Thiophene spacers impart crystallinity and enhance the efficiency of benzothiophene-based conjugated polymers for bulk heterojunction photovoltaics

Shang-Che Lan, Po-An Yang, Meng-Jie Zhu, Chia-Min Yu, Jian-Ming Jiang and Kung-Hwa Wei*

In this study we synthesized the donor–acceptor conjugated copolymers PBTT4BT and PBTT4BO featuring benzothiophene (BTT) units as donors and benzothiadiazole (BT) and benzoaxadiazole (BO) units, respectively, as acceptors, linked through 4-dodecylthiophene spacers. The presence of the spacer units enhanced not only the solubility of the synthesized polymers but also their molecular packing in the solid state; both of these polymers exhibited good crystallinity, as evidenced by a d-spacing of 23.8 Å in the (100) plane in their X-ray diffraction curves. When we used these synthesized polymers in bulk heterojunction photovoltaic device applications, the optimal device incorporating PBTT4BO/PC₆₁BM as the active layer exhibited a low efficiency of 3.2%, due to the poor solubility of PBTT4BO, whereas the optimal device incorporating the more-soluble PBTT4BT and PC₇₁BM displayed an efficiency of 4.4%, which is substantially 1.5% higher than that for the PBTTBT/PC₇₁BM device, where PBTTBT was formed by copolymerizing BTT and BT units without any spacer. After thermal annealing, the efficiency of the PBTT4BT/PC₇₁BM device improved further to 5.6%, with a V_OC value of 0.72 V, a J_SC value of 11.58 mA cm⁻² and a fill factor of 67%. The annealed PBTT4BT/PC₇₁BM active layer possessed a nanoscaled network-like morphology with rod-like PBTT4BT domains that were beneficial for charge separation and transport; accordingly, the power conversion efficiency of the annealed PBTT4BT/PC₇₁BM photovoltaic device was enhanced greatly over that of the as-cast PBTT4BT/PC₇₁BM device.

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Introduction

Polymer solar cells (PSCs) have attracted a great deal of attention because of their low cost, light weight, flexibility, and ease of fabrication relative to silicon-based solar cells.¹⁻³ Bulk heterojunctions (BHJs), in which a conjugated polymer as a p-type material is blended with a fullerene derivative (e.g., PC₆₁BM) as an n-type material, are the most successful active layer structures for PSCs. Recently, the power conversion efficiencies (PCEs) of some conjugated polymer-based BHJ devices have reached over 7% without the need to adopt new device architecture.¹ Ideally, the polymer in the active layer should have a broad absorption spectrum to absorb more photons, high hole mobility to transport carriers, and a suitable energy level offset with respect to the fullerene to afford a high open-circuit voltage (V_OC).

The rational design and synthesis of low-band gap conjugated polymers remains an important aspect of the quest for PSCs with high PCEs. The donor–acceptor (D/A) copolymer approach, where electron donor and electron acceptor units are copolymerized, is an effective means of obtaining conjugated polymeric materials exhibiting low band gaps as well as suitable energy level offsets with respect to the fullerenes.⁴ D/A polymers featuring a weak donor and a strong acceptor have displayed the ideal energy level offset with respect to fullerenes.⁴ Indeed, copolymerizing a weakly electron donating benzothiophene unit with a variety of strongly electron accepting units, such as thieno[3,4-b]thiophene,⁶ fluorinated benzo[1,2,5]thiadiazole (BT),⁶ benzo[1,2,5]oxadiazole (BO),⁶ and thieno[3,4-c]pyrrole-4,6-dione,⁶ has resulted in BHJ devices exhibiting PCEs ranging from 5 to 7%.

Another important feature of an ideal conjugated polymer is crystallinity, because crystalline polymers not only have better resistance to moisture and oxygen permeation, which result in longer device life time but also typically lead to higher hole mobilities. A case in point is poly(3-hexylthiophene) (P3HT), which can form highly crystalline states and nanoscaled bi-continuous networks with fullerenes upon thermal annealing in the active layer of BHJ devices, thereby providing quite-decent PCEs (4% or more), even though P3HT has a simple molecular structure.¹⁰ It is, however, difficult to predict a priori which molecular structures will result in crystalline polymers, even though some general directions (e.g., planarity,¹¹ regioregularity) can be followed; notably, most D/A copolymers are
amorphous materials. Only some specific monomer units, including thieno[3,2-b]thiophene,\textsuperscript{12} dithieno[3,2-b:2',3'-d]silole,\textsuperscript{13} and thieno[3,4-c]pyrrole-4,6-dione,\textsuperscript{14} have exhibited the potential to form crystalline polymers.

