ORIGINAL ARTICLE

Synthesis and characterization of alternating and random conjugated polymers derived from dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene and 2,1,3-benzothiadiazole derivatives

Qiang Su¹, Junfeng Tong², Jianfeng Li², Peng Zhang², Chunyan Yang², Caizhen Zhang¹, Feng Wang³, Dejia Chen⁴ and Yangjun Xia²

Alternating and random low band gap conjugated copolymers with dialkyloxy flanked-dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene derivatives (DTBDTs) as electron donor moieties and 5,6-di(dodecyloxy)-2,1,3-benzothiadiazole (BT) as electron acceptor moieties were synthesized and characterized. Both of the conjugated polymers exhibited extensive light absorption ability from approximately 330 to 680 nm with an optical band gap (E_g^{opt}) of approximately 1.82–1.87 eV. Unfortunately, the photovoltaic performance of the device derived from the alternating copolymer was limited by its poor solubility and low molecular weight. Compared with the alternating copolymer, the solubility, molecular weight and photovoltaic performance of the random copolymer were better, and maximal power conversion efficiencies (PCEs) of 3.15% and 4.73% were achieved in the photovoltaic cells (PVCs) with the random conjugated polymer as electron donor materials and [6,6]-phenyl-C₇₁ butyric acid methyl ester (PC₇₁BM) or indene-C₆₀ bisadduct (IC₆₀BA), respectively, as electron acceptor materials under 100 mW cm⁻² illumination (AM 1.5G).

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INTRODUCTION

Since the discovery of ultrafast photo-induced charge transfer between conjugated polymers (CPs) and fullerene,¹ polymer bulk heterojunction photovoltaic cells (PVCs) have attracted much attention owing to potential application in large area, flexible and inexpensive solar cells.² Extensive efforts involving the development of novel low band gap (LBG) CPs,^{3–21} optimization of the fabricating process²² and modifying the morphology of the donor and acceptor blend,^{23,24} and interfacial engineering²⁵ have been devoted to improve the power conversion efficiencies (PCEs) of PVCs. Among these efforts, the development of high-performance donor–acceptor (D–A) type LBG CPs is the most successful approach for achieving efficient PVCs, and many promising D–A-type LBG CPs have been developed in the last few decades.^{3–21,26–38} Among these materials, the most attractive sample is benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT)-based CPs.^{26–38} For example, Huang and colleagues reported a new and interesting BDT-based polymer (PBDT-DTNT) with naphtho[1,2-*c*:5,6-*c'*]bis-[1,2,5]thiadiazole as the new electron acceptor moiety, and this material exhibits PCEs as high as 6.0–8.4%.^{31,32} Hou and colleagues reported a series of LBG CPs based on BDT, and PCEs of 5.63–9.98% were achieved in the PVCs from the polymers.^{35–38}

As a notable aromatic analog of BDT, DTBDT possesses a highest occupied molecular orbital (HOMO) level that is similar to BDT as well as a larger coplanar core and extended conjugation length. It is believed that DTBDT-based CPs could provide some advantageous properties, such as enhanced charge-carrier mobility, decreased band gaps and facilitated exciton separation into free charge carriers, in contrast to BDT-based CPs.³⁹ Motivated by the attractive properties of DTBDT-based CPs, many high-performance DTBDT-based CPs have been reported since Hou and colleagues first introduced the 5,10-di-(2-hexyldecyloxy)-DTBDT to construct the D–A-type LBG CPs in 2012.⁴⁰ For example, Yu and colleagues presented a series of LBG CPs based on 5,10-dialkyl-DTBDT and alkyl 3-fluorothieno[3,4-*b*]thiophene-2-carboxylate in 2013.⁴¹ Recently, Hou and colleagues presented CPs derived from 5,10-di(alkylthieno-2-yl)-DTBDT and 2-(2-hexyldecyl)-sulfonylthieno[3,4-*b*]thiophene,⁴² and Kwon and colleagues reported CPs derived from 5,10-di(alkylthieno-2-yl)-DTBDT and 2,1,3-benzothiadiazole.⁴³ More recently, we reported an effective approach for tuning the optoelectronic properties of DTBDT-based CPs by changing the substituent groups on the DTBDT, and a series of D–A-type LBG CPs derived from DTBDTs and 3,6-bis(thieno-2-yl)-*N*,*N'*-dialkyl-1,4-dioxopyrrolo[3,4-*c*]pyrrole were prepared.⁴⁴ Although

