Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

Developing isomer-free fullerene bisadducts for efficient polymer solar cells

Zuo Xiao,‡ Xinjian Geng,‡ Dan He, Xue Jia and Liming Ding*

National Center for Nanoscience and Technology, Beijing 100190, China
E-mail: ding@nanoctr.cn

1. General characterization

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-400 spectrometer. Varying-temperature NMR spectra were measured on a Bruker Avance-500 spectrometer. High-resolution ESI mass spectra were measured on a Bruker Apex IV FTMS spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were conducted on a Shanghai Chenhua CHI620D voltammetric analyzer. All measurements were carried out in a one-compartment cell equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a Ag/Ag^+ reference electrode. Measurements were performed in ODCB/CH_3CN (9:1) solution containing tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte at 25 ºC under argon. For CV measurements, the scan rate is 0.1 V/s. For DPV measurements, the pulse width is 200 ms, the pulse period is 500 ms, the sample width is 16.7 ms, the pulse amplitude is 50 mV and the potential increment is 4 mV. All potentials were corrected against Fc/Fc^+. Single-crystal XRD analyses for compound **2** and *e*-PPMF were performed on a Rigaku MM007HF Saturn724+ diffractometer. Single-crystal XRD analysis for compound **3** was performed on a Rigaku RAPID-S diffractometer.

2. Synthesis

All reagents were purchased from Alfa Aesar Co., Aladdin Co., J&K Co., Rieke Metals Co. and other commercial suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. Di-ter-butyl-2-bromomalonate,[1] $C_{60}C(CO_2{}^tBu)_2$,[1] 1,4-dihydrobenzo[d][1,2]oxathiine 3-oxide,[2] $PC_{61}BM$,[3] PPDT2FBT[4] and PBDTTT-C-T[5] were prepared according to literatures.

Phenethyl 2-bromo-2-phenylacetate (PP-Br). To a solution of 2-bromo-2-phenylacetic acid (15.4 g, 71.6 mmol) and 2-phenylethanol (8.7 g, 71.3 mmol) in toluene (100 mL) was added sulfuric acid (2.5 g, 25.5 mmol). The reaction mixture was heated to reflux for 3 h. The side product (water) was removed by a knockout trap during refluxing. After cooling to room temperature, the reaction mixture was sequentially washed by water, $NaHCO_3$, and water. The solvent was removed under reduced pressure. Silica gel column chromatography using CH_2Cl_2 as the eluent gave pure PP-Br as a light-yellow oil (21.3 g, 66.8 mmol, 94%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.46-7.49 (m, 2H, Ar), 7.30-7.33 (m, 3H, Ar), 7.18-7.27 (m, 3H, Ar), 7.12-7.14 (m, 2H, Ar), 5.31 (s, 1H, C*H*), 4.37 (t, J = 6.9 Hz, 2H, CH_2), 2.93 (t, J = 6.9 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 168.08, 137.23, 135.81, 129.14, 128.85, 128.73, 128.64, 128.49, 126.62, 66.72, 46.82, 34.81.

***trans1*-AC$_{60}$BA/C$_{60}$ mixture.** C_{60} (10.0 g, 13.9 mmol) and anthracene (4.95 g, 27.8 mmol) were mixed in an agate mortar and then ground into a fine powder. The powder was transferred into a 25 mL flask equipped with a vacuum valve. The flask was vacuumized and put into a muffle furnace and kept at 240 ºC for 2 hrs. After cooling to room temperature, the solid was taken out of the flask and dispersed in CS_2 (200 mL) by using ultrasonics and then filtered. The solid was washed with CS_2 to give the *trans1*-AC$_{60}$BA/C$_{60}$ mixture (12.6 g). Thin layer chromatography (TLC) indicated a ~1:1 mixture of *trans1*-AC$_{60}$BA and C_{60}. *trans1*-AC$_{60}$BA was confirmed by ^{1}H NMR.[6] ^{1}H NMR ($CDCl_3/CS_2$, 400 MHz, δ/ppm): 7.81-7.83 (m, 8H, Ar), 7.49-7.51 (m, 8H, Ar), 6.07 (s, 4H, bridgehead C*H*).

Compound 1 and compound 2. To a suspension of *trans1*-AC$_{60}$BA/C$_{60}$ mixture (12.6 g) in CS_2 (1200 mL) were sequentially added di-tert-butyl-2-bromomalonate (16.4 g, 55.6 mmol) and DBU (8.5 g, 55.9 mmol). The mixture was stirred at room temperature for 16 h and then filtered. The filtrate was submitted to a silica gel column with CS_2 as the eluent. The first brown band was collected, giving a pure unreacted *trans1*-AC$_{60}$BA (1.8 g, 1.7 mmol). Then, the eluent was changed to CS_2:CH_2Cl_2 (3:1). The second greenish brown band was collected, giving the crude compound **1**. Using $CHCl_3$ to wash, pure **1** was obtained as a brown solid (3.0 g, 2.3

mmol). The third reddish brown band was collected, giving the crude compound **2**. Using $CHCl_3$ to wash, pure **2** were obtained as brown crystals (2.8 g, 2.2 mmol).

Compound **1**. ^1H NMR ($CDCl_3/CS_2$, 400 MHz, δ/ppm): 7.73-7.75 (m, 4H, Ar), 7.65-7.67 (m, 4H, Ar), 7.43-7.46 (m, 8H, Ar), 5.85 (s, 4H, bridgehead C*H*), 1.48 (s, 18H, C*H*$_3$). ^{13}C NMR ($CDCl_3/CS_2$, 100 MHz, δ/ppm): 161.60, 153.44, 153.04, 149.45, 147.70, 146.00, 145.68, 145.31, 144.70, 144.48, 141.84, 141.74, 141.62, 141.46, 141.37, 141.07, 138.28, 136.82, 126.96, 126.90, 125.56, 125.35, 83.27, 72.77, 70.39, 58.19, 27.65. ESI-HRMS (+): $C_{99}H_{39}O_4$ [M + H^+] calc. 1291.2843, found 1291.2848.

Compound **2**. ^1H NMR ($CDCl_3/CS_2$, 400 MHz, δ/ppm): 7.74-7.76 (m, 4H, Ar), 7.62-7.64 (m, 4H, Ar), 7.37-7.45 (m, 8H, Ar), 5.87 (s, 2H, bridgehead C*H*), 5.53 (s, 2H, bridgehead C*H*), 1.62 (s, 18H, C*H*$_3$). ^{13}C NMR ($CDCl_3/CS_2$, 100 MHz, δ/ppm): 162.56, 156.34, 151.71, 145.98, 145.90, 145.50, 145.27, 144.71, 144.58, 143.03, 142.76, 141.58, 141.52, 141.32, 140.99, 140.77, 139.10, 127.02, 126.95, 125.68, 83.30, 69.75, 69.59, 69.40, 59.01, 58.31, 55.45, 27.88. ESI-HRMS (+): $C_{99}H_{39}O_4$ [M + H^+] calc. 1291.2843, found 1291.2869. Single crystals of **2** were obtained by slowly diffusing ethanol into its CS_2 solution. Formula: $C_{102.5}H_{38}O_4S_7$; formula weight: 1557.75; crystal system: triclinic; space group: *P* -1; color of crystal: brown; unit cell parameters: a = 12.422(4) Å, b = 16.732(6) Å, c = 18.496(6) Å, α = 106.880(5)°, β = 94.237(3)°, γ = 108.521(3)°, V = 3429.30(19) Å^3; temperature for data collection: 173 K; $Z = 2$; final *R* indices [I >2σ(I)]: $R1 = 0.1046$, $wR2 = 0.2790$; GOF on F^2: 1.140. The crystallographic data have been deposited in Cambridge Crystallographic Data Centre (CCDC-1444239).

Compound 3. To a suspension of compound **1** (3.0 g, 2.3 mmol) and compound **2** (2.8 g, 2.2 mmol) in ODCB (400 mL) were sequentially added di-tert-butyl-2-bromomalonate (4.0 g, 13.6 mmol) and KO^{t}Bu solution (1 M in THF, 13.5 mL, 13.5 mmol). The mixture was stirred at room temperature for 15 min and quenched with water. The organic layer was submitted to a silica gel column with CS_2 as the eluent.

After removal of the colorless band (ODCB), the eluent was changed to CS_2:CH_2Cl_2 (2:1). The first brown band was collected, affording recovered **1** and **2** (1.1 g, 0.9 mmol). The second red band was collected, giving the crude compound **3**. After recrystallization in CS_2:EtOH, pure **3** was obtained as red crystals (3.6 g, 2.4 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.67-7.69 (m, 2H, Ar), 7.57-7.59 (m, 4H, Ar), 7.47-7.49 (m, 2H, Ar), 7.33-7.38 (m, 8H, Ar), 5.63 (s, 2H, bridgehead C*H*), 5.33 (s, 2H, bridgehead C*H*), 1.54 (s, 18H, C*H*$_3$), 1.43 (s, 9H, C*H*$_3$), 1.39 (s, 9H, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 162.82, 162.34, 156.63, 154.92, 151.94, 150.53, 149.45, 148.14, 147.13, 146.99, 146.38, 146.02, 145.77, 145.52, 145.40, 145.14, 144.94, 144.27, 143.89, 143.47, 143.38, 142.24, 142.04, 142.01, 141.84, 141.78, 140.87, 140.80, 140.74, 140.59, 131.80, 128.31, 128.18, 127.85, 126.97, 126.90, 126.87, 126.83, 126.22, 125.71, 125.51, 125.47, 125.34, 83.85, 83.68, 83.50, 71.97, 69.37, 69.26, 68.20, 68.01, 58.85, 58.12, 55.30, 54.37, 28.00, 27.97. ESI-HRMS (+): $C_{110}H_{57}O_8$ [M + H$^+$] calc. 1505.4048, found 1505.4021. Single crystals of **3** were obtained by slowly diffusing ethanol into its CS_2 solution. Formula: $C_{110}H_{56}O_8$; formula weight: 1505.54; crystal system: triclinic; space group: *P* -1; color of crystal: red; unit cell parameters: a = 14.1171(5) Å, b = 17.2567(7) Å, c = 18.6353(6) Å, α = 101.068(3)°, β = 102.967(3)°, γ = 96.525(3)°, V = 4283.1(3) Å^3; temperature for data collection: 100 K; *Z* = 2; final *R* indices [I >2σ(I)]: *R1* = 0.0745, *wR2* = 0.2242; GOF on F^2: 1.023. The crystallographic data have been deposited in Cambridge Crystallographic Data Centre (CCDC-1444242).

***e*-C$_{60}$[C(CO$_2$^{t}Bu)$_2$]$_2$.** A solution of compound **3** (3.6 g, 2.4 mmol) in toluene (500 mL) was heated to reflux for 3 h. Then, the solvent was removed under reduced pressure. The residue was submitted to a silica gel column with toluene as the eluent. The major reddish brown band was collected and evaporated under reduced pressure to give *e*-C_{60}[C(CO$_2$^{t}Bu)$_2$]$_2$ (2.7 g, 2.4 mmol, 17% overall yield based on 10 g C_{60}). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 1.63 (s, 9H, C*H*$_3$), 1.62 (s, 18H, C*H*$_3$), 1.60 (s, 9H, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 162.52, 162.50, 162.39, 147.97, 147.14, 146.49, 146.32, 146.30, 146.00, 145.43, 145.34, 145.22, 144.89, 144.52, 144.31, 143.97, 143.71, 143.34, 143.23, 142.80, 142.09, 141.69, 141.62, 141.58, 138.56, 138.46, 84.47, 84.45, 84.30, 72.30, 72.17, 70.95, 55.43, 53.14, 28.06, 28.05. ESI-HRMS (+): $C_{82}H_{36}O_8$ [M^+] calc. 1148.2405, found 1148.2380.

Compound 4. To a suspension of *trans1*-$AC_{60}BA$ (2.00 g, 1.86 mmol) in CS_2 (400 mL) was added 1,4-dihydrobenzo[d][1,2]oxathiine 3-oxide (2.50 g, 14.9 mmol). The mixture was heated to reflux for 5 h. The reaction mixture was cooled to room temperature and filtered. The solid was undissolved *trans1*-$AC_{60}BA$. The filtrate was submitted to a silica gel column with CS_2 as the eluent. The first brown band was unreacted *trans1*-$AC_{60}BA$, and it was combined with the undissolved *trans1*-$AC_{60}BA$ to give the recovered *trans1*-$AC_{60}BA$ (1.41 g, 1.31 mmol). The second brown band was collected and evaporated under reduced pressure to give the crude compound **4**. After washing with $CHCl_3$:hexane (1:1) to remove by-products, pure **4** was obtained as a brown solid (201 mg, 0.17 mmol, 9%) (31% yield when considering the recovered *trans1*-$AC_{60}BA$). Then, the eluent was changed to CH_2Cl_2:AcOEt (10:1). A colorless band was collected and evaporated under reduced pressure to give the recovered 1,4-dihydrobenzo[d][1,2]oxathiine 3-oxide (1.89 g, 11.3 mmol). ^1H NMR ($CDCl_3/CS_2$, 400 MHz, δ/ppm): 7.33-7.72 (br, Ar, two isomers), 5.11-5.75 (br, bridgehead C*H*, two isomers), 3.34-4.23 (br, CH_2, two isomers). ^{13}C NMR spectrum was not obtained due to the low solubility of the sample. ESI-HRMS (+): $C_{96}H_{29}$ [M + H^+] calc. 1181.2264, found 1181.2243.

Compound 5. To a suspension of compound **4** (150 mg, 0.13 mmol) in CS_2 (30 mL) was added 1,4-dihydrobenzo[d][1,2]oxathiine 3-oxide (437 mg, 2.60 mmol). The mixture was heated to reflux for 3 h. The reaction mixture was cooled to room temperature and filtered. The solid was undissolved **4**. The filtrate was submitted to a silica gel column with CS_2:CH_2Cl_2 (20:1) as the eluent. The first brown band was unreacted **4**, and it was combined with undissolved **4** to give the recovered **4** (63 mg, 0.05 mmol). The second orange band was collected and evaporated under reduced pressure to give compound **5** as an orange solid (37 mg, 0.03 mmol, 23%) (39% yield when considering the recovered **4**). Then, the eluent was changed to CH_2Cl_2:AcOEt (10:1). A colorless band was collected and evaporated under reduced pressure to give the recovered 1,4-dihydrobenzo[d][1,2]oxathiine 3-oxide (309 mg, 1.84 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.14-7.60 (br, 24H, Ar), 4.76-5.34 (br, 4H, bridgehead C*H*), 2.94-3.65 (br, 8H, C*H*$_2$). ^{13}C NMR spectrum was not obtained due to the low solubility of the sample. ESI-HRMS (+): $C_{104}H_{37}$ [M + H$^+$] calc. 1285.2890, found 1285.2877.

***e*-NC$_{60}$BA.** A solution of compound **5** (50 mg, 0.039 mmol) in toluene (10 mL) was heated to reflux for 2 h. Then, the solvent was removed under reduced pressure. The residue was submitted to a silica gel column with CS_2:hexane (1:1) as the eluent. The major reddish brown band was collected and evaporated under reduced pressure to give *e*-NC$_{60}$BA (34 mg, 0.037 mmol, 94%). ^{1}H NMR ($C_2D_2Cl_4$, 400 MHz, δ/ppm): 7.44-7.51 (br, 8H, Ar), 3.42-4.28 (br, 8H, C*H*$_2$). ^{13}C NMR ($C_2D_2Cl_4$, 100 MHz, δ/ppm): 161.18, 155.06, 154.07 (br), 149.82 (br), 148.63, 147.62, 146.83, 145.80 (br), 145.40, 144.65, 144.21, 144.16, 144.01, 143.43 (br), 142.43 (br), 141.90, 141.05 (br), 140.60 (br), 140.06 (br), 137.60, 137.33, 137.25, 135.82 (br), 134.64 (br), 127.30, 64.28, 63.97 (br), 44.69 (br), 44.40, 44.09. ESI-HRMS (+): $C_{76}H_{16}$ [M$^+$] calc. 928.1247, found 928.1224.

