

*Supporting Information*

**Face-to-face C<sub>6</sub>F<sub>5</sub>-[60]Fullerene Interaction for Ordering Fullerene Molecules and Application to Thin-film Organic Photovoltaics**

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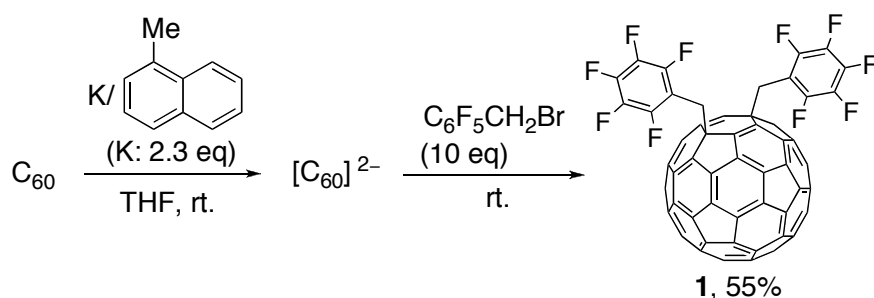
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**General** All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk technique under an argon atmosphere. HPLC analyses were performed on a Shimadzu LC-10A system equipped with SPD-M10A diode array detector and a Buckyprep column (Nacalai Tesque Inc., 4.6 mm ID x 250 mm). Preparative HPLC was performed on a Buckyprep column (20mm ID × 250 mm) using toluene/2-isopropanol (7/3) as eluent (flow rate 5 -15 mL/min, detected at 350 nm with an UV spectrophotometric detector, Shimadzu SPD-6A). Flash silica gel column chromatography was performed on silica gel 60N (Kanto, spherical and neutral, 140-325 mesh) as described by Still.<sup>1</sup> Gel permeation column chromatography was performed on a Japan Analytical Industry LC-9201 (eluent: toluene) with JAIGEL 2H and 3H polystyrene column. NMR spectra were measured with a JEOL ECA-500 (500 MHz) spectrometer. Spectra are reported in parts per million from internal tetramethylsilane ( $\delta$  0.00 ppm) for <sup>1</sup>H NMR, from solvent carbon (e.g.  $\delta$  77.00 ppm for chloroform) for <sup>13</sup>C NMR. High-resolution mass spectra were measured by APCI using a time-of-flight mass analyzer on a JEOL JMS-T100LC (AccuTOF) spectrometer.

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<sup>1</sup> Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

### Procedures for the preparation of 1,4-bis(pentafluorobenzyl)[60]fullerene (**1**)



To a freeze-thaw degassed mixture of C<sub>60</sub> (1000 mg, 1.39 mmol) and 1-methylnaphthalene (5.93 mL, 41.7 mmol, 30 equiv.) in 150 mL THF, metal potassium (124 mg, 3.19 mmol) was added in one portion. A dark red solution was produced after stirring under argon at room temperature for 3 hours. Pentafluorobenzyl bromide (3628 mg, 13.9 mmol) was then added. With stirring for additional 8 hours, the reaction mixture was quenched with aq. NH<sub>4</sub>Cl (0.5 mL). After concentration to a volume of ca. 10 mL, the desired product was precipitated by methanol. Purification on a silica gel column (eluent: first CS<sub>2</sub>/hexane = 1/1, then CS<sub>2</sub>) afforded 1,4-bis(pentafluorobenzyl)[60]fullerene **1** in 55% yield (830 mg). Further purification of sample for measurements and OPV evaluation was achieved with preparative HPLC (Buckyprep column, 20 mm ID x 250 mm, eluent: toluene/2-propanol = 7/3) and GPC (eluent: toluene). The compound as solid or in solution was stable under air.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 4.34 (d, <sup>2</sup>J<sub>H-H</sub> = 13.8 Hz, 2H, C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>), 4.36 (d, <sup>2</sup>J<sub>H-H</sub> = 13.8 Hz, 2H, C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 35.05 (2C, CH<sub>2</sub>), 57.68 (2C, sp<sup>3</sup>-C of C<sub>60</sub>), 109.70 (t, J<sub>C-F</sub> = 253 Hz, C<sub>6</sub>F<sub>5</sub>), 123.27 (C<sub>6</sub>F<sub>5</sub>), 127.96 (C<sub>6</sub>F<sub>5</sub>), 128.77 (C<sub>6</sub>F<sub>5</sub>), 136.56 (t, J<sub>C-F</sub> = 253 Hz, C<sub>6</sub>F<sub>5</sub>), 137.68, 138.55, 140.80, 141.73, 141.85, 142.08, 142.41, 142.48, 142.95, 143.12, 143.38, 143.75, 143.95, 143.98, 144.06, 144.12, 144.28, 144.39, 144.46, 144.97, 145.10, 145.43, 146.21, 146.47, 146.77, 146.79, 147.01, 147.65, 148.55, 149.94, 154.69; <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -137.78 (*o*-F), -152.34 (*m*-F), -159.32 (*p*-F); APCI-MS (-): *m/z* calcd for C<sub>74</sub>F<sub>10</sub>H<sub>4</sub> (M-H<sup>+</sup>), 1082.0153; found, 1082.0162. Anal. Calcd for C<sub>74</sub>F<sub>10</sub>H<sub>4</sub>: C, 82.08; H, 0.37. Found: C, 81.89; H, 0.57.

