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Graphical Abstract



Synthesis of fluorinated (benzotriazole (BTZ)- and benzodithiophene

(BDT)-based low-bandgap conjugated polymers for solar cell applications

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Supporting Information Placeholder

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A series of donor-acceptor (D-A) polymers (P1-P3) based on benzodithiophene (BDT) and electron-accepting benzotriazole (BTZ) units containing thiophene linkers with/without alkyl side-chains were designed and synthesized via Stille coupling polymerization method. The effects of polymers with multiple fluorinated BTZ groups on their thermal, optical, electrochemical, and photovoltaic properties were investigated. These polymers possessed the highest occupied molecular orbital (HOMO) levels ranged -5.38 to -5.6 eV and the lowest unoccupied molecular orbital (LUMO) levels ranged -3.55 to -3.57 eV, which covered broad absorption ranges with low optical bandgaps. The bulk heterojunction (BHJ) polymer solar cell (PSC) devices containing an active layer of D-A polymers blended with different weight ratios of electron-acceptor [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) were explored under 100 mW cm⁻² of AM 1.5 white-light illumination, where the maximum power conversion efficiency (PCE) value of 3% (with $J_{sc} = 7.70 \text{ mA/cm}^2$, FF = 54.04, and $V_{oc} = 0.72 \text{ V}$) was obtained in the PSC device consisting of polymer P3.

To generate unlimited energy directly from sunlight using photovoltaic (PV) technology has become an essential factor in order to meet the global energy demand. Organic solar cells consisting of conjugated polymers with promising state-of-the-art photovoltaic technology are due to several benefits, such as low-cost, light-weight, and large-area devices by using solution-processed roll-to-roll printing methods.^[1-7] In the past decade, significant progress^[11-14] in power conversion efficiencies (PCEs) over 11 % has been achieved in bulk heterojunction (BHJ) solar cell devices containing conjugated polymers as electron-donating materials with [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) along (or [6,6]-phenyl-C₆₁-butyric acid methyl ester, PC₆₁BM) as electron-accepting materials.^[8-10] Nevertheless, intensive attentions to solve the problems of polymer solar cells (PSCs) are required, including poor fill factor (FF), short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), morphology, and balanced charge mobilities.^[15] To meet the above challenges, it is necessary to develop novel alternating donor-acceptor (D-A) building blocks.^[16-18]

Recently, several low bandgap (LBG) polymer materials are designed to harvest higher amounts of light from the solar spectra and larger bandgaps in D-A polymers with a lower-lying highest occupied molecular orbitals (HOMO) and the higher-lying lowest unoccupied molecular orbital (LUMO), which provides an opportunity to increase the open circuit voltage.^[19-28] A high V_{oc} is readily achieved by tuning of HOMO energy level of donor, because the V_{oc} is directly proportional to HOMO level of donor and LUMO levels of

acceptor i.e PC₇₁BM or PC₆₁BM.^{[29],[30]} To increase the values of V_{oc} in conjugated polymers

while maintaining the bandgap constant, both HOMO and LUMO energy levels must be decreased simultaneously. Thus, the electron-withdrawing groups need to be placed alternatively on polymer backbones.^[31] The fluorine atom has been recently gained considerable attention as an electron-withdrawing group for high-performance polymer solar cells, which with a very small size can be easily introduced onto polymer backbones without effects compared with the other electron-withdrawing groups.^{[32],[33]} any steric Fluorine-substituted conjugated polymers exhibited higher thermal and oxidative stabilities, resistance to degradation, and inverted charge distribution in polymers. These unique features of the fluorine atom are due to the highest electronegative element and smallest electron-withdrawing group among all electron-withdrawing groups (e.g., cyano, nitro, and trifluoromethyl groups). Moreover, these fluorine atoms showed great influences on interand intra-molecular interactions.^[34-39] Furthermore, M. P. Felix and F. G. Michael et al. reported that the introduction of fluorine atoms onto polymer backbones decreased HOMO energy levels in the copolymers based on 2-alkyl-2H-benzotriazole derivatives as acceptor units and fluorine and carbzole as donor units with PCE values of 1.8 and 4.6%, respectively.^{[40],[41]}

The arrangements of alternating donor and acceptor units were highly effective to design photovoltaic polymers with desired intrinsic optoelectronic properties (such as light-harvesting windows and energy levels) by optimal selections of electron-donating

(donor) and electron-withdrawing (acceptor) building blocks. The benzodithiophene (BDT)

unit has emerged as an attractive donor building block for PSCs as well as small molecule organic solar cells (SMOSCs) owing to its high-coplanarity, π - π stacking, high-mobility and enhanced solubility. Moreover, BDT-based polymers exhibiting low HOMO levels potentially provide high open circuit voltages and different LUMO levels, which can be manipulated effectively through the use of various acceptors.^[42-51] Very recently, Zhong-Sheng Xu and coworkers reported a series of BDT-based polymers featuring mono-fluorinated benzothiadiazole unit as the electron-acceptor that displayed a highest PCE value of 6.2%.^[52]

In the spirit of further exploring structure-property and manipulation acceptor groups, herein we report the design, synthesis, and investigation of BDT and benzotriazole (BTZ) units as donor and acceptor, respectively. Three polymers (P1–P3) are developed to utilize multiple-fluorine-substituted benzene ring units in BTZ to fine tune the light absorption capabilities, V_{oc} values, and morphlogy due to favorable intramolecular charge transfer (ICT) between BDT and BTZ units.

2. Experimental Section

2.1. Materials

All of the chemicals and solvents were reagent grade and were purchased from Aldrich, ACROS, TCI, TEDIA, and Alfa-Aesar Chemical Co. Tetrahydrofuran (THF), toluene, and

without further purification.

2.2 Measurements and characterization

¹H and ¹³C NMR spectra were recorded using a Varian VNMRS-500 and 700 MHz spectrometer using $CDCl_3$ as the solvent and the chemical shifts are reported as δ values relative to a tetramethylsilane (TMS) internal standard. Elemental analyses were performed on a HERAEUS CHN-O RAPID elemental analyzer. Thermogravimetric analyses (TGA) were conducted on a TA Instruments Q500 instrument at a heating rate of 10°°C min⁻¹ under nitrogen. Gel permeation chromatography (GPC) was conducted using a Waters 1515 separation module, using polystyrene as a standard and THF as the eluent. UV-vis absorption spectra were recorded in dilute chloroform solutions (10⁻⁶ M) using an HP G1103A spectrophotometer. The solid films for UV-vis measurements were spin-coated on glass substrates from chlorobenzene solution with a concentration of 5 mg/mL. Cyclic voltammetry (CV) was measured using a BAS 100 electrochemical analyzer with a standard three-electrode electrochemical cell in anhydrous acetonitrile containing 0.1 Μ tetrabutylammonium hexafluorophosphate (TBAPF₆) at a scanning rate of 100 mV s⁻¹ at room temperature. The solutions were purged with nitrogen for 30 s during the CV measurements. In each case, a carbon rod coated with a thin layer of polymers as the working electrode, a platinum wire as the counter electrode, and a silver wire as the quasi-reference electrode were used. An Ag/AgCl (3M of KCl in acetonitrile) electrode served as the

reference electrode for all of the potentials quoted herein. The ferrocene/ferrocenium (Fc/Fc⁺)

redox couple was used as an external standard. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the onset oxidation and reduction potentials from the reference energy level of ferrocene (4.8 eV below the vacuum level), according to the following equations.^[53]

$$E_{\text{HOMO/LUMO}} = \left[-\left(E_{\text{onset}} - E_{\text{onset}(\text{Fc/Fc}^{+}\text{vs.Ag/Ag}^{+})}\right) - 4.8\right] \text{ eV}$$
(1)