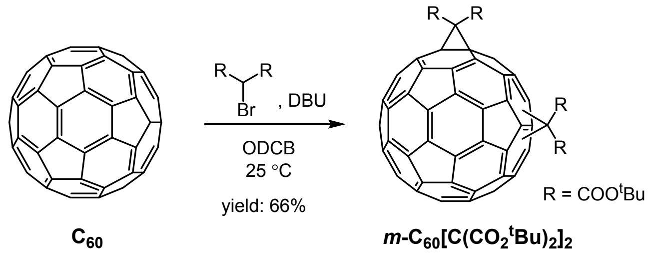
Compound 6. To a solution of compound **1** (2.00 g, 1.55 mmol) in ODCB (800 mL) were sequentially added PP-Br (1.98 g, 6.21 mmol) and KO^{t}Bu solution (1 M in THF, 6.21 mL, 6.21 mmol). The mixture was stirred at room temperature for 15 min and quenched with water. The organic layer was submitted to a silica gel column with CS_2 as the eluent. After removal of the colorless band (ODCB), the eluent was changed to CS_2:CH_2Cl_2 (2:1). The first greenish brown band was collected and evaporated under reduced pressure to give recovered **1** (910 mg, 0.71 mmol). The second red band was collected and evaporated under reduced pressure to give the crude compound **6**. After recrystallization in CH_2Cl_2:EtOH, pure **6** was obtained as red crystals (650 mg, 0.43 mmol, 27%) (50% yield when considering the recovered **1**). ^{1}H NMR ($CDCl_3$, 400

MHz, δ/ppm): 7.29-7.70 (m, 21H, Ar), 7.19-7.20 (m, 3H, Ar), 7.00-7.02 (m, 2H, Ar), 5.64 (s, 1H, bridgehead C*H*), 5.58 (s, 1H, bridgehead C*H*), 5.40 (s, 1H, bridgehead C*H*), 4.99 (s, 1H, bridgehead C*H*), 4.34 (t, J = 6.6 Hz, 2H, CH_2), 2.86 (t, J = 6.6 Hz, 2H, CH_2), 1.43 (s, 18H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 166.76, 162.37, 162.34, 156.55, 156.43, 154.83, 154.73, 152.21, 152.06, 150.75, 150.55, 149.47, 149.34, 148.10, 148.05, 147.10, 147.04, 146.95, 146.89, 146.62, 146.27, 146.09, 145.94, 145.92, 145.90, 145.74, 145.69, 145.65, 145.47, 145.04, 144.73, 144.71, 144.26, 144.16, 143.93, 143.70, 143.26, 143.17, 142.99, 142.71, 142.46, 142.18, 142.07, 141.97, 141.87, 141.84, 141.77, 141.72, 141.63, 141.54, 141.38, 140.86, 140.72, 140.69, 140.63, 140.56, 140.49, 137.42, 133.23, 131.71, 128.81, 128.61, 128.45, 128.08, 126.92, 126.84, 126.80, 126.76, 126.70, 126.64, 126.52, 125.75, 125.64, 125.59, 125.55, 125.42, 125.35, 83.90, 83.66, 72.04, 71.87, 71.23, 71.20, 69.31, 69.28, 69.20, 69.01, 66.67, 58.55, 58.44, 57.93, 57.86, 56.01, 54.30, 34.88, 27.95, 27.89. ESI-HRMS (+): $C_{115}H_{52}O_6K$ [M + K^+] calc. 1567.3396, found 1567.3419.

Compound 7. A solution of compound **6** (650 mg, 0.43 mmol) in toluene (100 mL) was heated to reflux for 3 h. Then, the solvent was evaporated under reduced pressure. The residue was submitted to a silica gel column with toluene as the eluent. The major reddish brown band was collected and evaporated under reduced pressure to give compound **7** (490 mg, 0.42 mmol, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.92-7.94 (m, 2H, Ar), 7.46-7.48 (m, 3H, Ar), 7.19-7.24 (m, 3H, Ar), 7.10-7.12 (m, 2H, Ar), 4.51 (t, J = 6.7 Hz, 2H, CH_2), 2.97 (t, J = 6.6 Hz, 2H, CH_2), 1.65 (s, 9H, CH_3), 1.64 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 166.46, 162.48, 149.57, 148.52, 147.20, 147.15, 146.47, 146.35, 146.32, 146.03, 145.98, 145.49, 145.36, 145.22, 145.17, 145.11, 145.01, 144.95, 144.81, 144.60, 144.59, 144.51, 144.47, 144.41, 144.32, 144.24, 144.20, 144.16, 143.99, 143.83, 143.80, 143.78, 143.73, 143.50, 143.36, 143.33, 143.30, 143.15, 142.82, 142.67, 142.00, 141.70, 141.61, 141.57, 141.19, 140.95, 140.59, 139.03, 138.63, 138.37, 137.25, 132.34, 132.22, 129.07, 128.85, 128.49, 128.46, 126.61, 84.43, 84.29, 75.52, 74.32, 72.41, 72.27, 67.02, 55.58, 54.64, 34.92, 28.08, 28.04. ESI-HRMS (+): $C_{87}H_{32}O_6$ [M^+] calc. 1172.2193, found 1172.2175.

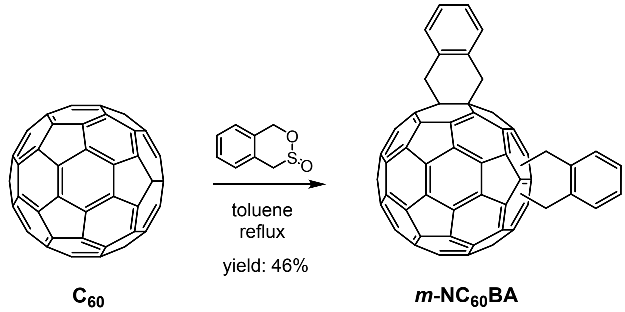
***e*-PPMF.** A solution of compound **7** (490 mg, 0.42 mmol) in ODCB (100 mL) was heated to reflux for 14 h. After cooling to room temperature, 1,10-phenanthroline monohydrate (85 mg, 0.43 mmol) and Ag_2CO_3 (59 mg, 0.21 mmol) were added to the solution. The mixture was heated to reflux, being irradiated under four lamps (13 W) for 7 h. The reaction mixture was cooled to room temperature and submitted to a flash column with CS_2:CH_2Cl_2 (2:1) as the eluent. The first reddish brown band was collected and evaporated under reduced pressure to give the crude *e*-PPMF. By using silica gel column with CS_2:CH_2Cl_2 (8:1) as the eluent, pure *e*-PPMF was obtained as a brown solid (172 mg, 0.18 mmol, 42%). ^1H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.92-7.95 (m, 2H, Ar), 7.46-7.50 (m, 3H, Ar), 7.19-7.24 (m, 3H, Ar), 7.11-7.13 (m, 2H, Ar), 4.51 (m, 2H, C*H*$_2$), 3.69 (dd, J = 62.7, 6.5 Hz, 2H, methano group C*H*$_2$), 2.98 (t, J = 6.7 Hz, 2H, C*H*$_2$). ^{13}C NMR ($CDCl_3$/CS_2, 100 MHz, δ/ppm): 166.32, 149.34, 149.10, 149.01, 148.87, 148.75, 148.17, 147.10, 147.07, 146.39, 146.36, 146.17, 146.12, 146.08, 145.88, 145.83, 145.38, 145.22, 145.09, 145.06, 144.95, 144.67, 144.61, 144.57, 144.55, 144.53, 144.47, 144.30, 144.24, 144.01, 143.84, 143.82, 143.63, 143.29, 143.09, 142.92, 141.99, 141.82, 141.74, 141.68, 141.09, 140.82, 140.49, 140.32, 140.27, 140.25, 139.27, 138.86, 137.22, 136.58, 136.57, 132.39, 132.21, 129.06, 128.80, 128.49, 128.47, 126.62, 76.28, 74.90, 71.89, 71.80, 66.90, 54.98, 35.03, 28.92. ESI-HRMS (+): $C_{77}H_{17}O_2$ [$M + H^+$] calc. 973.1223, found 973.1202. Single crystals of *e*-PPMF were obtained by slowly diffusing methanol into its toluene solution. Formula: $C_{77}H_{16}O_{2.6}$; formula weight: 982.42; crystal system: monoclinic; space group: P 21/c; color of crystal: brown; unit cell parameters: a = 23.316(7) Å, b = 10.157(3) Å, c = 17.402(5) Å, α = 90°, β = 98.718(5)°, γ = 90°, V = 4073(2) $Å^3$; temperature for data collection: 173 K; Z = 4; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.1015, $wR2$ = 0.2375; GOF on F^2: 1.438. The crystallographic data have been deposited in Cambridge Crystallographic Data Centre (CCDC-1444244).

***m*-$C_{60}[C(CO_2{}^tBu)_2]_2$**



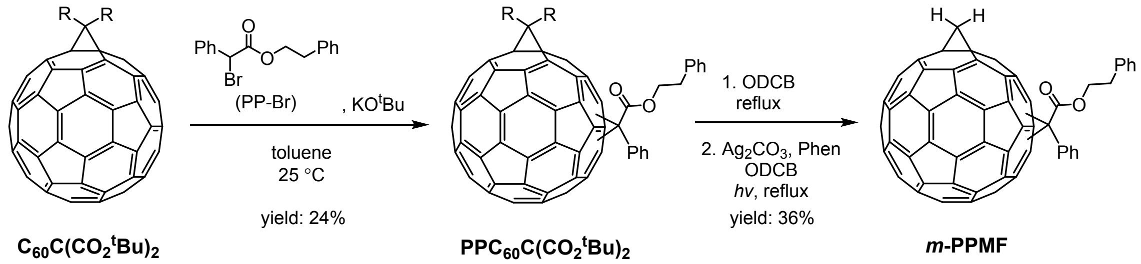
To a solution of C_{60} (1.00 g, 1.39 mmol) and di-tert-butyl-2-bromomalonate (820 mg, 2.78 mmol) in ODCB (70 mL) was added DBU (423 mg, 2.78 mmol). The mixture was stirred at room temperature for 1.5 h. The solution was submitted to a silica gel column with toluene/CS_2 (1:1) as the eluent. The major brownish red band was collected to give *m*-$C_{60}[C(CO_2{}^tBu)_2]_2$ (1.05 g, 66%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 1.55-1.71 (m, 36H, CH_3). ESI-HRMS (+): $C_{82}H_{36}O_8$ [M^+] calc. 1148.2410, found 1148.2399.

m-NC_{60}BA



To a suspension of C_{60} (500 mg, 0.69 mmol) in toluene (50 mL) was added 1,4-dihydrobenzo[d][1,2]oxathiine 3-oxide (234 mg, 1.39 mmol). The mixture was heated to reflux for 2 h. Then, the solvent was evaporated under reduced pressure. The residue was submitted to a silica gel column with CS_2:hexane (2:1) as the eluent. After the first band (C_{60}) and the second band (mono-adduct) being removed, the third brown band was collected and evaporated under reduced pressure to give *m*-NC_{60}BA (296 mg, 0.32 mmol, 46%). ^{1}H NMR ($C_2D_2Cl_4$, 400 MHz, δ/ppm): 7.45-7.85 (br, 8H, Ar), 3.42-4.95 (br, 8H, CH_2). ESI-HRMS (+): $C_{76}H_{16}$ [M^+] calc. 928.1247, found 928.1233.

m-PPMF



Step I: To a solution of $C_{60}C(CO_2{}^tBu)_2$ (2.00 g, 2.14 mmol) in toluene (200 mL) were sequentially added PP-Br (1.37 g, 4.29 mmol) and KO^tBu solution (1 M in THF, 4.29 mL, 4.29 mmol). The mixture was stirred at room temperature for 15 min and quenched with water. Toluene was evaporated under reduced pressure. The residue was submitted to a silica gel column with CS_2:CH_2Cl_2 (2:1) as the eluent. The first reddish brown band was unreacted $C_{60}C(CO_2{}^tBu)_2$. The second brown band was collected and evaporated under reduced pressure to give $PPC_{60}C(CO_2{}^tBu)_2$ as a brown solid (600 mg, 0.51 mmol, 24%).

Step II: A solution of $PPC_{60}C(CO_2{}^tBu)_2$ (600 mg, 0.51 mmol) in ODCB (100 mL) was heated to reflux for 14 h. After cooling to room temperature, 1,10-phenanthroline monohydrate (101 mg, 0.51 mmol) and Ag_2CO_3 (71 mg, 0.26 mmol) were added to the solution. The mixture was heated to reflux, being irradiated under four lamps (13 W) for 7 h. The reaction mixture was cooled to room temperature and submitted to a flash column with CS_2:CH_2Cl_2 (2:1) as the eluent. The first brown band was collected and evaporated under reduced pressure to give the crude *m*-PPMF. By using silica gel column with CS_2:CH_2Cl_2 (8:1) as the eluent, pure *m*-PPMF was obtained as a brown solid (180 mg, 0.19 mmol, 36%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.07-8.29 (m, 10H, Ar), 4.44-4.75 (m, 2H, C*H*$_2$), 3.44-4.06 (m, 2H, methano group C*H*$_2$), 2.92-3.18 (m, 2H, C*H*$_2$). ESI-HRMS (+): $C_{77}H_{16}O_2K$ [M + K$^+$] calc. 1011.0782, found 1011.0763.

3. NMR

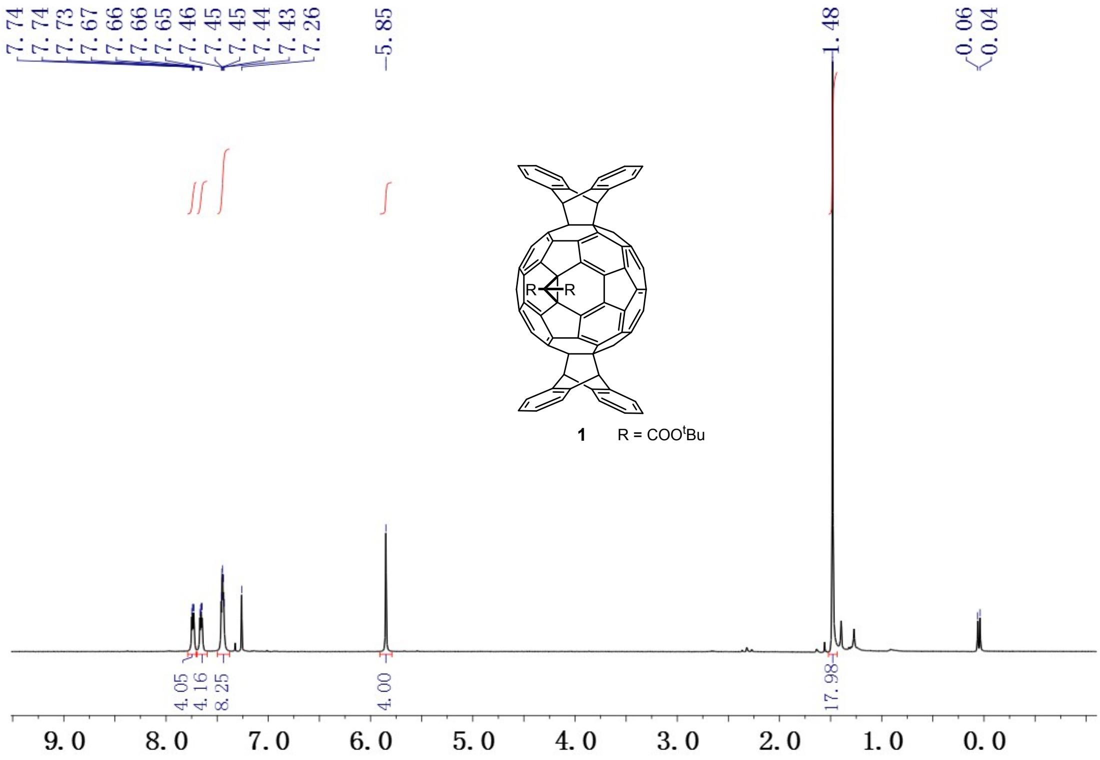


Figure S1. ^1H NMR spectrum of compound **1** (in $CDCl_3/CS_2$).

