

Highly Efficient Random Terpolymers for Photovoltaic Applications with Enhanced Absorption and Molecular Aggregation*

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Abstract A series of copolymers, based on benzo[1,2-b:4,5-b']dithiophene (BDT) as the electron donor and 2,1,3-benzothiadiazole (BT)/diketopyrrolo[3,4-c]pyrrole (DPP) as the electron acceptors, were synthesized for highly efficient polymer solar cells. By changing the BT/DPP ratio in the conjugated backbone, the absorption, energy levels, molecular aggregation and carrier mobility could be finely tuned. With increased DPP content, the absorption range was extended to the longer wavelength region with narrower bandgaps. The highest occupied molecular orbital (HOMO) levels were also raised up and the molecular aggregation was enhanced. The balance of these factors would afford a remarkable device performance enhancement. Polymer P3 with BT:DPP = 0.7:0.3 (molar ratio) exhibited the highest power conversion efficiency (PCE) of 9.01%, with open circuit voltage (V_{oc}) = 0.73 V, short current density (J_{sc}) = 18.45 mA·cm⁻², and fill factor (FF) = 66.9%. The PCE value was improved by 48.7% compared to P1 and by 117.6% compared to P7, respectively, indicating a great potential in photovoltaic application.

Keywords Polymer solar cells; Terpolymers; Complementary absorption; Molecular aggregation

INTRODUCTION

With growing concerns about the energy crisis and environmental pollution, there is a desire to use new and renewed energy resources as an alternative to replace the traditional fossil fuels. Among these new energy resources, solar energy has been attracting much attention due to their inexhaustible and pollution-free merits, the key points to meet future energy needs^[1, 2]. Solar cell is considered as one of the most promising heliotechnics for solar energy applications. Recently, bulk heterojunction (BHJ) polymer solar cells (PSCs) received considerable interest due to their low cost, light weight, easy fabrication of large area and flexible devices^[1–4]. The state-of-the-art device performance of PSCs has been exceeding 11%, demonstrating their attractively practical applications^[5].

Over the past decades, significant research efforts have been devoted to developing low-bandgap polymers to expand the absorption, which can harvest more solar energy^[6]. Unfortunately, the main challenge still lies in

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realizing panchromatic absorption with a single donor-acceptor (D-A) polymer^[6, 7]. To overcome the absorption limitation of the polymeric semiconductors, various strategies have been adopted. In recent years, tandem solar cells have been developed for expanding the absorption window to obtain high device efficiency^[8]. Tandem solar cells usually comprise multiple subcells with different absorption band stacked in series that can increase either the short current density (J_{sc}) and/or open circuit voltage (V_{oc})^[9]. However, the fabrication of a tandem device is extremely complicated in comparison to that of a single-junction device, bringing the meticulous processing procedures and high fabrication cost^[7, 10–13]. The defects in tandem solar cells also limit their practical usage in large-area devices.

To simplify the fabrication procedure, ternary blend solar cells have attracted considerable attention^[6, 14–16]. As an alternative strategy, ternary blend solar cells inherit the major benefits of incorporating multiple organic/polymer materials in tandem cells but retain the simple cell fabrication technology^[6, 14–16]. A multiple blend is expected to give steady energy level alignment, to afford more charge transfer channels in ternary blend devices, and to promote a smoother charge transfer compared with the binary PSCs^[6, 17]. Most recently, we demonstrated a efficient quaternary blend BHJ PSCs with power conversion efficiencies (PCEs) exceeding 10% by incorporating a series of highly crystalline copolymers as the additional donor materials and indene-C70 bisadduct (IC₇₀BA) as the additional acceptor material at the same time^[17]. However, one of the most challenging tasks in multiple blend solar cells is to balance the absorption and the morphology limitations. The morphology control of binary blends is already very complex. For multiple blends, the miscibility between polymer donors and fullerene derivatives would be disturbed, resulting in unfavorable interactions and deleterious morphology^[13, 18]. These unfavorable interactions might function as morphological traps and recombination centers, leading to a reduced photovoltaic performance in the multiple BHJ systems^[6]. Therefore, to obtain an optimized morphology, the additional polymer donors and/or fullerene derivatives with no more than 20 wt% are typically added in those highly efficient multiple blend solar cells^[14–17, 19, 20]. Such unbalanced composition ratio in active blends could also be hardly controlled to obtain a dramatically enlarged absorption, which constrained the light harvesting and efficiency improvements^[17, 20, 21]. On the other side, the poor reproducibility arising from the unmanageable complexity of morphology control would be a bottleneck for future commercialization.

Taking the above factors into account, a promising approach is to develop new terpolymer by copolymerizing more than two different chromophores with a complementary absorption range to broaden the absorption to match the solar spectrum^[13, 22–26]. Ternary copolymerization is an easy and effective method used to tune the optical and electronic properties of the conjugated copolymers. With appropriate choice of building blocks, the energy level, the absorption ability, the molecular packing and the solubility can be finely tuned *via* elaborately manipulating the corresponding chemical structures^[24, 27]. Moreover, tuning the molar ratio of the third component in the terpolymer backbone can provide a good balance between the required properties mentioned above^[24]. Tremendous efforts have been devoted to this field and a high efficiency over 8% has been reported^[28–32]. Terpolymers are good examples to further utilize the properties of the variable donors/acceptors^[27]. Comprehensive considerations should be taken when designing terpolymers, such as solubility, absorption spectrum, energy levels, carrier mobility, and blend morphology, *etc.* Thus, the terpolymer strategy is still of great interest and also of significant importance for developing high-performance photovoltaic copolymers.