 $Bandgap = E_{ox,onset} - E_{red,onset}$ (2)

4.8 eV is the energy level of ferrocene below the vacuum level and $E_{onset(Fe/Fe^+vs.Ag/Ag^+)} = 0.45$ eV. For the CV experiments with solid films of the polymers, which were performed by drop-casting films with similar thicknesses from THF solutions (5 mg mL⁻¹), the LUMO level of PC₇₁BM employed was in accordance with the literature data. The onset potentials were determined from the intersections of two tangents drawn at the rising currents and background currents of the CV measurements. The topologies of the films were investigated using atomic force microscopy (AFM, Veeco diInnova; scanning rate: 3–4 Hz), performed in the tapping mode in a dry environment at room temperature over a sampling area of $5 \times 5 \,\mu\text{m}^2$. The images had a resolution of 512×512 pixels and were acquired at an approximate scanning rate of 0.5 Hz. The images obtained were processed using diSPMLab software (Veeco). Surface morphologies and particle distributions were investigated using a thermal field emission scanning electron microscope (JEOL JSM-6500F).

The polymer solar cells (PSCs) in this study contained an active layer of polymers (P1–P3) blended with PC71BM in a solid film, which was sandwiched between a transparent indium/tin oxide (ITO) anode and a calcium cathode (see Fig. S1). Prior to device fabrication, the ITO-coated glass substrates $(1.5 \times 1.5 \text{ cm}^2)$ were subjected to cleaning with ultrasonication in detergent, deionized water, acetone, and isopropyl alcohol successively for 10 min each. After routine solvent cleaning, the substrates were treated with UV ozone for 15 min. Then, a modified ITO surface was obtained by the spin-coating of a layer of poly(ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (40 nm). After baking at 120 °C for 1 h, the substrates were transferred to a nitrogen-filled glove box. Subsequently, on the top of PEDOT:PSS layer, the active layer was prepared by spin-coating from blended solutions of polymers P1-P3:PC71BM (with 1:2 w/w) at a spin rate of 1500 rpm. The thickness of the active layer was typically 200 nm. Initially, the blended solutions were prepared by dissolving both polymers and $PC_{71}BM$ in trichlorobenzene (TCB) (20 mg mL⁻¹), followed by continuous stirring for 12 h at 50°C. In the slow-growth approach, the blended polymers in solid films were kept in the liquid phase after spin-coating by using a solvent with a high boiling point (e.g., in a glass Petri dish) and allowing the solvent to dry slowly. Finally, a calcium layer (30 nm) and a subsequent aluminum layer (60 nm) were thermally evaporated through a shadow mask at a pressure below 6×10^{-6} Torr, to obtain an active device area of 0.12 cm². The solar-cell testing was done inside a glove box under simulated

AM 1.5 G irradiation (100 mW/cm²) using a xenon-lamp-based solar simulator (Thermal

Oriel 1000 W). The light intensity was calibrated using a monosilicon photodiode with a KG-5 color filter (Hamamatsu). The external quantum efficiency (EQE) action spectra were obtained at short-circuit conditions. The light source was a 450 W xenon arc lamp (Oriel Instrument, model 6266) equipped with a water-based IR filter (Oriel Instruments, model 6123NS). The light output from the monochromator (Oriel Instruments, model 74100) was focused on the photovoltaic cell under test.

2.4 Synthesis

2.4.1 General suzuki-coupling procedures for 3a-3c:

A solution of dibromo compound **1a** or **1b** (1.0 equiv) and thiophene-2-boralone compound **2a** or **2b** (3.0 equiv) in a mixture anhydrous toluene (40 mL), 2 M aqueous sodium carbonate (NaCO₃) (10 mL) solution and a few drops of Aliquat 336 was degassed and purged with nitrogen. Afterward, tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (0.05 equiv) was added in one portion, and the reaction mixture was heated to 90°C with vigorous stirring until reaction completion by TLC analyses. After cooling to room temperature, the reaction mixture was poured into water and extracted with dichloromethane. The combined organic layer was washed thrice with water, once with brine and dried over anhydrous magnesium sulfate (MgSO₄). The solvent was evaporated and the residue was purified by column chromatography on silica gel using hexanes/dichloromethane (1/2, v/v) as eluent, and characterization analyses are shown as follows.

2.4.1.1 2-(3,5-Difluoro-4-(octyloxy)phenyl)-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole
(3a)

3a was prepared according to the general Suzuki-coupling procedure. **1a** (2.0 g, 3.9 mmol), **2a** (2.5 g, 11.6 mmol), Pd(PPh₃)₄ (225 mg, 0.17 mmol) were used and stirred at 90°C for 24 h. The resulting product **3a** was obtained as a green solid with a yield of 80%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.12 (d, *J* = 4.0 Hz, 2H), 8.06 (d, *J* = 9.0 Hz, 2H), 7.65 (s, 2H), 7.41 (d, *J* = 5.0 Hz, 2H), 7.21 (t, *J* = 4.0 Hz, 2H), 4.22 (t, *J* = 6.5 Hz, 2H), 1.83-1.77 (quin, *J* = 6.5 Hz, 2H), 1.52-1.46 (m, 2H), 1.34-1.29 (m, 8H), 0.88 (t, *J* = 6.5 Hz, 3H). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 157.01, 155.02, 142.98, 139.36, 128.18, 127.13, 126.00, 123.88, 123.73, 105.32, 105.25, 105.09, 75.14, 31.79, 29.97, 29.26, 29.21, 25.63, 22.64, 14.10. 2.4.1.2

2-(3,5-Difluoro-4-(octyloxy)phenyl)-4,7-bis(4-hexylthiophen-2-yl)-2H-benzo[d][1,2,3]triazol e (**3b**)

3b was prepared according to the general Suzuki-coupling procedure. **1a** (2.0 g, 3.9 mmol), **2b** (3.45 g, 11.6 mmol), Pd(PPh₃)₄ (225 mg, 0.17 mmol) were used and stirred at 90°C overnight. The resulting product **3b** was obtained as a light green solid with a yield of 84%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.04 (d, *J* = 9.0 Hz, 2H), 7.90 (d, *J* = 1.5 Hz, 2H), 7.60 (s, 2H), 6.99 (d, *J* = 1.5 Hz, 2H), 4.22 (t, *J* = 6.5 Hz, 2H), 2.70 (t, *J* = 8.0 Hz, 4H), 1.83-1.77

(quin, J = 6.5 Hz, 2H), 1.73-1.67 (quin, J ≥ 8.0 Hz, 4H), 1.52-1.46 (m, 2H), 1.44-1.38 (m, 4H), 1.35-1.29 (m, 16H), 0.91-0.87 (m, 9H). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 157.05, 157.00, 155.08, 155.02, 144.42, 142.96, 138.93, 134.44, 128.34, 123.76, 123.65, 120.81, 105.34, 105.27, 105.18, 105.11, 75.15, 31.79, 31.73, 30.64, 30.44, 29.96, 29.27, 29.21, 29.04, 25.63, 22.64, 14.11.

