Supporting Information

Molecular Engineering on Bis(Benzothiophene-S,S-Dioxide)-Based Large-Band Gap Polymers for Interfacial Modifications in Polymer Solar Cells

Guiting Chen,†,§,∥ Gaoheng Qian,†,∥ Shuwang Yi,† Zhicai He,*† Hong-Bin Wu,† Wei Yang,† Bin Zhang,*†,‡ Yong Cao†

†Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China.

‡Jiangsu Engineering Laboratory of Light-Electricity-Heat Energy-Converting Materials and Applications, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, School of Materials Science and Engineering, Changzhou University, Changzhou 213164, P. R. China.

§School of Chemistry and Environment, Jiaying University, Meizhou, 514015, P. R. China.

*Corresponding author. E-mail: zhicaihe@scut.edu.cn (Zhicai He);
msbinzhang@outlook.com (Bin Zhang)

Experimental Section

1. Synthesis
4-Bromo-2-ethylsulfanyl-1-iodo-benzene (1). 4-Bromo-2-fluoro-1-iodo-benzene (47.0 g, 156 mmol), ethanethiol (9.68 g, 156 mmol), K$_2$CO$_3$ (43.0 g, 312 mmol) and 200 mL of DMF were mixed under N$_2$. The reaction was heated to 100 °C and stirred overnight. After being cooled to room temperature, 300 mL of distilled water was added. The mixture was extracted with CH$_2$Cl$_2$ for three times. The combined organic layer was washed with distilled water and brine before dried over anhydrous MgSO$_4$. The organic solvent was distilled and the crude product was purified by column chromatography to afford 1 as colorless oil (47.6 g, 89%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 7.63-7.61 (d, $J = 10$ Hz, 1H), 7.24 (s, 1H), 6.98-6.96 (d, $J = 10$ Hz, 1H), 2.97-2.93 (q, $J = 6.7$ Hz, 2H), 1.41-1.39 (t, $J = 5$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$, δ): 144.55, 140.51, 129.26, 128.66, 122.93, 96.25, 28.04, 13.19.

4-Bromo-2-ethanesulfinyl-1-iodo-benzene (2). Compound 1 (34.3 g, 100 mmol) was dissolved in 200 mL of AcOH, after which 30% aqueous solution of H$_2$O$_2$ (11.3 mL, 100 mmol) was added dropwise at 0 °C. Then the mixture was stirred at room temperature overnight. 400 mL of distilled water was poured into the reaction, and the precipitate was collected via filtration. The crude product was purified by column chromatography to afford 2 as a white solid (27.6 g, 77%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 7.92-7.91 (d, $J = 5$ Hz, 1H), 7.67-7.65 (d, $J = 10$ Hz, 1H), 7.35-7.33 (dd, $J = 7.5$ Hz, $J = 2.5$ Hz, 1H), 3.13-3.09 (m, 1H), 2.84-2.80 (m, 1H), 1.31-1.28 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$, δ): 147.95, 140.65, 135.60, 130.14, 124.14, 89.51, 47.84, 6.06.

2,7-Bis(4-bromo-2-(ethanesulfinyl)phenyl)-9,9-bis(4-(2-ethylhexyloxy)phenyl)fl
**uorene (5).** Compound 4 (20.0 g, 24.2 mmol), 2 (26.1 g, 72.6 mmol), K$_2$CO$_3$ aqueous solution (2 M, 36.3 mL), Pd(PPh$_3$)$_4$ (2.80 g, 2.42 mmol) and 200 mL of THF were mixed together under argon. The reaction was heated to 70 °C and stirred for 24 h with argon protection. Then the THF was distilled and 200 mL of distilled water was added. The aqueous layer was extracted with CH$_2$Cl$_2$ for three times. The combined organic layer was washed with distilled water and brine before dried over anhydrous MgSO$_4$. The organic solvent was distilled and the crude product was purified by column chromatography to afford 5 as colorless oil (15.3 g, 61%). $^1$H NMR (500 MHz, CDCl$_3$, δ): 8.10 (s, 2H), 7.85-7.83 (d, $J = 10$ Hz, 2H), 7.62-7.60 (d, $J = 10$ Hz, 2H), 7.38-7.37 (m, 2H), 7.34-7.31 (m, 2H), 7.20-7.18 (d, $J = 10$ Hz, 2H), 7.13-7.01 (m, 4H), 6.82-6.67 (m, 4H), 3.76-3.72 (m, 4H), 1.85-1.82 (m, 4H), 1.70-1.62 (m, 2H), 1.42-1.24 (m, 18H), 0.91-0.83 (m, 16H). $^{13}$C NMR (75 MHz, CDCl$_3$, δ): 158.49, 153.26, 153.22, 143.38, 139.39, 138.31, 136.72, 136.33, 133.74, 131.84, 128.83, 128.80, 128.36, 127.63, 126.72, 123.03, 121.16, 114.33, 67.95, 64.48, 47.02, 39.36, 30.48, 29.06, 23.80, 23.02, 14.07, 11.08, 5.97. Anal. calcd for C$_{57}$H$_{64}$Br$_2$O$_4$S$_2$: C 66.01, H 6.22; found: C 65.69, H 6.48, S 6.55.

