

## SUPPORTING INFORMATION

### Amino-Fulleropyrrolidines as Electrotropic Additives to Enhance Organic Photovoltaics

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#### Materials and Methods

##### Materials

3-Dimethylamino-1-propanol (99%), triphenylphosphine (99%), diisopropyl azodicarboxylate (98%), aluminum oxide (activated, basic, Brockmann I), triethylamine (>99%), sarcosine (99%), 2,3,4-Trihydroxybenzaldehyde (98%) was purchased from Combi-Blocks and used without further purification. 6-Dimethylamino-1-hexanol (>97%) was purchased from TCI America and used without further purification. Fullerene-C<sub>60</sub> (99.95%) was purchased from Materials Technologies Research (MTR) and used without further purification. Chloroform-D (99.8%) was purchased from Cambridge Isotope Laboratories. Silica gel (200 x 400 mesh) was purchased from Sorbent Technologies. Tetrahydrofuran (99%, EMD) (THF) was dried over sodium/benzophenone ketyl, and distilled before use. Anhydrous magnesium sulfate, hexanes, chloroform, methanol, acetone, diethyl ether and dichloromethane were purchased from Fisher Scientific. PTB7 and PCE-10 were purchased from 1-Material and PC<sub>71</sub>BM was purchased from Nano-C. 2,3,4-tris((3-(dimethylamino)propyl)oxy)benzaldehyde and 2,3,4-tris((6-

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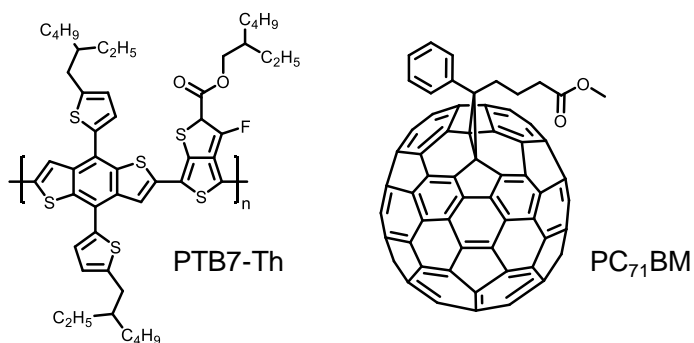
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(dimethylamino)hexyl)oxy)fulleropyrrolidine (C<sub>60</sub>-N-T<sub>3</sub>, previously referenced to as C<sub>60</sub>-N) was synthesized according to literature.<sup>1</sup> The active layer components, poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2-6-diyl)] (PTB7-Th) and [6,6]-Phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) were obtained from 1-Material and American Dye Source, respectively (chemical structures shown below). The cathode interlayer poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) was obtained from 1-Material. Synthesis of C<sub>60</sub>-N-T<sub>x</sub> (x= 3, 6 or 11) is described below.



## Instrumentation

<sup>1</sup>H-NMR spectra were recorded at 300 MHz on a Bruker-spectrospin or 500 MHz on an Ascend™ Bruker or 700 MHz on an Agilent Technologies (Varian) DD-2 and <sup>13</sup>C-NMR at 176 MHz on an Agilent Technologies Varian. Matrix assisted laser desorption ionization time of flight (MALDI-TOF) data were obtained on a Bruker microflex instrument using a microScout Ion Source and linear mode detection. The matrix used was [2-(4-hydroxyphenylazo)-benzoic acid] (HABA) which was drop cast from a 40 mg/mL solution in THF containing approximately 0.1 – 1 mg/mL of the analyte added to the mixture as a solution in either TFE. Current-voltage (I-V) characteristics were measured in a N<sub>2</sub> atmosphere (unless otherwise stated) using a Keithley 2400 source-meter under simulated AM1.5G irradiation using a 300 W Xe lamp solar simulator (Newport 91160). The light intensity was adjusted with an NREL-calibrated Si reference solar cell and KG-5 filter. The illuminated area (0.03025 cm<sup>2</sup> unless otherwise stated) was defined by a photomask with an aperture, the area of which was measured at NREL, and used in all reported PCE measurements.