2.4.1.3 4,7-Bis(4-hexylthiophen-2-yl)-2-(3,4,5-trifluorophenyl)-2H-benzo[d][1,2,3]triazole (3c)

3c was prepared according to the general Suzuki-coupling procedure. **1b** (2.0 g, 4.9 mmol), **2b** (4.4 g, 14.8 mmol), Pd(PPh₃)₄ (285 mg, 0.02 mmol) were used and stirred at 90°C for 24 h. The resulting product **3c** was obtained as a yellow solid with a yield of 70%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.14-8.11 (m, 2H), 7.87 (s, 2H), 7.60 (s, 2H), 7.00 (s, 2H), 2.70 (t, *J* = 8.0 Hz, 4H), 1.73-1.67 (quin, *J* = 6.5 Hz, 4H), 1.42-1.38 (m, 4H), 1.35-1.31 (m, 8H), 0.89 (t, *J* = 7.5 Hz, 6H). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 152.42, 150.47, 150.42, 144.43, 143.14, 139.18, 138.75, 135.29, 128.33, 123.93, 123.80, 120.96, 105.57, 105.52, 105.42, 105.36, 31.72, 30.62, 30.44, 29.04, 22.63, 14.11.

2.4.2 General bromination procedures for monomers M1-M3:

4,7-Di(2-thienyl)arene (**3a**, **3b** or **3c**) (1.0 equiv) was dissolved in a mixture solution of anhydrous chloroform (CHCl₃) (30 mL) and acetic acid (3 mL) under nitrogen and cooled to 0°C. *N*-bromosuccinimide (NBS) (2.0 equiv) was added portion wise over a period of 15 min protection in the dark. Then reaction mixture was allowed to warm to room temperature and

stirred for until the reaction completion by TLC analyses. After, the reaction mixture was

poured into water and extracted with dichloromethane. The combined organic layer was washed with water, once with brine and dried over anhydrous MgSO₄. The residue was purified by column chromatography on silica gel with hexanes/dichloromethane (1/2, v/v) to give the desired products. Their chemical characterization analyses are shown as follows.

2.4.2.1

4,7-*Bis*(5-*bromothiophen*-2-*yl*)-2-(3,5-*difluoro*-4-(*octyloxy*)*phenyl*)-2*H*-*benzo*[*d*][1,2,3]*triazole* (*M*1) **M1** was prepared according to the general bromination procedure, where **3a** (1.5 g, 2.9 mmol) and NBS (1.02 g, 5.7 mmol) were used. The resulting product **M1** was obtained as a yellow solid with a yield of 76%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.92 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 3.9 Hz, 2H), 7.38 (s, 2H), 7.11 (d, *J* = 3.9 Hz, 2H), 4.25 (t, *J* = 6.4 Hz, 2H), 1.85-1.78 (quin, *J* = 6.5 Hz, 2H), 1.53-1.49 (m, 2H), 1.34-1.31 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 142.70, 140.94, 131.31, 127.39, 123.45, 123.25, 114.07, 105.66, 105.27, 75.55, 32.22, 30.42, 29.71, 29.65, 26.06, 23.08, 14.54. MS (EI, *m/z*): calcd for C₂₈H₂₅Br₂F₂N₃OS₂: 679.0; found: 678.9. Anal. calcd (%) for C₂₈H₂₅Br₂F₂N₃OS₂: C, 49.35; H, 3.70; N, 6.17; found: C, 50.08; H, 3.81; N, 6.28. The detailed NMR and Mass spectra of **M1** are shown in Figs. S4-S6.

2.4.2.2

4,7-Bis(5-bromo-4-hexylthiophen-2-yl)-2-(3,5-difluoro-4-(octyloxy)phenyl)-2H-benzo[d][1,2,3]triaz ole (M2) mmol) and NBS (0.77 g, 4.4 mmol) were used. The resulting product **M2** was obtained as an orange solid with a yield of 78%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.88 (d, J = 7.7 Hz, 2H), 7.57 (s, 2H), 7.31 (s, 2H), 4.24 (t, J = 6.3 Hz, 2H), 2.60 (t, J = 7.7 Hz, 4H), 1.84-1.80 (quin, J = 6.3 Hz, 2H), 1.67-1.63 (quin, J = 7.0 Hz, 4H), 1.52-1.50 (m, 2H), 1.42-1.3 (m, 20H), 0.92-0.88 (m, 9H). ¹³C NMR (700 MHz, CDCl₃) δ (ppm): 156.66, 156.62, 155.23, 155.20, 143.03, 143.02, 142.31, 142.29, 142.27, 138.39, 136.69, 136.61, 134.06, 133.98, 127.28, 127.27, 122.80, 122.77, 122.74, 110.62, 105.08, 104.92, 75.12, 31.81, 31.67, 30.02, 29.70, 29.66, 29.30, 29.24, 28.98, 25.66, 22.66, 22.63, 14.11. MS (EI, m/z): calcd for C₄₀H₄₉Br₂F₂N₃OS₂: 849.2; found: 849.6. Anal. calcd (%) for C₄₀H₄₉Br₂F₂N₃OS₂: C, 56.54; H, 5.81; N, 4.94; found: C, 56.79; H, 5.91; N, 4.74. The detailed NMR and Mass spectra of **M2** are shown in Figs. S7-S9.

2.4.2.3 4,7-Bis(5-bromo-4-hexylthiophen-2-yl)-2-(3,4,5-trifluorophenyl)-2H-benzo[d][1,2,3]triazole (M3)

M3 was prepared according to the general bromination procedure, where **3c** (1.5 g, 2.6 mmol) and NBS (920 mg, 5.2 mmol) were used. The resulting product **M3** was obtained as an orange solid with a yield of 72%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.14-8.10 (m, 2H), 7.68 (s, 2H), 7.53 (s, 2H), 2.66 (t, J = 7.2 Hz, 4H), 1.71-1.64 (quin, J = 6.3 Hz, 4H), 1.42-1.34 (m, 12H), 0.89 (t, J = 6.9 Hz, 6H). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 143.15, 142.66, 138.25, 127.38, 123.24, 123.01, 110.89, 105.58, 105.23, 31.67, 29.72, 29.67,

calcd (%) for C₃₂H₃₂Br₂F₃N₃S₂: C, 51.97; H, 4.36; N, 5.68; found: C, 52.11; H, 4.47; N, 5.85. The detailed NMR and Mass spectra of **M3** are shown in Figs. S10-S12.

2.4.3 4,8-Bis(octyloxy)benzo[1,2-b:4,5-b']dithiophene (5)

Compound **4** (5.0 g, 22.7 mmol) was mixed with zinc powder (3.27 g, 50.0 mmol) and aqueous sodium hydroxide (NaOH) (60 mL, 12.0 wt%) solution under nitrogen. The resulting mixture was refluxed for 2 h. Then, 1-bromoctane (13.2 g, 68.2 mmol) and a catalytic amount of tetrabutylammonium bromide were sequentially added into the mixture solution. After being refluxed for overnight, the reaction was poured into cold water and extracted with diethyl ether. The organic layer was dried over anhydrous MgSO₄ and concentrated under vacuum. The crude product was purified by recrystallization from ethyl alcohol twice. The compound **5** was obtained as a white solid with a yield of 86%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.48 (d, *J* = 5.7 Hz, 2H), 7.36 (d, *J* = 5.4 Hz, 2H), 4.28 (t, *J* = 6.6 Hz, 4H), 1.92-1.83 (quin, *J* = 6.9 Hz, 4H), 1.42-1.34 (m, 20H), 0.89 (t, *J* = 6.9 Hz, 6H). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 144.52, 131.6, 130.14, 125.95, 120.3, 73.94, 31.82, 30.53, 29.41, 29.27, 26.07, 22.65, 14.1.