**9,9-Bis(4-(2-ethylhexyloxy)phenyl)fluorene-bis[2,3-b;6,7-b]3-bromo-benzo[b]thiophene (6).** Compound 5 (7.00 g, 6.75 mmol) was mixed with 150 mL of CF$_3$COOH and P$_2$O$_5$ (2.00 g, 14.1 mmol) at 0 °C. The reaction was stirred at room temperature for 24 h. After being mixed with 300 mL of distilled water, the precipitate was collected via filtration. The solid was dissolved in 150 mL of pyridine, which was heated to 120 °C and stirred overnight. The cooled solution was neutralized with
diluted aqueous solution of HCl, followed by extraction with CH$_2$Cl$_2$ for three times. The combined organic layer was washed with distilled water and brine before dried over anhydrous MgSO$_4$. The organic solvent was distilled and the crude product was purified by column chromatography to afford 6 as a white solid (3.70 g, 58%). $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 8.23 (s, 2H), 8.06 (s, 2H), 7.95 (s, 2H), 7.90-7.88 (d, $J = 10$ Hz, 2H), 7.51-7.49 (dd, $J = 7.5$ Hz, $J = 2.5$ Hz, 2H), 7.25-7.23 (d, $J = 10$ Hz, 4H), 6.80-6.78 (d, $J = 10$ Hz, 4H), 3.78-3.77 (d, $J = 5$ Hz, 4H), 1.69-1.64 (m, 2H), 1.28-1.26 (m, 12H), 0.89-0.85 (m, 16H). $^{13}$C NMR (75 MHz, CDCl$_3$, $\delta$): 153.61, 145.57, 136.66, 134.37, 134.35, 133.07, 130.32, 129.59, 124.44, 122.98, 120.67, 117.98, 115.53, 114.40, 109.56, 109.52, 65.57, 58.88, 34.63, 25.76, 24.32, 19.09, 18.28, 9.33, 6.36. Anal. calcd for C$_{53}$H$_{52}$Br$_2$O$_2$S$_2$: C 67.37, H 5.55, S 6.79; found: C 67.08, H 5.70, S 6.69.

9,9-Bis(4-(2-ethylhexyloxy)phenyl)fluorene-bis[2,3-b;6,7-b]-3-bromo-benzo[b]thiophene-$S,S$-dioxide (7). Compound 6 (4.73 g, 5.01 mmol) was dissolved in 50 mL of CH$_2$Cl$_2$. Then m-CPBA (3.81 g, 22.0 mmol) was added slowly at 0 °C. The mixture was allowed to be warmed to room temperature and stirred overnight. The reaction was washed with diluted aqueous solution of NaOH for three times, followed by being dried over anhydrous MgSO$_4$. The organic solvent was distilled and the crude product was purified by column chromatography to afford 7 as a white solid (4.15 g, 82%). $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 8.25 (s, 2H), 7.93-7.92 (d, $J = 5$ Hz, 2H), 7.71 (s, 2H), 7.70-7.68 (d, $J = 10$ Hz, 2H), 7.58-7.56 (d, $J = 10$ Hz, 2H), 7.16-7.14 (d, $J = 10$ Hz, 4H), 6.85-6.84 (d, $J = 5$ Hz, 4H), 3.81-3.80 (d, $J = 5$ Hz, 4H), 1.71-1.66 (m,
2H), 1.30-1.26 (m, 12H), 0.91-0.86 (m, 16H). $^{13}$C NMR (75 MHz, CDCl$_3$, δ): 159.08, 159.05, 140.43, 139.71, 137.66, 136.82, 134.10, 131.62, 130.25, 129.04, 125.54, 124.42, 123.11, 119.24, 115.04, 114.89, 70.44, 64.97, 39.32, 30.47, 29.04, 23.80, 23.00, 14.07, 11.09. Anal. calcd for C$_{53}$H$_{52}$Br$_2$O$_6$S$_2$: C 63.09, H 5.19, S 6.36; found: C 62.78, H 5.32, S 6.55.

