Supporting Information

Improving the stability of P3HT/PC_{61}BM solar cells by a thermal crosslinker

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1. Synthesis and characterization

NMR spectra were measured on a Bruker AVANCE-400 spectrometer. Mass spectra were measured on an Autoflex III (MALDI-TOF) spectrometer. Reagents and chemicals were purchased from Alfa-Aesar Co., TCI Co., or other commercial suppliers and used as received.

Synthesis of octane-1,8-diyl bis(3,4-dimethylbenzoate) (compound 2): In a 50 mL dry round bottom flask, a mixture of 3,4-dimethylbenzoic acid (500 mg, 3.33 mmol), 1, 8-octanediol (244 mg, 1.67 mmol), dicyclohexylcarbodiimide (DCC) (660 mg, 3.33 mmol), and dimethylamino-pyridine (DMAP) (50 mg, 0.41 mmol) in toluene (15 mL) were stirred at room temperature for 3 h. Then, the mixture was successively washed with 20% Na_{2}CO_{3} and water three times, and dried with anhydrous MgSO_{4}. Silica gel column chromatography afforded pure compound 2 (504 mg, yield: 74%). ^1H NMR (400 MHz, CDCl_{3}, δ): 7.73 (s, 2H, Ar), 7.69 (d, J = 7.9 Hz, 2H, Ar), 7.10 (d, J = 7.8 Hz, 2H, Ar), 4.21 (t, J = 6.7 Hz, 4H, OCH_{2}), 2.23 (s, 12H, CH_{3}), 1.64-1.73 (m, 8H, CH_{2}), 1.28-1.43 (m, 8H, CH_{2}); ^13C NMR (100 MHz, CDCl_{3}, δ): 167.06, 142.21,
MALDI-TOF-MS for C_{26}H_{34}O_{4} [M + Na^+] : 433.3.

Synthesis of octane-1,8-diyl bis(1,4-dihydrobenzo[d][1,2]oxathiine-6-carboxylate 3-oxide) (OBOCO): In a 50 mL dry round bottom flask, 2 (485 mg, 1.18 mmol), N-bromosuccinimide (NBS) (925 mg, 5.2 mmol), and benzoyl peroxide (BPO) (50 mg, 0.2 mmol) were added into CCl\(_4\) (20 mL) and the mixture was heated to reflux for 5 h. The float was then removed by filtration. The solvent was evaporated under vacuum. After a flash column chromatography, the crude bromination product was collected. \(^1\)H NMR indicates that it is a mixture of tetra- and multi-bromination compounds (Figure S3), and the separation of these compounds is very difficult. The mixture was directly used as the starting material for next step. The bromination product was mixed with rongalite (1.06 g, 7.08 mmol), tetrabutylammonium bromide (TBAB) (229 mg, 0.71 mmol), and a mixture of dimethyl formamide (DMF) and CH\(_2\)Cl\(_2\) (1:1, 12 mL). The reaction mixture was stirred at room temperature overnight. The reaction was stopped by adding water (20 mL). The product was extracted with CH\(_2\)Cl\(_2\) (20 mL) and dried with anhydrous sodium sulfate. Silica gel column chromatography afforded pure OBOCO (226 mg, yield: 36%). \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 8.00-8.03 (m, 2H, Ar), 7.89-7.92 (m, 2H, Ar), 7.29-7.32 (m, 2H, Ar), 5.36 (d, \(J = 13.86\) Hz, 2H, CH\(_2\)), 5.00-5.04 (m, 2H, CH\(_2\)), 4.38-4.43 (m, 2H, CH\(_2\)), 4.33 (t, \(J = 6.64\) Hz, 4H, OCH\(_2\)), 3.60-3.65 (m, 2H, CH\(_2\)), 1.74-1.79 (m, 4H, CH\(_2\)), 1.41-1.45 (m, 8H, CH\(_2\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), \(\delta\)): 165.83, 165.77, 137.85, 133.60, 131.60, 131.12, 131.02, 130.10, 130.03, 129.52, 128.93, 126.78, 126.14, 125.72,
65.37, 62.44, 62.17, 56.48, 56.02, 29.11, 28.65, 25.91. MALDI-TOF-MS for C_{26}H_{30}O_{8}S_{2} [M + Na^+] : 557.1.

**Synthesis of methyl 3,4-dimethylbenzoate**: In a 50 mL dry round bottom flask, a mixture of 3,4-dimethylbenzoic acid (500 mg, 3.33 mmol), methanol (106.6 mg, 3.33 mmol), dicyclohexylcarbodiimide (DCC) (660 mg, 3.33 mmol), and dimethylamino-pyridine (DMAP) (50 mg, 0.41 mmol) in CH_{2}Cl_{2} (10 mL) were stirred at room temperature for 3 h. Then, the mixture was successively washed with 20% Na_{2}CO_{3} and water three times, and dried with anhydrous MgSO_{4}. Silica gel column chromatography afforded pure methyl 3,4-dimethylbenzoate (460 mg, yield: 84%). \textsuperscript{1}H NMR (400 MHz, CDCl_{3}, δ): 7.83 (s, 1H, Ar), 7.78 (dd, J = 1.57 Hz, 7.85 Hz, 1H, Ar), 7.21 (d, J = 7.85 Hz, 1H, Ar), 3.91 (s, 3H, OCH_{3}), 2.33 (s, 3H, CH_{3}), 2.32 (s, 3H, CH_{3}).

