (100 nm) electrode was evaporated onto the top of copolymer film at 6×10^{-4} Pa. The effective area of one cell was 9 mm². Current density-voltage (*J*-*V*) characteristics were measured by a computer controlled Keithley 2602 source measurement unit in dark and under AM 1.5 illumination conditions, 100 mW/cm². All these measurements were carried out under ambient atmosphere at room temperature.

Monomer Synthesis

The synthetic routes of the monomers and copolymers are shown in Scheme 1. The detailed synthetic pathways are as follows.

2-(Tri-n-butylstannyl)-4-Hexyl thiophene (1)

Under argon atmosphere, 3-hexylthiophene (3.36 g, 20 mmol) and 50 mL freshly distilled dry THF were added in a 100 mL three-necked flask. *n*-Butyllithium (8.8 mL, 2.5 M in hexane, 22 mmol) was added dropwise at -78 °C, and the solution was stirred for 1 h at -78 °C, then tributyltin chloride (6 mL, 22 mmol) was added. The mixture was allowed up to room temperature slowly and stirred for another 24 h. Finally, the mixture was poured into 100 mL of cooled water, and extracted by hexane. The organic layer was dried over anhydrous MgSO₄. Removal of the solvent by rotary evaporation, a yellow-brown liquid **1** (8.25 g, 90%) was obtained. The crude product was used in next step without further purified.

¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.18 (s, 1 H, thienyl-H), 6.96 (s, 1 H, thienyl-H), 2.64 (t, 2 H, --CH₂), 1.62-1.54 (m, 8 H, --CH₂), 1.36-1.30 (m, 12 H, --CH₂), 1.11-1.06 (m, 6 H, --CH₂), 0.93-0.87 (m, 12 H, --CH₃).

2,5-Bis-(trimethylstannyl)thiophene (2)

Under argon atmosphere, thiophene (1.05 g, 12.5 mmol) and 50 mL freshly distilled dry THF were added in a 100 mL three-necked flask. *n*-Butyllithium (12.5 mL, 2.5 M in hexane, 62.5 mmol) was added dropwise at -78 °C, and the solution was stirred for 1 h at -78 °C, then trimethyltin chloride (18.7 mL, 75 mmol) was added. The mixture was allowed up to room temperature slowly and stirred for another 24 h. Finally, the mixture was poured into 100 mL of cooled water, and extracted by hexane. The organic layer was dried over anhydrous MgSO₄. Removal of the solvent by rotary evaporation, then recrystallized by isopropyl alcohol to obtain a white needle solid (1 g, 17.2%).

¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.40 (s, 2 H, thienyl-H), 0.39 (m, 18 H, –CH₃). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 143.0, 136.0, 1.01.



SCHEME 1 Synthetic route of the monomers and copolymers.

4,7-Bis-(4-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole (3) 4,7-Dibromo-2,1,3-benzothiadiazole (1 g, 3.4 mmol) and 2-(tri-*n*-butylstannyl)-4-hexyl thiophene (3.1 g, 6.8 mmol), Pd(PPh₃)₄ (0.084 g, 0.075 mmol), were dissolved in toluene (50 mL) and the mixture was refluxed for 48 h. After evaporating the solvent under reduced pressure, H₂O (50 mL) and chloroform (50 mL) were added. The organic layer was separated and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure. The pure product **3** was obtained as orange solid by column chromatography on silica gel (CH₂Cl₂/hexane = 1/8).

Yield: 1.08 g, 68%. ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.99 (s, 2 H, thienyl-H), 7.84 (s, 2 H, phenyl-H), 7.06 (s, 2 H, thienyl-H), 2.71 (t, 4 H, -CH₂), 1.72-1.60 (m, 8 H, -CH₂), 1.36-1.22 (m, 8 H, -CH₂), 0.94 (t, 6 H, -CH₃). MALDI-TOF MS (C₂₆H₃₂N₂S₃) *m/z*: calcd for 468.1; found 468.1.