Recently, a new planar donor, benzotriothiophene (BTT), was designed for the synthesis of a series of BTT-based copolymers for organic electronic device applications.\textsuperscript{25} The electron donating ability of BTT is slightly stronger than that of benzo-dithiophene; although it has an asymmetric structure, the copolymers of BTT and thiophene exhibited good crystallinity and high mobility, making them suitable for use in organic thin film transistors. Moreover, BTT has been copolymerized with benzo[1,2,5]thiadiazole (BT) to form a copolymer that has been used to fabricate BHJ solar cells exhibiting a PCE of 2.2%. This limited efficiency was due to the highly phase-separated active layer morphology, presumably because of the polymer's low solubility or miscibility.

In this present study, we wished to further improve the solubility of D/A copolymers incorporating BTT units and also enhance their crystallinity. It has been reported that D/A polymers featuring 4-alkylthiophene units as spacers between the D and A units can not only exhibit greater solubility\textsuperscript{16} but also enhance the crystalline potential because of the polymer's low steric demand on the planarity of the conjugated backbone when using 4-alkylthiophene.\textsuperscript{17} Here, we employed 4-dodecylthiophene as a spacer between BTT and BT monomer units to improve the solubility of their copolymer and to induce crystallinity in the copolymer. The presence of the thiophene-based spacer would, however, slightly elevate the energy level of the highest occupied molecular orbital (HOMO) of the polymer, relative to that of the corresponding polymer lacking the thiophene spacer, and, therefore, decrease the value of V\textsubscript{OC} of the resulting photovoltaic device. Accordingly, we also tested the effects of another acceptor, BO, because it has electron-withdrawing ability similar to that of BT, meanwhile it is more electronegative than BT and could maintain the HOMO energy level.\textsuperscript{12,16}

**Experimental**

**Materials and synthesis**

Unless stated otherwise, all reagents were purchased from chemical suppliers (Aldrich, Alfa, Acros, etc.) and used without further purification. All solvents were dried using appropriate agent(s) under purged N\textsubscript{2} prior to use. 5-(1-Octynonyl)benzo[1,2-b:3,4-b':5,6-d'']trithiophene (1),\textsuperscript{18} 2,5-dibromo-benzo[1,2,5]oxadiazole (2),\textsuperscript{19} 2-trimethylstannyl-4-dodecylthiophene,\textsuperscript{20} and 4,7-bis(5-bromo-4-dodecyl-thien-2-yl)benzo[1,2,5]thiadiazole (M3)\textsuperscript{21} were synthesized according to literature procedures.

5-(1-Octynonyl)-2,8-bis(trimethylstannyl)benzo[1,2-b:3,4-b':5,6-d'']trithiophene (M1). A two-neck round-bottom flask containing 1 (300 mg, 0.62 mmol) was evacuated and filled with N\textsubscript{2} for 3 times and then anhydrous tetrahydrofuran (THF, 20 mL) was added. tert-Butylithium (1.7 M in pentane, 1.3 mL, 2.2 mmol) was added drop wise into the flask at −78 °C and then the mixture was warmed to room temperature and stirred for a further 3 h. The reaction mixture was cooled to −78 °C again, trimethylchloride (1 M in hexane, 2.5 mL, 2.5 mmol) was added, and then the mixture was warmed to room temperature overnight. The reaction was quenched through the addition of water; the mixture was extracted with hexane (3 × 100 mL) and then the combined organic phases were dried (MgSO\textsubscript{4}) and concentrated. The crude product was washed alternately with triethylamine and hexane to afford a yellow viscous liquid (382 mg, 76%).\textsuperscript{1} H NMR (300 MHz, CDCl\textsubscript{3}); δ (ppm) 7.78 (s, 1H), 7.62 (s, 1H), 7.46 (s, 1H), 2.97 (m, 1H), 1.71 (m, 6H), 1.26–1.22 (m, 24H), 0.852 (t, J = 13.2 Hz, 6H), 0.48 (s, 18H).\textsuperscript{1} C NMR (300 MHz, CDCl\textsubscript{3}); δ (ppm) 199.68, 138.74, 137.67, 135.40, 134.41, 133.28, 132.49, 131.94, 130.55, 130.00, 129.90, 42.41, 38.11, 31.85, 29.64, 29.48, 29.28, 27.54, 22.63, 14.10.