¹School of Electronic and Information Engineering, Lanzhou Jiaotong University, Lanzhou, China; ²Key Laboratory of Optoelectronic Technology and Intelligent Control of Ministry Education, Lanzhou Jiaotong University, Lanzhou, China; ³Key Laboratory for Green Chemical Process of Ministry of Education, Wuhan Institute of Technology, Wuhan, China and ⁴School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, China

Correspondence: Dr Y Xia, Key Laboratory of Optoelectronic Technology and Intelligent Control of Ministry Education, Lanzhou Jiaotong University, Lanzhou 730070, China. E-mail: yxia73@126.com

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PVCs from the D–A-type LBG CPs with DTBDTs as electron donor units exhibit reasonably high PCEs of 3.5–7.6%,^{40–43} tailoring and enriching the family of DTBDT-based D–A-type LBG CPs remains insufficient compared with the BDT-based LBG CPs for high-performance PVCs.

In this study, an alternating low band gap conjugated copolymer derived from 5,10-di(2-ethylhexyloxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene and 5,6-di(dodecyloxy)-2,1,3-benzothiadiazole (BT) was synthesized and characterized. Despite the fact that the alternating conjugated polymer exhibited appropriate energy levels and extensive light absorption ability ranging from 330 to 676 nm, the photovoltaic performance of the device derived from the alternating copolymer was limited by its poor solubility and low molecular weight. To optimize the solubility and molecular weight of the alternating copolymer, 5,10-bis(2-butyloctyloxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene was introduced into the polymer, and a random conjugated polymer derived from 5,10-di(2-ethylhexyloxy)-dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene, 5,10-bis(2-butyloctyloxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene and 5,6-di(dodecyloxy)-2,1,3-benzothiadiazole with a feed molar ratio of 5:1:4 was synthesized. The solubility and molecular weight of the random copolymer increased, and HOMO and the lowest unoccupied molecular orbital (LUMO) energy levels of the random polymer were slightly different (HOMO energy levels, –5.33 vs –5.28 eV, LUMO energy levels, –3.51 vs –3.41 eV). In addition, maximal PCEs of 3.15 and 4.54% were achieved in the PVCs containing a random conjugated polymer as electron donor materials and [6,6]-phenyl-C₇₁ butyric acid methyl ester (PC₇₁BM) or indene-C₆₀ bisadduct (IC₆₀BA), respectively, as electron acceptor materials under 100 mW cm^{–2} illumination (AM 1.5G).

EXPERIMENTAL PROCEDURE

Materials

Unless otherwise specified, all of the reagents were obtained from Sigma-Aldrich (Shanghai, China), Acros (Beijing Innochem, Beijing, China) and TCI (Shanghai, China) Chemical and used as received. All of the solvents were further purified by typical procedures under a nitrogen flow. 2,7-Bis(trimethylstannyl)-5,10-di(2-ethylhexyloxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (**I**),⁴⁴ 4,7-dibromo-5,6-di(dodecyloxy)-2,1,3-benzothiadiazole (DBrBT)¹⁸ and IC₆₀BA⁴⁵ were synthesized according to a previously published procedure and characterized by ¹H NMR.

General methods

The ¹H NMR spectra were recorded on a Bruker DRX 400 spectrometer (Rheinstetten, Germany) operating at 400 MHz with tetramethylsilane as the reference. The polymerization reactions were carried using a mono-microwave system (NOVA, PreeKem Scientific Instruments, Shanghai, China). Analytical gel permeation chromatography was performed using a Waters GPC 2410 (Milford, MA, USA) in tetrahydrofuran relative to polystyrene standards. The thermal gravimetric analyses were conducted on a TGA 2050 (TA instruments, New Castle, DE, USA) thermal analysis system with a heating rate of 10 °C min^{–1} and a nitrogen flow rate of 20 ml min^{–1}. The UV–visible absorption spectra were measured on a UV-2550 spectrophotometer (Shimadzu, Kyoto, Japan). The cyclic voltammetry of the polymers were measured on CHI 660 electrochemical workstation (Shanghai Chenhua, Shanghai, China) at a scan rate of 50 mV s^{–1} with a nitrogen-saturated solution consisting of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile using a glass carbon electrode and a Ag/AgCl electrode as the working and reference electrodes, respectively. The surface roughness and morphology of the thin films were characterized by atomic force microscopy on an MFP-3D-SA (Asylum Research, Santa Barbara, CA, USA) in tapping mode.