In this work, we report a series of new random and conjugated terpolymers with donor (D)-acceptor (A1)-donor (D)-acceptor (A2) molecular configuration for PSCs, in which 2,1,3-benzothiadiazole (BT) and diketopyrrolo[3,4-c]pyrrole (DPP) are used as the first (A1) and second (A2) electron-accepting units, and benzo[1,2-b:4,5-b']dithiophene (BDT) as the electron-donating (D) unit, respectively. DPP has been used widely as an A unit for D-A type of copolymers for PSCs and organic field effect transistors (OFETs) due to its unique properties, such as high extinction coefficient, strong electron-accepting power and molecular planarity^[31–35]. DPP-based D-A copolymers exhibit a strong intramolecular charge transfer (ICT) absorption, which reaches more than 900 nm due to the presence of strong electron-deficient lactam rings^[23, 29–32]. BT has also attracted

much attention for its special property in control of the energy levels for D-A conjugated copolymers^[36–40]. Fluorination on BT units can reduce the highest occupied molecular orbital (HOMO) level and thus obtain a high V_{oc} in the related PSCs^[39, 41]. BDT is a weak donor with a structural symmetry and a rigid fused aromatic system, which can enhance the electron delocalization and the interchain interaction to improve the carrier mobility^[36]. The primary absorption peaks of the BDT-BT copolymers were often located at 400–600 nm^[37–40], whereas the PBDT-DPP copolymers had the absorption bands at 600–900 nm^[27]. Therefore, we could finely tune the absorption and energy levels by varying the BT/DPP ratio to provide broad absorption and suitable HOMO level. In addition, the morphology could also be optimized due to the totally different aggregation properties of BT and DPP units. The best performance is finally improved up to 9.01% for P3 with BT:DPP = 0.7:0.3 (molar ratio), which is the highest value for single-junction PSCs based on these terpolymers.

EXPERIMENTAL

Materials

PC₇₁BM was purchased from Solenne BV (Netherlands) with 99% purity. All the other chemicals were purchased as reagent grade from Aladdin, Adamas, Sigma-Aldrich, and Alfa Aesar Chemical Co., and used without further purification. All solvents for reactions were freshly distilled prior to use. The monomers BDT, BT and DPP (Scheme 1) were synthesized according to reported procedures^[40, 42, 43].

General Polymerization Procedures

Target copolymers were synthesized *via* the Stille coupling reaction. Monomers BDT, BT, DPP and degassed toluene (8 mL) were added to a two-necked flask. After being degassed with argon for several times, Pd₂(dba)₃ (2 mol%) and P(*o*-tol)₃ (8 mol%) were then added and the mixture was degassed with argon for several times again. After that, the reaction mixture was heated to 110 °C and kept for 24 h at the same temperature under constant stirring. Tributylstannylthiophene (2 mol%) was then added to the reaction mixture. After 2 h, 2-bromothiophene (2 mol%) was added. The mixture was stirred overnight to complete the end-capping reaction. Finally, the reaction mixture was dropped slowly into methanol (400 mL) to allow the precipitation of the crude polymer. The precipitate was filtered, washed with methanol and hexane in a Soxhlet apparatus to remove the oligomers and catalyst residue. Subsequently, the copolymer was extracted with chloroform. The extracted solution was condensed by evaporation and precipitated into methanol again. The precipitate was collected by filtration and dried in vacuum for 12 h to get the purified polymer.

Synthesis of P1

A mixture of BDT (0.3812 g, 0.3000 mmol) and BT (0.1980 g, 0.3000 mmol) in toluene was used to synthesize P1 according to the procedure described above with a yield of 80%, as a black solid product. ¹H-NMR (400 MHz, CDCl₃, δ): 7.46–7.31 (br, 2H, ArH), 7.22–6.74 (br, 6H, CH₂), 3.03–2.58 (br, 8H, CH₂), 2.10–1.96 (br, 6H, CH₂), 1.38–0.95 (br, 48H, CH₂), 0.95–0.63 (br, 18H, CH₃). Elemental analysis Calcd. (%) for C₆₈H₈₄F₂N₂S₇: C 68.53, H 7.10, N 2.35; Found: C 68.60, H 7.13, N 2.34.

Synthesis of P2

A mixture of BDT (0.3812 g, 0.3000 mmol), BT (0.1782 g, 0.2700 mmol) and DPP (0.0240 g, 0.0300 mmol) in toluene was used to synthesize P2, a black solid, according to the procedure described above with a yield of 85%. ¹H-NMR (400 MHz, CDCl₃, δ): 8.14–7.98 (br, 0.2H, ArH), 7.61–7.48 (br, 0.2H, ArH), 7.21–6.68 (br, 6H, CH₂), 4.19–3.85 (br, 0.4H, CH₂), 3.17–2.52 (br, 7.6H, CH₂), 2.17–2.02 (br, 5.8H, CH₂), 1.44–1.05 (br, 48.4H, CH₂), 1.05–0.69 (br, 18.6H, CH₃). Elemental analysis Calcd. (%) for (C₆₈H₈₄F₂N₂S₇)_{0.9}(C₇₂H₉₄N₂O₂S₆)_{0.1}: C 68.81, H 7.17, N 2.35; Found: C 68.87, H 7.25, N 2.33.

Synthesis of P3

A mixture of BDT (0.3812 g, 0.3000 mmol), BT (0.1386 g, 0.2100 mmol) and DPP (0.0612 g, 0.0900 mmol) in toluene was used to synthesize P3 according to the procedure described above with a yield of 83%. ¹H-NMR (400 MHz, CDCl₃, δ): 9.04–8.98 (br, 0.6H, ArH), 7.90–7.64 (br, 0.6H, ArH), 7.48–7.35 (br, 1.4H, CH₂),

7.17–6.74 (br, 6H, CH₂), 4.31–4.01 (br, 1.2H, CH₂), 3.10–2.50 (br, 6.8H, CH₂), 1.70–1.65 (br, 5.4H, CH₂), 1.46–1.22 (br, 49.2H, CH₂), 1.22–0.85 (br, 19.8H, CH₃). Elemental analysis Calcd. (%) for (C₆₈H₈₄F₂N₂S₇)_{0.7}(C₇₂H₉₄N₂O₂S₆)_{0.3}: C 69.38, H 7.32, N 2.34; Found: C 69.43, H 7.36, N 2.33.

Synthesis of P4

A mixture of BDT (0.3812 g, 0.3000 mmol), BT (0.0990 g, 0.1500 mmol) and DPP (0.1020 g, 0.1500 mmol) in toluene was used to synthesize P4 according to the procedure described above with a yield of 86%. ¹H-NMR (400 MHz, CDCl₃, δ): 9.31–8.01 (br, 1H, ArH), 7.84–7.54 (br, 1H, ArH), 7.41–7.32 (br, 1H, CH₂), 7.22–6.00 (br, 6H, CH₂), 4.28–3.90 (br, 2H, CH₂), 3.10–2.51 (br, 6H, CH₂), 1.77–1.66 (br, 5H, CH₂), 1.53–1.02 (br, 50H, CH₂), 1.02–0.86 (br, 21H, CH₃). Elemental analysis Calcd. (%) for (C₆₈H₈₄F₂N₂S₇)_{0.5}(C₇₂H₉₄N₂O₂S₆)_{0.5}: C 69.95, H 7.46, N 2.33; Found: C 70.06, H 7.49, N 2.31.