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

Compound **3** (1.00 g, 2.13 mmol) and *N*-bromosuccinimide (NBS) (0.84 g, 4.72 mmol) were resolved in mixed solvents (THF/HAc V/V = 1:1) (60 mL) in the dark. The resulting solution was stirred at room temperature under argon overnight. The organic phase and the water phase were separated from mixed solution. The organic phase was washed with brine and dried with sodium sulfate, filtered and the solvent evaporated under reduced pressure and further dried under high vacuum. A bright orange solid was obtained by column chromatography on silica gel with hexane (1.02 g, 77%).

¹H NMR (CDCl₃, 400 MHz, δ /ppm): 7.79–7.77 (d, 4 H, aryl-H), 2.68–2.64 (t, 4 H, --CH₂), 1.71–1.65 (t, 4 H), 1.42–1.36 (m, 12 H), 0.94–0.92 (t, 6 H, --CH₃). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 152.2, 143.1, 138.5, 128.1, 125.2, 124.7, 111.6, 31.6, 29.7, 29.6, 28.9, 22.6, 14.1.

5,15-Bis(4-brophenyl)-10,20-bis(4-(octyloxy) phenyl)porphyrin (5)

The monomer **5**, 5,15-bis(4-brophenyl)-10,20-bis(4-(octyloxy)-phenyl) porphyrin, was synthesized according to the methods reported in the literature²⁶ with some modification.

¹H NMR (CDCl₃, 400 MHz, δ /ppm): 8.90 (d, 4H, pyrrolic-H), 8.81 (d, 4H, pyrrolic-H), 8.10 (t, 8 H, Ar-H), 7.90 (d, 4H, Ar-H), 7.29 (d, 4H, Ar-H), 4.27 (t, 4H, OCH₂), 2.00 (t, 4H, CH₂), 1.54 (m, 20H, CH₂), 0.95 (t, 6H, CH₃), -2.80 (s, 2H, N-H). ¹³C NMR (CDCl₃):125.1, 119.9, 155.6, 160.8, 132.2, 137.7, 136.5, 103.1, 124.2, 127.4, 114.7, 156.7, 138.8, 128.5, 131.6, 122.2, 68.9, 29.6, 25.8, 28.9, 29.4, 31.8, 22.7, 14.4. MALDI-TOF MS (C₆₀H₆₀Br₂N₄O₂) *m/z*: calcd for 1026.3; found 1026.2.

5,15-Bis(4-brophenyl)-10,20-bis(4-(octyloxy)phenyl) porphyrin Zinc (6)

The solution of **5** (0.45 g, 0.44 mmol) in chloroform (200 mL) was added a solution of $Zn(OAc)_2$ (0.2 g, 1 mmol) in methanol (20 mL). The reaction mixture was refluxed for 1 h. After cooling to room temperature, the mixture was washed with water. The organic layer was dried over anhydrous MgSO₄ and concentrated. A purple-red solid of compound **6** was obtained (1.69 g, 97%).

¹H NMR (CDCl₃, 400 MHz, δ /ppm): 9.02–9.01 (d, 4 H, pyrrolic-H), 8.93–8.92 (d, 4 H, pyrrolic-H), 8.12–8.09 (t, 8 H,

 TABLE 1 Polymerization Results and Thermal Properties of the

 Porphyrin Copolymers

Copolymer	<i>M</i> _n (×10 ³)	<i>M</i> _w (×10 ³)	PDI	<i>T</i> _d (°C)	<i>T</i> g (°C
P1	5.2	11	1.8	310	66
P2	2.1	3.2	1.5	455	39

Ar-H), 7.91–7.89 (t, 4 H, Ar-H), 7.30–7.28 (d, 4 H, Ar-H), 4.28–4.25 (t, 4 H, $-OCH_2$), 2.02–1.98 (m, 4 H, $-CH_2$), 1.68– 1.61 (m, 4 H, $-CH_2$), 1.39–1.28 (m, 16 H, $-CH_2$), 0.98–0.95 (t, 6 H, $-CH_3$). ¹³C NMR (CDCl₃, 100 MHz, δ /ppm): 158.9, 150.8, 150.7, 149.8, 141.8, 135.7, 135.4, 134.8, 132.4, 131.7, 129.7, 122.2, 112.6, 68.4, 31.9, 29.5, 29.3, 26.2, 22.7, 14.1. MALDI-TOF MS ($C_{60}H_{58}Br_2N_4O_2Zn$) *m/z*: calcd for 1088.2; found 1088.1.