Preparation and characterization of the photovoltaic solar cells

A patterned indium tin oxide-coated glass with a sheet resistance of 10–15 Ω per square was cleaned by a surfactant scrub followed by a wet-cleaning process inside an ultrasonic bath beginning with de-ionized water, acetone and *iso*-propanol. After oxygen plasma cleaning for 5 min, a 40 nm thick poly-(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Bayer Baytron 4083, Leverkusen, Germany) anode buffer layer was spin-casted onto an indium tin oxide substrate and then dried by baking in a vacuum oven at 80 °C overnight. Then, the active layer, which had a thickness in the 70–80 nm range, was deposited on top of the PEDOT:PSS layer by spin-casting from a chlorobenzene solution containing alternating copolymer/[6,6]-phenyl-C₆₁ butyric acid methyl ester (PC₆₁BM) (1:1, 1:2, 1:3, 1:4, W/W), alternating copolymer/PC₇₁BM (1:1, 1:2, 1:3, 1:4, W/W), random copolymer/PC₆₁BM (1:2, W/W), random copolymer/PC₇₁BM (1:2, W/W) and random copolymer/IC₆₀BA (1:2, W/W). Then, an 8-nm calcium and a 100-nm aluminum layer were subsequently evaporated with a shadow mask under a vacuum of 1–5 × 10^{–5} Pa. The overlapping area between the cathode and anode defined the pixel size of device to be 0.1 cm². The thickness of the evaporated cathode was monitored by a quartz crystal thickness/ratio monitor (SI-TM206, Shenyang Sciens, Shenyang, China). Except for the deposition of the PEDOT:PSS layers, all of the fabrication processes were carried out in the controlled atmosphere of a nitrogen glove box (Etelux, Beijing, China) containing < 1 p.p.m. oxygen and moisture. The PCEs of the resulting polymer solar cells were measured under 1 sun, AM 1.5G (Air mass 1.5 global) irradiation using a solar simulator (XES-70S1, San-Ei Electric, Beijing, China) at 100 mW cm^{–2}. The current density–voltage (*J*–*V*) characteristics were recorded with a Keithley 2400 (USA) source-measurement unit. The spectral responses of the devices were measured with a commercial EQE/incident photon-to-charge carrier efficiency (IPCE) setup (7-SCSpecIII, Beijing 7-star, Beijing, China). A calibrated silicon detector was used to determine the absolute photosensitivity.

Synthesis of monomer and the polymers

Synthesis of 5,10-bis(2-butyloctyloxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (III). In a 50-ml flask, the diketone of **II** (0.5 g, 1.5 mmol), zinc powder (0.39 g, 6 mmol) and 15 ml distilled water were added. After the mixture was stirred for 15 min, 3 g NaOH was added and the solution was refluxed for 1 h. Then, 5-(bromomethyl)undecane (4.49 g, 18 mmol) and a catalytic amount of tetrabutylammonium bromide (Bu₄NBr) were added, and the solution was refluxed overnight. After the reaction mixture was cooled to ambient temperature, the resulting solution was poured into cold water, and hydrochloric acid (20 ml) was added to the mixture to adjust the pH (~3). Then, the mixture was extracted with chloroform, and the organic phase was dried over anhydrous Na₂SO₄. After the solvent was removed under reduced pressure, the crude product was purified over a silica gel column using hexane/chloroform (3:1, V/V) as an eluent. Compound **III** (0.75 g) was obtained as yellow oil in 75% yield. ¹H NMR (CDCl₃, 400 MHz), δ (p.p.m.): 7.56 (d, 2H), 7.32 (d, 2H), 4.22 (d, 4H), 2.12–2.06 (m, 2H), 1.71–1.31 (m, 32H), 0.89 (t, 12H). C₃₈H₅₄O₂S₄: C, 67.81; H, 8.39; O, 4.75. Found: C, 68.06; H, 8.42; O, 4.82. FAB-MS: 673.