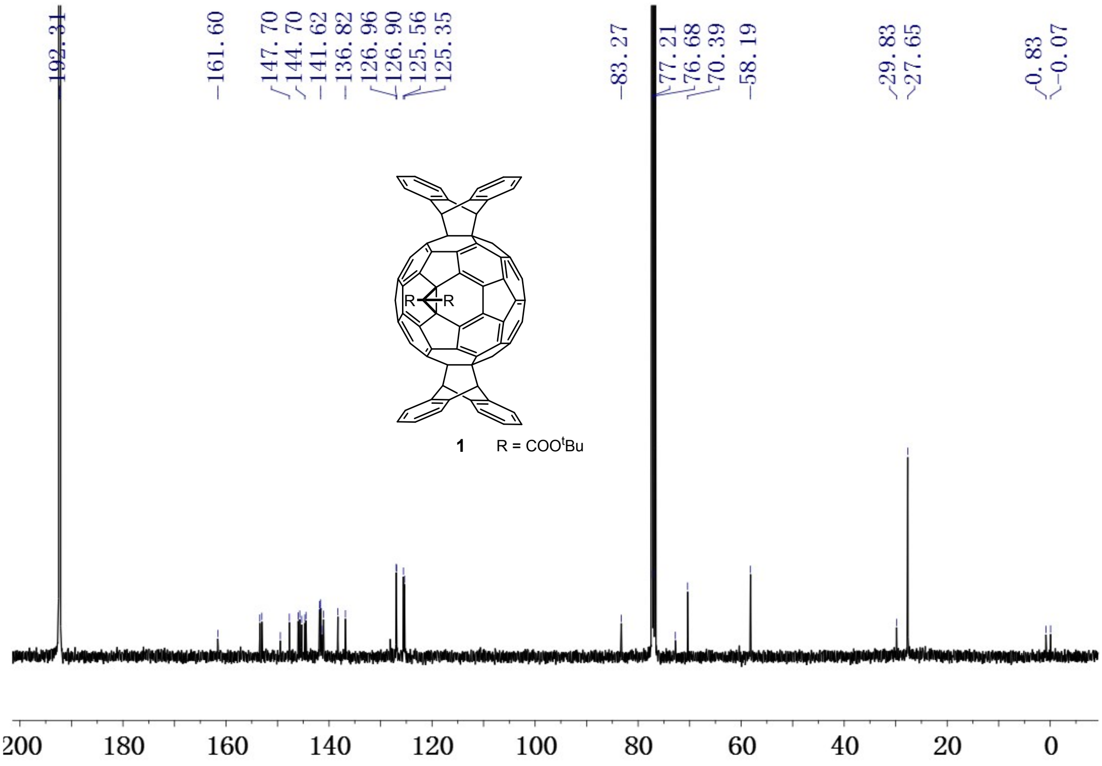


Figure S2. ^{13}C NMR spectrum of compound **1** (in $CDCl_3/CS_2$).

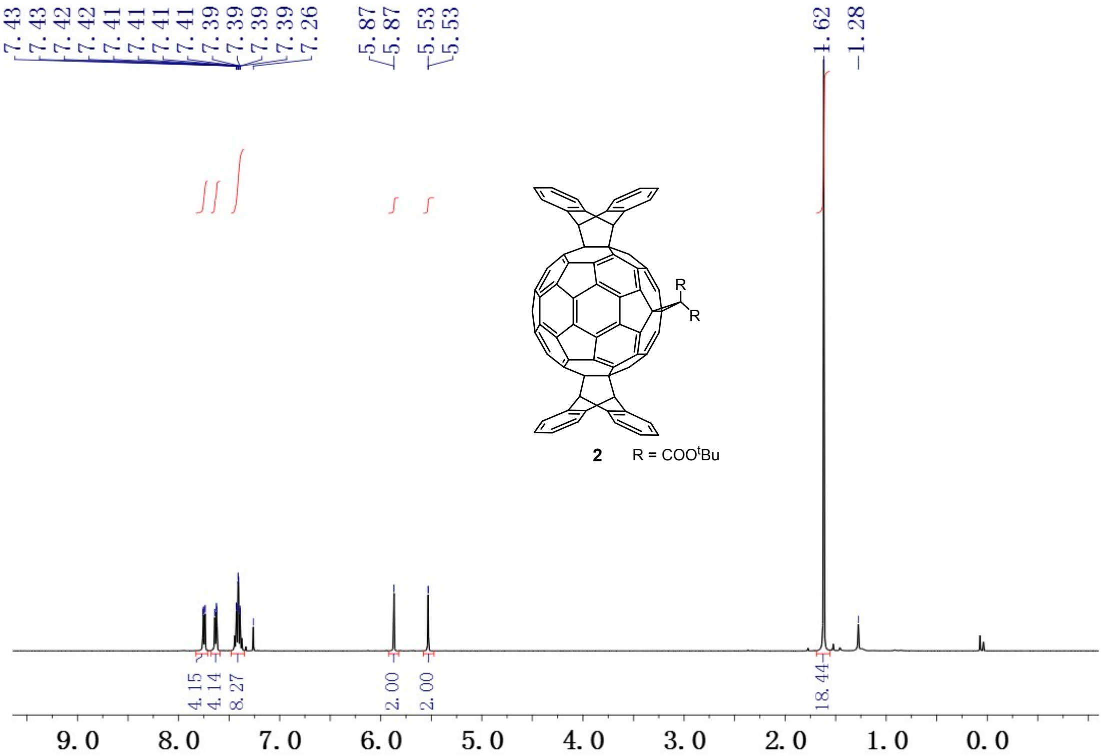


Figure S3. ^{1}H NMR spectrum of compound **2** (in $CDCl_3/CS_2$).

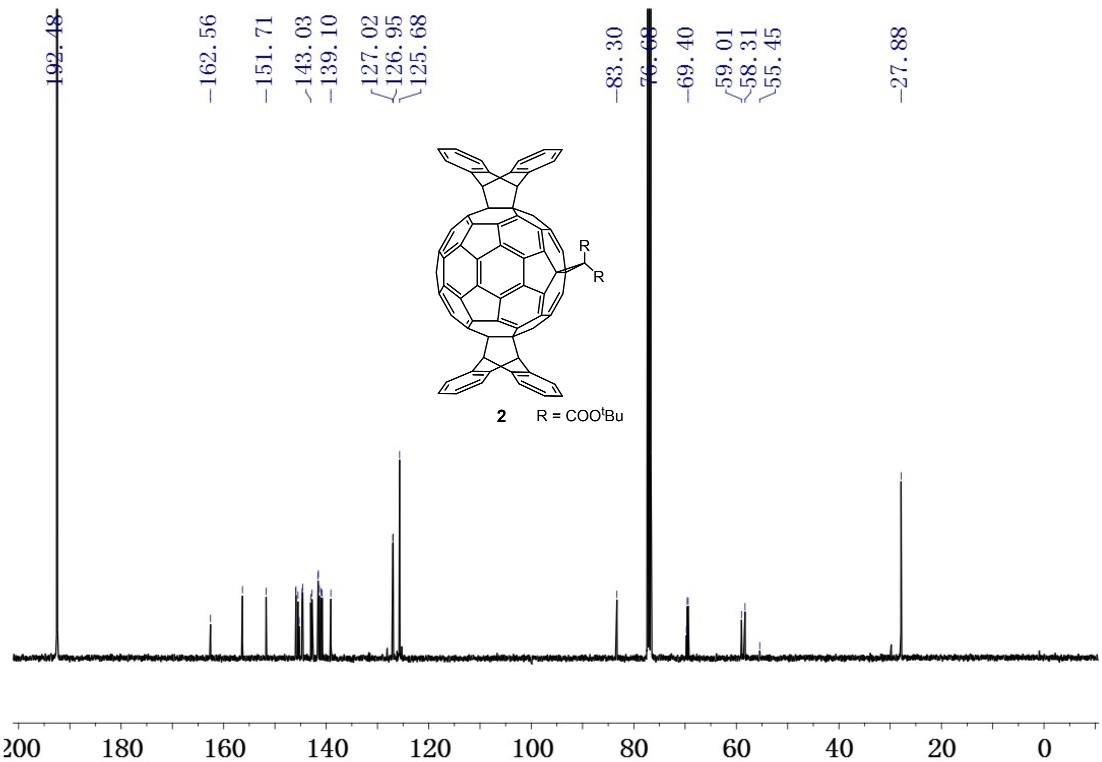


Figure S4. ^{13}C NMR spectrum of compound **2** (in $CDCl_3/CS_2$).

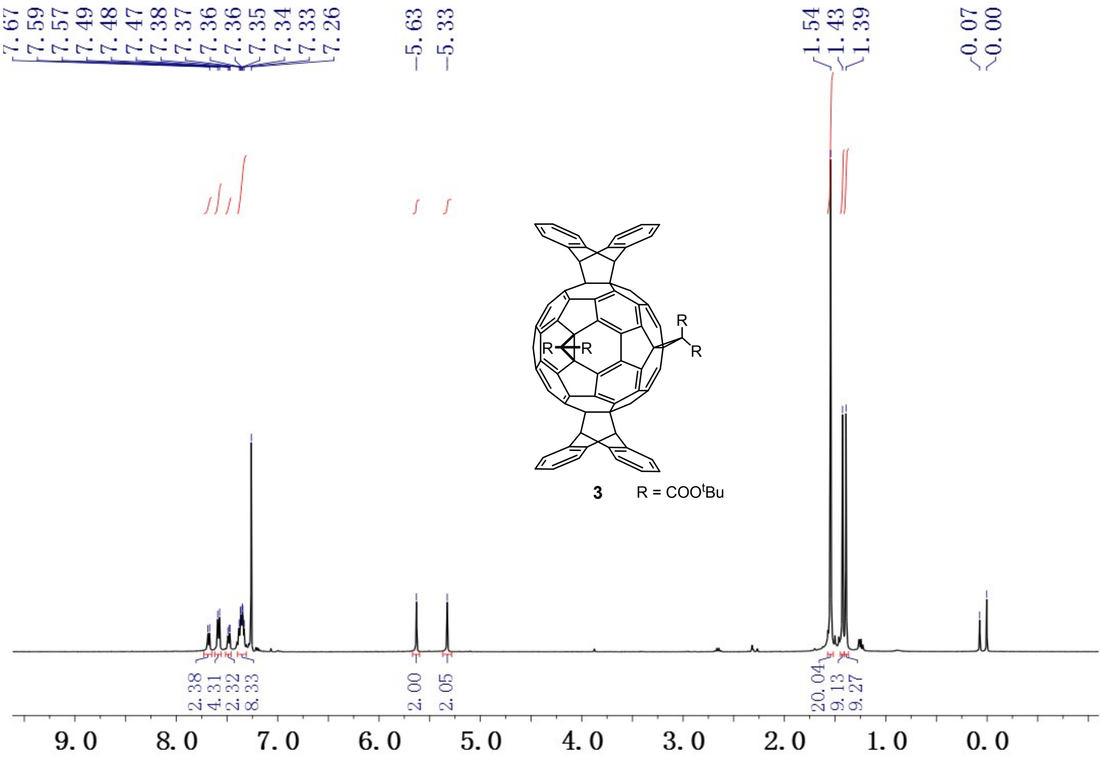


Figure S5. ^{1}H NMR spectrum of compound **3** (in $CDCl_3$).

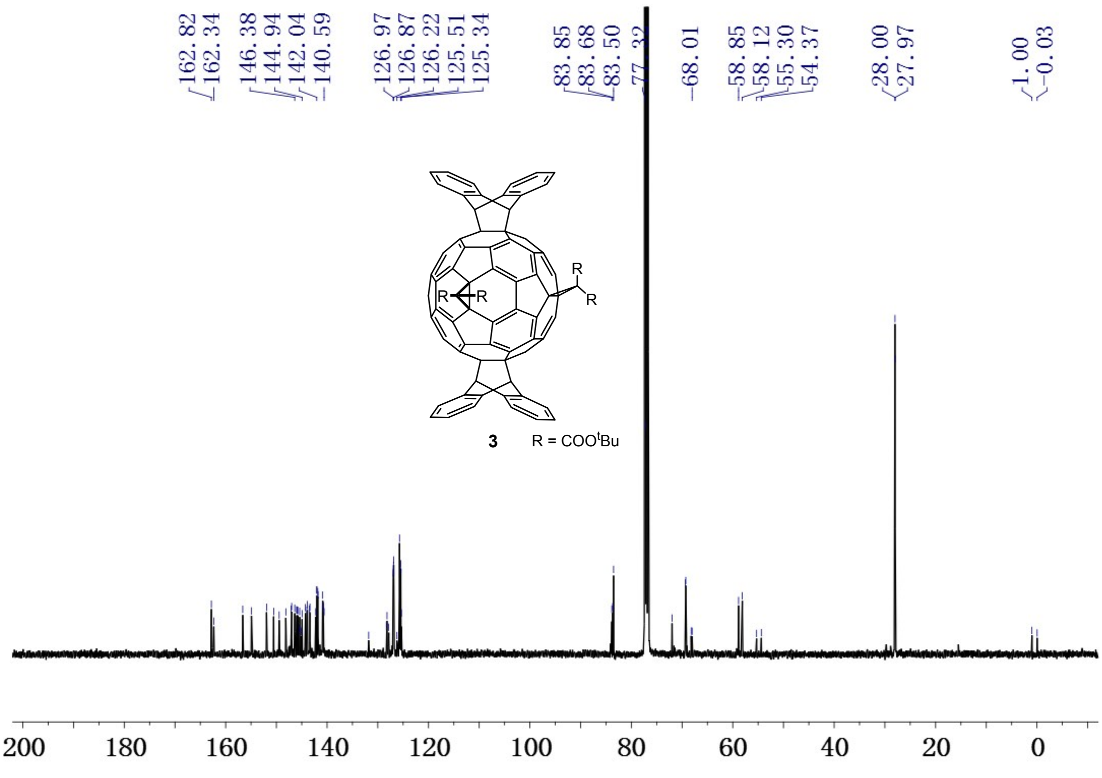


Figure S6. ^{13}C NMR spectrum of compound **3** (in $CDCl_3$).

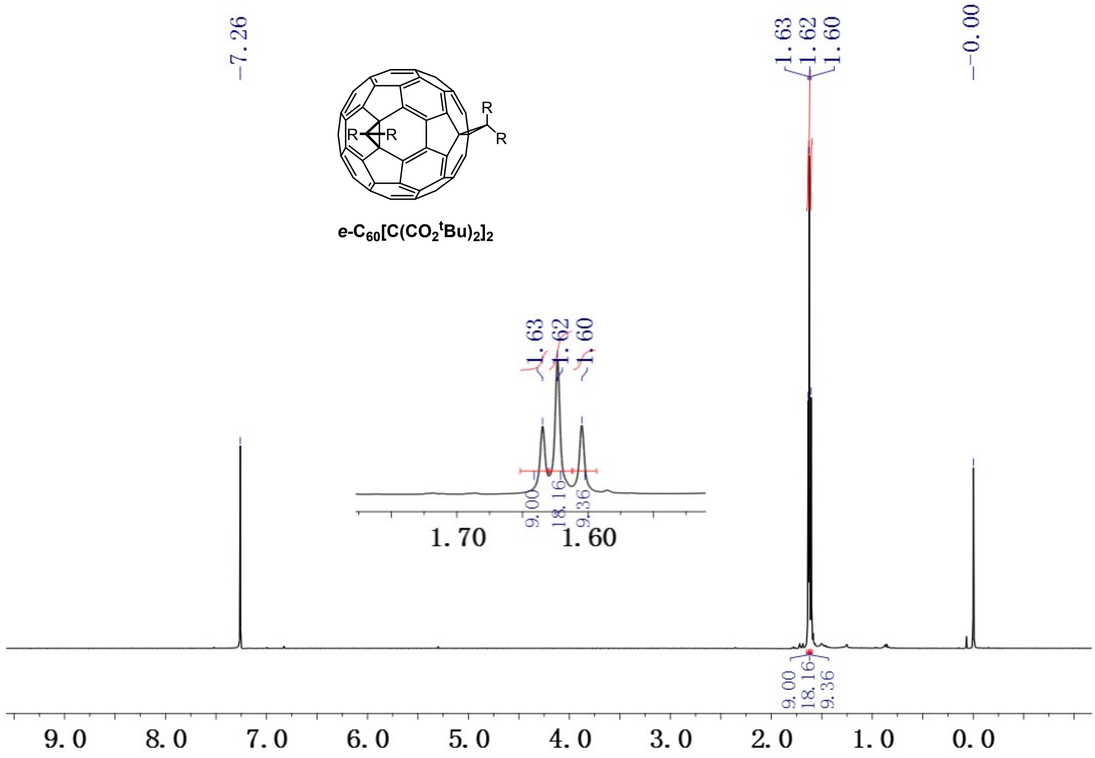


Figure S7. ^{1}H NMR spectrum of *e*-$C_{60}[C(CO_2{}^tBu)_2]_2$ (in $CDCl_3$).

