

## Supporting Information:

### Role of Intrinsic Photogeneration in Single Layer and Bilayer Solar Cells with C<sub>60</sub> and PCBM

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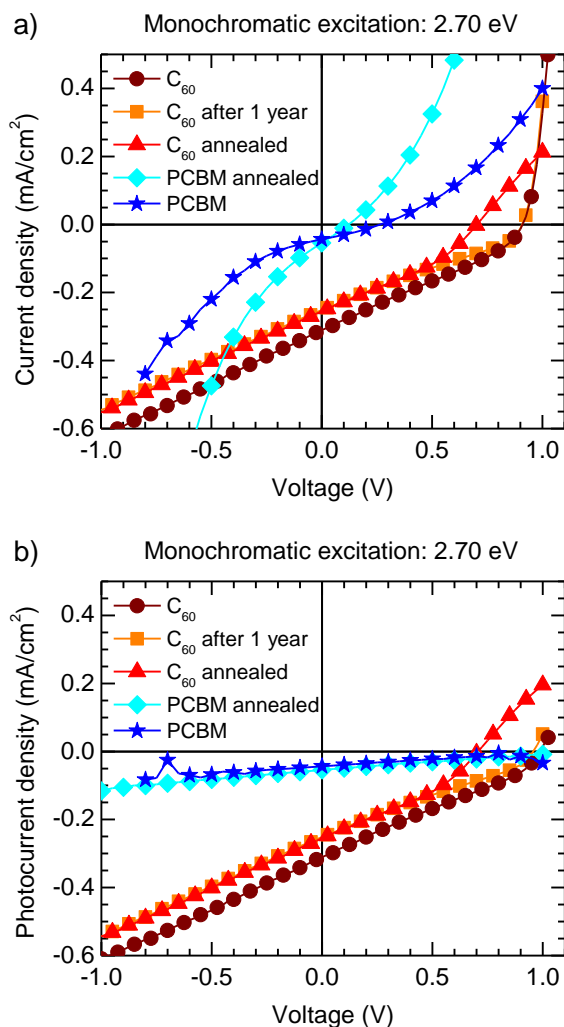
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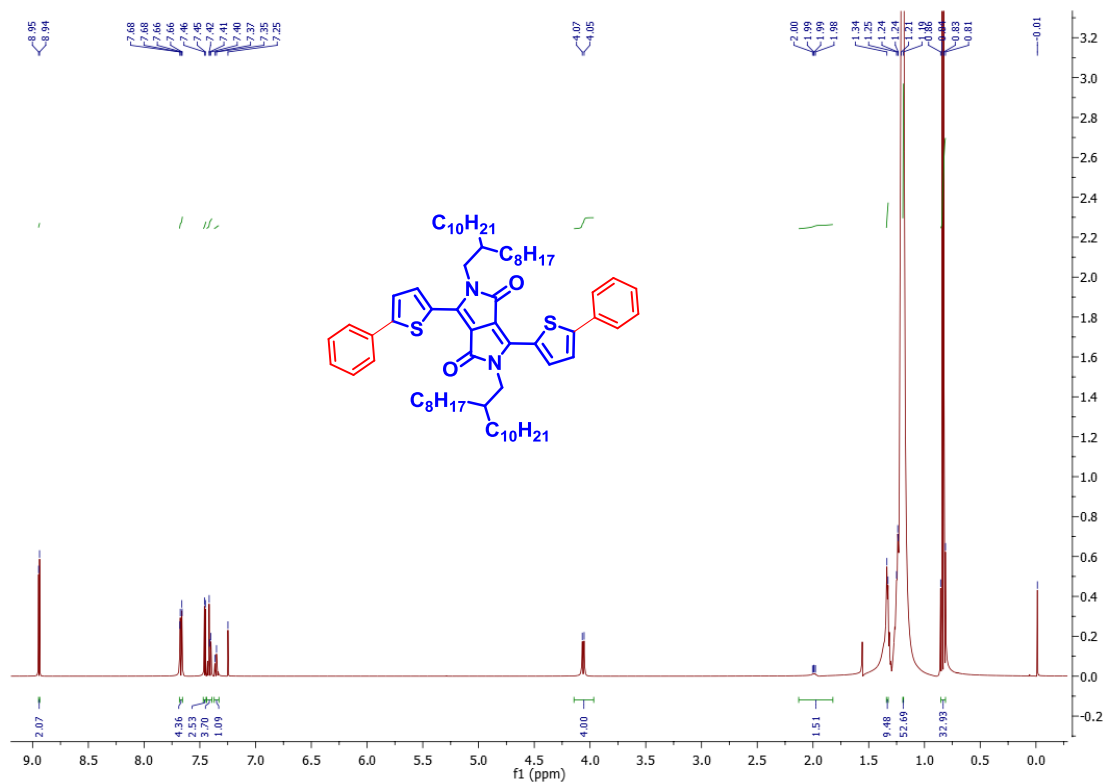
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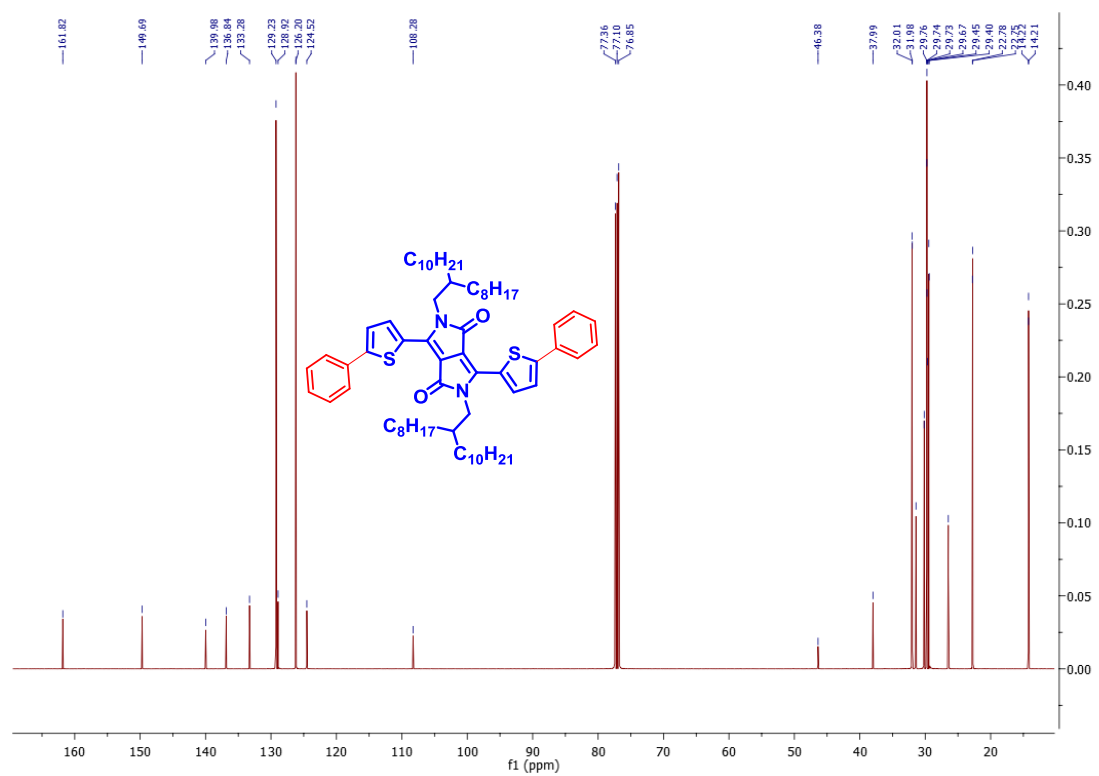
**Figure S1:** (a) Current and (b) Photocurrent (= Current minus Darkcurrent) for a  $C_{60}$ -only device measured immediately (wine circles), a  $C_{60}$ -only device stored in a nitrogen glovebox for one year (orange squares), a  $C_{60}$ -only device annealed at 140°C for 26 hours under nitrogen (red triangles), a PCBM-only device annealed at 140°C for 30 min and afterwards cooled down to 60°C in a time range of 30 min (cyan diamonds) and for a PCBM-only device which was not annealed and measured as cast (blue stars).

