

## Supporting Information

### Facile Synthesis of 56 $\pi$ -Electron 1,2-Dihydromethano-[60]PCBM and its Application for Thermally Stable Polymer Solar Cells

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**General.** All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk technique. All <sup>1</sup>H (500 MHz) and <sup>13</sup>C (125 MHz) spectra were recorded on Bruker AV500 spectrometers. Spectra were reported in parts per million from internal tetramethylsilane ( $\delta$  0.00 ppm) or residual protons of the deuterated solvent for <sup>1</sup>H NMR and from solvent carbon (e.g.  $\delta$  77.00 ppm for chloroform) for <sup>13</sup>C NMR. The Matrix for MALDI-TOF-MS used 2:1 mixture of alpha-cyano-4-hydroxycinnamic acid (CHCA)/2,5-dihydroxybenzoic acid (DHB) in acetonitrile. Silylmethyl[60]fullerene **2** and 1,2-dihydromethano[60]fullerene **3** were synthesized according to literature methods.<sup>1</sup> C<sub>60</sub> was purchased from American Dye Source. Unless otherwise noted, materials were purchased from Aldrich Inc., and used after appropriate purification.

#### Synthesis of Silylmethyl[60]fullerene **2** from [60]fullerene

<sup>1</sup> (a) Y. Matsuo, Y. Zhang, C.-Z. Li, H. Tanaka, E. Nakamura, *J. Am. Chem. Soc.*, **2011**, *133*, 8086. (b) Y. Matsuo, A. Iwashita, Y. Abe, C.-Z. Li, K. Matsuo, M. Hashiguchi, E. Nakamura, *J. Am. Chem. Soc.*, **2008**, *130*, 15429.

To a solution of C<sub>60</sub> (500 mg, 0.69 mmol) in anhydrous ODCB (100 mL) containing DMF (1.61 mL, 20.7 mmol) was added a THF solution of iPrOMe<sub>2</sub>SiCH<sub>2</sub>MgCl (3.45 mL, 0.60 M, 2.07 mmol) at room temperature. After stirring for 15 min, saturated aqueous NH<sub>4</sub>Cl solution (0.20 mL) was added to quench the reaction. The volatile components were removed under reduced pressure. The residue was then precipitated with Methanol. Chromatograph purification on a silica gel column (eluent: first n-hexane/CS<sub>2</sub>, then CS<sub>2</sub>) gave the compound (500 mg, 85 % yield). Spectral data was identical to the reported one.<sup>1</sup>

### Synthesis of 1,2-dihydromethano[60]fullerene **3** from Silylmethyl[60]fullerene **2**

To a solution of C<sub>60</sub>(CH<sub>2</sub>SiMe<sub>2</sub>O<sup>i</sup>Pr)H (270 mg, 0.32 mmol) in anhydrous ODCB (20 mL) was added a THF solution of t-BuOK (0.38 ml, 0.38 mmol, 1 M) at room temperature. After stirring for 10 min, CuCl<sub>2</sub> (508 mg, 1.92 mmol) was added. Stirring for 40 h at 100 °C, the resulting dark brown suspension was then quenched by 0.5 mL MeOH. The mixture was diluted with toluene and filtered through a pad of silica gel. The brown filtrate was evaporated to a small volume, and precipitation with MeOH afforded a crude product. Chromatograph purification on a silica gel column (eluent: first n-hexane/CS<sub>2</sub>, then CS<sub>2</sub>) gave C<sub>61</sub>H<sub>2</sub> (180 mg, 77 %). Spectral data was identical to the reported one.<sup>1</sup>

### Synthesis of methano-PC<sub>61</sub>BM **1** from 1,2-dihydromethano[60]fullerene **3**

To the dry pyridine (5 mL) solution of methyl-4-benzoylbutyrate tosylhydrazone (191 mg, 0.51 mmol), sodium methoxide (28 mg, 0.51 mmol) were added in one portion under an atmosphere of Argon. The mixture was stirred at room temperature for 10 mins. 1,2-dihydromethano[60]fullerene **3** (150 mg, 0.20 mmol) in anhydrous ODCB (30 mL) was then transferred to the resulting suspension. The reaction mixture was heated to 90 °C for 40 hours under argon. After cooling to room temperature, the solution was then precipitated with methanol. The dry solid was dissolved in anhydrous ODCB (10 mL), and then refluxed for 5 hours. Chromatograph purification on a silica gel column (eluent: first toluene/hexane = 1/4, then toluene/hexane = 1/1) gave product (43 mg, 23%).