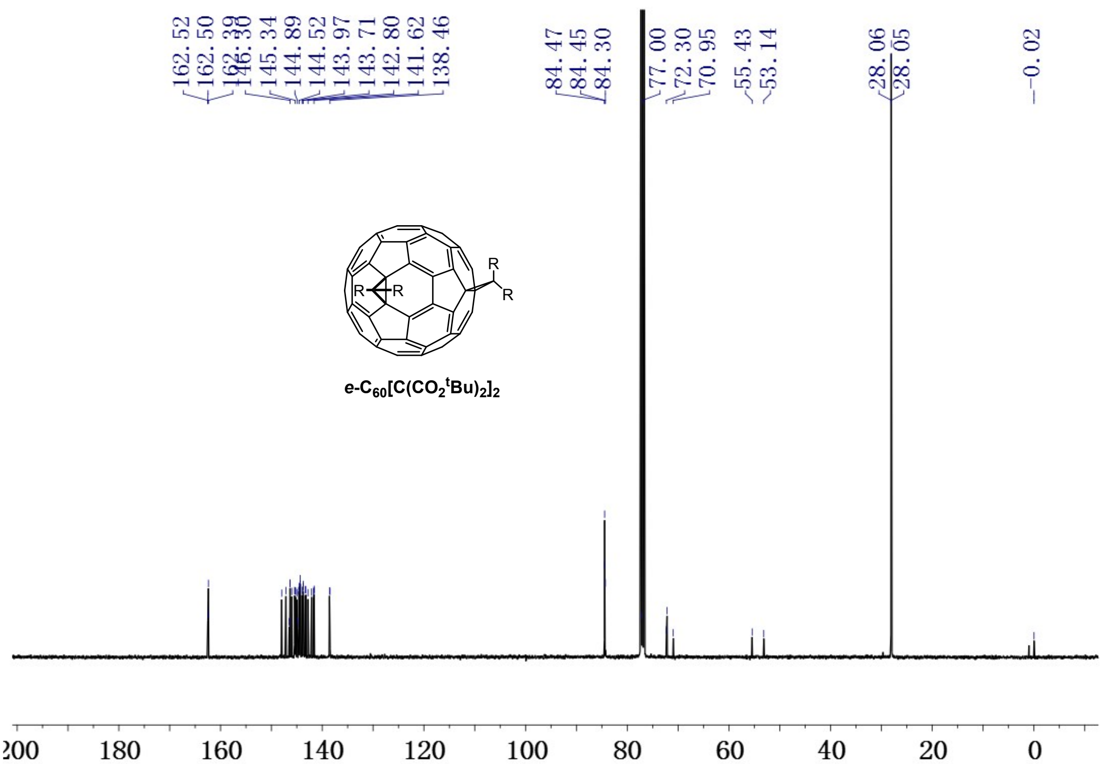


Figure S8. ^{13}C NMR spectrum of *e*-$C_{60}[C(CO_2{}^tBu)_2]_2$ (in $CDCl_3$).

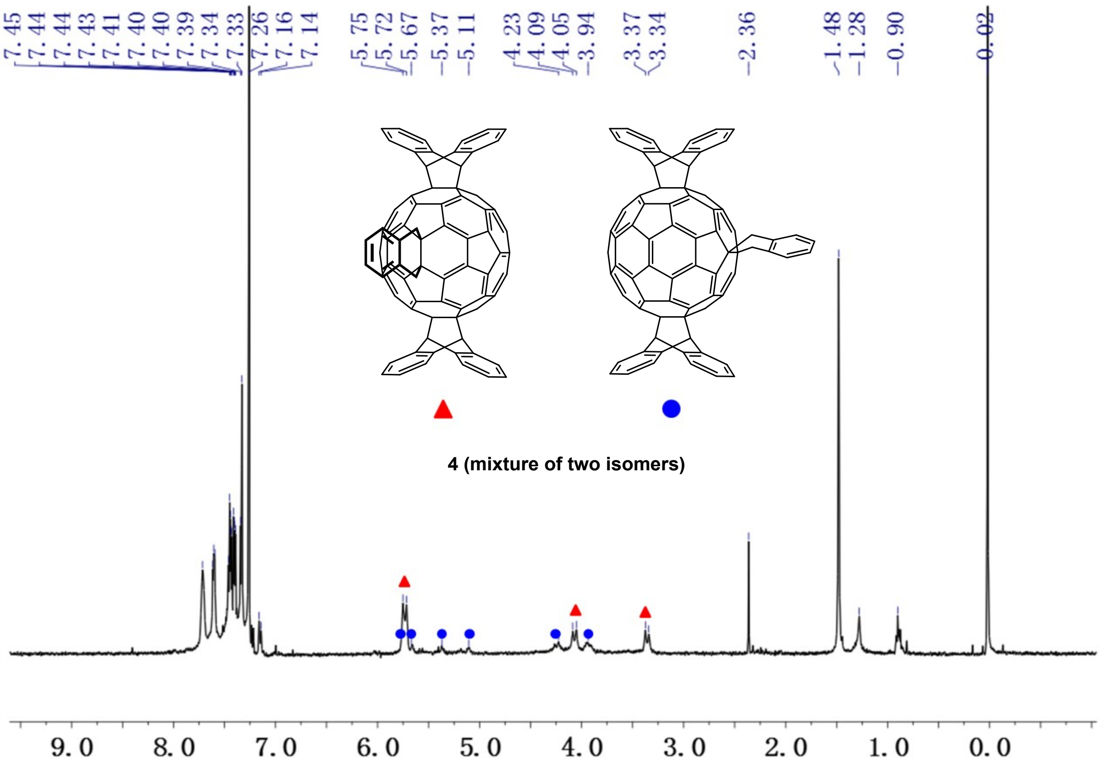


Figure S9. [1]H NMR spectrum of compound **4** (in $CDCl_3/CS_2$).

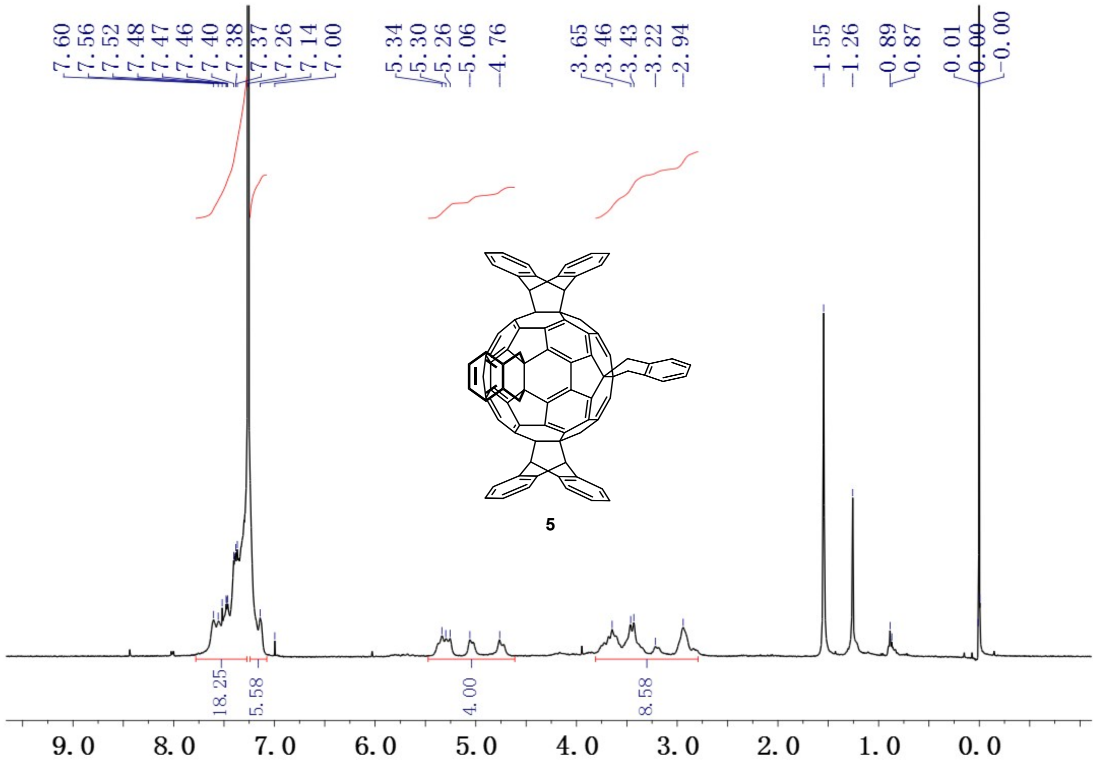


Figure S10. [1]H NMR spectrum of compound **5** (in $CDCl_3$).

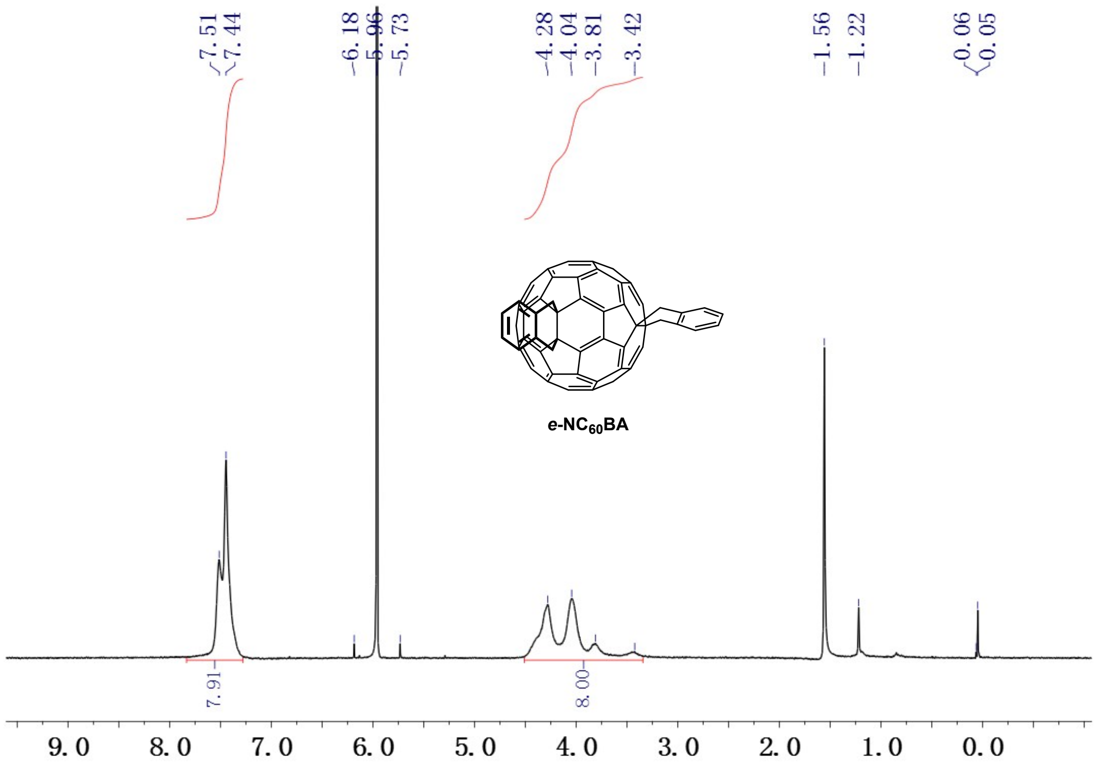


Figure S11. ^{1}H NMR spectrum of *e*-NC$_{60}$BA (in $C_2D_2Cl_4$).

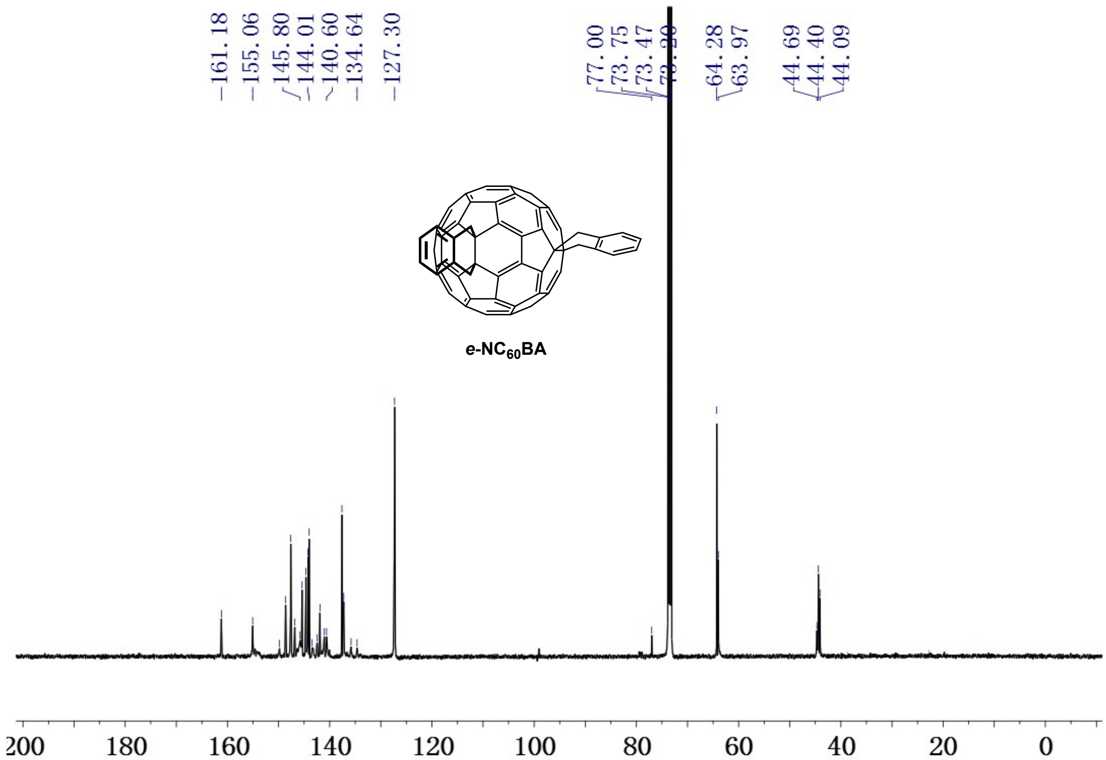
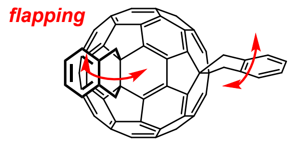


Figure S12. ^{13}C NMR spectrum of *e*-NC$_{60}$BA (in $C_2D_2Cl_4$).