9,9-Bis(4-hydroxyphenyl)fluorene-bis[2,3-b;6,7-b]-3-bromo-benzo[b]thiophene-$S,S$-dioxide (8). Compound 7 (3.00 g, 2.97 mmol) was dissolved in 50 mL of CH$_2$Cl$_2$, after which BBr$_3$ (2.24 g, 8.91 mmol) was added slowly at 0 °C. The reaction was allowed to be warmed to room temperature and stirred overnight. 100 mL of distilled water was added slowly, followed by distillation of the organic solvents and filtration. The solid was collected and washed with hot water for three times to afford crude 8 (2.0 g). The crude product was used to synthesize 9 without further purification due to its poor solubility in organic solvents.

9,9-Bis(4-(6-bromo-hexyloxy)phenyl)fluorene-bis[2,3-b;6,7-b]-3-bromo-benzo[b]thiophene-$S,S$-dioxide (9). Compound 8 (2.00 g), hexamethylene dibromide (1.87 g, 7.65 mmol), 30 mL of THF, 15 mL of DMSO, 5 mL of ethanol and NaOH (0.612 g, 15.3 mmol) were mixed under nitrogen. The reaction was heated to 80 °C and stirred overnight. After being cooled to room temperature, 50 mL of distilled water was poured into the reaction. The aqueous layer was extracted with CH$_2$Cl$_2$ for three times. The combined organic layer was washed with distilled water and brine before dried over anhydrous MgSO$_4$. The organic solvent was distilled and the crude product was purified by column chromatography to afford 9 as a white solid (1.98 g, 70%). $^1$H
NMR (500 MHz, CDCl₃, δ): 8.21 (s, 2H), 7.95 (s, 2H), 7.73-7.71 (d, J = 10 Hz, 2H), 7.68 (s, 2H), 7.59-7.57 (d, J = 10 Hz, 2H), 7.13-7.11 (d, J = 10 Hz, 4H), 6.82-6.81 (d, J = 5 Hz, 4H), 3.93-3.90 (t, J = 7.5 Hz, 4H), 3.41-3.38 (t, J = 7.5 Hz, 4H), 1.89-1.84 (m, 4H), 1.78-1.75 (m, 4H), 1.48-1.45 (m, 4H), 1.36-1.26 (m, 4H). ¹³C NMR (75 MHz, CDCl₃, δ): 159.01, 158.78, 140.39, 139.76, 137.74, 136.90, 134.26, 131.71, 130.24, 129.06, 125.60, 124.51, 123.13, 119.22, 114.90, 67.81, 64.95, 33.79, 32.61, 28.99, 27.84, 25.27. Anal. calcd for C₄₉H₄₂Br₄O₆S₂: C 52.99, H 3.81, S 5.77; found: C 52.66, H 3.60, S 6.00.

9,9-Bis(4-(6-(N,N-diethylamino)hexyloxy)phenyl)fluorene-bis[2,3-b;6,7-b]3-bromo-benzo[b]thiophene-S,S-dioxide (10). Compound 9 (1.11 g, 0.999 mmol) and 10 mL of DMF were mixed, after which K₂CO₃ (1.10 g, 7.99 mmol) and diethylamine (0.438 g, 5.99 mmol) was added. The reaction was heated to 100 °C and stirred overnight. After being cooled to room temperature, 30 mL of distilled water was poured into the mixture. The aqueous layer was extracted with CH₂Cl₂ for three times. The combined organic layer was washed with distilled water and brine before dried over anhydrous MgSO₄. The organic solvent was distilled and the crude product was purified by column chromatography to afford 10 as a white solid (0.941 g, 86%). ¹H NMR (500 MHz, CDCl₃, δ): 8.20 (s, 2H), 7.95 (s, 2H), 7.74-7.72 (d, J = 10 Hz, 2H), 7.70 (s, 2H), 7.61-7.60 (d, J = 5 Hz, 2H), 7.13-7.11 (d, J = 10 Hz, 4H), 6.82-6.80 (d, J = 10 Hz, 4H), 3.92-3.90 (t, J = 5 Hz, 4H), 2.88-2.86 (m, 8H), 2.74-2.71 (m, 4H), 1.77-1.74 (m, 4H), 1.31-1.28 (m, 24H). ¹³C NMR (75 MHz, CDCl₃, δ): 159.05, 158.72, 140.37, 139.73, 137.72, 136.95, 134.28, 131.73, 130.24, 129.08, 125.56,
124.50, 123.25, 119.29, 114.91, 112.68, 67.71, 64.96, 51.88, 46.50, 29.33, 28.96, 26.88, 25.75, 9.48. Anal. calcd for C\textsubscript{57}H\textsubscript{62}Br\textsubscript{2}N\textsubscript{2}O\textsubscript{6}S\textsubscript{2}: C 62.52, H 5.71, N 2.56, S 5.86; found: C 62.35, H 5.99, N 2.38, S 6.03.