**Synthesis of methyl 1,4-dihydrobenzo[d][1,2]oxathiine-6-carboxylate 3-oxide**: In a 50 mL dry round bottom flask, methyl 3,4-dimethylbenzoate (210 mg, 1.29 mmol), N-bromosuccinimide (NBS) (505 mg, 2.83 mmol), and benzoyl peroxide (BPO) (30 mg, 0.12 mmol) were added into CCl_{4} (10 mL) and the mixture was heated to reflux for 5 h. The float was then removed by filtration. The solvent was evaporated under vacuum. After a flash column chromatography, the crude product was collected and directly used as the starting material for next step. The crude bromination product was mixed with rongalite (0.53 g, 3.54 mmol), tetrabutylammonium bromide (TBAB) (115 mg, 0.35 mmol), and a mixture of dimethyl formamide (DMF) and CH_{2}Cl_{2} (1:1, 10 mL). The reaction mixture was stirred at room temperature overnight. The reaction
was stopped by adding water (10 mL). The product was extracted with CH₂Cl₂ (20 mL) and dried with anhydrous sodium sulfate. Silica gel column chromatography afforded pure methyl 1,4-dihydrobenzo[d][1,2]oxathiine-6-carboxylate 3-oxide (108 mg, yield: 37%). ¹H NMR (400 MHz, CDCl₃, δ): 7.98-8.05 (m, 1H, Ar), 7.87-7.96 (m, 1H, Ar), 7.29-7.32 (m, 1H, Ar), 5.34 (d, J = 13.89 Hz, 1H, CH₂), 4.99-5.04 (m, 1H, CH₂), 4.38-4.44 (m, 1H, CH₂), 3.93 (3H, OCH₃), 3.58-3.67 (m, 1H, CH₂); ¹³C NMR (100 MHz, CDCl₃, δ): 166.26, 166.21, 137.93, 133.63, 131.19, 131.12, 130.47, 130.05, 129.79, 129.57, 128.98, 126.86, 126.19, 125.75, 62.33, 62.05, 56.01, 52.36.
Fig. S1 $^1$H NMR of 2 (in CDCl$_3$).

Fig. S2 $^{13}$C NMR of 2 (in CDCl$_3$).
**Fig. S3** $^1$H NMR of the bromination product (in CDCl$_3$).

**Fig. S4** $^{13}$C NMR of the bromination product (in CDCl$_3$).
**Fig. S5** $^1$H NMR of OBOCO (in CDCl$_3$).

**Fig. S6** $^{13}$C NMR of OBOCO (in CDCl$_3$).
Fig. S7 $^1$H NMR of methyl 3,4-dimethylbenzoate (in CDCl$_3$).

Fig. S8 $^1$H NMR of 1,4-dihydrobenzo[d][1,2]oxathiine-6-carboxylate 3-oxide (in CDCl$_3$).
**Fig. S9** $^{13}$C NMR of 1,4-dihydrobenzo[d][1,2]oxathiine-6-carboxylate 3-oxide (in CDCl$_3$).
Fig. S10 Effect of OBOCO crosslinker on the characteristic absorption of P3HT/PC$_{61}$BM blend films. NA: not annealed; A: annealed at 150 °C for 20 min.

Weight ratio: P3HT/PC$_{61}$BM=1/1; OBOCO/PC$_{61}$BM=1:1.7
**Fig. S11** AFM height and phase images for the active layers containing compound 2, octane-1,8-diyl bis(3,4-dimethylbenzoate). Content: a) 0%, b) 5%, c) 10%, d) 15%, e) 20%, f) 25%.
2. Space charge limited current (SCLC) measurements

Charge carrier mobility was measured by the SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

\[ J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d} \]

where \( J \) is the current density, \( \mu \) is the zero-field mobility of electrons (\( \mu_e \)) or holes (\( \mu_h \)), \( \varepsilon_0 \) is the permittivity of the vacuum, \( \varepsilon_r \) is the relative permittivity of the material, \( d \) is the thickness of the blend film, and \( V \) is the effective voltage, \( V = V_{\text{appl}} - V_{\text{bi}} \), where \( V_{\text{appl}} \) is the applied voltage, and \( V_{\text{bi}} \) is the built-in potential which results from the difference in the work function of the anode and the cathode. Figure S12 shows \( J-V \) curves of the electron-only devices. Figure S13 shows \( J-V \) curves of the hole-only devices. The mobility was calculated from the \( J^{1/2}-V \) curves and listed in Table S1.

![Fig. S12](image)

**Fig. S12** a) \( J-V \) curves (in the dark) for electron-only devices based on P3HT:PC_{61}BM blend with 0%, 5%, 10%, 15%, 20%, and 25% OBOCO; the thicknesses for the blend films are 75 nm, 75 nm, 75 nm, 90 nm, 90 nm, and 100 nm, respectively. b) The corresponding \( J^{1/2}-V \) curves.
Fig. S13 a) $J$-$V$ curves (in the dark) for hole-only devices based on P3HT:PC$_{61}$BM blend with 0%, 5%, 10%, 15%, 20%, and 25% OBOCO; the thicknesses for the blend films are 95 nm, 95 nm, 100 nm, 100 nm, 105 nm, and 120 nm, respectively. b) The corresponding $J^{1/2}$-$V$ curves.

Table S1 The SCLC mobilities for devices with different OBOCO content.

<table>
<thead>
<tr>
<th>Content (%)</th>
<th>Electron mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>Hole mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
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<td>0</td>
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<td>25</td>
<td>$1.6 \times 10^{-6}$</td>
<td>$4.3 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
**Fig. S14** Optical microscopy images for the active layers before(left) and after(right) being heated at 150 °C for 100 h. a) without OBOCO; b) with 5% OBOCO.

**Fig. S15** Polarized light microscopy image for P3HT/PC_{61}BM blend film after annealing. Weight ratio: P3HT/PC_{61}BM=1/1.