**Methano-PC<sub>61</sub>BM** (mixture of isomers) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 2.02-2.23 (m, 2H, CH<sub>2</sub>), 2.37-2.90 (m, 4H, CH<sub>2</sub>), 3.08-3.14 (m, 0.4H, CH<sub>2</sub>), 3.34-3.38 (m, 0.2H,

$CH_2$ ), 3.42 (m, 0.6H,  $CH_2$ ), 3.59-3.78 (m, 3H,  $OCH_3$ ), 4.00-4.38 (m, 0.8H,  $CH_2$ ), 7.35-7.72 (m, 3.5H, Ar- $H$ ), 7.77-7.93 (m, 1.3H, Ar- $H$ ), 8.13-8.15 (m, 0.2H, Ar- $H$ );  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  22.18-22.50 (m), 33.50-34.06 (m), 48.79-49.31 (m), 50.77-50.95 (m), 51.61, 51.69, 51.74, 70.40, 70.60, 70.97, 71.45, 77.50-77.89, 78.98, 79.30, 79.85, 128.04, 128.13, 128.17, 128.24, 128.33, 128.39, 128.42, 128.44, 128.55, 129.03, 131.86, 131.95, 131.99, 132.02, 132.30, 136.12, 136.46, 136.91, 137.09, 138.03, 139.83, 140.65, 141.68, 142.10, 142.13, 142.17, 142.92, 142.99, 143.03, 143.28, 143.76-144.82, 145.05, 145.47, 145.62-146.37, 146.60, 147.80, 173.47-173.55. MALDI-TOF-MS (+): calcd. for  $[C_{73}H_{16}O_2]$ , 924.907, found.  $[M-H]^+$ , 923.987. Anal. Calcd for  $C_{73}H_{16}O_2$ : C, 94.80; H, 1.74. Found: C, 93.99; H, 1.65.

## 5. Devices Fabrication and Characterization

**Materials** [6,6]-Phenyl-C<sub>61</sub>-butyric methyl ester (PC<sub>61</sub>BM) was purchased from Nano-C. Poly(3-hexyl thiophene) (P3HT) was purchased from Rieke Metals. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron P VP AI 4083) was purchased from H.C. Stark. Materials were used as received.

### Devices Fabrication

Conventional PSCs structure based on ITO/PEDOT:PSS/BHJ(110±10nm)/CaAl are used. The ITO-coated glass substrates were cleaned by subsequently soaking in sonication bath containing detergent, acetone, DI-water and Isopropanol (IPA) for 15mins each, and surface treatment with O<sub>2</sub>-Plasma prior to fabricate. A 45 nm thick layer of PEDOT:PSS (Baytron 4083) was spincoated onto each substrate, and then baked at 140°C for 10 mins. The photoactive layer consisting P3HT and fullerene derivative (PC<sub>61</sub>BM, BisPC<sub>61</sub>BM and Methano-PC<sub>61</sub>BM, respectively) (1:1 w/w in chlorobenzene) was spincoated in N<sub>2</sub>-filled glovebox. The substrates were then annealed at 150°C for 10 mins. Finally, Ca (30nm) and Al (100 nm) were thermally deposited with a shadow mask producing individual devices measuring 10.08 mm<sup>2</sup> in area.

**Device Characterization** Photocurrent–voltage (J–V) measurements were performed using a Keithley 2400 in a nitrogen-filled glove box under AM1.5 illumination conditions at intensity of 100 mW/cm<sup>2</sup>. A NREL certified silicon photodiode with a

KG5 filter was used to calibrate. Device EQE spectra were obtained in air by comparison to a known AM1.5 reference spectrum for a calibrated silicon photodiode.