Synthesis of the Copolymer (P1)

To a 50 mL three-necked flask were added monomer **2** (139.8 mg, 0.3 mmol), **4** (0.2 mmol, 125.6 mg), **6** (108.8 mg, 0.1 mmol), and freshly distilled toluene (10 mL). The mixture was purged with nitrogen for 30 min. $Pd(PPh_3)_4$ (100 mg, 0.08 mmol) was added. After stirring at 110 °C for 3 days, the mixture was cooled to room temperature, the solvent was removed by rotary evaporation, and the residue was poured into 50 mL CH₃OH. The precipitate was filtered and washed with methanol and then the solid was purified successively by Soxhlet extraction in methanol, hexane, and chloroform for 24 h. The fraction extracted by chloroform was evaporated under reduced pressure, then precipitated in methanol, filtered, and finally dried over 24 h to obtain a dark purple solid.

Yield: 34.1%. ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 9.11–8.95 (br, pyrrolic-H), 8.35–7.42 (br, Ar-H), 4.37–4.17 (t, -OCH₂), 2.91–0.87 (br, alkyl-H). FT-IR (KBr, v_{max}/cm^{-1}): 2923, 2850, 1604, 1504, 1464, 1338, 1244, 1171, 997, 795. $M_w = 11 \text{ kg/mol}$, PDI = 1.8. According to the theoretical *x/y* ratio of 1:2, the ELEM. ANAL. for **P1** Calc.: C: 70.37, H: 5.91, N: 5.34, S: 13.73, C/S = 5.12. Found: C: 69.04, H: 6.10, N: 4.60, S: 13.63, C/S = 5.06.

Synthesis of the Copolymer (P2)

The synthetic procedure for **P2** was similar to that for **P1** while the molar ratio of monomer **2**: monomer **4**: monomer **6** is 5:4:1.

Yield: 30.3%. ¹H NMR (CDCl₃, 400 MHz, δ /ppm): 9.05–8.88 (br, pyrrolic-H), 8.34–7.10 (br, Ar-H), 4.26 (t, -OCH₂), 2.96–0.91 (br, alkyl-H). FT-IR (KBr, v_{max}/cm^{-1}): 2926, 2855, 1629, 1486, 1440, 1340, 1248, 1173, 1171, 995, 793. $M_w = 3.2$ kg/mol, PDI = 1.5. According to the theoretical *x/y* ratio of 1:4, the ELEM. ANAL. for **P2** Calc.: C: 68.76, H: 5.88, N: 5.26, S: 16.98, C/S = 4.05. Found: C: 68.62, H: 5.68, N: 4.75, S: 16.28, C/S = 4.21.

RESULTS AND DISCUSSION

Syntheses and Chemical Characterization

Following the synthetic routes of copolymers in Scheme 1, monomer 6 was reacted with carefully purified 2,5-bis

(trimethylstannyl)thiophene and 4,7-bis-(5-bromo-4-hexylthiophen-2-yl)benzo[1,2,5]thiadiazole by a palladium-catalyzed Stille coupling reaction. The obtained copolymers P1 and P2 were completely soluble in common organic solvents, such as THF and chloroform. The structures of copolymers were characterized by ¹H NMR spectroscopy and FT-IR. In the ¹H NMR spectra of copolymers the signals of the pyrrole-H of the porphyrin unit dominated in the region of 9.01-8.88 ppm, the alkyl chains appeared at 4.26-0.91 ppm, and other aromatic proton peaks located between 7.42 and 8.34 ppm. In the ¹H NMR spectrum of **P2**, the resonance integral ratio of signals of alkyl-H versus $-OCH_2$ is bigger than that of **P1**, indicating that there are more monomer 4 incorporated in P2. In the FT-IR spectra of P1 and P2, the strong stretching vibration of the C-C of porphyrin and C-H of aromatic ring are observed around 997 and 2921 cm⁻¹, respectively. Polymerization via Stille coupling yielded black-blue copolymers with average molecular weight (M_w) of 11.2 and 3.2 kg/mol and polydispersity index (PDI) of 1.8 and 1.5 for P1 and P2, respectively (Table 1). According to the theoretical x/y ratio of 1:2 for P1, the elemental analysis shows the theoretical calculation (such as C/S = 5.12) and experimental result (C/ S = 5.06) is almost consistent. For P2, the theoretical calculation (x/y ratio of 1:4, C/S = 4.05) is also approximate with the experimental result (C/S = 4.21).