2,7-Dibromo-5,10-bis(2-butyloctyloxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (IV). In a 150-ml flask, **III** (1.35 g, 2.0 mmol) was added to a solution consisting of 12 ml CHCl₃ and 6 ml acetic acid. *N*-bromosuccinimide (0.89 g, 5.0 mmol), which was dissolved in 6 ml chloroform, was added dropwise under dark conditions. After the mixture was stirred at ambient temperature overnight, the resulting solution was poured into 50 ml distilled water and extracted with chloroform three times. The combined organic phase was dried with anhydrous Na₂SO₄. The solvent was removed under reduced pressure, and the obtained crude product was purified by column chromatography on silica gel using hexane and CHCl₃ (10:1, V/V) as an eluent to afford **IV** as yellow solid (1.54 g, 92%). Melting point 146–148 °C. ¹H NMR (CDCl₃, 400 MHz), δ (p.p.m.): 7.29 (s, 2H), 4.18 (d, ³*J* = 6.4 Hz, 4H), 2.05–2.02 (m, 2H), 1.67–1.61 (m, 4H), 1.55–1.48 (m, 4H), 1.43–1.33 (m, 24H), 0.90 (t, ³*J* = 6.8 Hz, 12H). Calculated for C₃₈H₅₂Br₂O₂S₄, C, 54.93; H, 6.55; O, 3.85. Found: C, 55.01; H, 6.28; O, 3.91. FAB-MS: 831.

Scheme 1 Synthetic route for the monomers and polymers.

Table 1 Molecular weight, optoelectronic and thermal parameters of the polymers

Polymer	$M_n(\text{g mol}^{-1})$	$M_w(\text{g mol}^{-1})$	PDI	$E_g^{\text{opt}}(\text{eV})^a$	$E_{\text{ox}}^{\text{onset}}(\text{V})$	$E_{\text{HOMO}}(\text{eV})^b$	$E_{\text{LUMO}}(\text{eV})^c$	$T_d^5(^{\circ}\text{C})^d$
P1	9 650	20 500	2.12	1.87	0.88	−5.28	−3.41	416.0
P2	17 600	30 500	1.73	1.82	0.93	−5.33	−3.51	391.0

Abbreviations: LUMO, lowest unoccupied molecular orbital; PDI, polydispersity index.

^aCalculated by on-set band gap wavelength of the copolymers in thin film $E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}$.

^bCalculated by oxidation potential of the copolymer $E_{\text{HOMO}} = -e(E_{\text{ox}}^{\text{onset}} + 4.40)$ (eV).

^cCalculated from optical band gap and HOMO levels of the copolymers $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{\text{opt}}$ (eV).

^d5% weight loss temperature.

Synthesis of alternating copolymer P1

A mixture of toluene (6 ml) and *N,N*-dimethylformamide (DMF, 0.5 ml) was added to a 55-ml microwave tube containing **I** (266.0 mg, 0.3 mmol), **DBrBT** (199.4 mg, 0.3 mmol) and Pd(PPh₃)₄ (4.0 mg) in a glove box where the moisture and oxygen content was <1 p.p.m. Then, the tube was subjected to the following reaction conditions in a microwave reactor: 120 °C for 5 min, 140 °C for 5 min and 160 °C for 20 min. At the end of the polymerization process, the polymer was end-capped with 2-tri(butylstannyl)thiophene and 2-bromothiophene to remove the bromo and trimethylstannyl end groups. Then, the mixture was poured into methanol. The precipitated material was collected and extracted with ethanol, acetone, hexane and toluene in a Soxhlet extractor. The solution containing the copolymer in toluene was condensed to 20 ml and then poured into methanol (500 ml). The precipitate was collected and dried under vacuum overnight (yield: 75%). $M_n = 9\,650 \text{ g mol}^{-1}$ with a polydispersity index of 2.12.