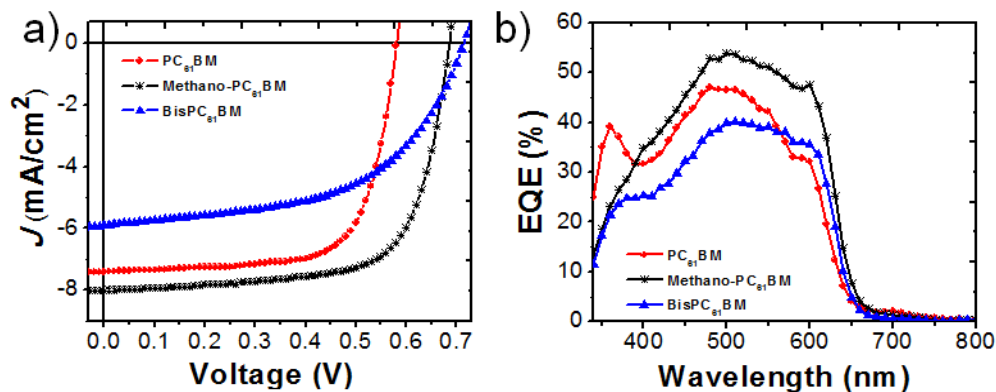


Figure S1. The J-V characteristics under 100mW/cm<sup>2</sup> (AM 1.5) (a) and EQE (b) of PC<sub>61</sub>BM (red), Methano-PC<sub>61</sub>BM **1** (black), and BisPC<sub>61</sub>BM (blue).

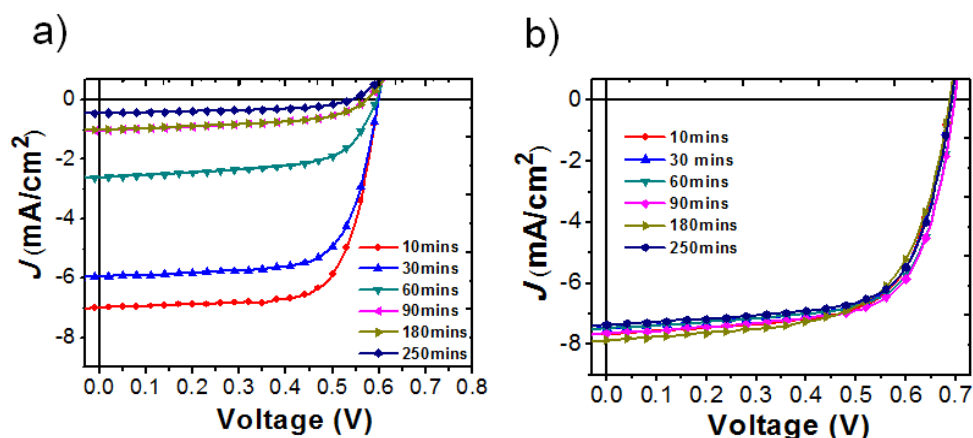


Figure S2. The J-V characteristics of (a) PC<sub>61</sub>BM and (b) Methano-PC<sub>61</sub>BM **1** with different annealing times at 150 °C. Annealing of devices were performed before the deposition of Ca/Al cathode.

Table S1. PSC Performance of PC<sub>61</sub>BM, Methano-PC<sub>61</sub>BM and BisPC<sub>61</sub>BM based OPV at optimum processed condition.

Devices	$V_{oc}$ [V]	$J_{sc}$ [mA/cm <sup>2</sup> ]	FF	PCE [%]
P3HT: PC <sub>61</sub> BM (1:1)	0.58	7.42	0.70	3.02
P3HT:1(1:1)	0.69	8.03	0.69	3.81
P3HT:BisPC <sub>61</sub> BM(1:1)	0.71	5.86	0.54	2.26