e-$NC_{60}BA$

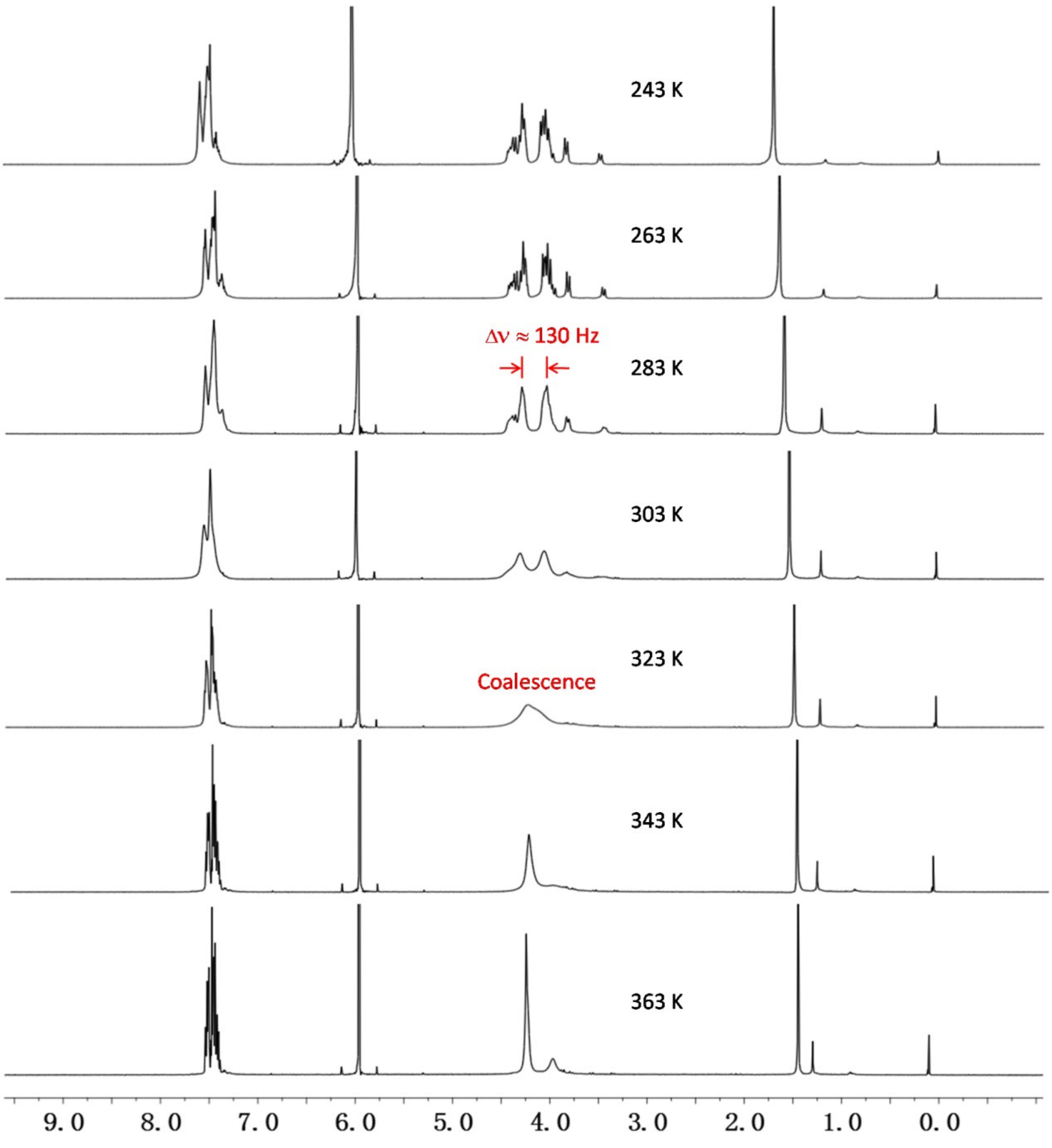


Figure S13. Dependence of ^{1}H NMR spectra for *e*-$NC_{60}BA$ on temperature. The free energy barrier (≈ 15 kcal/mol) for the flapping of *o*-quinodimethane side groups was calculated *via* equation: $\Delta G^{\neq} = 0.00458 \times Tc\ [9.97 + \log (Tc / \Delta\nu)]$ kcal/mol, where Tc is the coalescence temperature (323 K), Δν is the maximum peak-peak gap.[7]

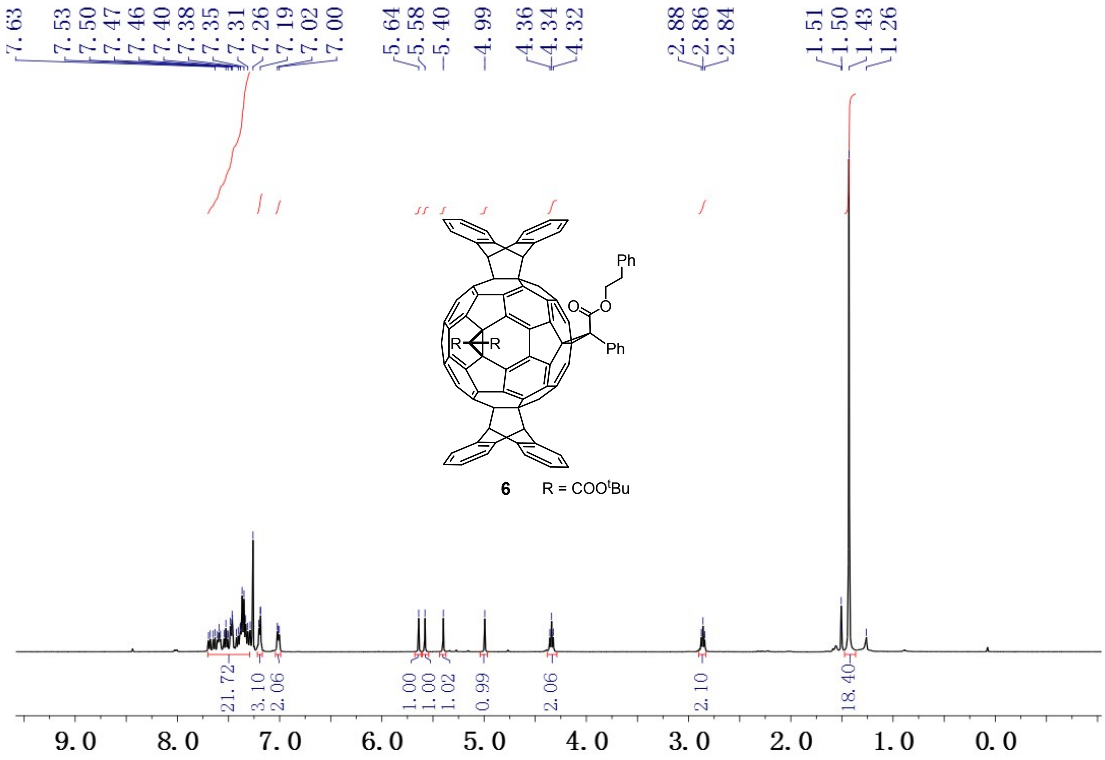


Figure S14. ^{1}H NMR spectrum of compound **6** (in $CDCl_3$).

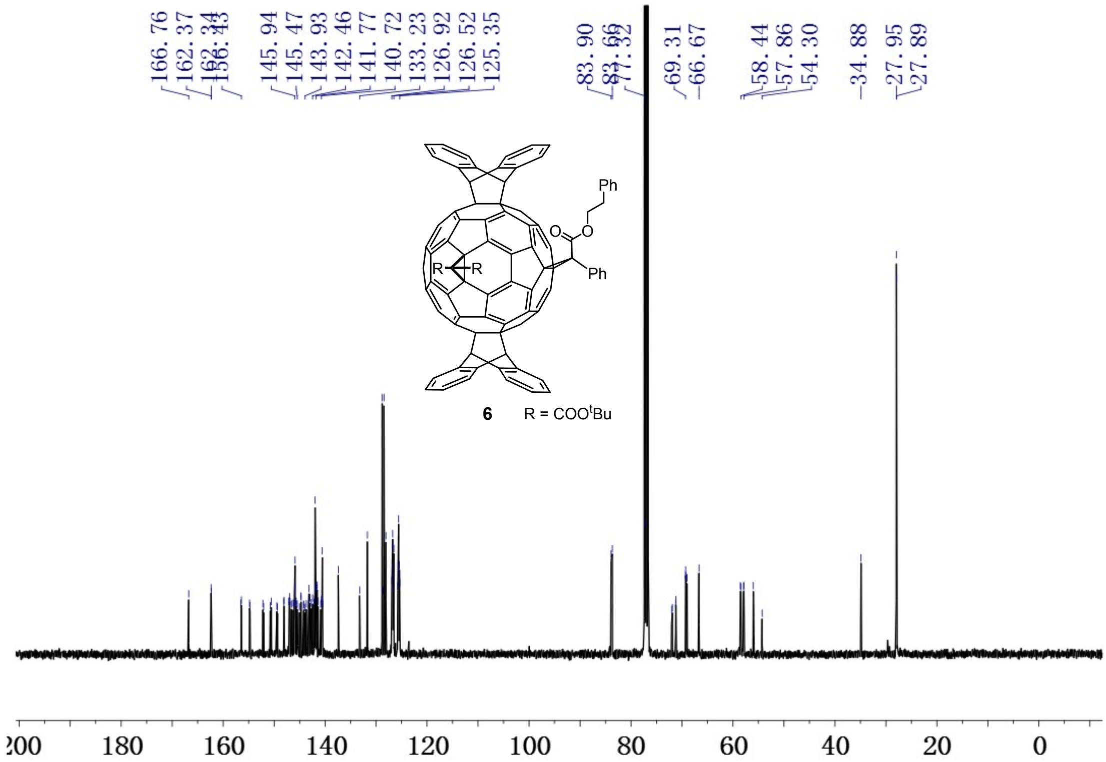


Figure S15. ^{13}C NMR spectrum of compound **6** (in $CDCl_3$).

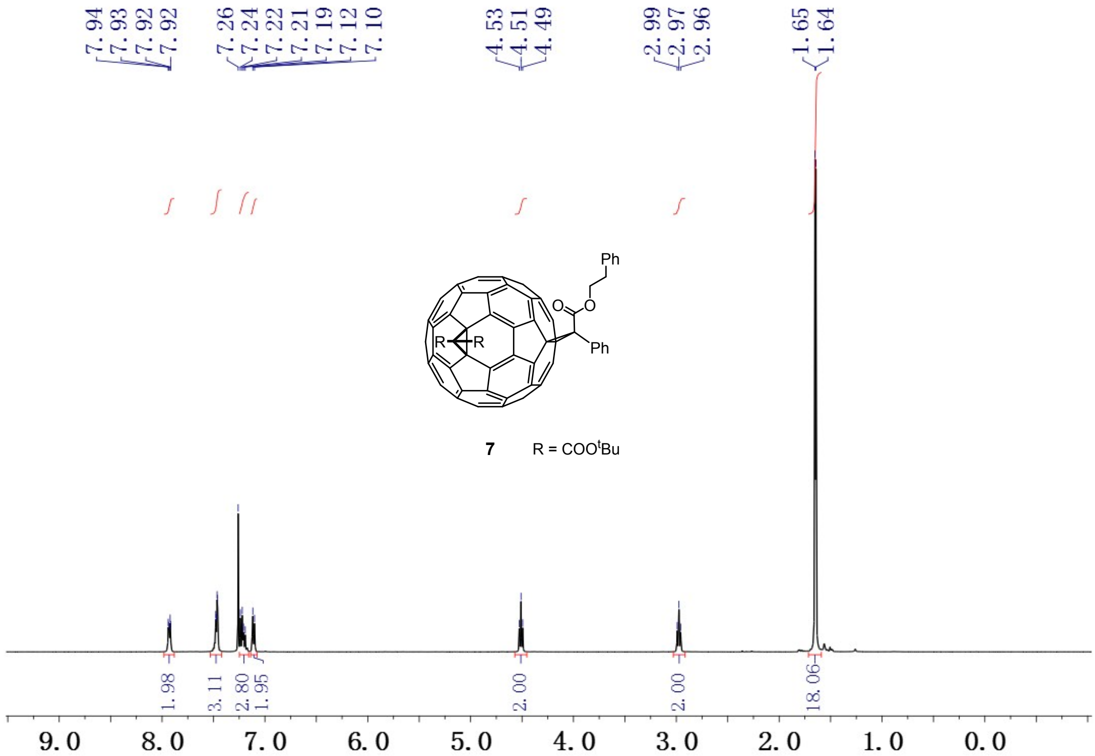


Figure S16. ^{1}H NMR spectrum of compound **7** (in $CDCl_3$).

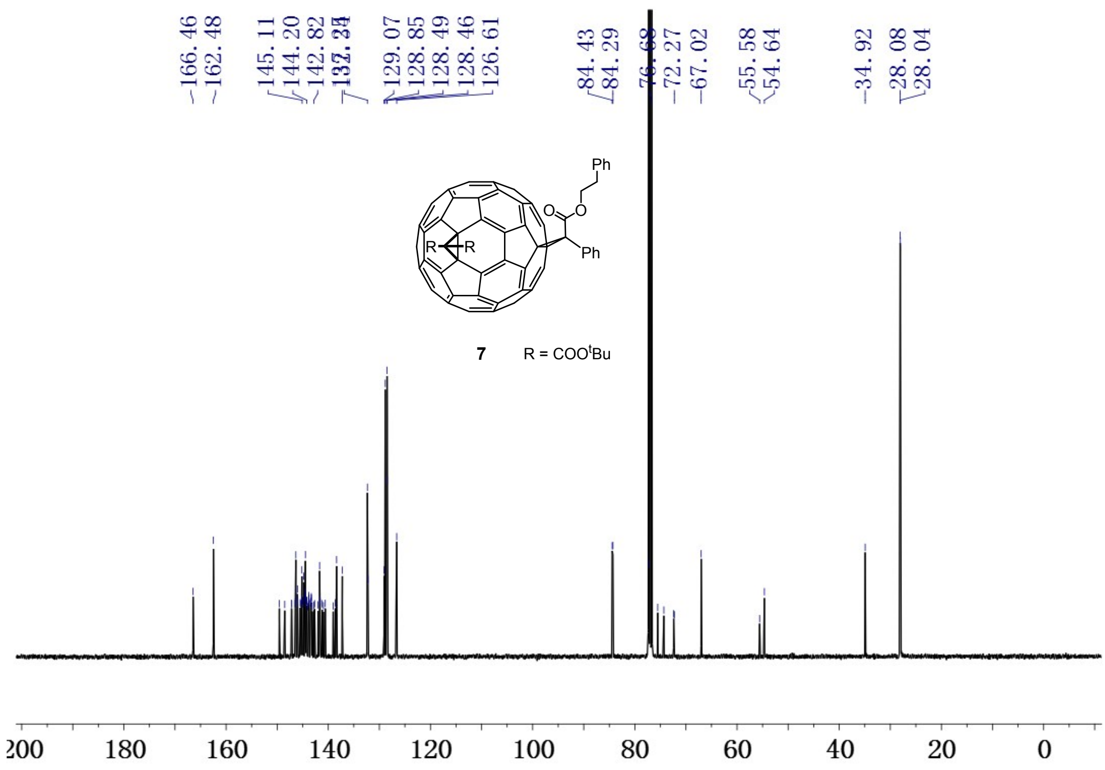


Figure S17. ^{13}C NMR spectrum of compound **7** (in $CDCl_3$).