4,7-Bis(4-dodecyl-thien-2-yl)benzo[1,2,5]oxadiazole (3). A two-neck round-bottom flask containing 2,5-dibromobenzo[1,2,5]oxadiazole (2, 3.00 g, 10.9 mmol), 2-trimethylstannyl-4-dodecylthiophene (10.4 g, 25.0 mmol), and tetrakis-(triphenylphosphine)palladium(0) [Pd(PPh\textsubscript{3})\textsubscript{4}, 606 mg, 0.52 mmol] was purged with N\textsubscript{2} for 20 min to remove O\textsubscript{2}. Anhydrous THF (30 mL) was added and then the mixture was heated under reflux. After 24 h, the mixture was cooled to room temperature and concentrated using a rotary evaporator. The crude product was purified through column chromatography (SiO\textsubscript{2}; EtOAc–hexanes, 5 : 95) to give an orange solid (5.61 g, 83%).\textsuperscript{1} H NMR (300 MHz, CDCl\textsubscript{3}); δ (ppm) 7.95 (d, J = 1.2 Hz, 2H), 7.549 (s, 2H), 1.68 (m, 4H), 1.33–1.25 (m, 36H), 0.875 (t, J = 13.2 Hz, 6H).\textsuperscript{1} C NMR (300 MHz, CDCl\textsubscript{3}); δ (ppm) 147.84, 145.05, 137.54, 130.16, 126.07, 122.06, 121.64, 31.92, 30.61, 30.45, 29.67, 29.62, 29.47, 29.36, 22.70, 14.13.

4,7-Bis(5-bromo-4-dodecyl-thien-2-yl)benzo[1,2,5]oxadiazole (M2). N-Bromosuccinimide (NBS, 3.10 g, 17.4 mmol) was added in portions to a stirred solution of 3 (5.00 g, 8.05 mmol) in dimethyl formamide (DMF, 40 mL) and then the mixture was stirred in the dark at room temperature for 8 h. Brine was added and then the aqueous phase was extracted with ether (3 × 200 mL). The combined organic phases were washed twice with brine, dried (MgSO\textsubscript{4}), and concentrated. The residue was purified through column chromatography (SiO\textsubscript{2}; CH\textsubscript{2}Cl\textsubscript{2}–hexanes, 10 : 90) to give an orange solid (5.62 g, 90%).\textsuperscript{1} H NMR (300 MHz, CDCl\textsubscript{3}); δ (ppm) 7.71 (s, 2H), 7.24 (s, 2H), 2.59 (4H, J = 15.6 Hz), 1.63 (m, 4H), 1.31–1.236 (m, 36H), 0.853 (t, J = 13.5 Hz, 6H).\textsuperscript{1} C NMR (300 MHz, CDCl\textsubscript{3}); δ (ppm) 147.47, 144.01, 137.10, 129.75, 127.98, 125.73, 121.40, 111.57, 31.92, 29.67, 29.58, 29.40, 29.36, 29.25, 22.69, 14.13.

PBT4BO. A solution of M1 (70 mg, 0.086 mmol) and M2 (67 mg, 0.086 mmol) in anhydrous toluene was purged with N\textsubscript{2} for 20 min to remove O\textsubscript{2}. Pd(PPh\textsubscript{3})\textsubscript{4} (9.9 mg, 10 mmol%) was added and then the solution was heated at 100 °C. After 48 h, an end-capping agent (2-triethylstannyl)thiophene (100 μL) was added; 4 h later, another end-capping agent, 2-bromothiophene (100 μL), was added and then the mixture was heated overnight. The temperature was lowered to 50 °C and the mixture was then added dropwise into stirred MeOH (40 mL). The precipitated polymer was filtered off. The solid was placed in a Soxhlet extractor and washed sequentially with acetone, hexane, and chloroform (CF). The CF solution was re-precipitated in MeOH to obtain the final polymer (70 mg, 66%). Anal. calcd: C, 74.08; H, 9.12; N, 2.30. Found: C, 73.66; H, 8.92; N, 1.98%.
PBTT4BT. Following the procedure described previously, the reaction of M1 (70 mg, 0.086 mmol) and M3 (68 mg, 0.086 mmol) in the presence of tri-o-tolyolphosphine [P(o-tol)], 2.1 mg, 8.0 mol%) and tris(dibenzylideneacetone) dipalladium (Pd2dba3, 1.6 mg, 2 mol%) provided the copolymer PBTT4BT (76 mg, 72%). Anal. calcd: C, 73.11; H, 9.00; N, 2.27. Found: C, 73.33; H, 9.22; N, 2.61%.