**General procedures for preparation of the target polymers.**

Palladium(0)-catalyzed Suzuki cross-coupling reactions were employed for polymerization procedures. Dibromo monomer (0.5 mmol), diboronic ester monomer (0.5 mmol), 15 mL of THF, Et\textsubscript{4}NOH (20% aq., 1.00 mL) and Pd(PPh\textsubscript{3})\textsubscript{4} (18 mg, 0.015 mmol) were mixed under argon flow. After being degassed for 10 mins, the reaction mixture was heated to 80 °C and stirred for 24 h under argon protection. After being cooled to room temperature, the mixture was poured into 200 mL of MeOH, and the precipitate was collected by filtration. Then the material was washed with hexane and acetone in a Soxhlet for 8 h, after which the solid was dissolved in 8 mL of THF, followed by filtration with a 0.45 μm polytetrafluoroethylene (PTEE). The solution was concentrated and precipitated from 150 mL of hexane to afford the target polymer.

PBSON-P: 10 (547.5 mg, 0.500 mmol) and 11 (165.0 mg, 0.500 mmol) were used to synthesize PBSON-P. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, δ): 8.25-8.24 (m, 2H), 8.11-8.05 (m, 2H), 7.78-7.72 (m, 4H), 7.66-7.62 (m, 2H), 7.51-7.42 (m, 4H), 7.19-7.16 (m, 4H), 6.85-6.83 (m, 4H), 3.92 (br, 4H), 2.51-2.37 (m, 12H), 1.86-1.84 (m, 4H), 1.45-1.25 (m, 24H). Anal. calcd for C\textsubscript{63}H\textsubscript{66}N\textsubscript{2}O\textsubscript{6}S\textsubscript{2}: C 74.67, H 6.76, N 2.76, S 6.33; found: C 74.32, H 6.99, N 2.91, S 6.60.

PBSON-FEO: 10 (547.5 mg, 0.500 mmol) and 12 (311.2 mg, 0.500 mmol) were
used to synthesize PBSON-FEO. \(^1\)H NMR (500 MHz, CDCl\(_3\), δ): 8.26 (br, 2H), 8.14-8.12 (m, 2H), 7.92-7.68 (m, 12H), 7.23-7.22 (m, 4H), 6.88-6.87 (m, 4H), 3.94 (br, 4H), 3.30-3.24 (m, 18H), 2.57-2.47 (m, 12H), 1.86-1.84 (m, 4H), 1.78 (br, 4H), 1.50-1.26 (m, 24H). Anal. calcd for C\(_{80}\)H\(_{90}\)N\(_2\)O\(_{10}\)S\(_2\): C 73.59, H 7.10, N 2.15, S 4.91; found: C 73.31, H 7.42, N 2.48, S 4.67.

2. General Measurements and Characterization

\(^1\)H NMR and \(^{13}\)C NMR spectra were carried out on a Bruker AV-500 spectrometer operating at 500 MHz (for \(^1\)H) and 75 MHz (for \(^{13}\)C) with tetramethylsilane (TMS) as the internal reference. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). Molecular weights of the polymers were determined by a Waters GPC 2410 in THF using a calibration curve with polystyrene standards. UV-vis absorption spectra were performed on a HP 8453 spectrophotometer. PL spectra were recorded on an Instaspec IV CCD spectrophotometer (Oriel Co.). CV were characterized on a CHI600D electrochemical workstation with a standard three electrodes cell based on a Pt wire counter electrode and a platinum (Pt) working electrode, against SCE as reference electrode at a scan rate of 50 mV s\(^{-1}\) within a nitrogen-saturated anhydrous solution of 0.1 mol L\(^{-1}\) tetrabutylammonium hexafluorophosphates (Bu\(_4\)NPF\(_6\)) in acetonitrile, versus Fe/Fc\(^+\) as the internal reference.