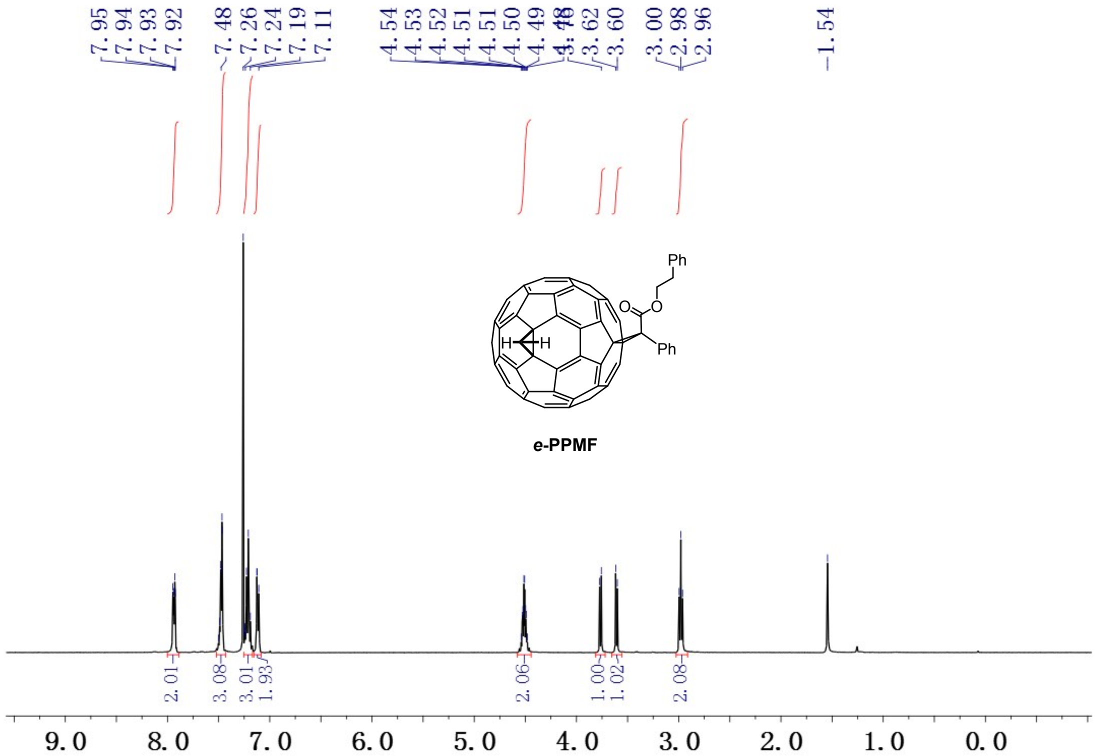


Figure S18. ^{1}H NMR spectrum of *e*-PPMF (in $CDCl_3$).

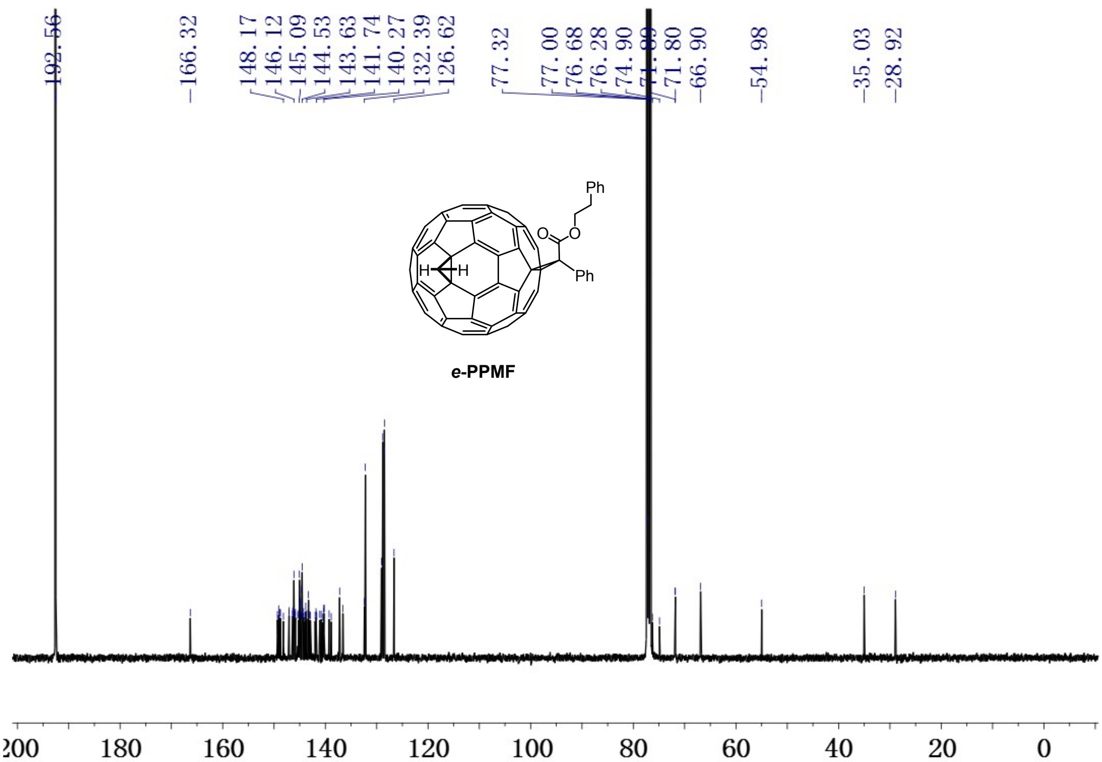


Figure S19. ^{13}C NMR spectrum of *e*-PPMF (in $CDCl_3/CS_2$).

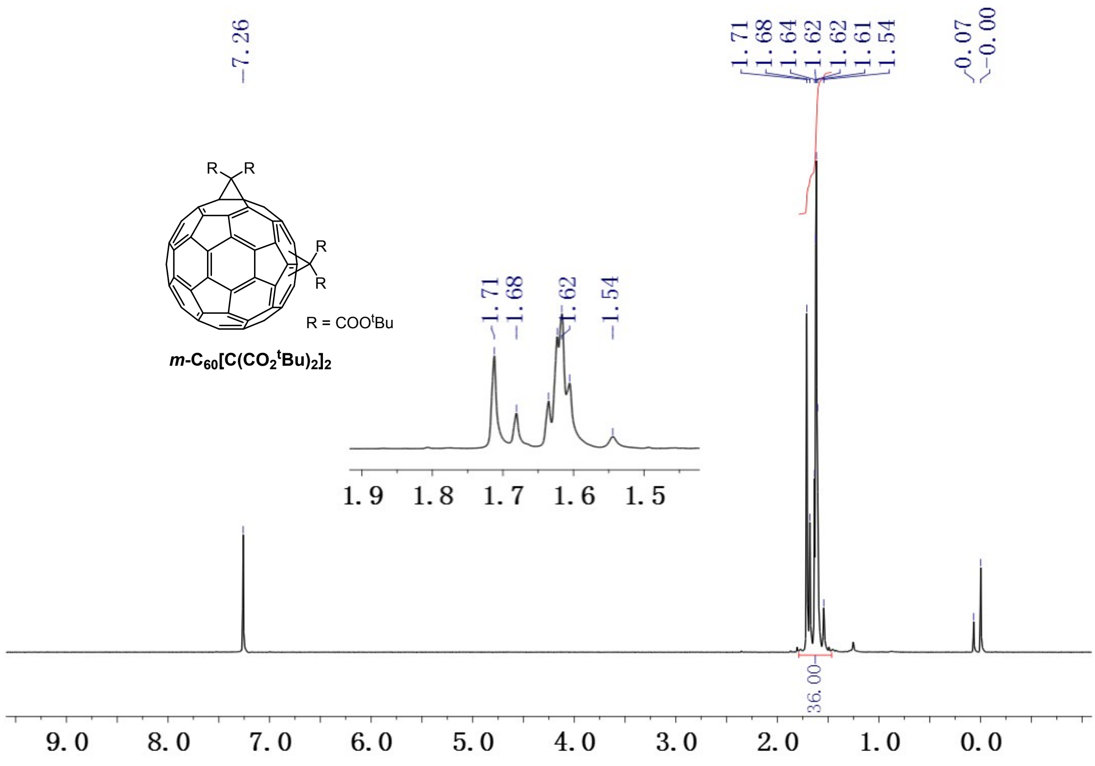


Figure S20. ^{1}H NMR spectrum of *m*-$C_{60}[C(CO_2{}^tBu)_2]_2$ (in $CDCl_3$).

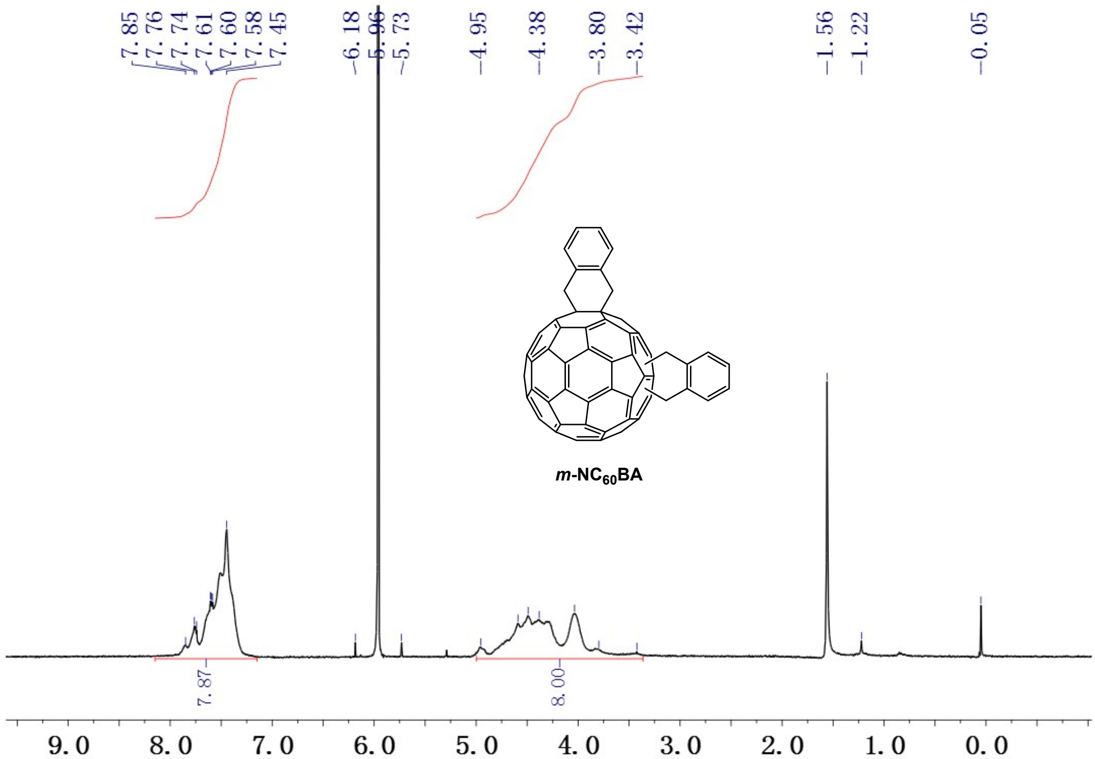


Figure S21. ^{1}H NMR spectrum of *m*-$NC_{60}BA$ (in $C_2D_2Cl_4$).

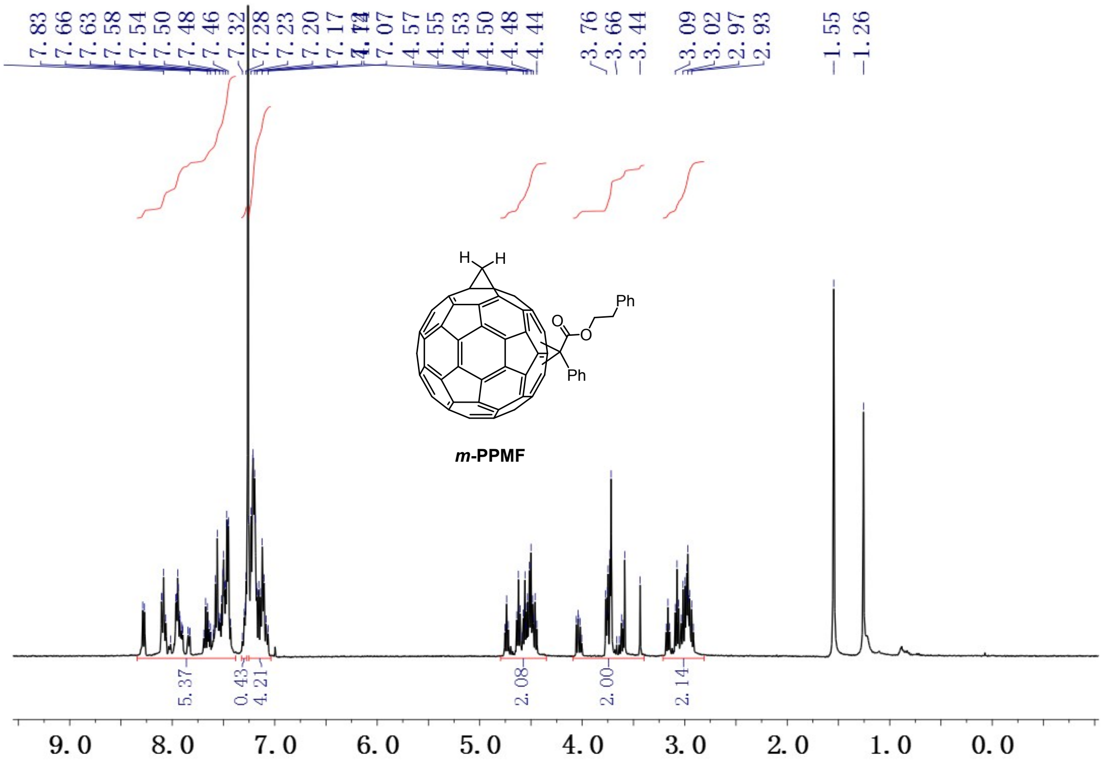


Figure S22. ^{1}H NMR spectrum of *m*-PPMF (in $CDCl_3$).

4. UV-vis absorption

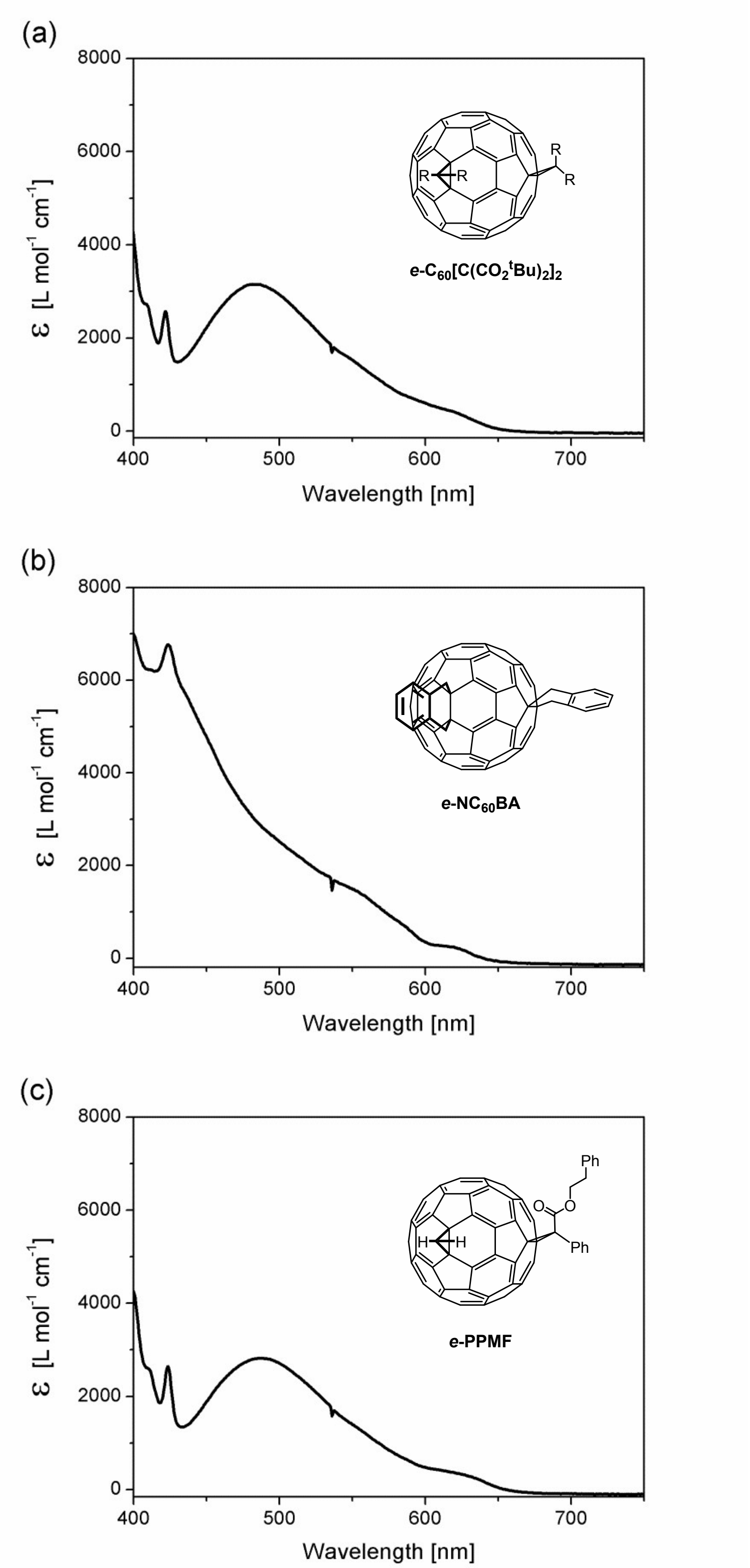


Figure S23. Absorption spectra for *e*-$C_{60}[C(CO_2{}^tBu)_2]_2$ (a), *e*-$NC_{60}BA$ (b) and *e*-PPMF (c) in $CHCl_3$.