PBTT4BO. Following the procedure described previously, the reaction of M1 (70 mg, 0.086 mmol) and M3 (25.2 mg, 0.086 mmol) in the presence of tri-o-tolyolphosphine [P(o-tol)], 2.1 mg, 8.0 mol%) and tris(dibenzylideneacetone) dipalladium (Pd2dba3, 1.6 mg, 2 mol%) provided the copolymer PBTT4BO (26 mg, 50%). Anal. calcd: C, 67.91; H, 6.84; N, 4.53. Found: C, 67.32; H, 6.92; N, 4.88%.

Measurements and characterization

$^1$H NMR spectra of solutions in CDCl$_3$ were recorded using a Varian UNITY-300 spectrometer. Chemical shifts are reported relative to the solvent signal. Mass spectra were recorded using a Micromass TRIO-2000 spectrometer. Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 apparatus operated at a heating rate of 20 °C min$^{-1}$ under a N$_2$ flow. The number- and weight-average molecular weights of the polymers were determined through size exclusion chromatography (SEC) using a Waters 1515 system, polystyrene standards, and THF as the eluent; the temperature of the system was set at 45 °C. UV-Vis absorption spectra were recorded using a Hitachi U-4100 spectrophotometer. Solution UV-Vis absorption spectra were recorded from 10$^{-3}$ M solutions in toluene. Polymer thin films were spin-coated from toluene solutions (1 mg mL$^{-1}$) onto a quartz substrate. Cyclic voltammetry (CV) was performed using a BAS 100 electrochemical analyzer operated at a scan rate of 50 mV s$^{-1}$. A three-electrode cell was used, with tetrabutylammoniumhexafluorophosphate (TBAPF$_6$, 0.1 M in MeCN) as the supporting electrolyte, a glassy carbon electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgNO$_3$ (0.01 M in MeCN) as the reference electrode. The ferrocene/ferrocenium ion (Fc/Fc$^+$) pair was used as the internal standard with the assumption that the energy level of Fe is 4.8 eV below vacuum. X-ray diffraction (XRD) patterns were recorded using a Bruker D8 high-resolution X-ray diffractometer operated in grazing incidence mode. Samples were prepared by drop-casting a solution of the polymer in toluene (1 mg mL$^{-1}$) onto a silicon wafer. Topographic and phase images of the active layers (surface area: 5 x 5 μm$^2$) were obtained using a Digital Nanoscope III atomic force microscope operated in the tapping mode under ambient conditions. The thickness of the active layer of the device was measured using a Veeco Dektak 150 surface profiler. Transmission electron microscopy (TEM) images were recorded using an FEI T12 transmission electron microscope; a low-energy electron beam (120 keV) provided sufficient contrast to distinguish the polymer-rich and fullerene-rich regions of the active layer in all of the samples without the need for heavy ion staining.

Fabrication and measurement of photovoltaic cells

The photovoltaic cells had the configuration glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):polystyresulfonate (PEDOT:PSS)/polymer:fullerene/Ca/Al. ITO-coated glass was pre-cleaned with detergent, DI water, acetone, and isopropanol in an ultrasonication bath (10 min each step) and then exposed to UV/ozone for 20 min. PEDOT:PSS was spin-cast onto the substrate and then annealed at 150 °C for 20 min in air. The active layer was spin-cast onto the PEDOT:PSS layer in a glove box, and then dried under N$_2$. To prepare the PBTT4BO cell, PBTT4BO (2 mg) and the fullerene (3 mg) were dissolved in CF (500 μL) at 60 °C; for the PBTT4BT cell, the polymer (6 mg) and the fullerene (9 mg) were dissolved in o-dichlorobenzene (DCB, 500 μL) at 80 °C; for the PBTT4BT cell, the polymer (2 mg) and the fullerene (4 mg) were dissolved in chlorobenzene (CB, 300 μL) at 80 °C. Ca (20 nm) and Al (100 nm), thermally deposited under vacuum, were used as the counter electrode. Each device featured four cells; the effective layer area of each cell was 0.04 cm$^2$. Annealing was performed by heating cells at a specific temperature for 20 min prior to deposition of the cathode.