## Organic Field-Effect Transistors

Fullerene-based field-effect transistors were fabricated through the top-contact and bottom-gate configuration. Heavily doped p-type silicon <100> substrates with a 300 nm thermal oxide layer were purchased from Montco Silicon Technologies INC. After cleaning the substrate by sequential ultrasonication in acetone and isopropyl alcohol for 15 min followed by air plasma treatment, the oxide layer was passivated with a thin divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB) buffer layer. 1 wt% BCB precursor solution in toluene was spun onto the silicon oxide at 4000 rpm and subsequently annealed at 250 °C overnight. The total capacitance density measured from parallel-plate capacitors was 10.6 nF/cm<sup>2</sup>. The different fullerene films were spin-coated from a 1 wt% chloroform solution at 2000 rpm. Interdigitated source and drain electrodes (W=1000 μm, L= 20/30 μm) were defined by evaporating a Ca (30 nm)/Al (100 nm) through a shadow mask from the resistively heated Mo boat at 10<sup>-7</sup> Torr. OFET characterization was carried out in a N<sub>2</sub>-filled glovebox using an Agilent 4155B semiconductor parameter S6 analyzer. The field-effect mobility was calculated in the saturation regime from the linear fit of (I<sub>ds</sub>)<sup>1/2</sup> vs V<sub>gs</sub>. The threshold voltage (V<sub>t</sub>) was estimated as the x intercept of the linear section of the plot of (I<sub>ds</sub>)<sup>1/2</sup> vs V<sub>gs</sub>. The sub threshold swing was calculated by taking the inverse of the slope of I<sub>ds</sub> vs V<sub>gs</sub> in the region of exponential current increase.

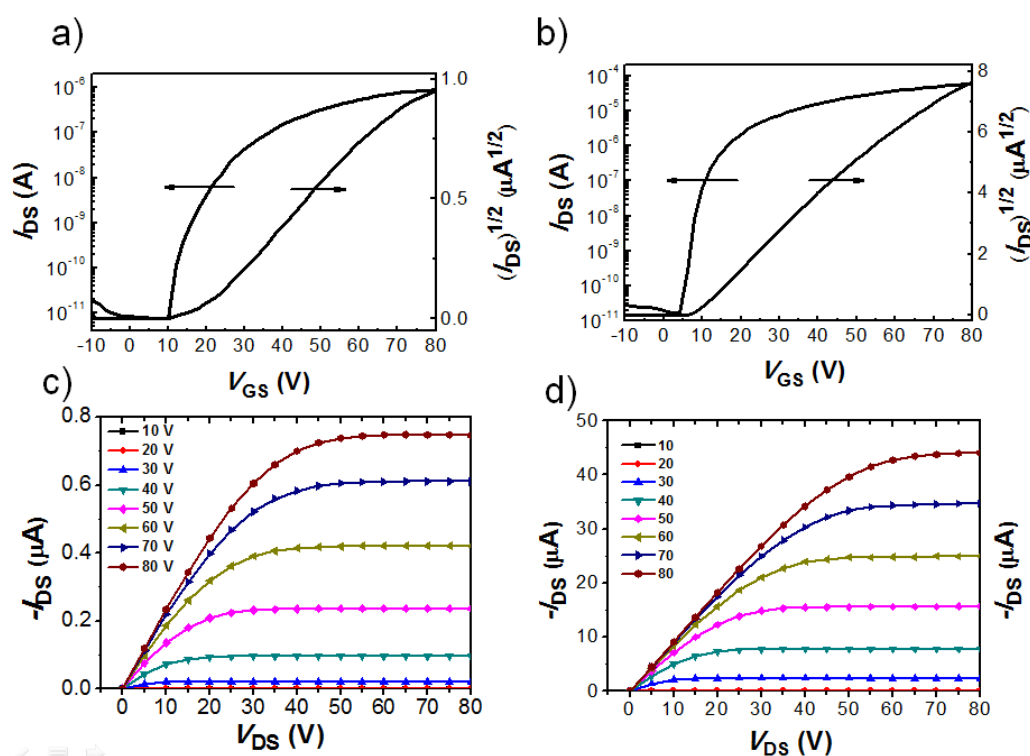


Figure S3. (a and b) Transfer characteristics of BisPC<sub>61</sub>BM and PC<sub>61</sub>BM. (c and d) Output current-voltage characteristics of BisPC<sub>61</sub>BM and PC<sub>61</sub>BM.

Table S2. FET Performance of PC<sub>61</sub>BM, Methano-PC<sub>61</sub>BM and BisPC<sub>61</sub>BM.

Materials	Mobility $\mu$ (cm <sup>2</sup> V <sup>-1</sup> S <sup>-1</sup> )	On/Off ratio	V <sub>t</sub> (V)
PC <sub>61</sub> BM	0.104	9.5 x 10 <sup>5</sup>	~11V
Methano-PC <sub>61</sub> BM 1	0.014	3.8 x 10 <sup>5</sup>	~20V
BisPC <sub>61</sub> BM	0.002	1.2 x 10 <sup>5</sup>	~19V