## Computational studies

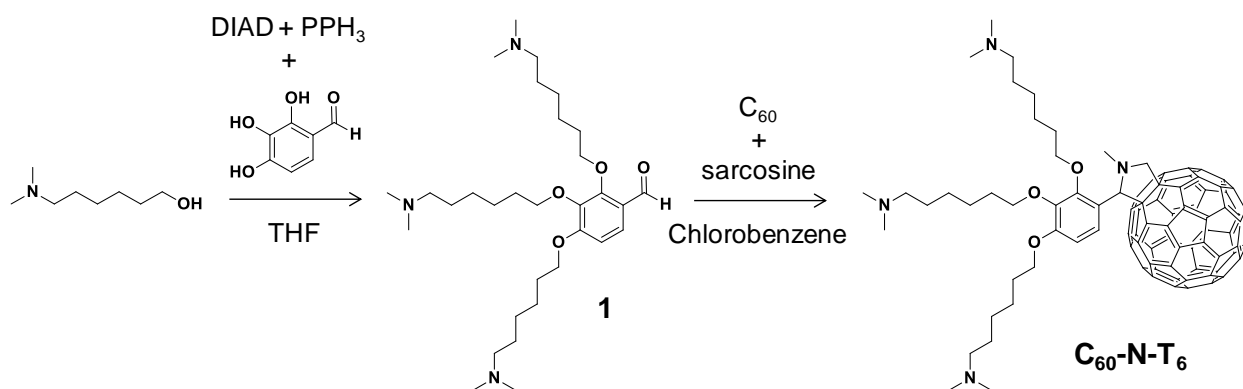
All quantum chemistry calculations were performed by Gaussian 09 Rev D.01 software.<sup>2</sup> The ground-state molecular geometries, dipole moments and electrostatic potential maps were calculated using density functional theory (DFT),<sup>3</sup> the B3LYP functional,<sup>4,5</sup> and the 6-31G(d, p) basis set. Molecular representations and Electrostatic potential maps were generated in GaussView.<sup>6</sup>

## Device fabrication and characterization

The inverted photovoltaic device architecture ITO/PFN (10 nm)/PTB7-Th:PC<sub>71</sub>BM (1:1.5)/MoO<sub>3</sub> (10 nm)/Al (100 nm) was utilized in this study. Device fabrication included the following steps. First, the patterned indium tin oxide (ITO)-covered glass substrates (resistivity of 20 Ω/sq, Thin Film Devices, Inc.) were cleaned in an ultrasonic bath with using Mucaso1™ (Sigma-Aldrich, pH

= 12 in deionized (DI) water), DI water (twice), acetone, and isopropyl alcohol sequentially for 10 minutes each. The substrates were dried overnight in an oven and exposed to UV/Ozone treatment for 20 min immediately prior to the next step. A 10 nm-thick PFN layer was spin-coated at 2500 rpm for 2 min from a 2 mg/ml methanol solution with a small amount (2  $\mu$ l/ml) of acetic acid. The PTB7-Th:PC<sub>71</sub>BM solution (1:1.5 by weight, 25 mg/ml in chlorobenzene with 3 v% of 1,8-diiodooctane) was mixed with a 0.5 v% of a stock solution (1 mg/ml in CB) of a dipolar additive (C<sub>60</sub>-N-T<sub>x</sub>, where x = 3, 6 or 11). The mixed solution was stirred overnight at 55 °C inside a glove box (N<sub>2</sub>, <1 ppm of O<sub>2</sub>, <1 ppm of H<sub>2</sub>O) and heated at 80 °C for 10 min prior to spin-coating. The active layer solution was spin-coated onto the ITO/PFN substrate at 1000 rpms for 2 min. Finally, a 10 nm-thick MoO<sub>3</sub> layer and a 100 nm-thick Al electrode were thermally evaporated at 1 $\times$ 10<sup>-6</sup> torr through a shadow mask. An overlap of the mask and patterned ITO substrate defined the 0.06 cm<sup>2</sup> device area. The current density - voltage (J - V) characteristics of the devices in a glove box were measured using a Keithley 2400 source-meter. The illumination was performed with an AM 1.5G solar simulator (Newport 91160, 100 mW/cm<sup>2</sup>), which was calibrated using a reference Si solar cell with a KG5 window (Newport certification). The Keithley 2400 source-meter was also used for the electric field poling.

