Electronic Supplementary Information

Alkylthiazole-based Semicrystalline Polymer Donors for Fullerene-free Organic Solar Cells

Junho Kim,a† Jinhyeon Kang,a† Ye-Seul Park,a Hyungju Ahn,b Seung Hun Eom,c Sung-Yeon Jang,*d and In Hwan Jung*a

a Department of Chemistry, Kookmin University, 77 Jeongneung-ro, Seongbuk-gu, Seoul 02707, Republic of Korea. ihjung@kookmin.ac.kr (I. H. J.)

b Pohang Accelerator Laboratory, POSTECH, Pohang, 37673 Republic of Korea

c Division of Advanced Materials, Korea Research Institute of Chemical Technology (KRICT), Daejeon 34114, Republic of Korea.

d School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 44919, Republic of Korea. E-mail: syjang@unist.ac.kr
EXPERIMENTAL SECTION

Synthesis of OTz

1-Bromodeca-2-one: 2-Decanone (10 g, 63.99 mmol) and urea (6.38 g, 106.23 mmol) were dissolved in glacial acetic acid (50 mL). The reaction mixture was stirred at room temperature for 15 min. A solution of bromine in glacial acetic acid (20 mL) was added dropwise to the reaction mixture, and the resultant mixture was stirred overnight at room temperature. Water was then added to the reaction mixture, which was twice worked up with dichloromethane, 10% sodium bicarbonate, and water. The organic phase was dried over anhydrous MgSO₄, and the solvent was removed by evaporation under reduced pressure. After the solvent was evaporated, the crude product was obtained as a yellow liquid. This product was used without further purification.

1-Thiocyanatodecan-2-one: Potassium thiocyanate (1.98 g, 20.41 mmol) was added to a solution of 1-bromodeca-2-one (4 g, 17.00 mmol) in ethanol (50 mL) and stirred at room temperature overnight. The reaction mixture was worked up with ethyl acetate and water. The organic phase was dried over anhydrous MgSO₄, and the solvent was removed by evaporation under reduced pressure. After the solvent was evaporated, the crude product was obtained as a yellow liquid. This product was used without further purification.

2-Bromo-4-octylthiazole (1): 1-Thiocyanatodecan-2-one (3.50 g, 16.4 mmol) was added to a 33% solution of HBr in AcOH (42 mL) and stirred overnight at room temperature. The reaction mixture was carefully neutralized with NaOH using an ice bath. The mixture was worked up with dichloromethane and water. The organic phase was dried over anhydrous MgSO₄, and the solvent was removed by evaporation under reduced pressure. After the solvent was evaporated, the residue was purified by column chromatography on silica gel (methylene chloride (MC): hexane = 3:2 v/v) to obtain as a brown oil (3.3 g, yield: 73%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 6.82 (s, 1H), 2.72 (t, J = 8.0 Hz, 2H), 1.66 (m, 2H), 1.28 (m, 10H), 0.87 (t, J = 8.0 Hz,
2,5-Bis(4-octylthiazol-2-yl)thiophene (3): 2-Bromo-4-octylthiazole (1) (1.43 g, 6.1 mmol), 2,5-bis(trimethylstannyl)thiophene (2) (1 g, 2.44 mmol), Pd$_2$(dba)$_3$ (65 mg, 0.07 mmol), and tri(ortolyl)phosphine (74 mg, 0.24 mmol) were dissolved in N$_2$-sparged toluene (40 mL). After the reaction mixture was refluxed at 110 °C for 48 h, it was cooled to room temperature and extracted with dichloromethane and water. The organic phase was dried over anhydrous MgSO$_4$, and the solvent was removed by evaporation under reduced pressure. After the solvent was evaporated, the residue was purified by column chromatography on silica gel (MC: hexane = 2:3 v/v) to give a brown oil (0.88 g, yield: 79%). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm): 7.46 (s, 2H), 6.85 (s, 2H), 2.80 (t, $J$ = 8.0 Hz, 2H), 1.75 (m 2H), 1.35 (m, 10H), 0.91 (t, $J$ = 8.0 Hz, 3H).