5. CV

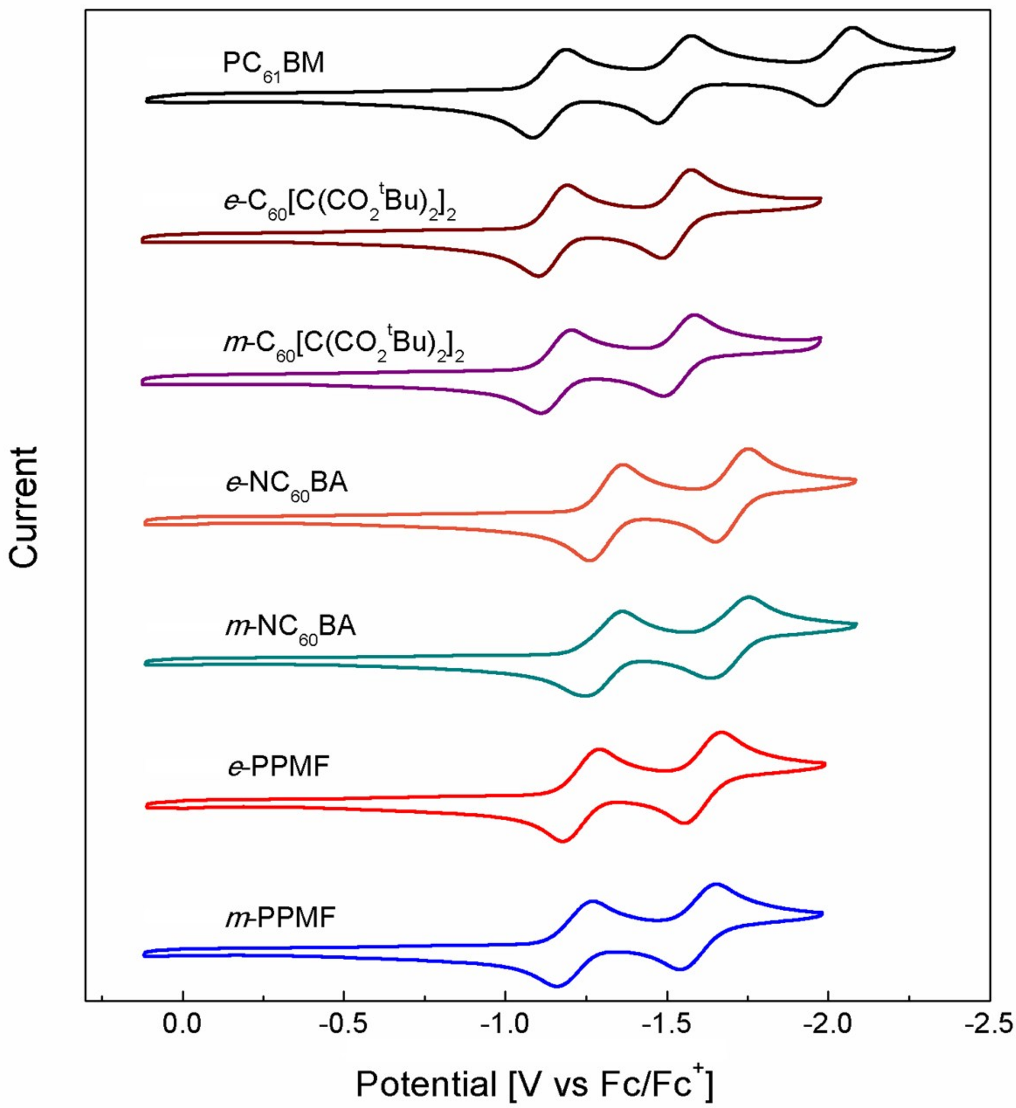


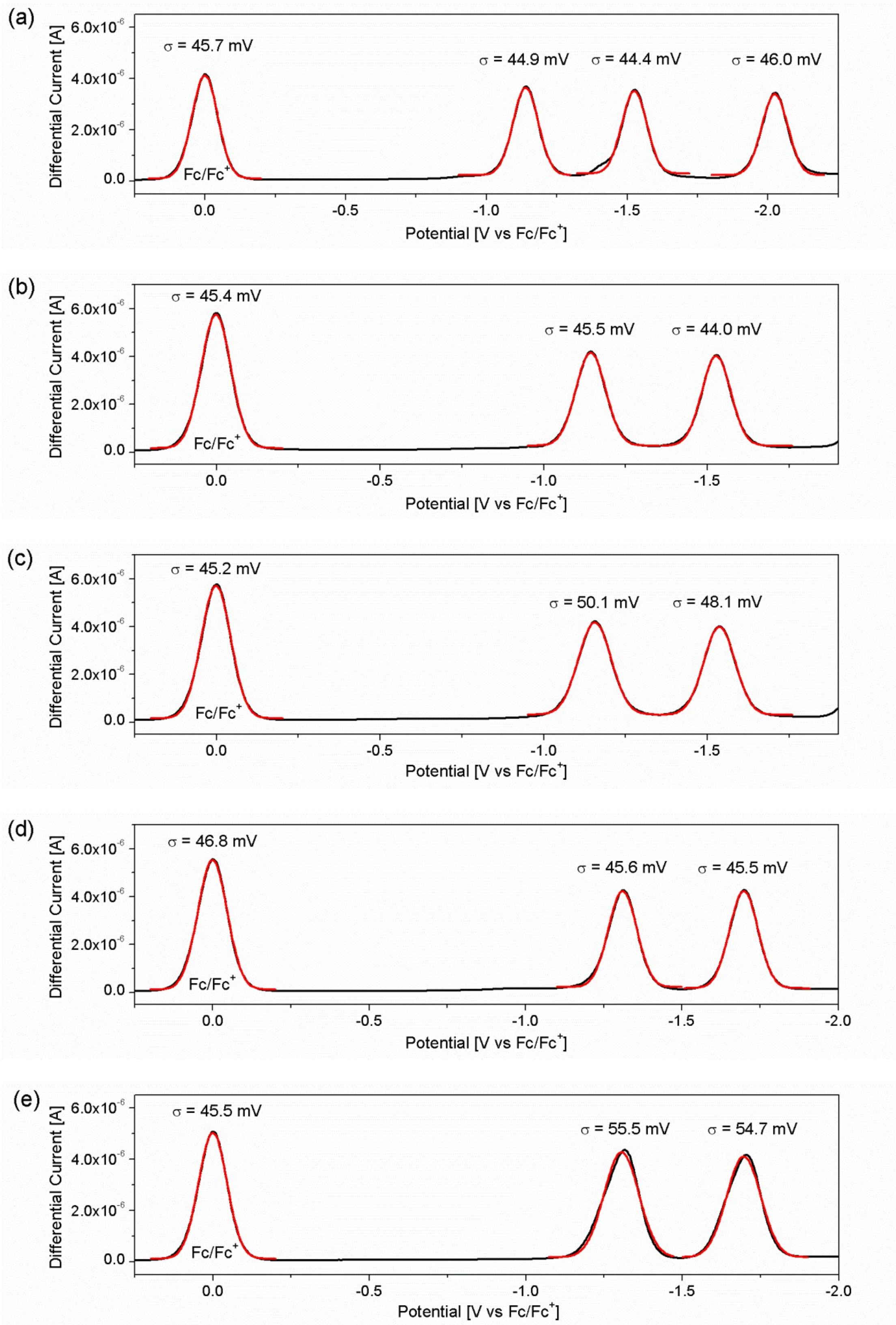
Figure S24. Cyclic voltammograms for $PC_{61}BM$, *e*-$C_{60}[C(CO_2{}^tBu)_2]_2$, *m*-$C_{60}[C(CO_2{}^tBu)_2]_2$, *e*-$NC_{60}BA$, *m*-$NC_{60}BA$, *e*-PPMF and *m*-PPMF.

Table S1. Electrochemical data.

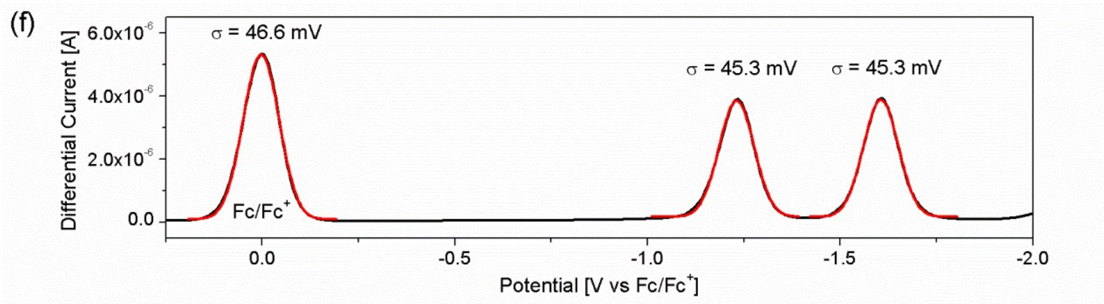
Compound	$E_{1/2}^{red1}$ [V]	$E_{1/2}^{red2}$ [V]	$E_{1/2}^{red3}$ [V]	LUMO [a] [eV]
$PC_{61}BM$	-1.15	-1.54	-2.03	-3.65
e-$C_{60}[C(CO_2{}^{t}Bu)_2]_2$	-1.15	-1.53	N. D. [b]	-3.65
m-$C_{60}[C(CO_2{}^{t}Bu)_2]_2$	-1.16	-1.54	N. D.	-3.64
e-$NC_{60}BA$	-1.31	-1.70	N. D.	-3.49
m-$NC_{60}BA$	-1.31	-1.70	N. D.	-3.49
e-PPMF	-1.24	-1.61	N. D.	-3.56
m-PPMF	-1.22	-1.60	N. D.	-3.58

[a] LUMO = -(4.8 + $E_{1/2}^{red1}$) eV
[b] not detected

6. DPV



(a)
σ = 45.7 mV
σ = 44.9 mV
σ = 44.4 mV
σ = 46.0 mV
Fc/Fc+
Differential Current [A]
Potential [V vs Fc/Fc+]
(b)
σ = 45.4 mV
σ = 45.5 mV
σ = 44.0 mV
Fc/Fc+
Differential Current [A]
Potential [V vs Fc/Fc+]
(c)
σ = 45.2 mV
σ = 50.1 mV
σ = 48.1 mV
Fc/Fc+
Differential Current [A]
Potential [V vs Fc/Fc+]
(d)
σ = 46.8 mV
σ = 45.6 mV
σ = 45.5 mV
Fc/Fc+
Differential Current [A]
Potential [V vs Fc/Fc+]
(e)
σ = 45.5 mV
σ = 55.5 mV
σ = 54.7 mV
Fc/Fc+
Differential Current [A]
Potential [V vs Fc/Fc+]



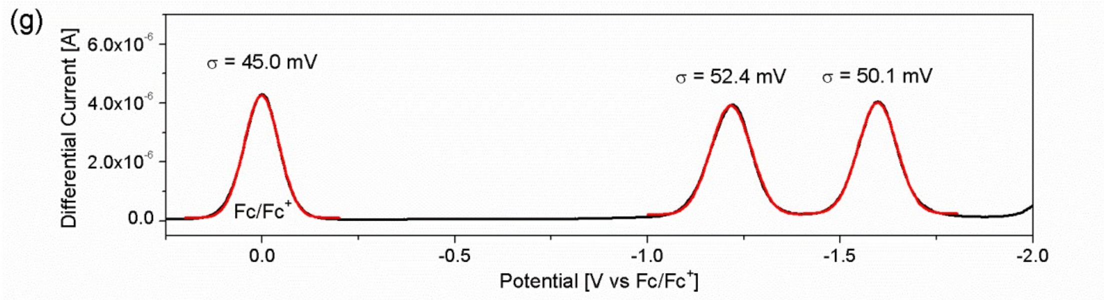


Figure S25. Differential pulse voltammograms for $PC_{61}BM$ (a), *e*-$C_{60}[C(CO_2{}^tBu)_2]_2$ (b), *m*-$C_{60}[C(CO_2{}^tBu)_2]_2$ (c), *e*-$NC_{60}BA$ (d), *m*-$NC_{60}BA$ (e), *e*-PPMF (f) and *m*-PPMF (g). All peaks were fitted with Gaussian model (red lines).

7. Device fabrication and measurements

Inverted solar cells

The patterned ITO glasses with a sheet resistance of 15 $\Omega\, sq^{-1}$ were ultrasonically cleaned using detergent, distilled water, acetone and isopropanol sequentially, then UV-ozone treatment was performed. ZnO precursor was prepared according to literature.[8] The precursor solution was spin-coated onto ITO glass (4000 rpm for 30 s). The films were annealed at 200 °C for 30 min in air. ZnO film thickness is about 30 nm. The optimized active layers were made as follows:

P3HT:fullerene solar cells. A blend of P3HT:fullerene in ODCB (1:1 w/w, 38 mg/mL) was spin-coated onto ZnO layer (800 rpm for 30 s). The films were put into glass petri dishes to undergo solvent annealing, then they underwent thermal annealing at 150 °C for 10 min. The film thickness is ~250 nm.

PPDT2FBT:fullerene solar cells. A blend of PPDT2FBT:fullerene in CB (1:1.5 w/w, 34 mg/mL) with 2 vol% DPE was spin-coated onto ZnO layer (800 rpm for 60 s). Then MeOH was spin-cast onto the film (3500 rpm for 30 s). The film thickness is ~290 nm.

PBDTTT-C-T:fullerene solar cells. A blend of PBDTTT-C-T:fullerene in ODCB (1:1.5 w/w, 25 mg/mL) with 3 vol% DIO was spin-coated onto ZnO layer (900 rpm for 60 s). The film thickness is ~90 nm.