Thermal Properties

The thermal properties of the copolymers were investigated by performing the differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurement, and the corresponding data were summarized in Table 1. As shown in Table 1, the glass transition temperature (T_g) of **P1** and **P2** was observed to be 66 °C and 39 °C, respectively. The TGA curves (Fig. 2) of two copolymers showed that 5% weight loss temperatures (T_d) are at 310 °C and 455 °C, respectively. The T_d values of both polymers are higher than 300 °C, indicating that two copolymers own the better thermal stability. The good thermal stability of the two copolymers is adequate for their applications in PSCs and other optoelectronic devices.²⁷

Photophysical Properties

The photophysical properties of the copolymers were investigated by UV-visible and fluorescence spectroscopy in diluted $CHCl_3$ solution and thin films on quartz plates. For comparison, we also measured the UV-visible spectra of reference



FIGURE 1 The chemical structure of copolymers.



FIGURE 2 TGA plots of the copolymers with a heating rate of 20 °C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

 P_{Zn}^{26} and monomer 3 in diluted CHCl₃. P_{Zn} showed a sharp Soret-band at 420 nm and weak Q-bands at 549 and 589 nm. And the monomer 3 exhibited two strong absorption peaks at 313 and 460 nm. After copolymerization, monomer 3 was successfully incorporated in the polymer backbone, thus, broad and strong absorption spectra of copolymers from 300 to 800 nm were obtained as expected. It is worthwhile to note that the copolymers not only hold the strong Soret-band but also possess much more broadened and stronger absorption at the locations of the Q-bands. The UVvisible spectra of copolymers in thin films are shown in Figure 3. Compared with those in solution, the spectra of copolymer films were improved significantly in intensity as well as breadth. As shown in Figure 3, the Soret-bands of P1 and P2 are respectively located at 439 nm and 442 nm, which are broadened and red-shifted by 14 and 18 nm compared with those in solution. On the other hand, the Q-bands of copolymer films located at 566 and 587 nm, respectively, are 14 and 39 nm red-shifted than those in solution apparently. The improvement of spectra in films can be attributed to the partial formation of J-aggregates (head-to-tail arrangement) through π - π stacking in the solid phase.²⁸ Those results showed that the introduction of BTZ moiety into main chains of the porphyrin polymers can markedly improve absorption in the red region. Moreover, it can be seen that Q-bands of P2 red-shifted than that of P1 in films. Thus, we can conclude that the absorption spectra would be



FIGURE 3 UV–Vis spectra of copolymers and reference P_{Zn} in CHCl₃ solutions and in thin films.

broadened in the red region with increasing the content of **BTZ** moieties in the main chain of the porphyrin polymers.

The photoluminescence (PL) spectra of copolymers and P_{Zn} were measured in the chloroform and thin films spin-coated on quartz plates (shown in Table 2 and Fig. 4). P_{Zn} showed two emission peaks at 600 nm and 650 nm. P1 and P2 exhibited the maximum emission peaks (λ_{em}) at 692 nm and 697 nm, respectively, and obtain red-shifted spectra in comparison with that of P_{Zn} , which conforms to the fact that played out in UV-visible spectra. We also measured the PL spectra of the two copolymers in thin films, and the maximum emission peaks (λ_{em}) of P1 and P2 are 783 and 772 nm, respectively. The large red-shift of λ_{em} observed from solution to solid thin film of porphyrin copolymers is similar to that observed from the UV-visible absorption spectra.