3. Polymer Solar cells Fabrication
3.1. Conventional PSCs

Patterned ITO-coated glass substrate was used as the anode. After the substrate was cleaned carefully, dried and plasma treated with oxygen, a 40 nm thin layer of PEDOT:PSS by spin-coating was used to modify the ITO substrate, followed by baking at 150 °C for 10 min. The substrate was then taken into a nitrogen-filled glove box, and an 90 nm blend active layer of PTB7-Th:PC71BM (1: 1.5, w/w) or PBDB-T:ITIC (1: 1, w/w) was deposited by spin-casting from its solution in a solvent mixture of chlorobenzene and 1,8-diiodooctane (97: 3, v/v) or in chlorobenzene with 0.5% 1,8-diiodooctane solvent for PTB7-Th:PC71BM and PBDB-T:ITIC, respectively. The resulting polymer CIL was spin-coated from 0.2 mg mL\(^{-1}\) solution in MeOH (in the presence of 0.5 v% TFA). Finally, an 80 nm thin layer of Al was thermally deposited as the cathode through a shadow mask (defined active area of 0.16 cm\(^2\)) in a chamber. The Al cathode thickness was monitored upon deposition by using a crystal thickness monitor (Sycon).

3.2. Inverted PSCs

The resulting polymer CIL was spin-coated from MeOH (in the presence of 0.5 v% TFA) solution with concentration of 2 mg mL\(^{-1}\) on the surface of precleaned ITO. An 90 nm blend active layer of PTB7-Th:PC71BM (1: 1.5, w/w) was spin-coated from its solution in a solvent mixture of chlorobenzene and 1,8-diiodooctane (97: 3, v/v). A 10 nm MoO\(_3\) layer and a 100 nm Al layer were subsequently evaporated through a shadow mask to define the active area of the device (~0.16 cm\(^2\)) and form the anode.
4. Polymer Solar Cells Characterization

The thickness of PEDOT:PSS and active layers were determined with Profilometry (Veeco Dektak150), and the thickness of polymeric CILs were tested by a step profiler. Device fabrication was finished in an N₂ atmosphere dry-box (Vacuum Atmosphere Co.). The $J-V$ characteristic was measured with a Keithley 236 source meter. The spectral response was recorded with a commercial photomodulation spectroscopic setup (Oriel). A calibrated Si photodiode was used to determine the photosensitivity. PCE was measured under an AM 1.5G solar simulator (Oriel model 91192). The power of the sun simulation was calibrated before the testing using a standard silicon solar cell.

Scheme S1. Synthetic Routes for the Monomers and Polymers
Figure S1. $^1$H NMR spectrum of compound 5.
Figure S2. $^{13}$C NMR spectrum of compound 5.

Figure S3. $^1$H NMR spectrum of compound 6.

Figure S4. $^{13}$C NMR spectrum of compound 6.
Figure S5. $^1$H NMR spectrum of compound 7.

Figure S6. $^{13}$C NMR spectrum of compound 7.

Figure S7. $^1$H NMR spectrum of compound 9.
Figure S8. $^{13}$C NMR spectrum of compound 9.

Figure S9. $^1$H NMR spectrum of compound 10.

Figure S10. $^{13}$C NMR spectrum of compound 10.
Figure S11. TGA curves of PBSON-P and PBSON-FEO.

Figure S12. $J$-$V$ characteristics of the conventional and inverted architectures with PFN CILs under AM 1.5G irradiation.

Table S1. Photovoltaic Performance of the Conventional and Inverted PSCs with PFN CILs under AM 1.5G Irradiation

<table>
<thead>
<tr>
<th>Device structure</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
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<tbody>
<tr>
<td>conventional</td>
<td>0.73</td>
<td>-16.81</td>
<td>70.47</td>
<td>8.65</td>
</tr>
<tr>
<td>inverted</td>
<td>0.79</td>
<td>-17.16</td>
<td>70.96</td>
<td>9.62</td>
</tr>
</tbody>
</table>
Figure S13. $J-V$ characteristics of the conventional architectures of PBDB-T:ITIC system with different CILs under AM 1.5G irradiation.

Table S2. Photovoltaic Performance of the Conventional PSCs of PBDB-T:ITIC System with Different CILs under AM 1.5G Irradiation

<table>
<thead>
<tr>
<th>CIL</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF  (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH (0.5% TFA)</td>
<td>0.670</td>
<td>13.88</td>
<td>51.32</td>
<td>4.77</td>
</tr>
<tr>
<td>PBSON-P</td>
<td>0.893</td>
<td>14.67</td>
<td>61.01</td>
<td>8.01</td>
</tr>
<tr>
<td>PBSON-FEO</td>
<td>0.885</td>
<td>14.66</td>
<td>58.36</td>
<td>7.57</td>
</tr>
</tbody>
</table>
Figure S14. Static water contact angle images of (a) ITO/active layer, (b) ITO/active layer/PBSNO-P, and (c) ITO/active layer/PBSNO-FEO substrates.