The photovoltaic characteristics were measured using a Keithley 2400 source meter under simulated AM 1.5G illumination at 100 mW cm$^{-2}$; a Xe lamp-based Newport 66902150 W solar simulator with an AM1.5G filter was used as the white light source. A silica photodiode (Hamamatsu S1133) was employed as a standard to confirm the light intensity.

Results and discussion

Synthesis and thermal characteristics

Scheme 1 displays the synthesis of the BTT donor (M1) and the BT and BO acceptor units (M2 and M3, respectively); they were all prepared with slight modifications of literature procedures.14,15,18 We performed the copolymerizations of these D and A units using the Stille cross-coupling method (Scheme 2); PBTT4BT was synthesized using a catalysis system containing Pd$_2$dba$_3$ and P(o-tol). The alkyl chains attached to the spacer and D units provided PBTT4BT with good solubility in DCB, CF, and THF, resulting in a decent molecular weight ($M_n = 20$ kDa; PDI = 9.0). PBTT4BO would have precipitated during polymerization when using Pd$_2$dba$_3$ and P(o-tol) as the catalyst system; therefore, we used a relatively weaker catalyst [Pd(PPh$_3$)$_4$] for its
polymerization. Nevertheless, PBTT4BO still exhibited poor solubility and could be dissolved only in toluene and CF. The portion of PBTT4BO soluble in THF was used for SEC analysis, providing a molecular weight of 6 kDa and a PDI of 6.2. These two polymers also exhibited good thermal stability, each with a thermal degradation temperature (at 5% weight loss) higher than 350 °C. Of the two polymers, PBTT4BO had the lower decomposition temperature, probably because of its lower molecular weight and the greater ring strain of its oxadiazole rings. Table 1 summarizes the GPC and TGA data of the two polymers.

Optical properties

Fig. 1 displays normalized UV-Vis absorption spectra of diluted solutions of the polymers in toluene and of their thin films; Table 2 summarizes the numerical data. In solution, PBTT4BT and PBTT4BO provided similar absorption profiles, with absorption peaks near 350, 600, and 700 nm. The peak located near 600 nm was due to internal charge transfer (ICT) from the D to the A; the peak located near 700 nm was the vibronic peak attributable to π–π interactions between polymer chains. The vibronic peaks for the PBTT4BT and PBTT4BO films were more intense in the solid state than in solution, presumably because of stronger π–π interactions in the solid films. The optical bandgaps, which were calculated from the onsets of the spectrum profiles for the thin films, for PBTT4BO and PBTT4BT were 1.63 and 1.64 eV, respectively. These nearly identical bandgaps suggest that BT and BO have roughly similar electron-withdrawing abilities.

Electrochemical properties

We used CV to determine the energy levels of the HOMOs and the lowest unoccupied molecular orbitals (LUMOs) of the conjugated polymers. Fig. 2 presents the onset oxidation and reduction potentials with respect to Fc/Fc⁺; both polymers underwent quasi-reversible oxidation processes and reversible reduction processes. The HOMO and LUMO energy levels for PBTT4BO were −5.32 and −3.58 eV, respectively; for PBTT4BT they were −5.24 and −3.59 eV, respectively. The band gap energies of PBTT4BT determined using CV are in close agreement with their optical band gap energies deduced from their UV-Vis absorption spectra, whereas the CV band gap was slightly larger than the optical band gap in the case of PBTT4BO. The HOMO energy level of PBTT4BO was lower than that of PBTT4BT, due to the oxygen atom being more electronegative than a sulfur atom; as a result, PBTT4BO had a larger energy level offset with respect to the fullerene.
Computational study