2,5-Bis(5-bromo-4-octylthiazol-2-yl)thiophene (4): 2,5-Bis(4-octylthiazol-2-yl)thiophene (3) (1 g, 2.1 mmol) and NBS (0.94 g, 5.3 mmol) were dissolved in dimethylformamide (DMF) (60 mL) and stirred at room temperature overnight. The reaction mixture was then poured into water. The organic phase was extracted with dichloromethane and water and dried over anhydrous MgSO$_4$. The solvent was removed by evaporation under reduced pressure. After the solvent was evaporated, the residue was purified by column chromatography on silica gel (MC: hexane = 1:2 v/v). The resulting product was recrystallized using MC and MeOH to give a pure yellow solid (1.1 g, 83%). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm): 7.20 (s, 2H), 2.66 (t, $J$ = 8.0 Hz, 2H), 1.65 (m, 2H), 1.25 (m, 10H), 0.82 (t, $J$ = 8.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm): 159.88, 157.22, 138.74, 126.64, 103.81, 32.02, 29.85, 29.55, 29.50, 29.35, 28.85, 22.83, 14.28.
Polymerization

2,5-Bis(5-bromo-4-octylthiazol-2-yl)thiophene (4) (0.3 mmol), BDT derivatives (0.3 mmol), and palladium catalyst, Pd(PhH)₄ (0.009 mmol), were added to a 25 mL two-necked round-bottom flask under a nitrogen atmosphere. The mixture was dissolved in N₂-sparged toluene (7 mL), stirred at 110 °C for 24 h, and then cooled to room temperature. The polymer was subsequently precipitated by addition of methanol (200 mL) and filtered through a Soxhlet thimble. The precipitate was purified by Soxhlet extraction with acetone, hexane, and chloroform. The polymer was recovered as a solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum.

PTBOTz: OTz (190 mg, 0.3 mmol), (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (271 mg, 0.3 mmol), and Pd(PPh₃)₄ (11 mg, 0.009 mmol) were used for Stille polymerization. Yield: 289 mg (92%). Anal. calcd. for C₆₀H₇₆N₂S₇: C, 68.65; H, 7.30; N, 2.67; S, 21.38. Found: C, 67.92; H, 7.29; N, 2.87; S, 21.52.

POBOTz: OTz (190 mg, 0.3 mmol), (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (232 mg, 0.3 mmol), and Pd(PPh₃)₄ (11 mg, 0.009 mmol) were used for Stille polymerization. Yield: 215 mg (78%). Anal. calcd. for C₅₂H₇₂N₂O₂S₅: C, 68.09; H, 7.92; N, 3.06; O, 3.49; S, 17.44. Found: C, 67.74; H, 7.92; N, 3.22; S, 17.02.

PSBOTz: OTz (190 mg, 0.3 mmol), (4,8-bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (291 mg, 0.3 mmol), and Pd(PPh₃)₄ (11 mg, 0.009 mmol) were used for Stille polymerization. Yield: 318 mg (95%). Anal. calcd. for C₆₀H₇₆N₂S₉: C, 64.73; H, 6.89; N, 2.52; S, 25.87. Found: C, 64.04; H, 6.81; N, 2.69; S, 26.83.
**Device fabrication:** Each indium-doped tin oxide (ITO) substrate was cleaned for 20 min by sonication in acetone, distilled water (DW), and ethanol. Bulk heterojunction (BHJ) OSCs were fabricated using an inverted structure (ITO/ZnO/BHJ/MoO$_3$/Ag). First, ZnO was prepared via a sol–gel process as the electron transport layer. For the precursor solution used in the ZnO sol–gel synthesis, 0.45M zinc acetate dihydrate ($\text{Zn}(\text{Ac})_2\cdot2\text{H}_2\text{O}$, Sigma-Aldrich) and ethanolamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$, Sigma-Aldrich) were dissolved in 2-methoxyethanol under vigorous stirring for 3 h at 60°C. The ITO substrates were subjected to a UV–O$_3$ treatment for 20 min. The ZnO precursor solution was spin-coated onto the treated ITO substrates at 2000 rpm for 30 s. The ZnO-coated ITO substrates were then placed onto a hotplate at room temperature and heated to 220 °C. When the target temperature was reached, the substrates were immediately removed from the hot plate to cool. For the preparation of the BHJ layer, each donor and IDIC were dissolved in chloroform at a mass ratio of 1:1.4. The concentration at this time was 10 mg mL$^{-1}$ based on the donor material. A 1 vol% solution of 1,8-diiodooctane (DIO, TCI) was used as an additive. The mixtures were stirred at 40 °C for 3 h in a N$_2$-filled glove box, and the objected BHJ solutions were subsequently spin-coated onto the ZnO-coated ITO substrates at 4500 rpm for 30 s. The 8 nm MoO$_3$ and 100 nm of Ag were deposited by thermal evaporation (base pressure $< 10^{-6}$ Torr) as hole-blocking layer and electrode, respectively.