### Synthesis



### Scheme S1. Synthesis of C<sub>60</sub>-N-T<sub>6</sub>

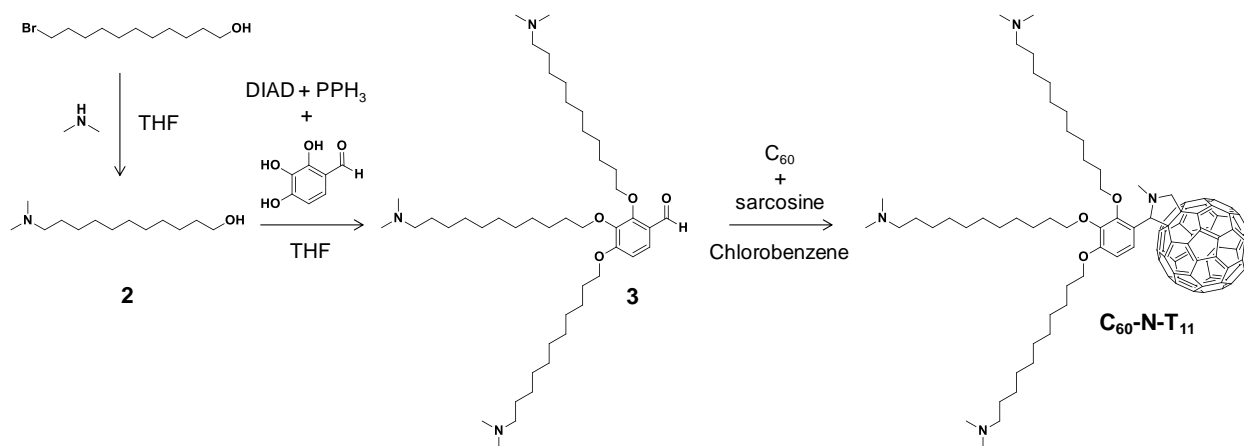
#### 2,3,4-tris((6-(dimethylamino)hexyl)oxy)benzaldehyde (**1**).

A 2-neck, 250 mL roundbottom flask equipped with a magnetic stir bar, inlet adapter, addition funnel and septa was flushed with nitrogen, followed by addition of 2,3,4-trihydroxybenzaldehyde (1.0 g, 6.5 mmol), 6-dimethylamino-1-hexanol (3.20 g, 22.1 mmol), triphenylphosphine (5.79 g, 22.1 mmol) and THF (anhydr, 30 mL). The mixture was cooled to 0 °C with an ice bath while stirring under nitrogen. Diisopropyl azodicarboxylate was added to the addition funnel, dissolved in THF (anhydr, 15 mL) and added dropwise to the reaction mixture. After complete addition the flask was removed from the ice bath and stirred at room temperature for five hours. The reaction was concentrated and the resulting crude mixture was washed with Hex:Et<sub>2</sub>O (1:1), filtering off the white phosphine-oxide byproduct through Celite. The filtrate was concentrated, dissolved in DCM and washed with 1M HCl (aq) (50 mL, 3x). The aqueous fractions were combined and washed with DCM until the organic phase no longer contained a UV-active compound (tested on

UV-active TLC plates under short-wave 254 nm light). The acidic aqueous layer was neutralized with sodium carbonate (sat., aq.) and the product was extracted into DCM. The combined organic phases were dried with MgSO<sub>4</sub> (anhydr), filtered and concentrated to obtain a brown oil. The crude product was further purified using basic alumina (activated Brockman I) eluting with DCM:MeOH:TEA (98:1:1) yielding (once concentrated) **1** as a light yellow oil (1.06 g, 30%). <sup>1</sup>H NMR (700 MHz, Chloroform-*d*) δ 10.22 (s, 1H), 7.54 (dd, *J* = 9.0, 1.3 Hz, 1H), 6.68 (d, *J* = 8.9 Hz, 1H), 4.13 (t, *J* = 6.7 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 3.94 (t, *J* = 6.6 Hz, 2H), 2.25 – 2.21 (m, 6H), 2.20 – 2.13 (m, 18H), 1.83 (dt, *J* = 13.6, 6.6 Hz, 2H), 1.75 (dp, *J* = 18.5, 6.8 Hz, 4H), 1.50 – 1.41 (m, 6H), 1.39 – 1.31 (m, 6H), 1.26 – 1.17 (m, 6H). <sup>13</sup>C NMR (176 MHz, Chloroform-*d*) δ 189.20, 159.16, 156.69, 140.99, 123.87, 123.49, 108.16, 77.16, 75.29, 73.74, 68.87, 59.95, 59.87, 59.85, 45.62, 30.33, 30.22, 29.19, 27.86, 27.80, 27.77, 27.49, 27.42, 27.28, 26.19, 26.11, 26.07.