Due to different band gap correlations for PBTT4BO and PBTT4BT in optical and electrochemical properties, the computational analyses were performed to obtain the relationship between band gap and energy levels of PBTT4BO and PBTT4BT. Quantum-chemical calculations were based on the method of density functional theory (DFT) at the B3LYP/6-31G* level. To simplify the calculation, only three repeat units were taken, with which alkyl chains were replaced by methyl groups. Fig. 3 displays the calculated electron density distributions and the energy levels of HOMOs and LUMOs for PBTT4BO and PBTT4BT. Both of the polymers show similar electron density distributions; the electron density of HOMO was distributed along the backbone of polymers with the electron density of LUMO mainly located at the acceptor unit. The correlation of calculated band gap energies for PBTT4BO and PBTT4BT (1.94 vs. 1.91 eV) is in agreement with the observation of the UV-Vis spectrum (1.63 vs. 1.64 eV).

The theoretical calculation indicated that both the LUMO and HOMO energy levels of PBTT4BO are deeper than those of PBTT4BT, which is partly in agreement with the CV experiments where the HOMO of PBTT4BO is deeper than that of

| Table 2 Optical and electrochemical properties of PBTT4BO and PBTT4BT |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | \( \lambda_{\text{max}} \) (nm) | \( \lambda_{\text{onset}} \) (nm) | \( E_{\text{g opt}}^a \) (eV) | HOMO\(^b\) (eV) | LUMO\(^b\) (eV) | \( E_{\text{g EC}}^c \) (eV) |
| PBTT4BO        | 600             | 766             | 1.63             | -5.32           | -3.38           | 1.74            |
| PBTT4BT        | 690             | 768             | 1.64             | -5.24           | -3.59           | 1.65            |

\(^a\) Optical bandgap calculated from the absorption onset in the film. \(^b\) HOMO and LUMO energy levels determined using the equations HOMO = \(-4.8 + E_{\text{ox}}^\text{red}\) eV and LUMO = \(-4.8 + E_{\text{ox}}^\text{red}\) eV. \(^c\) Electrochemical bandgap calculated from LUMO − HOMO.
BTT4BT, and the LUMOs for BTT4BO and BTT4BT are identical. This difference in the LUMOs determined from the theoretical calculations and CV measurement is probably due to the fact that the LUMO of conjugated polymers is difficult to be accurately measured in the CV experiment.

XRD analysis and molecular packing

To investigate the molecular packing of PBTT4BO and PBTT4BT in the solid state, we performed XRD analyses of their as-cast thin films that we had drop-cast from toluene solutions onto silica substrates and after annealing at 150 °C for 20 min. Fig. 4 displays the XRD patterns of the as-cast and annealed polymer films. For the as-cast PBTT4BT film, the only reflection peak appeared at a 2θ value of 3.7°, corresponding to edge-on lamellar stacking in the (100) plane with a d-spacing of 23.8 Å. After annealing, a higher-order reflection peak appeared at a 2θ value of 7.7°, arising from the (200) plane with a d-spacing of 11.6 Å, along with a more-intense (100) peak. Hence, the degree of crystallinity of PBTT4BT improved appreciably after thermal annealing. The chains of PBTT4BT predominantly adopted a layered structure with an edge-on orientation relative to the substrate; this structure would presumably assist charge carrier transport in the vertical direction. Recently, it has been suggested that the curvature of a polymer backbone would greatly affect its stacking. The less curvature in the polymer backbone results in more crystallinity in the polymer thin film. The PBTT4BT featured thiophene spacer has less curvature than BT and BT copolymer without the spacer, as determined in our DFT simulations. Hence, PBTT4BT reveals crystallinity, whereas BTT–BT does not exhibit crystallinity as shown in Fig. 4. The PBTT4BO film displayed the same single reflection peak and tendency as that of PBTT4BT, however it lacked another higher-order reflection peak in the (200) plane, indicating that the tendency of PBTT4BT to crystallize was greater than that of PBTT4BO; a similar heteroatom effect is evident in, for example, the crystallinity of dithieno[3,2-b:2′,3′-d]silole and cyclopenta[2,1-b:3,4-b′]dithiophene. The larger size of the sulfur atom increases the spacing between the polymer chains and improves polymer reorganization. In addition, PBTT4BO is less soluble than PBTT4BT, resulting in faster precipitation after solvent evaporation and decreasing the amount of time available for self-organization.