Synthesis of P5

A mixture of BDT (0.3812 g, 0.3000 mmol), BT (0.0594 g, 0.0900 mmol) and DPP (0.2788 g, 0.2100 mmol) in toluene was used to synthesize P5 according to the procedure described above with a yield of 81%. ¹H-NMR (400 MHz, CDCl₃, δ): 9.32–8.68 (br, 1.4H, ArH), 7.69–7.44 (br, 1.4H, ArH), 7.38–7.31 (br, 0.6H, CH₂), 7.22–6.66 (br, 6H, CH₂), 4.40–3.80 (br, 2.8H, CH₂), 3.18–2.53 (br, 5.2H, CH₂), 1.84–1.70 (br, 4.6H, CH₂), 1.46–1.01 (br, 50.8H, CH₂), 1.01–0.86 (br, 22.2H, CH₃). Elemental analysis Calcd. (%) for (C₆₈H₈₄F₂N₂S₇)_{0.3}(C₇₂H₉₄N₂O₂S₆)_{0.7}: C 70.51, H 7.60, N 2.32; Found: C 70.62, H 7.67, N 2.30.

Synthesis of P6

A mixture of BDT (0.3812 g, 0.3000 mmol), BT (0.0198 g, 0.0300 mmol) and DPP (0.1836 g, 0.2700 mmol) in toluene was used to synthesize P6 according to the procedure described above with a yield of 88%. ¹H-NMR (400 MHz, CDCl₃, δ): 9.36–8.39 (br, 1.8H, ArH), 7.97–7.43 (br, 1.8H, ArH), 7.34–7.30 (br, 0.2H, CH₂), 7.14–6.80 (br, 6H, CH₂), 4.11–3.90 (br, 3.6H, CH₂), 3.07–2.50 (br, 4.4H, CH₂), 1.69–1.66 (br, 4.2H, CH₂), 1.50–1.01 (br, 51.6H, CH₂), 1.01–0.87 (br, 23.4H, CH₃). Elemental analysis Calcd. (%) for (C₆₈H₈₄F₂N₂S₇)_{0.1}(C₇₂H₉₄N₂O₂S₆)_{0.9}: C 71.08, H 7.74, N 2.31; Found: C 71.14, H 7.79, N 2.29.

Synthesis of P7

A mixture of BDT (0.3812 g, 0.3000 mmol) and DPP (0.2040 g, 0.3000 mmol) in toluene was used to synthesize P7 according to the procedure described above with a yield of 82%. ¹H-NMR (400 MHz, CDCl₃, δ): 9.45–8.28 (br, 2H, ArH), 7.65–7.37 (br, 2H, ArH), 7.15–6.72 (br, 6H, CH₂), 4.24–3.86 (br, 4H, CH₂), 3.14–2.53 (br, 4H, CH₂), 1.76–1.65 (br, 4H, CH₂), 1.51–1.00 (br, 52H, CH₂), 1.00–0.85 (br, 24H, CH₃). Elemental analysis Calcd. (%) for C₇₂H₉₄N₂O₂S₆: C 71.36, H 7.82, N 2.31; Found: C 71.44, H 7.87, N 2.28.

Measurements and Characterization

General information

¹H-NMR test was conducted on a Bruker ARX 400 NMR spectrometer with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. Elemental analysis (EA) was performed on a Carlo Erba 116 elemental analyzer. UV-Vis spectra were obtained on a HITACHI U2910 spectrophotometer. Thermal gravity analysis (TGA) and differential scanning calorimetry (DSC) were conducted on a TA Instrument Model SDT Q600 simultaneous TGA/DSC analyzer at a heating rate of 10 K·min^{−1} under a N₂ flow rate of 90 mL·min^{−1}. Atomic force microscope (AFM) images were obtained on a Bruker Innova SPM system.

Cyclic voltammetry measurements

Cyclic voltammetry (CV) measurement was conducted on a CHI660 potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV·s^{−1}, with Ag/AgCl as the reference electrode and a platinum wire as the counter electrode in the solution of *n*-Bu₄NClO₄ in CH₃CN (0.1 mol·L^{−1}) saturated with anhydrous nitrogen. The redox couple of ferrocene/ferrocenium (Fc/Fc⁺) was used as the external standard. The studied copolymers were drop-coated on the platinum plate working electrodes from dilute solutions in CHCl₃. The HOMO and lowest unoccupied molecular orbital (LUMO) energy values (in eV) were calculated by using Eqs. (1) and (2),

respectively^[17, 44–46]:

$$E_{\text{HOMO}} = -e (E_{\text{onset, ox}} + 4.4) \quad (1)$$

$$E_{\text{LUMO}} = -e (E_{\text{onset, re}} + 4.4) \quad (2)$$

Hole and electron mobility measurements

The hole-only and electron-only device structures are glass/indium tin oxide (ITO)/PEDOT:PSS/polymer:PC₇₁BM/MoO₃/Au and glass/Al/polymer:PC₇₁BM/Al, respectively. The hole and electron mobility was measured by using the space charge limited current (SCLC) method, determined by fitting the dark current to the model of a single carrier with the Eq. (3)^[47–50]:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3} \quad (3)$$

Here, J is the current measured in dark; μ is the zero-field mobility; ϵ_0 is the permittivity of free space which is $8.854 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$; ϵ_r is the relative dielectric constant of the small molecules which is assumed to be around 3; d is the thickness of the active layer, which is around 110 nm; and V is the voltage drop across the device, $V = V_{\text{appl}} - V_{\text{bi}} - V_{\text{a}}$, where V_{appl} is the external applied voltage, V_{a} is the voltage drop due to contact resistance and series resistance across the electrodes which is around 30 Ω obtained from a reference device without the active layer, and V_{bi} is the built-in voltage due to the difference in work function of the two electrodes, which is close to 0. The hole and electron mobility is calculated from the slope of $J^{1/2}$ - V curve.