*2,3,4-tris((6-(dimethylamino)hexyl)oxy)fulleropyrrolidine (C<sub>60</sub>-N-T<sub>6</sub>).*

A 2-neck, 500 mL round-bottom flask equipped with a magnetic stir bar, inlet adapter, septum, and Vigreux column was flushed with nitrogen, followed by addition of **1** (196 mg, 0.37 mmol), fullerene-C<sub>60</sub> (396 mg, 0.54 mmol), sarcosine (100 mg, 1.10 mmol) and chlorobenzene (200 mL). The mixture was degassed with nitrogen and then heated to reflux for 12 hours. The reaction was concentrated, dissolved in chloroform and filtered. The resulting filtrate was concentrated and then dissolved in carbon disulfide (CS<sub>2</sub>). The crude mixture was added to silica gel, wet packed with hexanes, and eluted with CS<sub>2</sub>, followed by CH<sub>2</sub>Cl<sub>2</sub>:TEA:MeOH (95:5:5). The first brown band that eluted was collected and concentrated, dissolved in chloroform, filtered through a 1 μm PTFE filter and precipitated into acetone. The precipitate was washed with acetone and dried to obtain **C<sub>60</sub>-N-T<sub>6</sub>** as a brown solid (157 mg, 33 %). <sup>1</sup>H NMR (700 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.8 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 1H), 5.35 (s, 1H), 4.95 (d, *J* = 9.3 Hz, 1H), 4.24 (d, *J* = 9.2 Hz, 1H), 4.15 – 4.03 (m, 2H), 3.95 (ddt, *J* = 33.0, 9.3, 6.4 Hz, 2H), 3.89 – 3.74 (m, 2H), 2.77 (s, 3H), 2.26 (dt, *J* = 14.9, 7.9 Hz, 6H), 2.23 – 2.06 (m, 18H), 1.85 – 1.68 (m, 4H), 1.57 (dtd, *J* = 13.4, 6.7, 3.2 Hz, 2H), 1.48 (dq, *J* = 18.9, 7.5 Hz, 8H), 1.42 – 1.29 (m, 6H), 1.23 (qd, *J* = 11.0, 9.3, 6.1 Hz, 4H). <sup>13</sup>C NMR (176 MHz, Chloroform-*d*) δ 156.86, 155.20, 154.37, 154.17, 153.09, 152.64, 147.39, 147.38, 147.18, 146.83, 146.47, 146.34, 146.28, 146.22, 146.16, 146.15, 146.03, 145.84, 145.67, 145.65, 145.64, 145.41, 145.39, 145.34, 145.32, 145.32, 145.20, 145.18, 144.67, 144.52, 144.44, 143.16, 143.07, 142.74, 142.71, 142.66, 142.62, 142.37, 142.34, 142.26, 142.24, 142.19, 142.16, 142.07, 141.96, 141.77, 141.75, 141.68, 141.28, 140.23, 140.18, 139.56, 139.46, 136.69, 136.52, 136.05, 134.79, 124.31, 122.59, 108.52, 77.16, 76.49, 73.81, 73.26, 70.03, 69.26, 68.57, 60.00, 59.94, 59.89, 53.05, 45.62, 45.60, 45.58, 40.28, 30.67, 30.06, 29.48, 27.96, 27.81, 27.79, 27.66, 27.52, 27.40, 26.50, 26.22, 26.17. MALDI-TOF (*m/z*): [M+H]<sup>+</sup> calculated for: C<sub>93</sub>H<sub>63</sub>N<sub>4</sub>O<sub>3</sub>: 1284.49, found: 1284.45.