2.4.4 2,6-Dibromo-4,8-bis(octyloxy)benzo[1,2-b:4,5-b']dithiophene (6)

Compound **5** (4.46 g, 10.0 mmol) was dissolved in anhydrous $CHCl_3$ (100 mL) and cooled to 0°C under nitrogen. Bromine (3.2 g, 20.0 mmol) in methylene chloride (60 mL) was slowly dropped to the reaction solution, and then the reaction was allowed to warm to room

temperature and stirred for 4 h. After completion, the solvent was removed by evaporation.

The residue was recrystallized by hexane. The compound **5** was obtained as a white solid with a yield of 90%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.42 (s, 2H), 4.18 (t, *J* = 6.5 Hz, 4H), 1.86-1.80 (quin, *J* = 7.0 Hz, 4H), 1.55-1.50 (m, 4H), 1.39-1.31 (m, 16H), 0.91 (t, *J* = 6.5 Hz, 6H). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 142.53, 131.15, 130.88, 123.12, 114.96, 74.16, 31.81, 30.42, 29.35, 29.24, 25.96, 22.66, 14.12.

2.4.5 2,6-Bis(trimethyltin)-4,8-dioctyloxybenzo[1,2-b;3,4-b]dithiophene (7)

Compound **6** (5.0 g, 8.3 mmol) was dissolved in tetrahydrofuran (THF) (100 mL) which was cooled down to -78°C under nitrogen. *n*-Butyllithium (*n*-BuLi) (7.3 mL, 2.5 M in *n*-hexane) was added slowly over a period for 15 min, and then the reaction mixture was stirred for 30 min. Then, trimethyltin chloride (18 mL, 1 M in *n*-hexane) was added in one portion, and the reactant turned to clear rapidly. The resulting mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with cool water (200 mL) and extracted with diethyl ether. The combined organic layer was washed with water, and dried over anhydrous MgSO₄. After removing solvent under vacuum, the residue was recrystallized by ethyl alcohol twice. The compound **7** was obtained as a colorless solid with a yield of 72%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.50 (s, 2H), 4.28 (t, *J* = 6.4 Hz, 4H), 1.90-1.83 (quin, *J* = 6.4 Hz, 4H), 1.60-1.53 (m, 4H), 1.36-1.29 (m, 16H), 0.88 (t, *J* = 6.0 Hz, 6H), 0.44 (s, 18H). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 143.40, 140.78, 134.32, 133.28, 128.31,

49.76; H, 7.05; found: C, 50.01; H, 7.12.

2.4.6 General Still-coupling polymerization procedures for polymers P1-P3:

Dibromo monomer (M1, M2 or M3) (1.0 equiv) and distannyl monomer 7 (1.0 equiv) in anhydrous toluene (15 mL) were degassed with nitrogen. Then $Pd(PPh_3)_4$ (1.5 mol %) was added in one portion. The reaction mixture was heated to reflux for 24 h under nitrogen. After, an excess amount of 2-bromothiophene (0.34 g, 2.0 mmol) was added the trimethyl stannyl groups as an end-capped and reacted for 2 h. The reaction mixture was cooled to room temperature and poured into methanol (200 mL) for precipitation. The precipitated solid was collected and was further purified by Soxhlet extraction with methanol, hexane, acetone, and CHCl₃. Finally, the remaining solid was dried under vacuum to afford the desired polymer.

2.4.6.1 **P1**: **P1** was prepared according to the general Still-coupling polymerization procedure. Monomers **M1** (0.68 g, 1.0 mmol) and **7** (0.74 g, 1.0 mmol) were used. The **P1** was obtained as a black solid with a yield of 80%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.95-7.44 (br, 10H), 4.22 (br, 6H), 1.90-1.81 (br, 10H), 1.55-1.12 (br, 36H), 0.91 (br, 9H). 2.4.6.2 **P2**: **P2** was prepared according to the general Still-coupling polymerization procedure. Monomers **M2** (0.85 g, 1.0 mmol) and **7** (0.74 g, 1.0 mmol) were used. The **P2** was obtained as a black solid with a yield of 88%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 0.88 (br, 15).

2.4.6.3 **P3**: **P3** was prepared according to the general Still-coupling polymerization procedure. Monomers **M3** (0.74 g, 1.0 mmol) and **7** (0.74 g, 1.0 mmol) were used. The **P3** was obtained as a black solid with a yield of 82%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.11-7.33 (br, 8H), 4.26 (br, 4H), 2.96 (br, 4H), 1.90-1.81 (br, 18H), 1.39-1.33 (br, 22H), 0.89 (br, 12H).

3. Results and discussion

3.1 Synthesis and thermal stability

The synthetic routes of monomers M1-M3 and polymers P1-P3 are shown in Scheme 1. The syntheses of compounds 1a,^[54] 1b,^[54] and $4^{[55]}$ are followed by the previous literature. Three 4,7-dibromo-2-(phenyl)-2*H*-benzotriazoles (1a and 1b) with different substitution patterns on the phenyl group are subjected to Suzuki reaction conditions with 3-hexylthiophene-2-boronicacidpinacol ester and thiophene-2-boronicacidpinacol ester to give the substituted BTZ (i.e., 3a-3c). After bromination of the prepurified compounds 3a-3c in CHCl₃ with *N*-bromosuccinamide (NBS), pure dibromo monomers M1-M3 could be obtained in reasonable yields, and the purities of M1-M3 are proven by EA data demonstrated in Fig. S13.

The stannylated BDT was polymerized with the corresponding monomers M1–M3 by Stille-coupling, in which polymers P1–P3 were obtained in very good yields, respectively. All

and polydispersity indices (PDI = M_w/M_n) were subjected to Soxhlet extraction with various solvents or simply filtered through a plug of celite. After dissolving the polymers again in a small amount of an appropriate solvent (e.g., CHCl₃) the polymers could be precipitated from methanol. The polymers were collected through filtration and dried in vacuum. To determine the actual ratio between M1–M3 and 7 in the polymers, their chemical compositions were characterized by ¹H NMR spectroscopy. The actual and feed ratios of these polymers are in good agreements. Detailed synthetic procedures and characterization data are given in the Experiment Section. All polymers exhibit good solubilities in common organic solvents such as chloroform, THF, DCB, and TCB, etc. at room temperature. As summarized in Table 1, the number-average molecular weights (M_n) , weight-average molecular weights (M_w) and PDI values of P1-P3 were determined by GPC using THF as eluent against polystyrene standards. These results show that considerable molecular weights were obtained in these polymers, where the values of M_n were ranged among 163000–32400g/mol with PDI values of 1.1–1.3. Among all polymers, P1 showed a remarkably higher molecular weight of 32400g/mol. This could be attributed to the lack of alkyl chains on thiophene of poymer backbone along with a more planar structure, which led to higher molecular weight. The thermal stabilities of conjugated polymers play a key role for device fabrication. The thermal stabilities of P1-P3 were investigated using thermogravimetric analyses (TGA), and their corresponding results are summarized in Fig. S2 and Table 1. It is apparent that all polymers exhibited excellent thermal stabilities as the temperatures for 5% weight loss (under nitrogen) were found to be 368–391°C. Due

to the highest molecular weight and the most planar backbone conformation by the density functional theory (DFT) calculations of **P1** in these polymers, **P1** showed the highest decomposition temperature at 391°C. Whereas, polymer **P2** exhibited the lowest decomposition temperature at 368°C lower than **P3** (381°C), because of three fluorine-substituted phenyl pendant attached to the BTZ unit for **P3** in contrast to the alkoxy-substituted phenyl pendant for **P2**. Thus, these polymers showed sufficient thermal stabilities for the applications of polymer solar cells and other optoelectronic devices.