Device fabrication and characterization

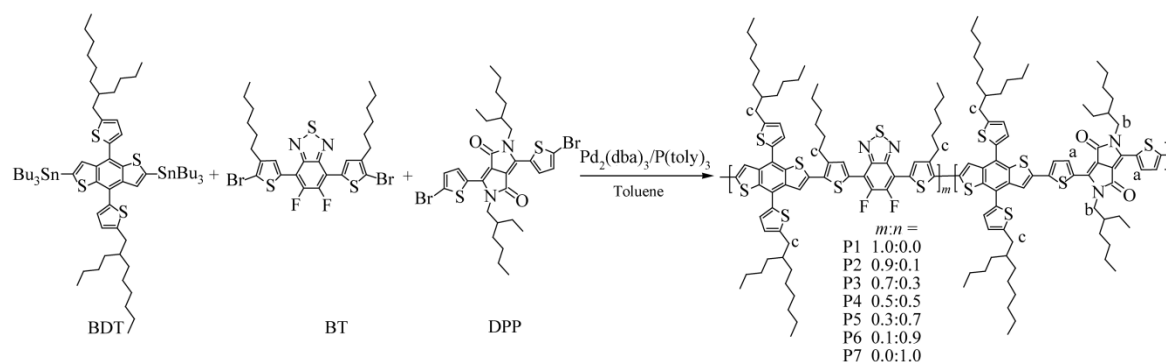
The device structure was ITO/ZnO/copolymer:PC₇₁BM/MoO₃/Ag. A pre-patterned ITO (sheet resistance = 15 Ω -square⁻¹) glass substrate was ultrasonicated successively in detergent, deionized water, acetone, and isopropanol. After that, the substrate was dried by high pressure airflow and treated with UV exposure for 20 min in a UV-ozone chamber. ZnO electron transport layer was prepared by spin coating at 5000 r·min⁻¹ from a ZnO precursor solution (diethyl zinc, 2 mol·L⁻¹ in toluene was diluted with 10 part of tetrahydrofuran) to form a thin film of 35 nm thickness, which was baked on a hot plate at 150 °C for 20 min. The substrate was taken into high purity argon filled glove box ($< 1 \times 10^{-7}$ mol/L O₂ and H₂O). A chlorobenzene (CB) solution of the active layer with different weight ratio of copolymer/PC₇₁BM was spin-coated onto the surface of the substrate. The optimized overall concentration was 21 mg·mL⁻¹ with a D/A ratio of 1:2 ($W:W$). 1,8-Diiodooctane (DIO, 3% solution by volume) was added as an additive to optimize the blend morphology. The optimized spin-speed was adjusted from 600 r·min⁻¹ to 1500 r·min⁻¹. A MoO₃ layer (*ca.* 10 nm) and an Ag cathode (*ca.* 80 nm) were finally deposited onto the surface of the active layer in an evaporation chamber under high vacuum ($\leq 10^{-4}$ Pa). For the preparation of the hole-only device of ITO/PEDOT:PSS/copolymer:PC₇₁BM/MoO₃/Au, MoO₃ (10 nm) was evaporated onto the surface of the active layer before Au (80 nm) deposition. But for the electron-only device of glass/Al/copolymer:PC₇₁BM/Al, Al (100 nm) was evaporated before and after the active layer deposition. The thickness of active layer was detected by using a Bruker Inova atomic microscope at stepping mode. The device area was exactly fixed at 0.04 cm². I - V characterization was performed on a computer-controlled Keithley 2400 Source Measurement system with a solar simulator as the light source. The external quantum efficiency (EQE) values were tested with a Newport QE test Model 77890 (Newport Co., Ltd.) during illumination with monochromatic light from a xenon lamp. A solar simulator was used as the light source, and the light intensity was monitored by using a standard Si solar cell.

RESULTS AND DISCUSSION

Characterization and Thermal Properties

Molecular structures of the monomers, the target copolymers, and the synthetic route to the polymers are shown in Scheme 1. Detailed procedures and characterizations are described in the Experimental Section. The ¹H-NMR spectra of the copolymers are shown in Fig. 1. Three typical chemical shifts were enframed with green

rectangles, and the corresponding protons were marked in Scheme 1. The enhanced intensity of protons a and b with decreased intensity of proton c were observed clearly when increasing the content of DPP unit, which indicated that these polymers were successfully synthesized with the exact molecular structures. The resulting copolymers exhibited good solubility in chloroform and chlorobenzene. The number-average molecular weights (M_n) of these copolymers were determined to be in the range of 41–67 kDa with a relatively low polydispersity index (PDI) of 1.5–2.6 (Table 1).



Scheme 1 Synthetic route of the copolymers

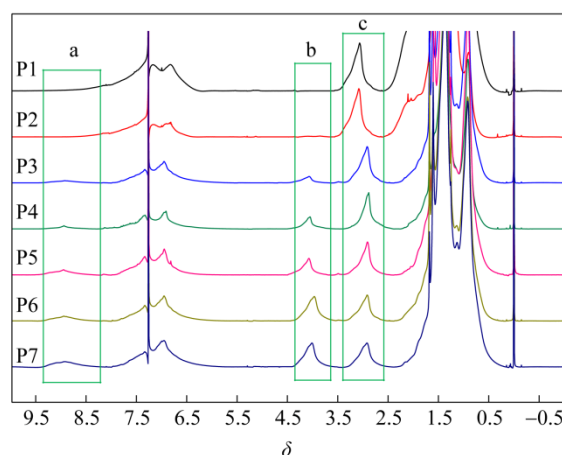


Fig. 1 ^1H -NMR spectra of the copolymers

Table 1 Molecular weights and thermal properties of copolymers

Polymer (BT:DPP)	Yield (%)	M_n ($\text{kg}\cdot\text{mol}^{-1}$)	M_w ($\text{kg}\cdot\text{mol}^{-1}$)	PDI	T_d ($^{\circ}\text{C}$)
P1 (1.0:0.0)	80	41.2	81.3	1.97	356
P2 (0.9:0.1)	85	49.7	74.2	1.49	356
P3 (0.7:0.3)	83	50.3	76.1	1.51	350
P4 (0.5:0.5)	86	51.5	80.4	1.56	340
P5 (0.3:0.7)	81	57.0	148.5	2.61	337
P6 (0.1:0.9)	88	63.4	162.0	2.55	336
P7 (0.0:1.0)	82	67.9	175.2	2.58	335

TGA showed that all the copolymers exhibited good thermal stabilities with the onset degradation temperatures (T_d , 5% weight loss) above 330 $^{\circ}\text{C}$ (Fig. 2a). The gradually decreased T_d values indicated that the BT-containing copolymers were more stable than the DPP-containing counterparts. DSC was also performed to measure the glass transition behaviors of these copolymers. No endo- or exothermal signals were observed in the range of 0–250 $^{\circ}\text{C}$ from the second heating and cooling runs (Fig. 2b), implying that these polymers were

thermally robust. The resulting characterization and thermal analysis data are listed in Table 1.