## Scheme S2. Synthesis of **C<sub>60</sub>-N-T<sub>11</sub>**

### *11-(dimethylamino)undecan-1-ol (2).*

A pressure flask equipped with a magnetic stir bar was dried and flushed with nitrogen, followed by addition of 11-bromo-1-undecanol (16.0 g, 63.7 mmol) and dimethylamine (200 mL, 2M in THF). The pressure flask was capped and the mixture was heated to 60 °C for 24 hours, followed by cooling with an ice bath and adding to Et<sub>2</sub>O (200 mL). The precipitate was filtered off and washed with Et<sub>2</sub>O. The resulting filtrate was washed with Na<sub>2</sub>CO<sub>3</sub> (sat. aq.), brine and water, then the organic layer was dried with MgSO<sub>4</sub> (anhydr), filtered and concentrated to obtain **2** as a light yellow crystalline solid (13.3 g, 97%). <sup>1</sup>H NMR (700 MHz, Chloroform-*d*) δ 3.55 (s, 1H), 3.51 (t, *J* = 6.8 Hz, 2H), 2.21 – 2.16 (m, 2H), 2.15 (s, 6H), 1.48 (p, *J* = 6.8 Hz, 2H), 1.39 (p, *J* = 7.4 Hz, 2H), 1.33 – 0.99 (m, 14H). <sup>13</sup>C NMR (176 MHz, Chloroform-*d*) δ 77.16, 62.51, 59.96, 45.43, 32.95, 29.66, 29.63, 29.62, 29.58, 29.54, 27.63, 27.56, 25.91.

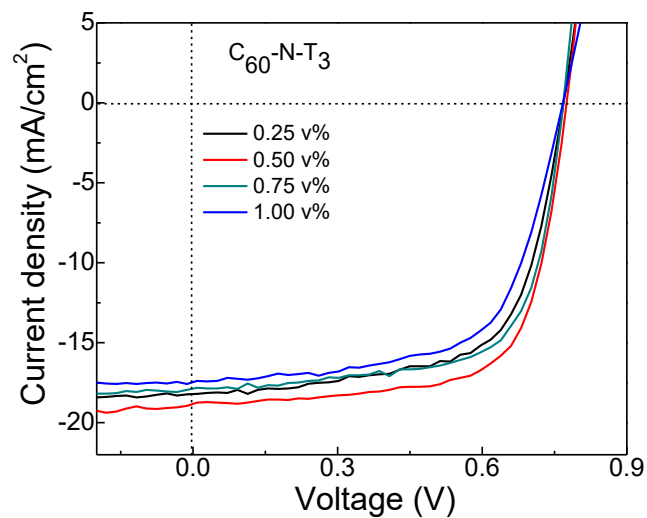
### *2,3,4-tris((11-(dimethylamino)undecyl)oxy)benzaldehyde (3)*

A 2-neck, 250 mL roundbottom flask equipped with a magnetic stir bar, inlet adapter, addition funnel and septa was flushed with nitrogen, followed by addition of 2,3,4-trihydroxybenzaldehyde (1.0 g, 6.5 mmol), 11-(dimethylamino)undecan-1-ol (4.75 g, 22.1 mmol), triphenylphosphine (5.79 g, 22.1 mmol) and THF (anhydr, 30 mL). The mixture was cooled to 0 °C with an ice bath while stirring under nitrogen. Diisopropyl azodicarboxylate was added to the addition funnel, dissolved in THF (anhydr, 15 mL) and added dropwise to the reaction mixture. After complete addition the flask was removed from the ice bath and stirred at room temperature for five hours. The reaction was concentrated and the resulting crude mixture was washed with Hex:Et<sub>2</sub>O (1:1), filtering off the white phosphine-oxide byproduct through Celite. The filtrate was concentrated, dissolved in DCM and washed with 1M HCl (aq) (50 mL, 3x). The aqueous fractions were combined and washed with DCM until the organic phase no longer contained a UV-active compound (tested on UV-active TLC plates under short-wave 254 nm light). The acidic aqueous layer was neutralized with sodium carbonate (sat., aq.) and the product was extracted into DCM. The combined organic phases were dried with MgSO<sub>4</sub> (anhydr), filtered and concentrated to obtain **3** as a brown oil (4.89 g, 30% yield). <sup>1</sup>H NMR (700 MHz, Chloroform-*d*) δ 10.09 (s, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.87 (t, *J* = 6.5 Hz, 2H), 3.81 (t, *J* = 6.6 Hz, 2H), 2.08 (t, *J* = 7.8 Hz, 6H), 2.06 – 1.98 (m, 18H), 1.68 (p, *J* = 6.7 Hz, 2H), 1.61 (dq, *J* = 15.5, 7.0 Hz, 4H), 1.41 – 1.25 (m, 12H), 1.20 – 1.06 (m, 36H). <sup>13</sup>C NMR (176 MHz,