Synthesis of random copolymer P2

The random copolymer was synthesized according to the procedure used for the alternating copolymer except that the polymerization was carried out with

266.0 mg of **I** (0.3 mmol), 159.5 mg of **DBrBT** (0.24 mmol) and 50.0 mg of **IV** (0.06 mmol). Yield: 85%. $M_n = 17\,600 \text{ g mol}^{-1}$ with a polydispersity index of 1.73.

RESULTS AND DISCUSSION

Synthesis and characterization of the polymers

Scheme 1 shows the synthetic routes for the monomer and conjugated copolymers. Compounds **I**⁴⁴ and **DBrBT**¹⁸ were synthesized according to previously reported procedures and characterized by ¹H NMR before use. Alternating copolymer **P1** was synthesized by Pd(0)-catalyzed Stille coupling polymerization in a toluene and DMF solution under mono-microwave heating conditions. Unfortunately, obtained **P1** exhibits poor solubility and a low molecular weight ($M_n = 9.65 \text{ kDa}$). To improve the solubility of dialkylalkoxy-flanked-DTBDT-based low band gap CPs, random copolymer **P2** derived from **I**, **IV** and **DBrBT** using a molar ratio of 5:1:4 was synthesized (Scheme 1). Random copolymer **P2** has a number-average molecular

Figure 1 Thermal gravimetric analysis of the polymers.

Figure 2 Normalized absorption (Abs) and PL spectra of the alternating copolymer (a) and random copolymer (b) in a chloroform solution and thin film. PL, photoluminescence.

weight of $M_n = 17.6$ kDa with a polydispersity index of 1.73 (Table 1). **P2** exhibits better solubility than **P1** in common organic solvents, such as chloroform and toluene. Both copolymers exhibit good thermal stability with 5% weight loss at a temperature (T_d) of ~ 391 – 416 °C under a nitrogen atmosphere (Table 1 and Figure 1), demonstrating their sufficiently high thermal stability for applications in PVCs.

Figure 3 Electrochemical curves for the polymers.

Optical and electrochemical properties of the polymers

Figures 2a and b show the normalized UV–visible absorption and photoluminescence spectra of the copolymers in a tetrahydrofuran solution and a solid thin film. In solution, alternating copolymer **P1** exhibits two absorption peaks at 398 and 601 nm with a shoulder absorption peak at 558 nm. The photoluminescence emission peaks of **P1** in solution and a solid thin film are ~ 657 and 682 nm, respectively. The on-set band gap wavelengths of **P1** are red shifted ~ 14 nm from the solution to the film (Figure 2a), and the E_g^{opt} of **P1**, which was estimated from the on-set band gap wavelength of **P1** in a solid thin film, was ~ 1.87 eV. Random copolymer **P2** exhibits two absorption peaks at 398 and 553 nm with a shoulder absorption peak at 602 nm. The photoluminescence emission peaks of **P2** in solution and a solid thin film are ~ 654 and 675 nm, respectively. The on-set band gap wavelengths of **P2** are red shifted ~ 25 nm from the solution to the film, and the corresponding E_g^{opt} of **P2**, which was estimated from the on-set band gap of **P2** in solid thin film is ~ 1.82 eV (Figure 2b). On the basis of the results in Figures 2a and b, **P2** in the solid thin film exhibited more extensive absorption of light ranging from 400 to 520 nm and a narrower band gap compared with those for **P1** in a solid thin film (Figures 2a and b). In addition, the solid state photoluminescence of **P1** and **P2** are completely quenched by PC₆₁BM, which may be owing to ultrafast photo-induced charge transfer from the polymer to PC₆₁BM.^{36,37} These results indicated that the copolymers are viable electron donor materials for applications in PVCs.

The electrochemical behaviors of the copolymer films were investigated by cyclic voltammetry in a nitrogen-saturated solution consisting of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile with a glass carbon electrode and a Ag/AgCl electrode as the working and reference electrodes, respectively. We recorded the oxidation process for the copolymers in a solid thin film. The on-set oxidation potentials of **P1** and **P2** are 0.88 and 0.93 V, respectively (Figure 3, Table 1). The redox potential of Fc/Fc⁺ under these conditions was +0.40 V, which is assumed to have an absolute energy level of -4.8 eV to vacuum for calibration. Therefore, the HOMO levels of **P1** and **P2** calculated from the empirical formula ($E_{\text{HOMO}} = -e(E_{\text{ox}}^{\text{onset}} + 4.40)$ (eV)^{46,47}) are approximately -5.28 and -5.33 eV, respectively. Unfortunately, the reduction potential could not be obtained in a cathodic scan of the polymers. Therefore, the LUMO energy levels of **P1** and **P2** were estimated from their E_{HOMO} and E_g^{opt} to be approximately -3.41 and -3.51 eV, respectively, where $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{\text{opt}}$ (eV).