Photovoltaic devices

We fabricated solar devices having the configuration glass/ITO/PEDOT:PSS/polymer:fullerene/Ca/Al. Fig. 5 displays the J–V curves of these devices under AM 1.5G conditions; Table 3 summarizes the photovoltaic parameters. Because of the low solubility of PBTT4BO, its active layer could be spin-coated only from CF, providing a layer thickness of approximately 100 nm. The PCE of the device incorporating PBTT4BO was higher when it was blended with PC61BM than with PC71BM, presumably because of greater phase separation in the active layer. The highest measured PCE for the as-cast PBTT4BO/PC61BM-containing device was 2.9%, with a Voc value of 0.75 V, a Jsc value of 7.14 mA cm−2, and a fill factor (FF) of 54%; the average efficiency measured over 20 devices was 2.3%. We observed a slight improvement in performance for the device that had been subjected to annealing: values of Voc, Jsc, and FF of 0.75 V, 7.54 mA cm−2, and 55%, respectively, resulting in an efficiency of 3.2% (average efficiency for 20 devices: 2.7%).

Because PBTT4BT had better solubility in DCB, we used it as the processing solvent to prepare the active layer. The device incorporating the as-cast PBTT4BT/PC61BM blend as the active layer exhibited a PCE of 3.9%, while that of the as-cast PBTT4BT/PC71BM device was 4.4% with a Voc value of 0.69 V, a Jsc value of 11 mA cm−2, and an FF of 58%. The lower open-circuit voltage for this device is due to the higher HOMO energy level of PBTT4BT elevated by the thiophene spacer. Comparing to the BHJ device of PBTTBT, where PBTTBT was produced by copolymerization of BT and BT units, the...
efficiency of the BHJ PBTT4BT device improves greatly (4.4 vs. 1.5%), presumably due to the better solubility and the crystalline nature of PBTT4BT that gives better miscibility and charge mobility in the active layer. After thermal treatment at 150 °C for 20 min, the photovoltaic parameters for the PBTT4BT/PC71BM device were all enhanced, with a Voc value of 0.72 V, a Jsc value of 11.58 mA cm⁻², and an FF of 67%, resulting in a device efficiency of 5.6%.

### Table 3 Photovoltaic properties of PBTT4BO and PBTT4BT blends with fullerene derivatives

<table>
<thead>
<tr>
<th>Active layer (polymer-fullerene = 1 : 1.5 wt%)</th>
<th>Annealing</th>
<th>Voc (V)</th>
<th>Jsc (mA cm⁻²)</th>
<th>FF (%)</th>
<th>PCE (avg°) (%)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBTT4BO/PC61BM</td>
<td>—</td>
<td>0.75</td>
<td>-7.14</td>
<td>54</td>
<td>2.9 (2.3)</td>
<td>117</td>
</tr>
<tr>
<td>PBTT4BO/PC61BM</td>
<td>100 °C per 20 min</td>
<td>0.76</td>
<td>-7.54</td>
<td>55</td>
<td>3.2 (2.7)</td>
<td>108</td>
</tr>
<tr>
<td>PBTT4BO/PC71BM</td>
<td>—</td>
<td>0.79</td>
<td>-3.17</td>
<td>57</td>
<td>1.4 (1.2)</td>
<td>75</td>
</tr>
<tr>
<td>PBTT4BT/PC61BM</td>
<td>—</td>
<td>0.70</td>
<td>-8.90</td>
<td>62</td>
<td>3.9 (3.6)</td>
<td>90</td>
</tr>
<tr>
<td>PBTT4BT/PC71BM</td>
<td>—</td>
<td>0.69</td>
<td>-10.98</td>
<td>58</td>
<td>4.4 (4.3)</td>
<td>85</td>
</tr>
<tr>
<td>PBTT4BT/PC71BM</td>
<td>150 °C per 20 min</td>
<td>0.72</td>
<td>-11.58</td>
<td>67</td>
<td>5.6 (5.5)</td>
<td>97</td>
</tr>
<tr>
<td>PBTTBT/PC71BM</td>
<td>—</td>
<td>0.84</td>
<td>-3.90</td>
<td>46</td>
<td>1.5 (1.2)</td>
<td>65</td>
</tr>
</tbody>
</table>

° Average PCE calculated from 20 cells.