Chloroform-*d*)  $\delta$  188.77, 158.93, 156.46, 140.78, 123.53, 123.22, 107.84, 77.16, 75.07, 73.50, 68.67, 61.97, 59.77, 45.32, 32.87, 30.12, 30.00, 29.53, 29.51, 29.50, 29.50, 29.48, 29.48, 29.47, 29.46, 29.45, 29.44, 29.43, 29.42, 29.41, 29.40, 29.38, 29.29, 29.19, 28.99, 27.61, 27.59, 27.57, 27.39, 27.37, 27.36, 27.35, 25.96, 25.88, 25.86, 25.82.

*2,3,4-tris((11-(dimethylamino)undecyl)oxy)fulleropyrrolidine (C<sub>60</sub>-N-T<sub>11</sub>).*

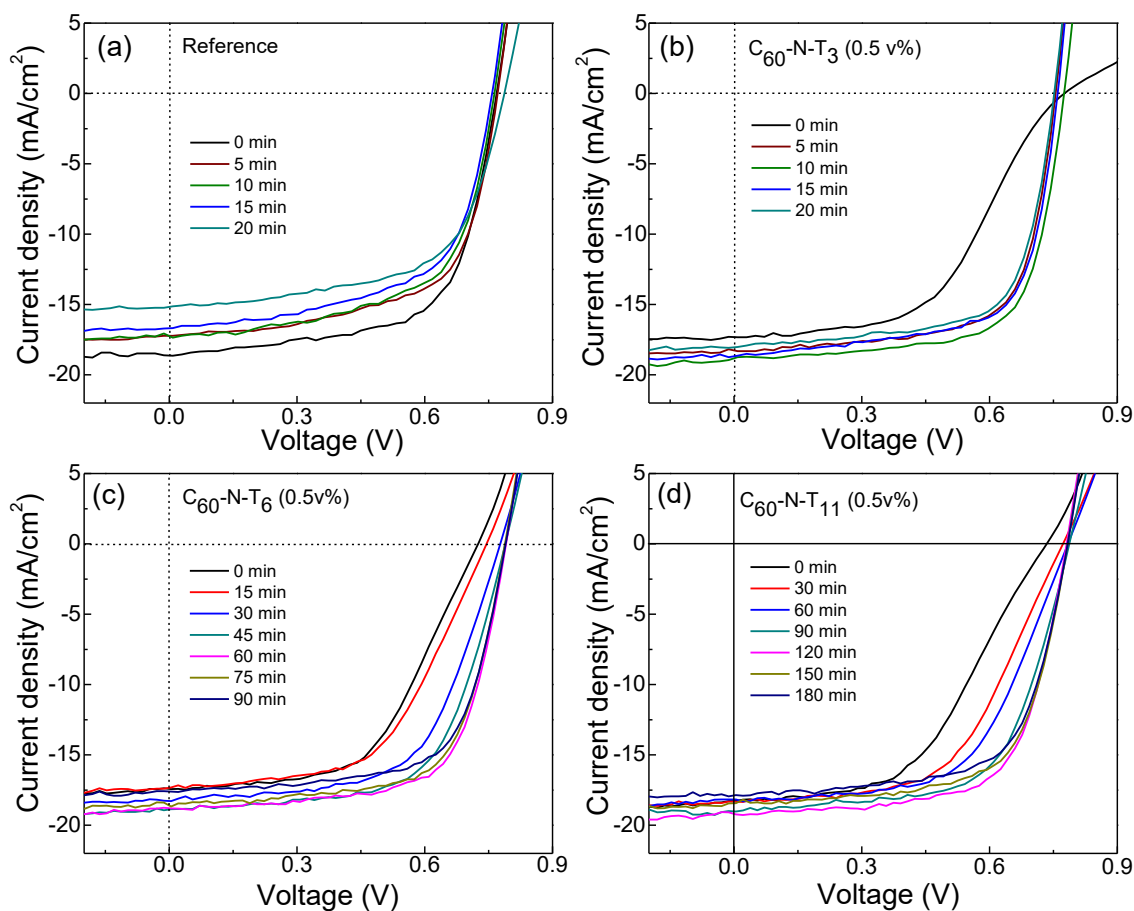
A 2-neck, 500 mL round-bottom flask equipped with a magnetic stir bar, inlet adapter, septum, and Vigreux column was flushed with nitrogen, followed by addition of **3** (273 mg, 0.37 mmol), fullerene-C<sub>60</sub> (396 mg, 0.54 mmol), sarcosine (100 mg, 1.10 mmol) and chlorobenzene (200 mL). The mixture was degassed with nitrogen and then heated to reflux for 12 hours. The reaction was concentrated, dissolved in chloroform and filtered. The resulting filtrate was concentrated and then dissolved in carbon disulfide (CS<sub>2</sub>). The crude mixture was added to silica gel, wet packed with hexanes, and eluted with CS<sub>2</sub>, followed by CH<sub>2</sub>Cl<sub>2</sub>:TEA:MeOH (95:5:5). The first brown band that eluted was collected and concentrated, dissolved in chloroform, filtered through a 1  $\mu$ m PTFE filter and precipitated into acetone. The precipitate was washed with acetone and dried to obtain C<sub>60</sub>-N-T<sub>11</sub> as a brown solid (294 mg, 54 %). <sup>1</sup>H NMR (700 MHz, Chloroform-*d*)  $\delta$  7.57 (d, *J* = 8.6 