3.2 Optical and electrochemical properties

The photophysical properties of the polymers in chloroform solutions and solid films were investigated by UV-vis absorption spectroscopy. The UV-vis absorption spectra are shown in Figs. 1a and 1b, and the absorption maxima (for both solutions and solid films) and the optical bandgaps ($E_{g,opt}$) are listed in Table 2. All polymers in solution state showed similar absorption spectra and exhibited two main absorption peaks at ca. 400 and 500 nm. The shorter wavelength absorption bands located between 385 and 411 nm were correspondent to the π - π * transitions of polymer backbones. On other hand, the longer absorption bands located between 505 and 524 nm were mainly due to the intramolecular charge transfer (ICT) interactions from the donor BDT units to acceptor fluorine substituted BTZ moieties, which is a typical characteristic for D-A polymers. These similar characteristic bands were also obtained in solid films. All polymers have absorption maxima accompanied by a distinctive shoulder, indicating a substantial degree of backbone

coplanarity. The blue-shift of 12 nm in polymer P2 was likely originated from the reduced

backbone coplanarity, which was due to the high alkylation density and interchain repulsions and thus to induce less aggregation in solution. Whereas polymer P3 showed a red shift of 19 nm, as a result of three fluorine-substituted phenyl pendant attached to the BTZ unit to promote backbone coplanarity. As expected, all three polymers demonstrated a red shifted absorption from solutions to solid films in Fig. 1b. The absorption maxima of P1-P3 were in the range of 508–534 and 560–618 nm for solutions and solid films, respectively. Whereas P3 showed a little blue-shifted absorption maximum at 576 nm and a shoulder peak at 619 nm in contrast to P2. The optical bandgaps $(E_{g,opt})$ of P1, P2, and P3 in solid films were calculated to be 1.79, 1.77, and 1.81 eV, respectively, from the absorption edges of the corresponding UV-vis absorption spectra (see Table 2). In order to investigate the temperature effect on absorption spectra of polymers, we carried out UV-Vis experiments at various temperatures between 20-50°C in chloroform solutions. As shown in Fig. S3, the absorption spectra of polymers P1-P3 displayed a systematic trend of an absorption peak broadening accompanied with a blue-shift upon increasing temperature. At elevated temperatures, all polymers are well dissolved and disaggregated. The blue-shift and broadening of the absorption band are also related to the thermally induced less-restricted and less-planar conformation distributions at higher temperatures.^{[56],[57]} These results imply that it is an efficient way to design LBG photovoltaic polymers to have higher light-harvesting capabilities by tuning various electron-acceptor moieties.

HOMO/LUMO levels), the electrochemical properties of polymers P1-P3 were investigated by CV measurements. The electrochemical properties, such as the onset potentials of oxidation and reduction processes, (i.e., the estimated positions of the upper edges of valence bands (HOMO) and the lower edges of conduction bands (LUMO), respectively) and the electrochemical bandgaps of all polymers are summarized in Table 2. As shown in Fig. 2, the oxidation onsets of P1, P2, and P3 were achieved to be 1.03, 1.09, and 1.20 V, which corresponded to HOMO energy levels of -5.38, -5.44, and -5.60 eV, respectively. Comparing HOMO energy levels of P1-P3, it showed a lower HOMO level in P3 due to one more fluorine atom in the polymer pendant. This result implies that **P3** is promising for achieving a higher V_{oc} value in PSCs than its counterparts **P1** and **P2**. Moreover, the reduction onsets of P1, P2, and P3 were measured to be -0.80, -0.85, and -0.78 V, which correspond to LUMO energy levels of -3.55, -3.50, and -3.57 eV, respectively. Hence, the introduction of fluorine units seems to affect mostly the HOMO energy levels of the resulting polymers while the LUMO energy levels remained almost constant. In summary, these polymers P1–P3 showed roughly similar optical and electronic bandgaps.

3.3. Theoretical studies

To further understand the geometrical structures and absorption spectra of one repeating unit for these polymers (**P1-P3**), we carried out the density functional theory (DFT) calculations using the Gaussian 09 software package. We optimized the ground state geometries of all polymers at the

B3LYP/6-31G level. The obtained minima are further confirmed by vibrational frequency

calculations at the same level; only the lowest energy conformation is reported here. The optimized geometries are shown in Fig. 3. Table S1 summarizes the dihedral angles of their optimal geometries. Furthermore, calculated dihedral also the average angles between we BDT-thophene-BTZ units to estimate the coplanarity of molecular backbone; the values are 3.0°, 6.7°, and 4.2° between BDT-thophene units and 2.8°, 2.7°, and 0.1° between thophene-BTZ units for P1, P2, and P3, respectively. These results imply that P2 features the most twisted conformation among three polymers. Anchoring the alkyl side chain on thiophene implies more molecular twist between BDT-thiophne, which reduces the coplanarity of polymer backbone. Whereas, the dihedral angles between thiophene-BTZ units are very low and mostly similar, and the coplanarity with the lowest dihedral angle ($\varphi_2 = 0.1^\circ$) of **P3** is induced in the presence of three fluorine-substituted phenyl pendant attached to the BTZ unit.

Using the optimized structures of all these polymers (**P1-P3**) with the B3LYP function, as shown in Figs. 4 and 5 we have plotted the iso-surfaces (iso-value=0.02) of the frontier molecular orbitals (FMOs) for all these polymers. The results show that the molecular orbitals of HOMO and LUMO for all these polymers are predominantly localized in the backbone. The molecular orbitals of the HOMO electronic densities are mainly located on the backbones of these polymers, whereas the contribution to LUMO is mainly from the terminal group of BTZ unit. The detailed analysis of these wavelength absorptions as well as their main contributions to the first excitation can be made on the basis of time-dependent DFT (TDDFT) calculations as collected in Table S1. For the S0 \rightarrow oscillator strengths of 0.853, 0.802, and 0.641, respectively, resulting mainly from the HOMO \rightarrow LUMO transition. All these theoretical calculations are highly supportive to the experimental results.

3.4 Photovoltaic properties

The motivation to design and synthesize these D-A polymers containing BDT and BTZ moieties is to look for new LBG polymers for the application of PSCs. The BHJ photovoltaic devices were fabricated with a configuration of ITO/PEDOT:PSS(40nm)/(**P1–P3**):PC₇₁BM(200nm)(1:2, w/w)/Ca(30nm)/Al(60nm). Fig. 6 showed the current density–voltage (*J–V*) curves for polymers under the condition of AM 1.5G simulated solar illumination at 100 mW/cm². The photovoltaic properties, including the open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and PCE values, of the polymers for PSC devices are summarized in Table 3. The PSC devices based on polymers **P1–P3** showed different V_{oc} values in the range of 0.58–0.72 V, which are related to the differences between the HOMO energy levels of the polymers and the LUMO energy levels of the PC₇₁BM. Comparing photovoltaic properties of **P1–P3**, the PSC device based on **P3** showed the best photovoltaic performance with the highest measured PCE value of 3.00%, with $J_{sc} = 7.70$ mA/cm², *FF* = 54.04, and $V_{oc} = 0.72$ V.