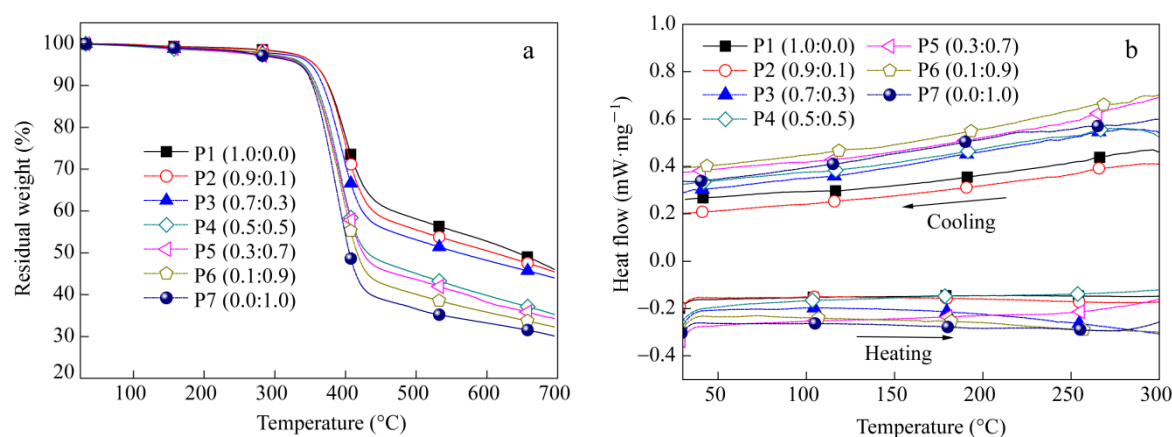


Fig. 2 TGA (a) and DSC (b) curves of the copolymers under inert atmosphere at a scan rate of $10 \text{ K} \cdot \text{min}^{-1}$

Optical Properties

UV-Vis absorption spectra of these copolymers in chloroform solutions ($0.02 \text{ mg} \cdot \text{mL}^{-1}$) and in thin films are shown in Figs. 3(a) and 3(b), respectively. As shown in Fig. 3, all these copolymers exhibit an absorption peak around 300–500 nm, which is ascribed to the π - π^* transition. It is more interesting that the absorption peaks in the longer wavelength region are gradually changing, which is attributed to the intramolecular charge transfer (ICT) from BDT units to BT or DPP units^[23]. This ICT absorption is around 500–700 nm for P1, and 600–850 nm for P7, and both of them are not well matched with the solar spectrum. The maximum peak of P7 shows a large red-shift over 160 nm in comparison to that of P1, which indicates that a good complementary absorption will be obtained if both BT and DPP units are built in one molecular backbone. When the terpolymer strategy was used, the ICT absorption band shows progressively bathochromic-shift with increased DPP content. When the ratio of BT/DPP is over 0.5:0.5, the main absorption in the longer wavelength region will red-shift, while the absorption in the shorter wavelength will slightly decrease. On the contrary, when the ratio of BT/DPP is less than 0.5:0.5, the absorption in the longer wavelength region tends to stabilize, but it decreases dramatically in the shorter wavelength region. In addition, the shoulder absorption of the copolymers increases gradually around 750 nm, which is due to the strong aggregation property of these DPP-based copolymers. Therefore, there is a balance between the absorption and molecular aggregation during the formation of the blend film. From the on-set absorption edge in the film state, the optical bandgaps (E_g^{opt}) of these polymers are calculated to vary between 1.73 and 1.43 eV for P1–P7, respectively. The optical data are given in Table 2.

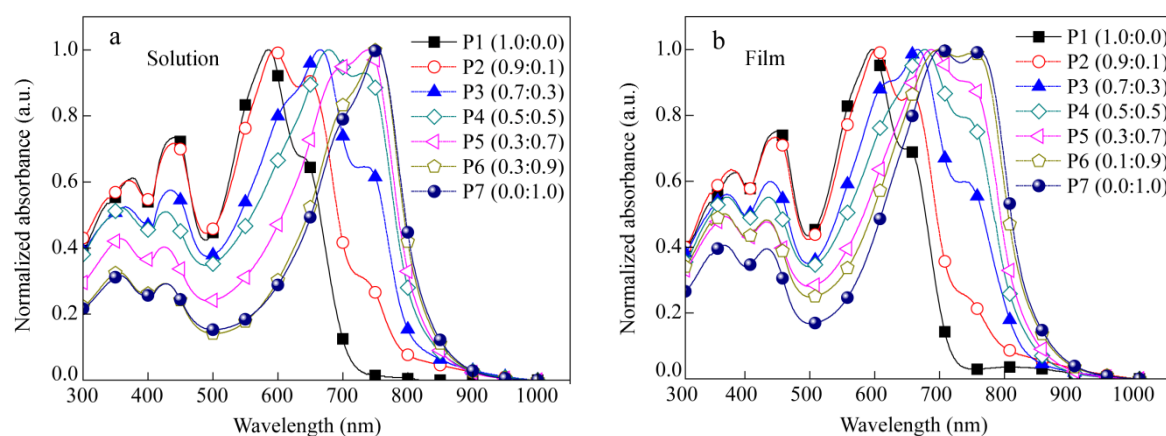


Fig. 3 Normalized UV-Vis absorption spectra of the copolymers in chloroform solutions (a) and thin films (b)

Electrochemical Properties

To investigate BT/DPP ratio effect on the energy levels of these random copolymers, CV measurements were carried out. Figure 4 shows the CV curves of the copolymer films. Clearly, both absolute values of the reduction and the oxidation onsets decrease gradually with increased DPP content, which indicates that the LUMO level is gradually lowered but the HOMO level is gradually elevated. The LUMO levels are calculated to vary from -2.97 eV to -3.16 eV, and the HOMO levels from -5.32 eV to -5.20 eV. Thus, the electrochemical bandgaps (E_g^{CV}) is calculated to vary from 2.35 eV to 2.04 eV. The variation trend is in accordance with that from the UV-Vis measurement. It is well known that a low-lying HOMO level would contribute to achieving a high V_{oc} , while a broader absorption would favor for obtaining higher J_{sc} in PSCs. Therefore, a satisfactory device performance requires the balance of a rational energy level control and an absorption manipulation in the terpolymers. The electrochemical data are also summarized in Table 2.