Electrochemical Properties

The electrochemical behaviors of the copolymers were investigated by cyclic voltammetry (CV) for determining the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the conjugated copolymers. Figure 5 showed the cyclic voltammograms of copolymer films on Pt electrodes in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte and saturated calomel electrode (SCE) was used as reference electrode. **P2** shows an irreversible oxidation peak and a quasi-reversible reduction peak. However, **P1** shows two irreversible oxidation peaks and a

TABLE 2 UV-Vis, PL Spectral Data, and Electrochemical Properties of the Porphyrin Copolymers

	Solution λ_{max} (nm) ^a		Film λ_{max} (nm) ^b					
Copolymer	UV	PL	UV	PL	HOMO ^c (eV)	LUMO ^c (eV)	E_{g}^{ec} (eV)	$E_{g}^{opt}(eV)$
P1	425	692	439	783	-5.12	-3.50	1.62	1.51
P2	425	697	442	771	-5.21	-3.45	1.76	1.50

^a Measured in chloroform solution.

^b Polymer cast from chloroform solution.

^c Energy levels calculated from the cyclic voltammogram.



FIGURE 4 PL spectra of copolymers in CHCl₃ solution and in films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

quasi-reversible reduction peak. Onset potentials are values obtained from the intersection of the two tangents drawn at the rising current and the baseline changing current of the CV curves. **P1** and **P2** have onset oxidation potentials at 0.72 and 0.81 eV, and onset reduction potentials at -0.90 and -0.95 eV, respectively. The potential of Hg/Hg₂Cl₂ reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple, which has a known reduction potential of -4.8 eV. The HOMO and LUMO energy levels of copolymers were calculated from the onset oxidation potentials ($E_{\rm ox}$) and onset reductive potentials ($E_{\rm red}$), respectively, according to the following equations:



FIGURE 5 Cyclic voltammograms of copolymers in $CH_3CN/0.1$ M Bu_4NPF_6 at 50 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

HOMO =
$$-e(E_{ox} + 4.40)$$
 (eV);
LUMO = $-e(E_{red} + 4.40)$ (eV);
 $E_g^{ce} = e(E_{ox} - E_{red})$ (eV)

Therefore, the energy levels of HOMO/LUMO for **P1** and **P2** are estimated to be -5.12/-3.50 eV and -5.21/-3.45 eV, and the calculated HOMO-LUMO energy gap are 1.62 and 1.76 eV, respectively. The location of HOMO and LUMO energy levels of the donor polymers are very important for application in efficient photovoltaic cell. The HOMO energy level of an ideal donor polymer should be lower than the air



FIGURE 6 Band diagram for the donor polymers **P1**, **P2**, and the acceptor $PC_{61}BM$. Dashed lines indicate the thresholds for air stability (-5.2 eV) and effective charge transfer to PCBM (-3.8 eV).

Copolymers	Copolymer/PC ₆₁ BM (w/w)	$V_{\rm oc}$ (V)	J _{sc} (mA/cm ²)	FF	PCE (%)
P1	1:1	0.53	3.38	0.26	0.46
	1:2	0.55	3.13	0.26	0.45
	1:3	0.54	2.80	0.24	0.36
P2	1:1	0.57	4.10	0.36	0.84
	1:2	0.62	5.03	0.29	0.91
	1:3	0.57	3.99	0.36	0.83

TABLE 3 Photovoltaic Performances of the Porphyrin Copolymers

oxidation threshold (ca. -5.2 eV) to ensure the good air stability (i.e., resistant to oxidation).²⁹ Furthermore, the relatively low HOMO of the polymers may lead to a high opencircuit potential ($V_{\rm oc}$) value for the photovoltaic cell.³⁰ The HOMO energy level of P2 is 0.09 eV lower than P1, indicating that P2 would own higher $\mathit{V}_{\rm oc}$ value. On the other hand, a donor polymer intended for use with a soluble fullerene acceptor (e.g., $PC_{61}BM$) should have an LUMO offset of ~0.3-0.4 eV relative to $PC_{61}BM$ (-4.2 eV) for the effective charge transfer. A complete picture of the band structure of P1, P2, and the acceptor $PC_{61}BM$ is presented in Figure 6. The first dashed line indicates the threshold for air stability (-5.2)eV), and the second dashed line represents the threshold value for an effective charge transfer from the polymers to $PC_{61}BM$ (-3.8 eV). As seen from Figure 6, both the HOMO and LUMO of the polymers are close to the ideal range. With the introduction of BTZ moieties, the LUMO energy levels of **P1** and **P2** are lower than that of **P-PTT** and **P-POT**.²⁶ At the same time, the HOMO energy levels of P1 and P2 are also lower than that of P-PTT and P-POT, which promise higher V_{oc} values.