In comparison with **P1**, polymer **P2** with alkyl side chains on thiophene linker has a stronger electron-donating trend to induce a higher oxidation strength of 1.09 V (vs 1.03 V of **P1**) and a deeper lying HOMO level of 5.44 eV (vs 5.38 eV of **P1**).^{[58],[59]} The oxidation potential of polymer **P3** incorporated with the electron-withdrawing BTZ unit showed the highest value of 1.20 V, so **P3**

had the same electron-donating BDT moiety, **P3** with alkyl side chains on thiophene linker and all-fluorine-substituted benzene ring units in BTZ unit has the strongest electron-withdrawing tendency to enhance the oxidation strength (high oxidation state) of the polymer.

Due to the lowest HOMO level of **P3**, its PSC device achieved the largest V_{oc} value of 0.72 V so as to acquire the highest PCE value (3.00%). On the other hand, the PSC device containing **P1** obtained the smallest V_{oc} of 0.58 V and thus to have the lowest PCE value of 1.23% owing to the highest HOMO level of 5.38 eV. The external quantum efficiency (EQE) spectra (matched with absorption properties of all polymers) of PSC devices containing **P1–P3** are demonstrated in Fig. 7, where the PSC device containing **P3** exhibited the highest EQE value about 43 % at 545 nm. This may attributed to the highest efficiency of light absorption for **P3** in the visible region of 400 to 700 nm.

The surface morphological studies of the active layer in PSC devices were investigated by atomic force microscopy (AFM) (tapping mode) to record heights and phase images ($5 \times 5 \mu m^2$) of the polymer blend films (**P1–P3**:PC₇₀BM, 1:2 w/w). The AFM phase (2-D) and height (3-D) graphs of all blended polymer films with PC₇₀BM showed in Figs. 8 and 9, respectively. The root-mean square (RMS) values of roughnesses of **P1**, **P2**, and **P3** measured by the topographic images were 10.22, 8.07, and 8.37 nm, respectively. Due to the highest molecular weight of **P1**, the largest RMS value of 10.22 nm in **P1** indicated the worst solubility with the most large-scaled phase separation, which decreased the film quality and thus to result in the lowest PCE value of 1.23% in the PSC device. The most efficient PSC device with the maximum PCE value of 3.00% was achieved by the active layer of **P3**:PCBM (1:2 w/w) with the medium roughness value of 8.37 nm, which possessed higher roughness and PCE values than its analogous polymer **P2**.

4. Conclusions

In summary, three new conjugated polymers **P1–P3**, which were based on electron-donating BDT and electron-accepting BTZ units containing multiple fluorine-substituted benzene ring along with thiophene linkers with/without alkyl side-chains, were designed and successfully synthesized for BHJ PSCs. All polymers demonstrated good solubilities in common organic solvents and possessed excellent thermal stabilities. The optical properties showed that these new polymers revealed strong π - π stacking and an enhanced absorption-maximum band in solid films due to strong ICT in the polymer backbone. Thus, the optical and electrochemical bandgaps and energy levels of the polymer pendants. Furthermore, among PSC devices fabricated from the active layer of **P1–P3**:PC₇₁BM (1:2, w/w), **P3** illustrated the best photovoltaic properties with the highest PCE value of 3.00%, $J_{sc} = 7.70 \text{ mA/cm}^2$, FF = 54.04, and $V_{oc} = 0.72 \text{ V}$. This work demonstrates that D-A polymer **P3** containing electron-donating BDT and electron-accepting multiple fluorinated BTZ units along with thiophene linkers with alkyl side-chains can enhance the photovoltaic performance of PSC devices. Our study provides a new concept of polymer design towards low bandgap conjugated polymers for the fabrication of efficient BHJ PSCs.

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References

- [1] Yu G, Gao J, Hummelen JC, Wudl F, Heeger AJ. Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor heterojunctions. Science 1995; 270: 1789–91.
- [2] Lu LY, Yu LP. Understanding low-bandgap polymer PTB7 and optimizing polymer solar cells based on it. Adv Mater 2014; 26: 4413–30.
- [3] Li G, Zhu R, Yang Y. Polymer solar cells. Nat Photonics 2012; 6: 153–61.

- [5] Cheng YJ, Yang SH, Hsu CS. Synthesis of conjugated polymers for organic solar cell applications. Chem Rev 2009; 109: 5868–23.
- [6] Deng P, Zhang Q. Recent developments on isoindigo-based conjugated polymers. Polym Chem 2014; 5: 3298–05.
- [7] Sondergaard R, Hosel M, Angmo D, Larsen-Olsen TT, Krebs FC. Roll-to-roll fabrication of polymer solar cells. Mater Today 2012; 15: 36–49.
- [8] Brabec CJ, Gowrisanker S, Halls JJM, Laird D, Jia S, Williams SP. Polymer-fullerene bulk-heterojunction solar cells. Adv Mater 2010; 22: 3839–56.
- [9] Yang X, Chueh CC, Li CZ, Yip HL, Yin P, Chen H, Chen WC, Jen AKY. High-efficiency polymer solar cells achieved by doping plasmonic metallic nanoparticles into dual charge selecting interfacial layers to enhance light trapping. Adv Energy Mater 2013; 3: 666–73.
- [10] Chen M, Fu W. Shi M, Hu Х, Pan J, Ling J, Li Η, Chen H. An ester-functionalized diketopyrrolopyrrole molecule with appropriate energy levels for application in solution-processed organic solar cells. J Mater Chem A 2013; 1: 105–11.
- [11] He ZC, Zhong CM, Su SJ, Xu M, Wu HB, Cao Y. Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure. Nat Photonics 2012; 6: 591–95.

- J, Li G, Yang Y. A polymer tandem solar cell with 10.6% power conversion efficiency. Nat Commun 2013; 4: 1446–56.
- [13] Green MA, Emery K, Hishikawa Y, Warta W, Dunlop ED. Solar efficiency tables.Journal progress in photovoltaics: research and applications 2013; 21: 1–11.
- [14] Bian L, Zhu E, Tang J, Tang W, Zhang F. Recent progress in the design of narrow bandgap conjugated polymers for high-efficiency organic solar cells. Prog Polym Sci 2012; 37: 1292–31.
- [15] Brabec CJ, Heeney M, McCulloch I, Nelson J. Influence of blend microstructure on bulk heterojunction organic photovoltaic performance. Chem Soc Rev 2011; 40: 1185–99.
- [16] Dang D, Zhou P, Peng Q, He K, Jiang H, Yang P, Tan H, Wang Y, Liu Y, Lei G, Zhu W. Improved photovoltaic performance of two-dimensional low-bandgap conjugated polymers with thieno[3,2-b]thiophene and diketopyrrolopyrrole units by altering pendent position of conjugated side chain. Dyes and Pigments 2014; 109: 6–12.
- [17] Zhou P, Dang D, Fan J, Xiong W, Yang C, Tan H, Wang Y, Liu Y, Zhu W. Increasing thiophene spacers between thieno[3,2-b]thiophene and benzothiadiazole units in backbone to enhance photovoltaic performance for their 2-D polymers. Dyes and Pigments 2015; 112: 99–04.

[18] Chen Y, Zhang SQ, Wu Y, Hou JH. Molecular design and morphology control towards

efficient polymer solar cells processed using non-aromatic and non-chlorinated solvents. Adv Mater 2014; 26: 2744–49.