Table 2 Optical and electrochemical data of the copolymers

Polymer (BT:DPP)	Abs. (nm)		E_g^{opt} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{CV} (eV)
	λ_{max}^{sol}	λ_{max}^{film}				
P1 (1.0:0.0)	585, 638	589, 642	1.73	-5.32	-2.97	2.35
P2 (0.9:0.1)	595, 648	595, 649	1.58	-5.29	-2.99	2.30
P3 (0.7:0.3)	665, 732	658, 730	1.52	-5.28	-3.00	2.28
P4 (0.5:0.5)	678, 733	668, 730	1.49	-5.26	-3.01	2.25
P5 (0.3:0.7)	739	679, 735	1.47	-5.24	-3.03	2.21
P6 (0.1:0.9)	752	690, 745	1.44	-5.21	-3.09	2.12
P7 (0.0:1.0)	754	694, 754	1.43	-5.20	-3.16	2.04

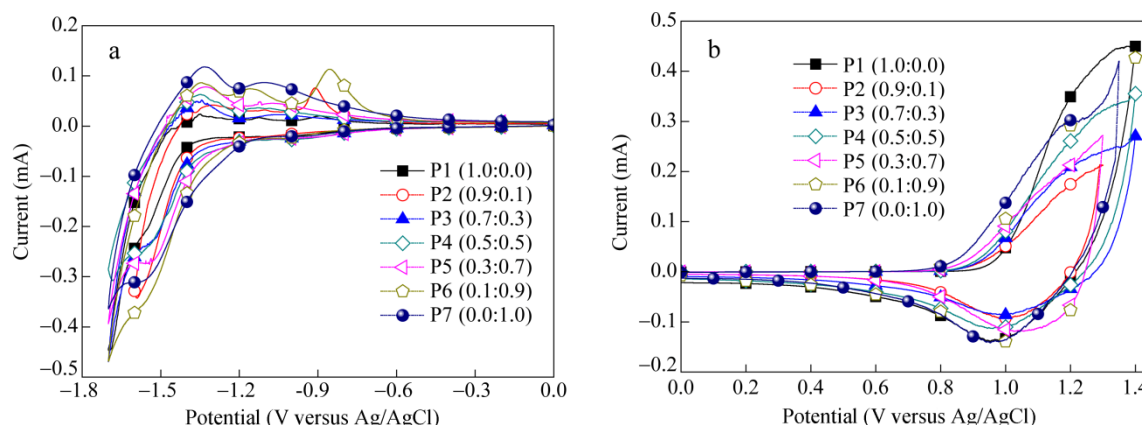


Fig. 4 The reduction scanning curves (a) and oxidation scanning curves (b) of the copolymer films from CV measurements

Photovoltaic Properties

To explore the BT/DPP ratios effect on photovoltaic property, inverted PSCs were fabricated and evaluated with a device configuration of glass/ITO/ZnO/copolymer:PC₇₁BM/MoO₃/Ag, in which the copolymers were used as the donor materials and PC₇₁BM as the acceptor. The optimization process involved varying D/A weight ratios, solvent additives, active layer thicknesses, and spin-coating temperatures. Figure 5 shows the resulting optimized device performance. It was seen that V_{oc} gradually decreased with increasing the DPP content, which was consistent with the HOMO level variation of the copolymers. P1 device without DPP component exhibited the highest V_{oc} of 0.76 V, with a J_{sc} of 12.57 mA·cm⁻² and fill factor (FF) of 63.4%, giving rise to a PCE of 6.06%. By increasing the DPP content, both the J_{sc} and FF obviously improved at first and then decreased gradually. The highest J_{sc} value, 18.52 mA·cm⁻², was obtained when BT and DPP were used in equal molar amount. Such a high J_{sc} value would be mainly due to the more effective solar spectrum absorption. However, the highest FF value of 66.9% was achieved when BT:DPP = 0.7:0.3, which might originate from the best morphology of the

corresponding blend. The J_{sc} in this sample was also as high as $18.45 \text{ mA}\cdot\text{cm}^{-2}$, very close to the highest J_{sc} , which was likely due to the relatively wide absorption range and effective exciton dissociation as well as excellent charge collection. Therefore, the optimal device performance reached up to 9.01%, with a V_{oc} of 0.73 V. When the DPP amount was more than that of BT, the V_{oc} reached a stable level of 0.71 V, but the J_{sc} dropped dramatically, accompanied with a slowly decreased FF value. P7 device without BT component gave the lowest PCE of 4.16%, with a V_{oc} of 0.71 V, a J_{sc} of $9.93 \text{ mA}\cdot\text{cm}^{-2}$, and a FF of 59.1%. This could be attributed to the relatively narrow absorption and less effective exciton dissociation as well as poor charge collection. The highest series resistance (R_s) value of $15.1 \text{ }\Omega\cdot\text{cm}^2$ for P7 device was another evidence of the inferior exciton dissociation with more charge recombination. The photovoltaic parameters are summarized in Table 3.