**Synthesis of 2,5-bis(2-octyldodecyl)-3,6-bis(5-phenylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (Ph-TDPP-Ph)**

A mixture of phenylboronic acid (0.079 g, 0.64 mmol) and potassium carbonate (0.089 g, 0.64 mmol) in toluene/ethanol (3:1, 60 mL) was stirred at 50°C for 30 min. Then the compound 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.3 g, 0.29 mmol) was added in one portion, the reaction mixture was heated at 110°C for 12 h and then cooled to room temperature. Dichloromethane (100 mL) and water (200 mL) were added and the layers separated. The organic layer was concentrated *in vacuo*. Further purification was carried out by column chromatography on silica gel eluting with hexane/ethyl acetate (5%) to give the compound Ph-TDPP-Ph as a dark blue solid (0.22 g, 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.94 (d, *J* = 8 Hz, 2H), 7.67 (dd, *J* = 8.5, 1.3 Hz, 4H), 7.45 (d, *J* = 4.2 Hz, 3H), 7.44 – 7.39 (m, 4H), 7.35 – 7.37 (m, *J* = 7.5 Hz, 1H), 4.06 (d, *J* = 4 Hz, 4H), 1.98 – 2.00 (m, 2H), 1.19 – 1.34 (m, 62H), 0.81 – 0.86 (m, 12H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.82, 149.69, 139.98, 136.84, 133.28, 129.23, 128.92, 126.20, 124.52, 108.28, 46.38, 37.99, 32.01, 31.98, 29.76, 29.74, 29.45, 29.40, 22.78, 22.75, 14.22, 14.21 ppm. ESI-MS calculated for C<sub>66</sub>H<sub>96</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: *m/z*: 1012.69; found: 1014.12.



**Figure S2:  $^1\text{H}$  NMR spectrum of Ph-TDPP-Ph**



**Figure S3:  $^{13}\text{C}$  NMR spectrum of Ph-TDPP-Ph**

### Synthesis of the polymer PCDTBT<sub>co</sub>

PCDTBT<sub>co</sub> (poly[(*N*-heptadecan-9'-yl)-2,7-carbazole-*alt*-5,5-(4',7'-bis(thien-2-yl)-2',1',3'-benzothiadiazole)]<sub>0.7</sub>-*stat*-[*N,N'*-bis(4-methylphenyl)-*N,N'*-diphenylbenzidine-*alt*-5,5-(4',7'-bis(thien-2-yl)-2',1',3'-benzothiadiazole)]<sub>0.3</sub>) was synthesized via Suzuki coupling according to the following procedure. The molar ratio of the carbazole, the phenyl-substituted benzidine, and the bisthierylbenzothiadiazole units in PCDTBT<sub>co</sub> is 0.7:0.3:1.

A Schlenk flask was charged with the monomers 2,7-bis-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-*N*-(heptadecan-9''-yl)-carbazole (0.368 g, 0.560 mmol), *N,N'*-bis(4-methylphenyl)-*N,N'*-bis((4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)phenyl)-benzidine (0.184 g, 0.239 mmol), 4,7-bis(5'-bromo-thien-2'-yl)-2,1,3-benzothiadiazole (0.367 g, 0.800 mmol) and 12 mL of toluene under argon. One drop of Aliquat 336 and 20 mL of 2 M Na<sub>2</sub>CO<sub>3</sub> solution were added and the mixture was degassed by three freeze-thaw cycles. Afterwards, 14 mg of tetrakis(triphenylphosphine)palladium(0) were added and followed by again three freeze-thaw cycles. The reaction mixture was then stirred under reflux in an argon atmosphere for 90 h before bromobenzene (0.126 g, 0.800 mmol) was added. After 2 h, phenylboronic acid (0.098 g, 0.800 mmol) was added and the reaction mixture was again refluxed overnight. The reaction mixture was allowed to cool to room temperature and the polymer was precipitated into methanol/water (10:1). Soxhlet extraction was carried out using acetone and toluene. The reduced toluene fraction was precipitated into methanol/water (10:1) and dried in vacuum overnight, yielding 0.163 g (28 %) of PCDTBT<sub>co</sub> as a dark-red powder. A molecular weight of 45,000 gmol<sup>-1</sup> (*M*<sub>w</sub>) and 31,000 gmol<sup>-1</sup> (*M*<sub>n</sub>) was determined by high temperature polymer size exclusion chromatography in trichlorobenzene at 160°C with a polydispersity index of 1.44.

<sup>1</sup>H NMR (300 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 120 °C): δ = 0.66-0.91 (m, CH<sub>3</sub>), 0.93 - 1.49 (m, CH<sub>2</sub>), 2.08 (br, carbazole-CH<sub>2</sub>), 2.22 - 2.48 (m, benzidine-CH<sub>3</sub>, carbazole-CH<sub>2</sub>), 4.67 (br, CH), 6.76 - 8.27 (m, ar-CH). Broadened and multiple signals are due to atropisomerism. From the integration of the signal for the CH<sub>2</sub> group in the swallow-tail spacer of the carbazole unit (2.08 ppm) and the combined signal for the methyl group in the benzidine units and the other CH<sub>2</sub> group in the carbazole spacer (2.22 - 2.48 ppm), a molar ratio of 0.7:0.3:1 was calculated.