### DSC characterization of thermotropic crystalline phase

Differential scanning calorimetry (DSC) measurement was performed on a NETZSCH DSC204 Phoenix calorimeter (DSC 204/F1). Under N<sub>2</sub> gas, samples were investigated at a scanning rate of 10 °C/min with applying two heating and cooling cycles.

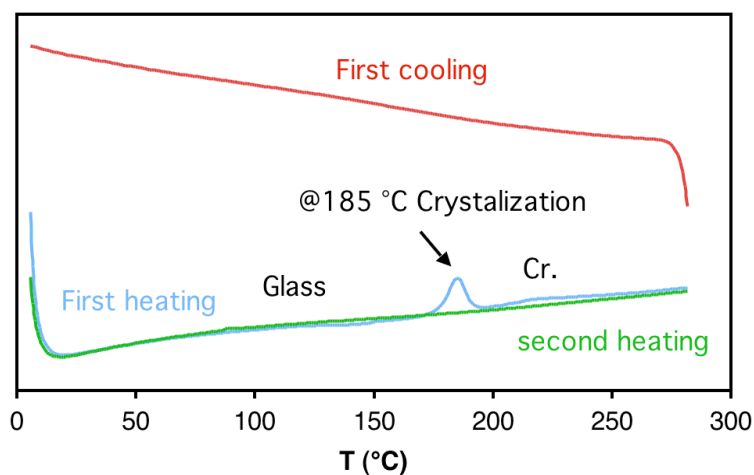


Figure S1. DSC curves of compound **1**. An exothermic peak at 185 °C shows the crystallization process to form higher ordered structure.

### Powder X-ray diffraction analysis of compound **1**

Powder X-ray diffraction study was carried out on a Rigaku R-AXIS RAPID II imaging plate diffractometer using Cu-K $\alpha$  radiation. The measurement temperatures were varied using the temperature controller Rigaku CGD-4 under N<sub>2</sub> gas. Samples were grinded down and packed into glass capillaries.

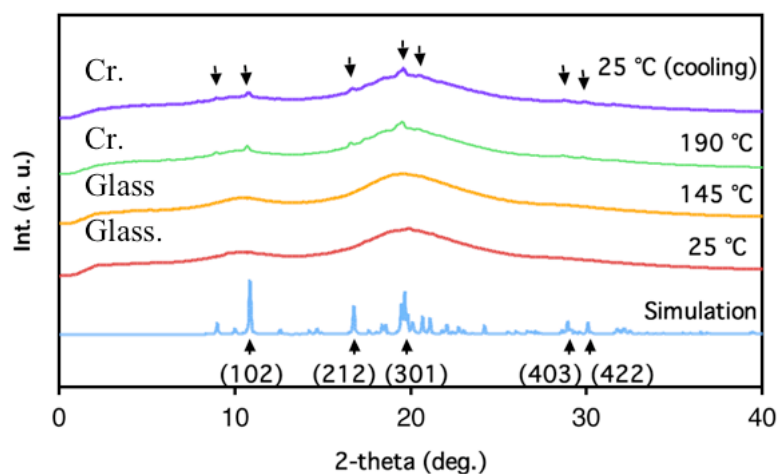


Figure S2. Variable temperature XRD patterns. Thermotropic crystalline phase has been

revealed. Blue line: A simulated pattern from X-ray single crystal analysis of **1**; red line: diffraction pattern at 25 °C; orange line: at 145 °C; green line: at 190 °C; purple line: diffraction pattern after cooling to 25 °Cs.

### TG-DTA measurement of compound **1**

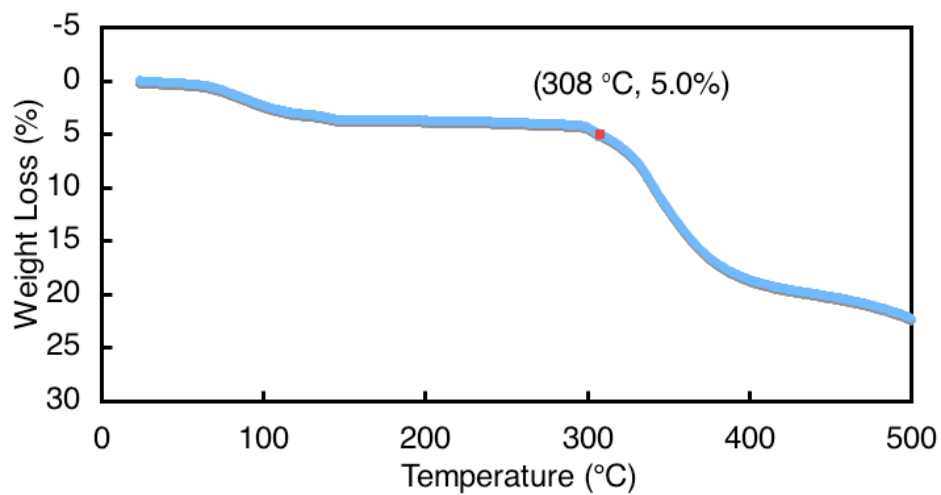


Figure S3. TG-DTA curves of compound **1** under N<sub>2</sub>. The decomposition temperature ( $T_{95} = 308$  °C) was determined as the temperature at which 5% weight loss occurred.