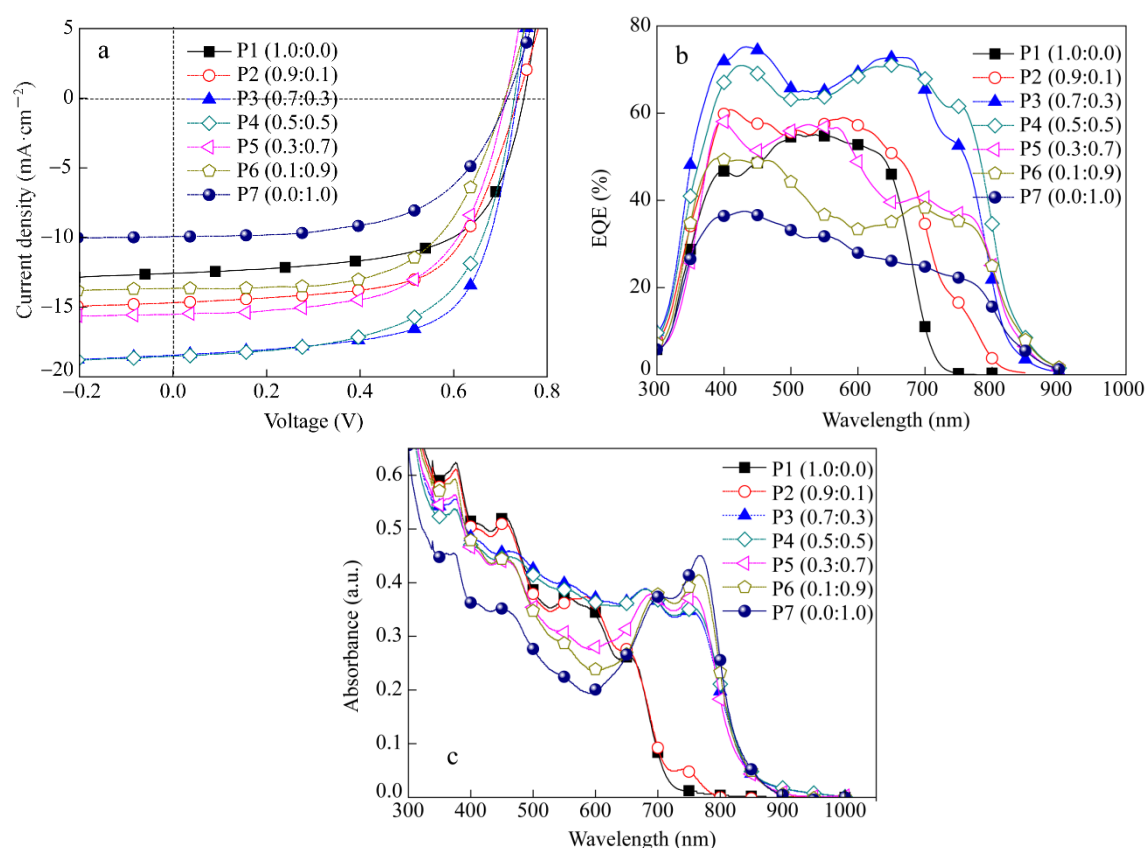


Fig. 5 (a) J - V curves of the PSCs; (b) EQE curves of the PSCs; (c) UV-Vis spectra of copolymer:PC₇₁BM blends

Table 3 Photovoltaic properties of the PSCs

Polymer (BT:DPP)	V_{oc} (V)	J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	FF (%)	PCE _{max} (%) / PCE _{ave} (%)	R_s^a ($\Omega\cdot\text{cm}^2$)	R_{sh}^b ($\Omega\cdot\text{cm}^2$)	μ_h^c ($\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$)	μ_e^d ($\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$)
P1 (1.0:0.0)	0.76	12.57	63.4	6.06/5.87	7.6	623.1	9.4×10^{-5}	1.9×10^{-4}
P2 (0.9:0.1)	0.74	14.70	64.4	7.01/6.72	7.4	630.9	1.8×10^{-4}	2.7×10^{-4}
P3 (0.7:0.3)	0.73	18.45	66.9	9.01/8.80	5.6	884.9	4.2×10^{-4}	4.6×10^{-4}
P4 (0.5:0.5)	0.72	18.52	62.2	8.29/8.01	6.6	872.6	5.6×10^{-4}	4.4×10^{-4}
P5 (0.3:0.7)	0.71	15.52	61.3	6.74/6.45	8.1	604.9	2.9×10^{-4}	2.4×10^{-4}
P6 (0.1:0.9)	0.71	13.65	61.1	5.90/5.74	10.7	538.9	1.6×10^{-4}	1.8×10^{-4}
P7 (0.0:1.0)	0.71	9.93	59.1	4.16/4.02	15.1	376.2	7.4×10^{-5}	1.6×10^{-4}

^a R_s is series resistance; ^b R_{sh} is shunt resistance; ^c μ_h is hole mobility; ^d μ_e is electron mobility.

Improvement of J_{sc} by using terpolymer strategy was further confirmed by EQE measurement (Fig. 5b). PSC based on P1 without DPP units exhibited an EQE response up to 700 nm, with a top EQE value of 55%. With increased DPP content, PSCs based on the related copolymers showed extended EQE response to longer wavelength. P3 device with BT:DPP = 0.7:0.3 exhibited a wide EQE response with the highest EQE value, while P4 with BT:DPP = 0.5:0.5 showed the widest EQE response, which were in correspondence with the optical absorption of the related blend films (Fig. 5c). However, P5, P6 and P7 devices exhibited sharply decreased EQE values in the overall spectrum range, regardless of their good absorption in the longer wavelength (Fig. 3). This was mainly rooted from their inferior morphology for effective charge dissociation and transportation.

To further understand the reason of J_{sc} enhancement by terpolymers strategy, carrier mobility of the active blend films was measured. A hole-only device structure of glass/ITO/PEDOT:PSS/polymer:PC₇₁BM/MoO₃/Au and an electron-only device structure of glass/Al/polymer:PC₇₁BM/Al were used for the hole mobility (μ_h) and electron mobility (μ_e) measurements. Figure 6 shows the $J^{1/2}$ - V curves of the resulting hole-only and electron-only devices. The carrier mobility exhibited a similar trend to their J_{sc} variations. P1 without DPP had a hole/electron mobility of $9.4 \times 10^{-5}/1.9 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, while P7 without BT showed a relatively low hole/electron mobility of $7.4 \times 10^{-5}/1.6 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. When the BT/DPP ratio was 0.7:0.3 and 0.5:0.5, the hole/electron mobility was improved to $4.2 \times 10^{-4}/4.6 \times 10^{-4}$ and $5.6 \times 10^{-4}/4.4 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, respectively, with more balanced μ_e/μ_h values of 1.1 and 0.8 at the same time, indicating their better charge transportation properties. Detailed carrier mobility data are summarized in Table 3 for comparison.