Photovoltaic Properties

The bulk heterojunction solar cells of ITO/PEDOT:PSS/ copolymer:PC₆₁BM/LiF/Al device structures with different weight ratios of P1 or P2 to $PC_{61}BM$ were fabricated to investigated the photovoltaic properties. We have measured the photovoltaic properties of the devices in copolymers:PC₆₁BM weight ratio (1:1, 1:2, and 1:3). The photovoltaic parameters including the short-circuit current density $(J_{\rm sc})$, the open-circuit voltage $(V_{\rm oc})$, the fill factor (FF), and power conversion efficiency (PCE), are summarized in Table 3. For **P1**, the copolymers: $PC_{61}BM$ weight ratio doesn't affect the performance very much. However, it dose have effect on **P2**. When the copolymers: $PC_{61}BM$ weight ratio is 1:2, the PSCs devices exhibited the best performances. Under standard global AM 1.5 solar conditions and with copolymers:PC₆₁BM weight ratio of 1:2, the photovoltaic cells based on copolymer P2 exhibits the better photovoltaic performances ($J_{sc} = 5.03 \text{ mA/cm}^2$, $V_{oc} = 0.62 \text{ V}$, FF = 0.29, and PCE = 0.91%) than **P1** based devices ($J_{sc} = 3.13 \text{ mA/cm}^2$, $V_{\rm oc} = 0.55$ V, FF = 0.28, and PCE = 0.45%) . Figure 7 shows the *J–V* curves of the devices for **P1** and **P2** with the copolymers:PC₆₁BM weight ratio of 1:2. Compared with previous copolymers **P-PTT** and **P-POT**¹¹ the J_{sc} values of **P1** and **P2** is much higher than those of **P-PTT** (2.03 mA/cm²) and

P-POT (1.70 mA/cm²). This result indicates that the introduction of the electron deficient BTZ moieties in the backbone of the porphyrin copolymers can achieve higher J_{sc} due to the red-shifted and broadened UV-visible spectra in the red region. The short-circuit current for P2 is higher compared to P1, which implies that the increase molar ratio of BTZ moiety in the polymer improved the photovoltaic performances. In general, a higher $V_{\rm oc}$ could result from the lower HOMO energy levels of the studied copolymers because $V_{\rm oc}$ is related to the energy differences between the HOMO of the donor (conjugated polymer) and the LUMO of the acceptor.¹⁶ In Table 3, **P2** possesses the higher $V_{\rm oc}$ than P1, which conforms to the result of the discussion in the electrochemical properties. Furthermore, the $V_{\rm oc}$ values of P1 and P2 are both higher than P-PTT (0.46 eV) and P-POT (0.46 eV), which are also due to the lower HOMO energy levels of the former. In summary, the photophysical and electrochemical properties of these porphyrin copolymers, P1 and P2, possess red-shifted and broadened UV-visible spectra and lower HOMO energy levels, which, respectively, caused the higher J_{sc} and V_{oc} values than **P-PTT** and **P-POT** and resulted in the higher power conversion efficiencies.



FIGURE 7 J-V curves of the photovoltaic cells based on **P1** and **P2** (copolymers:PC₆₁BM, 1:2, w/w) under the illumination of AM 1.5, 100 mW/cm². [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

In summary, two novel low band gap conjugated copolymers P1 and P2 containing porphyrins, thiophenes, and BTZ moieties, have been successfully synthesized via the Stille coupling reaction. The research results showed that the introduction of BTZ moiety in the conjugated main chain of the porphyrin copolymers can broaden the absorption spectra in the range of 450-750 nm. With the introduction of BTZ moieties, the LUMO energy levels of the copolymers were lowered to -3.50 and -3.45 eV and the HOMO energy levels were lowered to -5.12 and -5.21 eV, resulting energy gaps lowered to 1.62 and 1.76 eV, respectively. The lowered energy gaps promised the red-shifted and broadened spectra which lead to higher J_{sc} and the lower located HOMO energy levels result the higher $V_{\rm oc}$. Thus, the synthesized porphyrin copolymers in this article could reach a promising PCE of 0.91% which is a relatively high PCE value in porphyrin polymers applied in PSCs.

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