- [19] Yang M, Peng B, Liu B, Zou Y, Zhou K, He Y, Pan C, Li Y. Synthesis and photovoltaic properties of copolymers from benzodithiophene and thiazole. J Phys Chem C 2010; 114: 17989–94.
- [20] Price SC,. Stuart AC, You Y. Low Band Gap Polymers based on benzo[1,2-b:4,5-b']dithiophene: rational design of polymers leads to high photovoltaic performance. Macromolecules 2010; 43: 4609–12.
- [21] Deng P, Lei Y, Wu B, Zheng X, Lu Y, Zhu F, Ong BS. Synthesis, field-effect and photovoltaic properties of random difluorobenzothiadiazole-isoindigo electron donor-acceptor polymers. Dyes and Pigments 2016; 134: 251–57.
- [22] Zhang Y, Zou JY, Cheuh CC, Yip HL, Jen AKY. Significant improved performance of photovoltaic cells made from a partially fluorinated cyclopentadithiophene/benzothiadiazole conjugated polymer. Macromolecules 2012; 45: 5427–35.
- [23] Guo X, Zhang MJ, Cui CH, Hou JH, Li YF. Efficient polymer solar cells based on poly(3-hexylthiophene) and indene– c_{60} bisadduct fabricated with non-halogenated solvents. ACS Appl Mater Interfaces 2014; 6: 8190–98.

solar cells. RSC Adv 2014; 4: 16681–85.

- [25] Chueh CC, Yao K, Yip HL, Chang CY, Xu YX, Chen KS, Li CZ, Liu P, Huang F, Chen YW, Chen WC, Jen AKY, Non-halogenated solvents for environmentally friendly processing of high-performance bulk-heterojunction polymer solar cells. Energy Environ. Sci 2013; 6: 3241–48.
- [26] Ai L, Ouyang XH, Liu QD, Wang SY, Peng RX, Islam A, Ge Z.Y. Effective side chain selection for enhanced open circuit voltage of polymer solar cells based on 2D-conjugated anthracene derivatives. Dyes and Pigments 2015; 115: 73–80.
- [27] Park SH. Bulk heterojunction solar cells with internal quantum efficiency approaching 100%. Nature Photon 2009; 3: 297–02.
- [28] Patra D, Sahu D, Padhy H, Kekuda D, Chu CW, Wei KH, Lin HC. Fine tuning of homo energy levels for low-bandgap photovoltaic copolymers containing cyclopentadithienopyrrole and bithiazole units. Macromol Chem Phys 2011; 212: 1960–70.
- [29] Zhang F, Jespersen KG, Björström C, Svensson M, Andersson MR, Sundström V, Magnusson K, Moons E, Yartsev A, Inganäs O. Influence of solvent mixing on the morphology and performance of solar cells based on polyfluorene copolymer/fullerene blends. Adv Funct Mater 2006; 16: 667–74.

- [30] Chen MH. Efficient polymer solar cells with thin active layers based on alternating polyfluorene copolymer/fullerene bulk heterojunctions. Adv Mater 2009; 21:4238–42.
- [31] Brabec CJ, Shaheen SE, Winder C,. Sariciftci NS, Denk P. Effect of LiF/metal electrodes on the performance of plastic solar cells. Appl Phys Lett 2002; 80: 1288–90.
- [32] Chen HY, Hou J, Zhang S, Liang Y, Yang G, Yang Y, Yu L, Wu Y,Li G. Polymer solar cells with enhanced open-circuit voltage and efficiency. Nat. Photonics 2009; 3: 649–53.
- [33] Singh A,Singh R, Lin CM, Pola MK, Chang CK, Wei KH, Lin HC. Novel fluoride-substituted donor/acceptor polymers containing benzodithiophene and quinoxaline units for use in low-band gap solar cells. European Polymer Journal 2016; xxx: xxx-xxx.
- [34] Wong S, Ma H, Jen AKY, Barto R, Frank CW. Highly fluorinated trifluorovinyl aryl ether monomers and perfluorocyclobutane aromatic ether polymers for optical waveguide applications. Macromolecules 2003; 36: 8001–07.
- [35] Cher KR, Suss HI, Hulliger J. Fluorine in crystal engineering—"the little atom that could". Chem Soc Rev 2005; 34: 22–30.
- [36] Pagliaro M, Ciriminna R. New fluorinated functional materials. J Mater Chem 2005; 15: 4981–91.
- [37] Babudri F, Farinola GM, Naso F, Ragni R. Fluorinated organic materials for electronic and optoelectronic applications: the role of the fluorine atom. Chem Commun 2007; 1003–22.

Weinheim; 2004.

- [39] Wang Y, Parkin SR, Gierschner J, Watson MD. Highly fluorinated benzobisbenzothiophenes. Org Lett 2008; 10: 3307–10.
- [40] Pasker FM, Klein MFG, Sanyal M, Barrena E, Lemmer U, Colsmann A, Höger S. Photovoltaic response to structural modifications on a series of conjugated polymers based on 2-aryl-2h-benzotriazoles. J Polym Sci Part A: Polym Chem 2011; 49: 5001–11.
- [41] Klein MFG, Pasker FM, Kowarik S, Landerer D, Pfaff M, Isen M, Gerthsen D, Lemmer U, Hoger S, Colsmann A. Carbazole–phenylbenzotriazole copolymers as absorber material in organic solar cells. Macromolecules 2013; 46: 3870–78.
- [42] Kranthiraja K, Gunasekar K, Chakravarthi N, Song M, Moon JH, Lee JY, Kang IN, Jin SH. Synthesis and characterization of alkoxyphenylthiophene substituted benzodithiophene-based 2D conjugated polymers for organic electronics applications. Dyes and Pigments 2015; 123: 100–111.
- [43] Dong Y, Hu X, Duan C, Liu P, Liu S, Lan L, Chen D, Ying L, Su S, Gong X, Huang F, Cao Y. A series of new medium-bandgap conjugated polymers based on naphtho[1,2-c:5,6-c]bis(2-octyl-[1,2,3]triazole) for high-performance polymer solar cells. Adv Mater 2013; 25: 3683–88.

[44] Zhou H, Yang L, Stuart AC, Price SC, Liu S, You W. Development of fluorinated

benzothiadiazole as a structural unit for a polymer solar cell of 7 % efficiency. Angew Chem Int Ed 2011; 50: 2995–98.

- [45] Price SC, Stuart AC, Yang L, Zhou H, You W. Fluorine substituted conjugated polymer of medium band gap yields 7% efficiency in polymer–fullerene solar cells. J Am Chem Soc 2011; 133: 4625–31.
- [46] Liu L, Zhang Lipeng, Li M, Guo Y, Song J, Wang H. Random dithienosilole-based terpolymers: synthesis and application in polymer solar cells. Dyes and Pigments 2016; 130: 63–69.
- [47] Jiang JM, Raghunath P, Lin YC, Lin HK, Ko CL, Su YW, Lin MC, Wei KH. Linear solubilizing side chain substituents enhance the photovoltaic properties of two-dimensional conjugated benzodithiophene-based polymers. Polymer 2015; 79: 262–70.
- [48] JiangJM, Raghunath P, Lin HK, Lin YC, Lin MC, Wei KH. Location and number of selenium atoms in two-dimensional conjugated polymers affect their bandgap energies and photovoltaic performance. Macromolecules 2014; 47: 7070–80.
- [49] Patra D, Huang TY, Chiang CC, Maturana ROV, Pao CW, Ho KC, Wei KH, Chu CW. 2-alkyl-5-thienyl-substituted benzo[1,2-b:4,5-b]dithiophene-based donor molecules for solution-processed organic solar cells. ACS Appl Mater Interfaces 2013; 5: 9494–00.
- [50] Lang C, Fan J, Gao Y, Liu M, Zhang Y, Guo F, Zhao L. Synthesis, characterization and

Pigments 2017; 137: 50–57.