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 1H), 5.35 (s, 1H), 4.94 (d, *J* = 9.3 Hz, 1H), 4.24 (d, *J* = 9.3 Hz, 1H), 4.08 (t, *J* = 6.5 Hz, 2H), 3.94 (ddd, *J* = 33.8, 15.6, 7.6 Hz, 2H), 3.84 (h, *J* = 9.3 Hz, 2H), 2.77 (s, 3H), 2.36 – 2.17 (m, 24H), 1.93 – 1.65 (m, 6H), 1.62 – 1.40 (m, 12H), 1.39 – 1.10 (m, 36H). <sup>13</sup>C NMR (176 MHz, Chloroform-*d*)  $\delta$  156.86, 155.15, 154.41, 154.14, 153.11, 152.65, 147.35, 147.14, 146.82, 146.49, 146.30, 146.29, 146.25, 146.16, 146.12, 145.99, 145.81, 145.65, 145.62, 145.60, 145.37, 145.35, 145.31, 145.28, 145.16, 145.14, 144.65, 144.64, 144.51, 144.40, 143.01, 142.68, 142.67, 142.60, 142.57, 142.35, 142.33, 142.32, 142.25, 142.20, 142.16, 142.13, 142.03, 141.93, 141.73, 141.71, 141.68, 141.30, 140.17, 140.14, 139.52, 139.48, 136.67, 136.48, 136.09, 134.79, 124.22, 122.48, 108.44, 77.16, 76.43, 73.85, 73.32, 70.01, 68.64, 59.85, 53.00, 45.37, 40.26, 30.63, 30.05, 29.96, 29.85, 29.82, 29.80, 29.77, 29.75, 29.70, 29.67, 29.65, 29.55, 29.50, 27.62, 27.58, 27.56, 27.55, 26.45, 26.24, 26.16. MALDI-TOF (*m/z*): [M+H]<sup>+</sup> calculated for: C<sub>108</sub>H<sub>93</sub>N<sub>4</sub>O<sub>3</sub>: 1494.72, found: 1494.47.



**Figure S1.** Current density-voltage characteristics of the devices with different amount of  $C_{60}$ -N- $T_3$  dipole additives under the simulated solar irradiation after -2 V poling.

**Table S1.** Device performance of the electrochromic solar cells with different amount of  $C_{60}$ -N- $T_3$  dipole additives under the simulated solar irradiation after -2 V poling.