### Morphological analyses

Fig. 6 presents atomic force microscopy (AFM) images of various active layers incorporating PBTT4BT and PBTT4BO. Fig. 6(a) and (b) display the height and the phase image for the as-cast and the annealed films of PBTT4BO/PC61BM, respectively. The phase images of both of these polymer films revealed phase-aggregation, with the thermally treated film featuring slightly rougher and slightly larger aggregated domains; this
aggregation was probably due to the poor solubility of PBTT4BO. In both cases the diameters of aggregates were approximately 150–200 nm. The aggregation became much more pronounced in the case of PBTT4BO/PC71BM [Fig. 6(c)], consistent with the sharp drop in efficiency of the corresponding device. Fig. 6(e) and (f) reveal that the as-cast PBTT4BT/PC71BM film was relatively homogeneous and remained so after thermal treatment, with the roughness in both cases being 3.3 nm, without any apparent aggregation. The PCE of the annealed PBTT4BT/PC71BM device was, however, substantially improved over that of its as-cast device, indicating that AFM analysis of the surface morphology could not differentiate the actual morphology of the active layer.

Fig. 7 presents TEM images of the PBTT4BO/PC61BM and PBTT4BT/PC71BM films. The dark and bright regions in these images correspond to fullerene-rich and polymer-rich domains, respectively, due to the electron density of the fullerenes (density: ca. 1.5 g cm\(^{-3}\)) being higher than that of the polymers (density: ca. 1.1 g cm\(^{-3}\)).Fig. 7(a) reveals that the diameter of each dark region in the PBTT4BO/PC61BM film was approximately 50 nm; this domain size is too large to provide enough interfaces for exciton dissociation. After annealing, the phase-separation between the polymer and fullerene domains in the PBTT4BO/PC61BM film was more complete [Fig. 7(b)], indicating that PBTT4BO had greater crystallinity; these domains provided better channels for charge transport, thereby improving the performance of the devices. Fig. 7(c) displays a rather uniform PBTT4BT/PC71BM morphology that resulted because PBTT4BT and PC71BM were mixed well in DCB. Fig. 7(d) reveals a network-like morphology in the annealed PBTT4BT/PC71BM film, where PBTT4BT appeared as rod-like crystalline domains (width: ca. 5 nm) distributed in the fullerene matrix. This nanoscale phase separation in the annealed PBTT4BT/PC71BM film appears to be optimal, producing a more than 25% enhancement in the PCE of the annealed device relative to that for the as-cast case (5.6 vs. 4.4%).

### Conclusions

We have synthesized two new crystalline D/A polymers, PBTT4BO and PBTT4BT, that feature benzo tri thiophene units as donor moieties and benzo thiadiazole and benzoxadiazole units, respectively, as acceptor moieties, separated by 4-dode cyli thiophene spacers. The HOMO and LUMO energy levels for PBTT4BO were \(-5.32\) and \(-3.58\) eV, respectively; for PBTT4BT, they were \(-5.24\) and \(-3.59\) eV, respectively, resulting in a band gap of approximately 1.63 eV. Both PBTT4BO and PBTT4BT formed edge-on lamellae that stacked in the (100) plane with a \(d\)-spacing of 23.8 \(\AA\), as evidenced from their XRD patterns. The degrees of crystallinity of PBTT4BT and PBTT4BO were improved appreciably after annealing at 150 °C for 20 min. The as-cast PBTT4BT/PC71BM photovoltaic devices exhibited an optimal PCE of 4.4%, which is substantially higher than that of 1.5% for the PBTTBT/PC71BM device, where PBTTBT was formed by copolymerizing BTT and BT units without any spacer. For the annealed PBTT4BT/PC71BM photovoltaic devices, the PCE improved to 5.6%—an enhancement of more than 25% after annealing, presumably because PBTT4BT formed rod-like crystalline domains (width: ca. 5 nm) distributed in the fullerene matrix, as determined by transmission electron microscopy. Due to the poor solubility of PBTT4BO and its low molecular weight, the fabrication of the PBTT4BO into reasonable photovoltaic devices was severely limited. Therefore, the comparison of the photovoltaic performances of the BTT4BO and BT4BT case reflects more on the device differences than on the molecular differences.

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### Notes and references