Photovoltaic properties of the polymers

Alternating copolymer **P1**, which is a potential electron donor material for PVCs, was used in a device configuration consisting of indium tin

Table 2 Photovoltaic parameters of the polymer solar cells based on **P1** and **P2**

Active layer	Weight ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	η (%)
P1:PC ₆₁ BM	1:1	0.80	4.24	43.0	1.45
P1:PC ₆₁ BM	1:2	0.77	4.68	46.6	1.68
P1:PC ₆₁ BM	1:3	0.78	4.27	39.0	1.30
P1:PC ₆₁ BM	1:4	0.76	3.26	41.0	1.02
P1:PC ₇₁ BM	1:1	0.83	3.76	45.0	1.40
P1:PC ₇₁ BM	1:2	0.77	6.61	40.0	2.04
P1:PC ₇₁ BM	1:3	0.78	5.69	42.0	1.86
P1:PC ₇₁ BM	1:4	0.75	4.58	44.6	1.53
P2:PC ₆₁ BM	1:2	0.76	5.43	58.3	2.41
P2:PC ₇₁ BM	1:2	0.76	6.76	61.4	3.15
P2:IC ₆₀ BA	1:2	0.93	7.87	64.6	4.73

Figure 4 J/V (a) and IPCE (b) characteristics of the PVCs derived from alternating copolymer **P1** and fullerene derivatives with an optimal weight ratio of 1:2. IPCE, incident photon-to-charge carrier efficiency; PL, photoluminescence; PVC, photovoltaic cell.

oxide/PEDOT:PSS/active layer/Ca/Al with PC₆₁BM or PC₇₁BM as the electron acceptor materials. The blending weight ratio of **P1** and PC₆₁BM (or PC₇₁BM) was optimized from 1:1 to 1:4, and the thickness of the blend film was fixed at ~50–60 nm. The fabricated PVCs were tested under AM 1.5G illumination at an irradiation intensity of 100 mW cm^{-2} , and the resulting device performances are summarized in Table 2. On the basis of the results in Table 2, the

Figure 5 J/V (a) and IPCE (b) characteristics of the PVCs derived from random copolymer **P2** and fullerene derivatives with a weight ratio of 1:2. IPCE, incident photon-to-charge carrier efficiency; PL, photoluminescence; PVC, photovoltaic cell.

devices with a **P1**/PC₆₁BM (or PC₇₁BM) blending weight ratio of 1:2 exhibited the best performances (Table 2, Figure 4a). In addition, maximal PCEs of 1.68 and 2.04% were achieved in the PVCs from **P1** with PC₆₁BM and/or PC₇₁BM as electron acceptor materials. The IPCE curves of the devices based on the **P1**/PC₆₁BM (or PC₇₁BM) blends with a weight ratio of 1:2 are shown in Figure 4b. The device based on the **P1**/PC₆₁BM (W:W; 1:2) blend exhibited a photoresponse in the range of 300–708 nm, and the device based on the **P1**/PC₇₁BM (W:W; 1:2) blend exhibited a photoresponse in the range of 300–721 nm. An IPCE of 30–40% ranging from 380 to 670 nm was observed for the device based on the **P1**/PC₇₁BM (W:W; 1:2) blend, which was larger than that of 10–20% for the device based on the **P1**/PC₆₁BM (W:W; 1:2) blend. The improvements in J_{SC} and IPCE in the devices where PC₇₁BM was used as the electron acceptor material may be owing to the stronger absorption of PC₇₁BM in the visible region compared with that of PC₆₁BM.⁴