$C_{60}$ -N (v%)	$J_{sc}$ ( $mA/cm^2$ )	$V_{oc}$ (V)	FF (%)	$\eta$ (%)
0.25	18.15	0.77	65.52	9.14 (9.0±0.2)
0.5	18.89	0.78	69.05	10.11 (9.7±0.4)
0.75	17.89	0.77	68.78	9.45 (9.3±0.2)
1.00	17.33	0.77	63.91	8.51 (8.2±0.3)



**Figure S2.** Current density-voltage characteristics of the devices with poling (-2 V) time, (a) Reference sample, (b) Devices with  $C_{60}$ -N-T<sub>3</sub> dipole additives, (c) Devices with  $C_{60}$ -N-T<sub>6</sub> dipole additives and (d) Devices with  $C_{60}$ -N-T<sub>11</sub> dipole additives.

**Table S2.** Device performance of the reference cells with poling time.

Time (min)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF (%)	η (%)
0	18.41	0.77	64.91	9.19 (9.0±0.2)
5	18.21	0.77	63.47	8.91 (8.8±0.1)
10	18.21	0.76	62.16	8.64 (8.5±0.14)
15	17.52	0.76	61.09	8.52 (8.3±0.2)
20	16.00	0.78	61.19	7.70 (7.5±0.2)



**Table S3.** Device performance of the electrochromic cells with C<sub>60</sub>-N-T<sub>3</sub> additive with poling time.

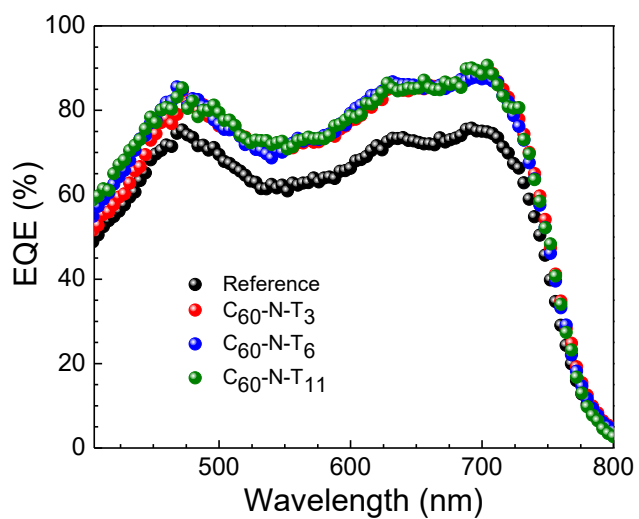
<b>Time (min)</b>	<b>Jsc (mA/cm<sup>2</sup>)</b>	<b>Voc (V)</b>	<b>FF (%)</b>	<b>η (%)</b>
0	17.26	0.78	50.23	6.79 (6.4±0.4)
5	18.25	0.76	68.98	9.51 (9.2±0.3)
10	18.89	0.78	69.05	10.11 (9.7±0.4)
15	18.53	0.76	68.65	9.66 (9.5±0.2)
20	17.91	0.75	68.95	9.28 (9.1±0.2)

**Table S4.** Device performance of the electrochromic cells with C<sub>60</sub>-N-T<sub>6</sub> additive with poling time.

<b>Time (min)</b>	<b>Jsc (mA/cm<sup>2</sup>)</b>	<b>Voc (V)</b>	<b>FF (%)</b>	<b>η (%)</b>
0	17.41	0.72	55.04	6.94 (6.7±0.3)
15	17.28	0.74	55.41	7.13 (6.9±0.2)
30	18.13	0.78	61.02	8.59 (8.3±0.3)
45	18.85	0.79	63.35	9.46 (9.3±0.2)
60	18.83	0.79	67.79	10.09 (9.8±0.3)
75	18.49	0.79	67.30	9.81 (9.4±0.4)
90	17.58	0.79	67.27	9.35 (9.2±0.2)

**Table S5.** Device performance of the electrochromic cells with C<sub>60</sub>-N-T<sub>11</sub> additive with poling time.

Time (min)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF (%)	η (%)
0	18.29	0.73	49.24	6.59 (6.2±0.4)
30	18.30	0.77	55.24	7.80 (7.6±0.2)
60	18.23	0.78	58.56	8.36 (8.4±0.2)
90	18.89	0.79	63.73	9.47 (9.2±0.3)
120	19.12	0.78	66.78	10.01 (9.7±0.3)
150	18.48	0.78	66.61	9.64 (9.4±0.3)
180	17.78	0.78	66.51	9.26 (9.0±0.3)



**Figure S3.** EQE spectra of the corresponding champion devices

## References

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