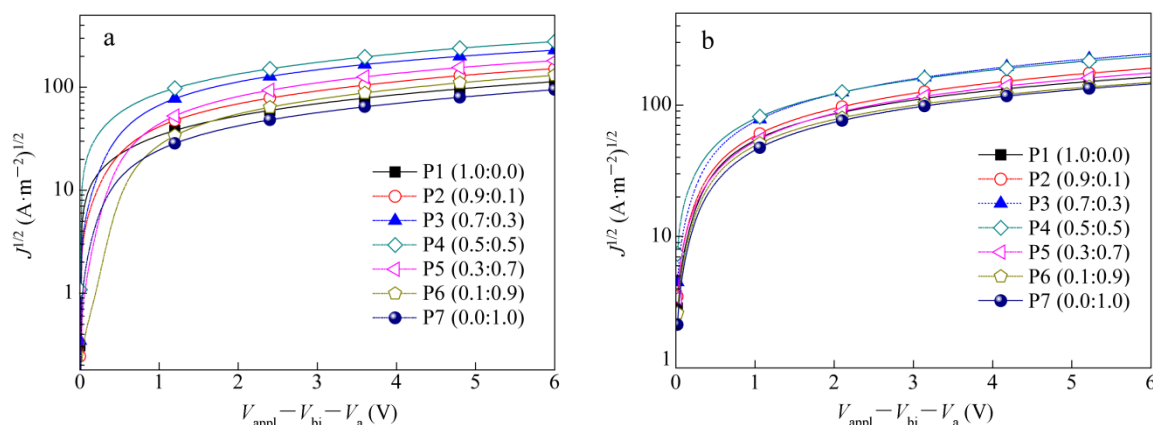


Fig. 6 $J^{1/2}$ - V curves of the hole-only devices (a) and electron-only devices (b) based on the blends of copolymer:PC₇₁BM

Morphology Studies

The morphology of the active blends plays a key role in the final device performance of the related PSCs. Thus, AFM was used to study the morphology of the copolymer-fullerene blends. Figure 7 shows the height images and phase images of the optimized active blends. The P1-based active layer exhibited extremely smooth topography with a small root-mean-square roughness (RMS) of 0.80 nm. RMS values were enlarged gradually with increase in DPP content, which were determined to be 1.01, 1.34, 1.51, 1.82, 2.20 and 3.43 nm for P2, P3, P4, P5, P6 and P7, respectively. The increased roughness resulted mainly from strong aggregation nature of the DPP units. The higher aggregation property could lead to a larger phase domain size during film formation, which could be usually found in DPP-containing polymer blend films, especially for P7. By varying the BT/DPP ratio, the morphology could thus be finely tuned. P3 exhibited the optimized morphology with fibril-like domains around 10–20 nm throughout the whole active layer. The high quality morphology of P3:PC₇₁BM would be responsible for the excellent exciton dissociation and charge transportation with a less charge recombination, which would give rise to high J_{sc} and FF values in the corresponding devices. The results demonstrate that the terpolymer strategy is an effective way to control the morphology for achieving high-performance PSCs.

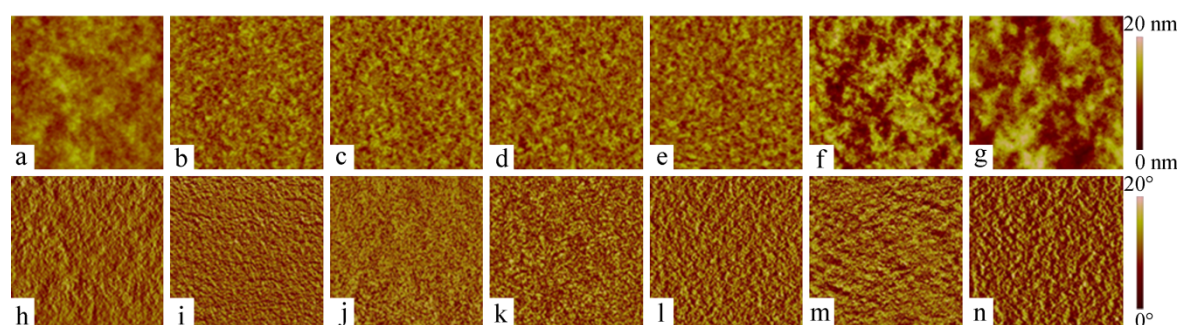


Fig. 7 AFM height images (a, b, c, d, e, f, g) and phase images (h, i, j, k, l, m, n) of the copolymer-based active blends: (a, h) P1:PC₇₁BM; (b, i) P2:PC₇₁BM; (c, j) P3:PC₇₁BM; (d, k) P4:PC₇₁BM; (e, l) P5:PC₇₁BM; (f, m) P6:PC₇₁BM; (g, n) P7:PC₇₁BM (AFM image size: 5 μm $\times$ 5 μm)

CONCLUSIONS

In conclusion, we have successfully synthesized and characterized a series of BDT-containing terpolymers by varying the BT/DPP ratio as the first and second acceptor units. The BT and DPP units had totally different absorption properties, energy levels and aggregation nature. Therefore, these properties could be finely tuned by controlling the BT/DPP ratio in the resulting copolymers. By increasing the DPP content, the absorption range extended effectively to longer wavelength region. P4 with equal BT and DPP amount exhibited the best absorption, giving the highest J_{sc} of up to 18.52 $\text{mA}\cdot\text{cm}^{-2}$. Increasing the DPP unit also made HOMO level rise up, leading to a decreased V_{oc} . The morphology of the active blends exhibited high dependence on the BT/DPP ratio. Rougher topography with relatively larger domain size could be observed in the higher content DPP-containing copolymers, which made J_{sc} and FF increase first and then decrease gradually. Finally, the P3 device with BT:DPP = 0.7:0.3 exhibited the best PCE of 9.01%, which was improved by 48.7% compared to the P1 device, and by 117.6% compared to the P7 device, respectively. These results give a good example for the design of highly efficient terpolymers by fine-tuning absorption and molecular aggregation.

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