**General Characterizations:** $^1$H NMR spectra were recorded at 25°C on a Bruker Ascend TM-400 spectrometer, with tetramethylsilane as an internal reference in CDCl$_3$. The absorption spectra were recorded on a SHIMADZU/UV-2550 model UV–vis spectrophotometer. Cyclic voltammetry was performed at a scan rate of 30 mV s$^{-1}$ on a BASi 100B/W electrochemical
analyzer with a three-electrode cell with 0.1 N Bu₄NBF₄ solution in acetonitrile. The polymer film was coated onto a working electrode by dipping the electrode into a polymer solution in chloroform. All measurements were calibrated against an internal standard of ferrocene (Fc), the ionization potential (IP) of which is −4.8 eV for the Fc/Fc⁺ redox system. GPC was conducted at 145 °C using o-dichlorobenzene as the eluent.

**Device analysis:** The \( J-V \) characteristics of the OSCs were measured using a Keithley 2401 instrument and a solar simulator with a 150 W (Newport) light source. The light intensity was adjusted using a KG-5 filter-covered monosilicon detector calibrated by the National Renewable Energy Laboratory (NREL). The EQE spectra were obtained by passing 400 W Xe lamplight through a monochromator using a filter of appropriate wavelength (McScience, K3100 IQX). The chopping frequency (i.e., 100 Hz) was measured from 300 to 950 nm. The space–charged-limit current (SCLC) was used to calculate the charge mobility of the active layers. All SCLC measurements were carried in the dark condition. An electron-only device (ITO/ZnO/active layer/ZnO/Ag) and a hole-only device (ITO/PEDOT:PSS/active layer/MoOₓ/Ag) were fabricated for measurement of the hole and electron mobilities, respectively. The mobility was calculated via the Mott–Gurney law in an SCLC trap-free regime. Cross-sectional images of the devices were obtained by field-emission scanning electron microscopy (FE-SEM) (JEOL JSM-7401F, JEOL, Ltd.). TEM images were obtained on a JEM-2100F (JEOL, Ltd.).

**Two-dimensional grazing-incidence X-ray diffraction (2D-GIXD) experiments:** 2D-GIXD measurements were performed under vacuum at the PLS-II 9A beamline of the Pohang
Accelerator Laboratory in Korea. The samples were prepared on ZnO-modified Si substrates under the same conditions as those used for the fabrication of solar-cell devices. The wavelength of the X-ray was 0.1120 nm, and the incidence angle was 0.12°. The 2D-GIXD patterns were recorded using a 2D-CCD detector (MX225-HS, Rayonix LLC, USA); the X-ray irradiation time was 10 s.
Scheme S1. Synthesis procedure for the OTz compound and the polymers containing the OTz moiety. Reaction conditions: i) urea, Br$_2$, GAA, r.t.; ii) KSCN, ethanol, r.t.; iii) HBr, acetic acid, r.t.;

Scheme S2. Estimated cost for PTBOTz
Figure S1. $^1$H NMR spectrum of compound 1.
Figure S2. $^1$H NMR spectrum of compound 3.
Figure S3. $^1$H NMR spectrum of compound 4 (OTz).
Figure S4. $^1$H NMR spectrum of PTBOTz.
Figure S5. $^1$H NMR spectrum of POBOTz.
Figure S6. $^1$H NMR spectrum of PSBOTz.
Figure S7. Thermogravimetric analysis curves of PTBOTz, POBOTz, and PSBOTz.
Figure S8. Optimized molecular structures calculated by the DFT method at the B3LYP/6-31G(d,p) level.
Figure S9. UPS spectra of PTBOTz, POBOTz and PSBOTz film at (a) the onset ($E_F$) and high binding energy cutoff ($E_{cut}$) region.
Figure S10. $J-V$ characteristics of PTBOTz:IDIC photovoltaic devices at different weight ratios (w/w) between PTBOTz and IDIC.
Figure S11. $J$–$V$ characteristics of PTBOTz:IDIC photovoltaic devices fabricated at different spin-coating speeds.
Figure S12. Average values of photovoltaic parameters, PCE, $J_{\text{SC}}$, $V_{\text{OC}}$ and FF of 10 devices
Figure S13. $J-V$ characteristics of hole-only devices (ITO/PEDOT:PSS/pristine polymer film/MoO$_x$/Ag) of PTBOTz, POBOTz and PSBOTz.
Figure S14. Cross-sectional SEM images of PTBOTz, POBOTz, and PSBOTz.
Figure S15. Thermal stability of the devices at 85°C in glove box (O_2, 50–60 ppm).