The photovoltaic properties of random copolymer **P2** were explored in using the indium tin oxide/PEDOT:PSS/active layer/Ca/Al device configuration with **P2** as the electron donor material and PC₆₁BM, PC₇₁BM and IC₆₀BA as electron acceptor materials. The weight ratio of the electron donor materials and electron acceptor materials was

fixed at 1:2, and the thickness of the blend films was ~ 80 – 90 nm. The fabricated PVCs were tested under AM 1.5G illumination at an irradiation intensity of 100 mW cm^{-2} . The parameters of the devices based on **P2** are summarized in Table 2. The J/V curves and IPCEs of the devices based on **P2** are shown in Figures 5a and b. PCEs of 2.41, 3.15 and 4.73% were achieved for the devices based on the **P2/PC₆₁BM** (W:W, 1:2), **P2/PC₇₁BM** (W:W, 1:2) and **P2/IC₆₀BA** (W:W, 1:2) blends, respectively. The performances (J_{sc} , FF and IPCEs) of the devices based on **P2** improved compared with those of the devices based on **P1** (Figures 4b and 5b). This improvement may be owing to the better solubility and higher molecular weight of **P2** compared with those of **P1**. However, the V_{oc} of the devices based on the **P2/IC₆₀BA** blend increased from 0.76 to 0.93 V compared with the devices based on the **P2/PC₆₁BM** and **P2/PC₇₁BM** blends (Table 2, Figure 5a). These results may be owing to the higher LUMO of IC₆₀BA ($\text{LUMO}_{\text{PC}_{61}\text{BM/PC}_{71}\text{BM}} = -3.9 \text{ eV}$, $\text{LUMO}_{\text{IC}_{60}\text{BA}} = -3.76 \text{ eV}$).^{45,48}

Morphological characterization

Film surface morphology has a key role in the efficiency of bulk heterojunction PVCs. The atomic force microscopy height and phase images of the active layer surface for **P1:PC₇₁BM** (1:1, 1:2 and 1:3) were recorded (Supplementary Figure S1). The scan size was $10 \mu\text{m} \times 10 \mu\text{m}$. The obtained root-mean-square roughness (RMS) values were 1.31, 2.10 and 2.53 nm for the **P1:PC₇₁BM** blends (1:1, 1:2 and 1:3, respectively). Although the 1:1 **P1:PC₇₁BM** blend exhibited a relatively smooth surface morphology, the device based on **P1:PC₇₁BM** (1:1) exhibited a lower J_{sc} value than those for the other blend ratios, which may be due to its lower EQE value. In addition, the height and phase images of the active layer surface of **P2:PC₇₁BM** and **P2:IC₆₀BA** are shown in Supplementary Figure S2. The **P2:PC₇₁BM** and **P2:IC₆₀BA** blend films exhibited a surface roughness with a RMS of 1.76 and 1.30 nm, respectively. The relatively smooth surface of **P2:IC₆₀BA** may induce slightly better contact between the active layer and the cathode, which may lead to an enhanced J_{sc} and FF.

CONCLUSIONS

Herein, an alternating low band gap conjugated copolymer derived from 5,10-di(2-ethylhexyloxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]-dithiophene and 5,6-di(dodecyloxy)-2,1,3-benzothiadiazole (BT) was synthesized and characterized. This alternating conjugated polymer exhibited extensive light absorption ability ranging from 330 to 676 nm with a HOMO energy level of -5.23 eV and a LUMO energy level of -3.46 eV . Next, a random conjugated polymer derived from 5,10-di(2-ethylhexyloxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]-dithiophene, 5,10-bis(2-butyloctyloxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene and 5,6-di(decyloxy)-2,1,3-benzothiadiazole with a feed ratio molar ratio of 5:1:4 was synthesized. Compared with the alternating copolymer, the solubility and molecular weight of the random copolymer increased. In addition, the HOMO energy level of the random copolymer decreased slightly, and the LUMO energy levels of the random copolymer increased slightly (-5.33 eV vs -5.28 eV , -3.51 eV vs -3.41 eV). The performances of the PVCs based on the random polymer improved, and maximal PCEs of 2.41, 3.15 and 4.73% were achieved in the PVCs where the random conjugated polymer acted as the electron donor material and PC₆₁BM, PC₇₁BM or IC₆₀BA, respectively, acted as the electron acceptor material using a weight ratio of 1:2 under 100 mW cm^{-2} illumination (AM 1.5G).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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