- [51] Li M, Liu L, Zhao C, Zhou Y, Guo Y, Song Jinsheng, Hua Wang. Side chain engineering of dithienosilole-based polymers for application in polymer solar cells. Dyes and Pigments 2016; 134: 480–486.
- [52] Xu Z, Luo G, Yu J, Yin X, Zhu E, Zhang F, Wu H, Tang W. Side-chain manipulation on accepting units of two-dimensional benzo[1,2-b:4,5-b']dithiophene polymers for organic photovoltaics. Polym Chem 2016; 7:1486–93.
- [53] Li KC, Huang JH, Hsu YC, Huang PJ, Chu CW, Lin JT, Ho KC, Wei KH, Lin HC. Tunable novel cyclopentadithiophene-based copolymers containing various numbers of bithiazole and thienyl units for organic photovoltaic cell applications. Macromolecules 2009; 42: 3681–93.
- [54] Wettach H, Pasker F, Hoger S. 2-aryl-2h-benzotriazoles as building blocks for new low-bandgap poly(arylene–ethynylene)s. Macromolecules 2008; 41: 9513–15.
- [55] Hou J, Park MH, Zhang S, Yao Y, Chen LM, Li JH, Yang Y. Bandgap and molecular energy level control of conjugated polymer photovoltaic materials based on benzo[1,2-b:4,5-b']dithiophene. Macromolecules 2008; 41: 6012–18.
- [56] Zhao J, Li Y, Hunt A, Zhang J, Yao H, Li Z, Zhang J, Huang F, Ade H, Yan He. A difluorobenzoxadiazole building block for efficient polymer solar cells. Adv Mater 2016; 28: 1868–1873.

[57] Hedström S, Henriksson P, Wang E, Andersson MR, Persson Petter . Temperature-dependent

optical properties of flexible donor-acceptor polymers. J Phys Chem C 2015; 119: 6453-6463.

- [58] Zhou H, Yang L, Xiao S, Liu S, You W. Donor-acceptor polymers incorporating alkylated dithienylbenzothiadiazole for bulk heterojunction solar cells: pronounced effect of positioning alkyl chains. Macromolecules 2010; 43: 811–820 811.
- [59] Najari A, Beaupré S, Berrouard P, Zou Y, Pouliot J-R, Pérusse CL, Leclerc M. Synthesis and characterization of new thieno[3,4-c] pyrrole-4,6-dione derivatives for photovoltaic applications. Adv Funct Mater 2011; 21: 718–728.

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Schemes and List of Figures

Scheme 1. Synthesis routes of the monomers M1–M3 and polymers P1–P3.

Fig. 1. Normalized UV–vis absorption spectra of P1–P3 (a) in dilute chloroform solutions (10^{-6} M) and (b) in solid films.

Fig. 2. Cyclic voltammograms of **P1–P3** in solid films measured at a 100 mV s⁻¹ (in a 0.1 M solution of TBAPF₆ in acetonitrile).

Fig. 3. Optimized geometries of one repeating unit for polymers (a) **P1** (b) **P2**, and (c) **P3**, respectively (calculated by using B3LYP/6-31G level).

Fig. 4. Frontier molecular orbital distributions of one repeating unit for HOMO levels of polymers (a)

P1, (b) P2, and (c) P3, respectively.

Fig. 5. Frontier molecular orbital distributions of one repeating unit for LUMO levels of polymers (a)

P1, (b) P2, and (c) P3, respectively.

Fig. 6. J-V curves E spectra of **P1–P3**:PC₇₁BM (1:2, w/w) for PSCs under AM 1.5 G simulated solar illumination at 100 mW cm⁻².

Fig. 7. EQE spectra of **P1–P3**:PC₇₁BM (1:2, w/w) for PSCs under AM 1.5 G simulated solar illumination at 100 mW cm⁻².

Fig. 8. 2-D AFM images of blends of the polymers (a) P1 (b) P2, and (c) P3 with $PC_{71}BM$ (1:2, w/w); image size: $5 \times 5 \mu m^2$.

Fig. 9. 3-D AFM images of blends of the polymers (a) P1 (b) P2, and (c) P3 with $PC_{71}BM$ (1:2, w/w); image size: 5 × 5 μ m².

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polymer	M_n^a (g mol ⁻¹)	$M_{\rm w}^{\ a} ({\rm g \ mol}^{-1})$	$\text{PDI}^a (M_w/M_n)$	$T_{\rm d}^{\ b} (^{\rm o}{\rm C})$		
P1	32400	44700	1.3	391		
P2	17100	19300	1.1	368		
Р3	16300	21900	1.3	381		

Table 1 Molecular weights and thermal properties of P1–P3.

^aDetermined by GPC using polystyrene standard and THF as an eluent.

^b5% weight loss measured by TGA at a heating rate of 10 °C min⁻¹ under nitrogen.

Table 2 Optical and electrochemical properties of P1–P3.

polymer	$\lambda_{ m max,abs}$ (nm)		$E_{\mathrm{g,opt}}^{d}$	$E_{\mathrm{ox,onset}}^{e}(\mathbf{V})/$	$E_{\rm red,onset}^{e}$ (V)/	$E_{\rm g,CV}^{f}$
	solution ^a	film ^b	(eV)	HOMO (eV)	LUMO (eV)	(eV)
P1	517	568	1.79	1.03/-5.38	-0.80/-3.55	1.83
P2	505	582	1.77	1.09/-5.44	-0.85/-3.50	1.94
P3	524	576, 619 ^c	1.81	1.20/-5.60	-0.78/-3.57	2.03

^a Diluted chloroform solutions (10⁻⁶ M).

^b Solid film spin-cast on a glass substrate from chloroform solution.

^c Shoulder peak.

^d Calculated from the absorption band edge of the polymer films, $E_{g,opt} = 1240/\lambda_{edge}$.

^e Measured using CV.

^f Calculated from the HOMO and LUMO energy levels.

Table 3 Photovoltaic properties of PSC devices^{a,b,c} containing P1–P3:PC₇₁BM(1:2,w/w).

polymer	V _{oc} (V)	$J_{\rm sc}~({\rm mA/cm}^2)$	FF	PCE (%)
P1	0.58	4.93	43.0	1.23
P2	0.65	5.33	51.4	1.78
Р3	0.72	7.70	54.0	3.00

^aDevice fabricated with a configuration of ITO/PEDOT:PSS/(**P1–P3**):PC₇₁BM/Ca/Al.

^bSpin-coated from TCB solution.

^cMeasured under AM 1.5G simulated solar illumination at 100 mW/cm².













P3











Highlights

- A series of low–band gap conjugated polymers **P1-P3** have been synthesized.
- All polymers exhibited good solubility in common organic solvents.
- Fluorinated BTZ units play important roles in ICT and photovoltaic performance.
- Optical and electronic energy levels could be tuned.
- Polymer **P3** exhibited the highest PCE value of 3.00% with PC₇₁BM.