Finally, MoO_3 (~6 nm) and Ag (~80 nm) were successively evaporated onto the active layer under a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the devices is 4 mm^2. The thicknesses for the active layers were measured by using a KLA Tencor D-120 profilometer. *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter and a Xenon-lamp-based solar simulator (Enli Tech, AM

1.5G, 100 mW/cm²). The illumination intensity of solar simulator was determined by using a monocrystalline silicon solar cell (Enli SRC2020, 2cm×2cm) calibrated by NIM. The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

Electron-only devices

The structure for electron-only devices is Al/active layer/Ca/Al. Al (~80 nm) was evaporated onto a glass substrate. A blend of P3HT:fullerene in ODCB (1:1 w/w, 38 mg/mL) was spin-coated onto Al. Ca (~5 nm) and Al (~100 nm) were successively evaporated under a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

8. *J-V* curves and EQE spectra

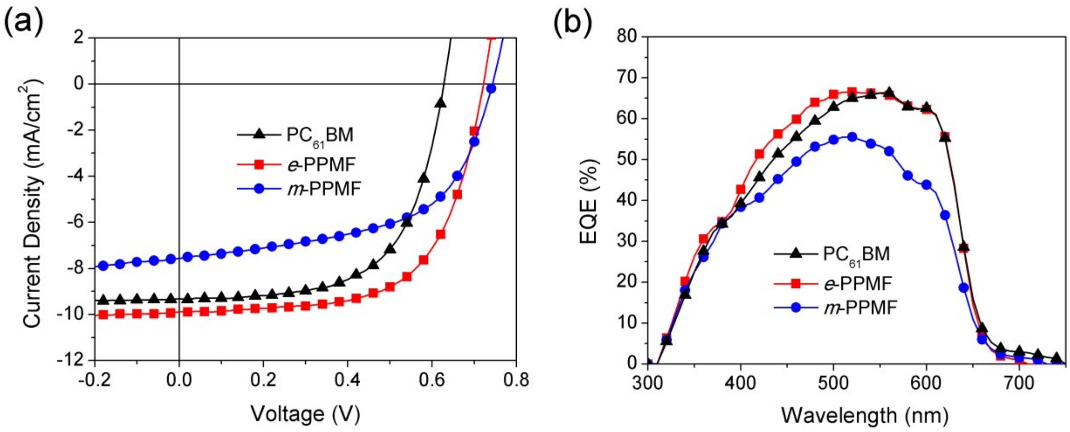


Figure S26. *J–V* curves (a) and EQE spectra (b) for P3HT:fullerene solar cells. The integrated photocurrent from EQE spectra for P3HT:$PC_{61}BM$, P3HT:*e*-PPMF and P3HT:*m*-PPMF solar cells are 9.37, 9.53 and 7.52 mA/cm², respectively.

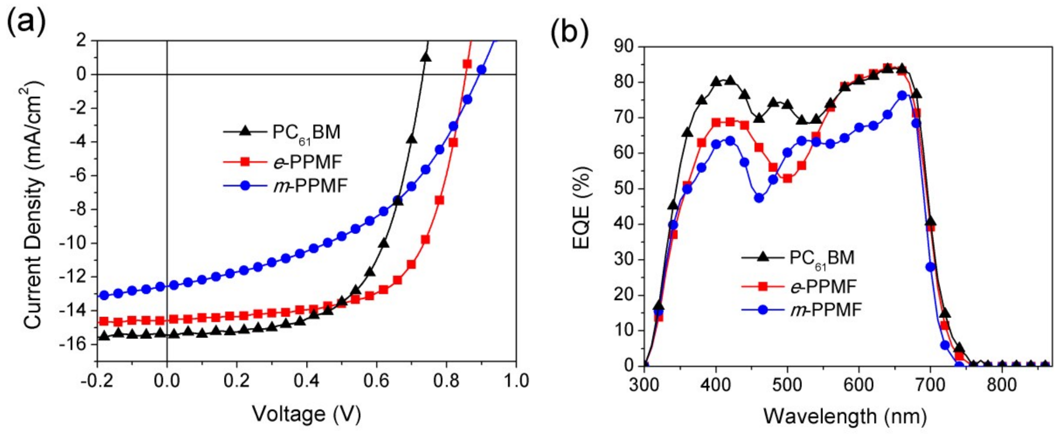


Figure S27. *J–V* curves (a) and EQE spectra (b) for PPDT2FBT:fullerene solar cells. The integrated photocurrent from EQE spectra for PPDT2FBT:$PC_{61}BM$, PPDT2FBT:*e*-PPMF and PPDT2FBT:*m*-PPMF solar cells are 15.82, 14.49 and 12.88 mA/cm^2, respectively.

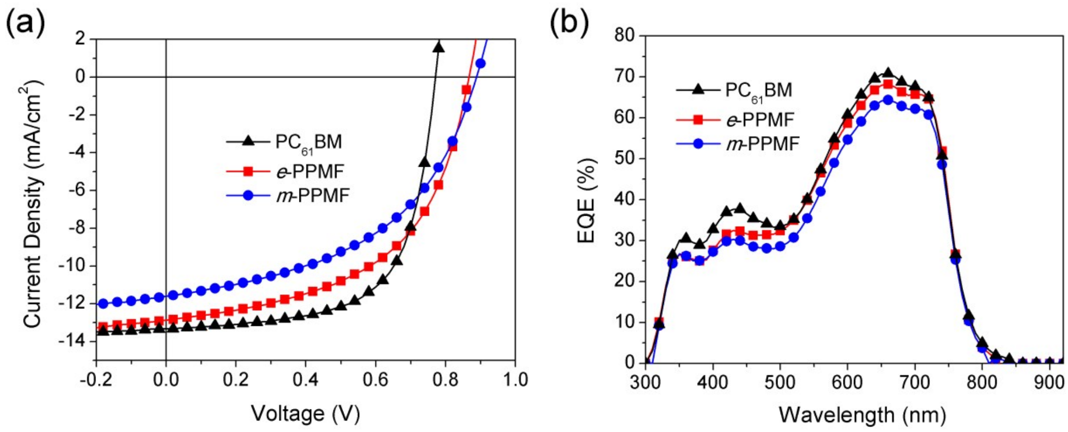


Figure S28. *J–V* curves (a) and EQE spectra (b) for PBDTTT-C-T:fullerene solar cells. The integrated photocurrent from EQE spectra for PBDTTT-C-T:$PC_{61}BM$, PBDTTT-C-T:*e*-PPMF and PBDTTT-C-T:*m*-PPMF solar cells are 12.83, 12.30 and 11.44 mA/cm^2, respectively.

9. Space-charge limited current (SCLC) measurements

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

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility of electron (μ_e), ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, d is the thickness of the blend film, and V is the effective voltage, $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode workfunction difference. Figure S29 shows J-V curves for the electron-only devices. The mobilities were calculated from the slope of $J^{1/2}$-V plots.

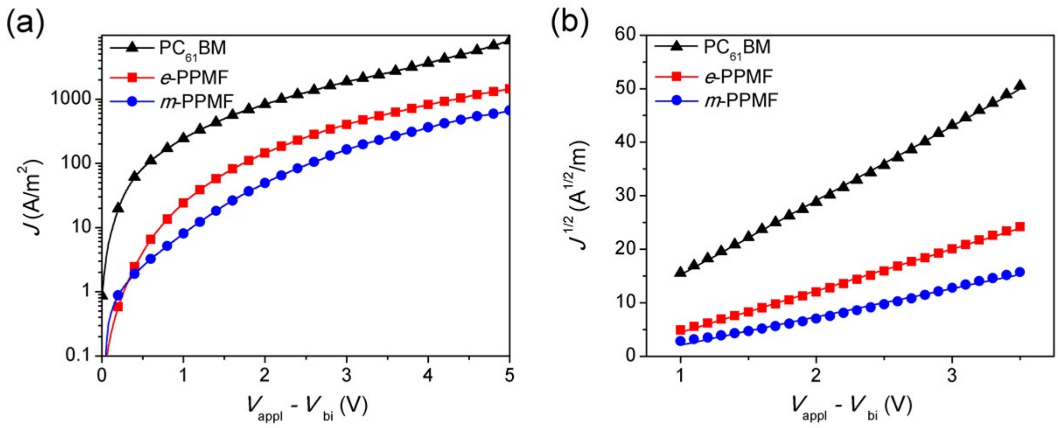


Figure S29. J–V curves (a) and the corresponding $J^{1/2}$–V plots (b) for electron-only devices based on P3HT:$PC_{61}BM$, P3HT:*e*-PPMF and P3HT:*m*-PPMF blend films (in the dark). The thicknesses for the blend films are 247, 247 and 256 nm, respectively. μ_e for $PC_{61}BM$, *e*-PPMF and *m*-PPMF are 7.49×10^{-4}, 2.35×10^{-4} and 1.21×10^{-4} cm^2 V^{-1} s^{-1}, respectively.

10. AFM

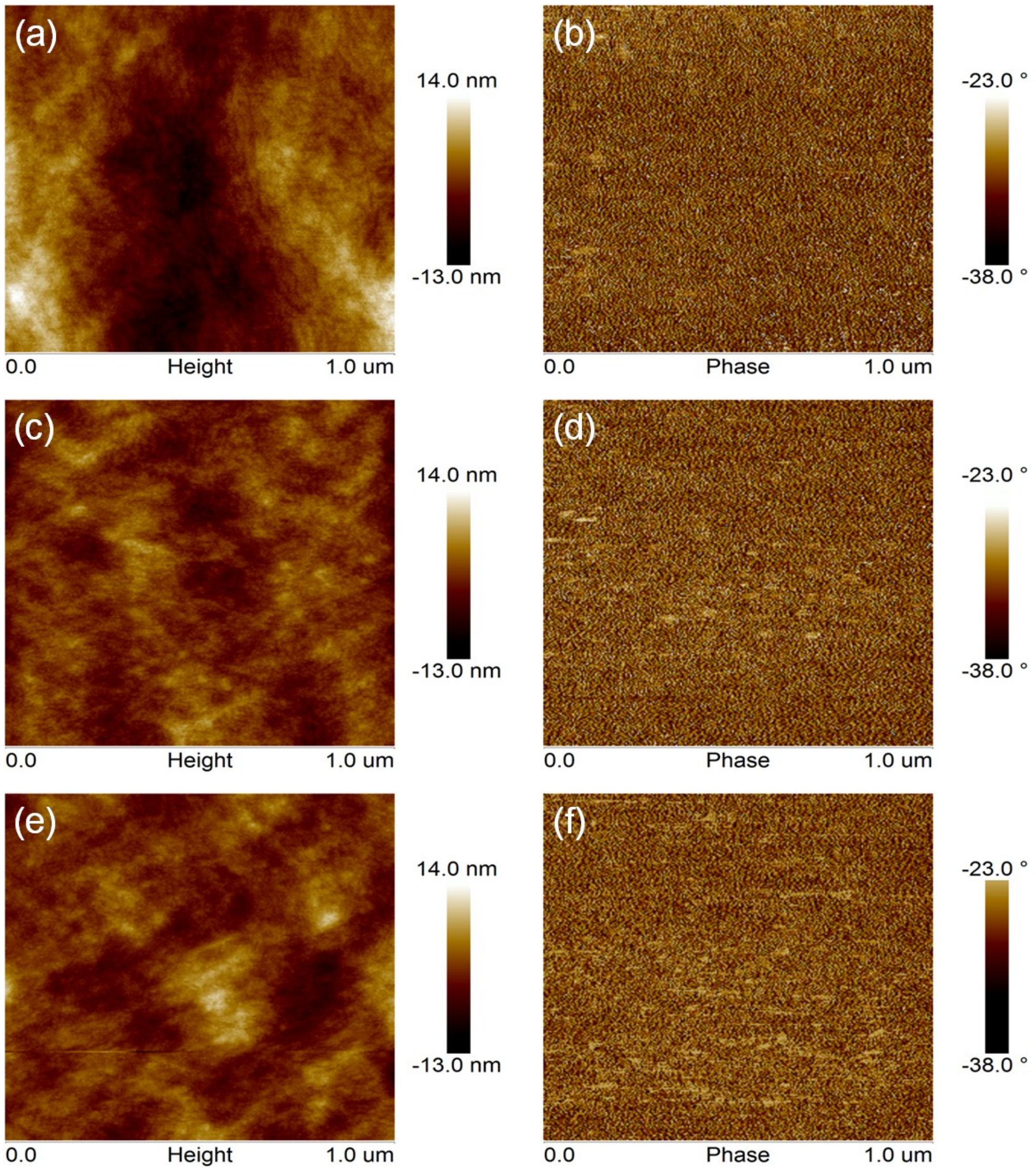


Figure S30. AFM height (left) and phase (right) images for the blend films. (a) and (b), P3HT:PC_{61}BM blend; (c) and (d), P3HT:*e*-PPMF blend; (e) and (f), P3HT:*m*-PPMF blend.

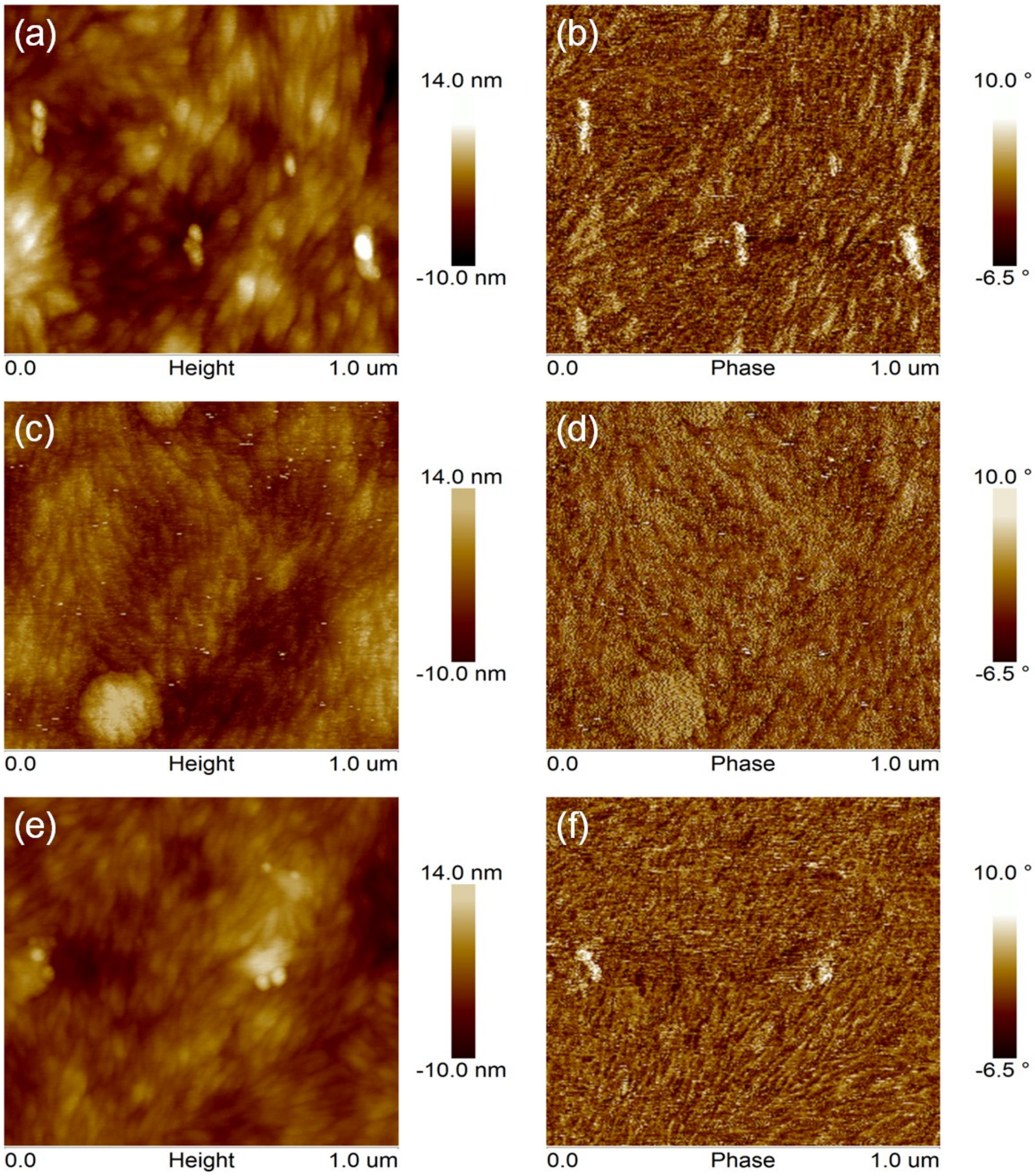


Figure S31. AFM height (left) and phase (right) images for the blend films. (a) and (b), PPDT2FBT:$PC_{61}BM$ blend; (c) and (d), PPDT2FBT:*e*-PPMF blend; (e) and (f), PPDT2FBT:*m*-PPMF blend.

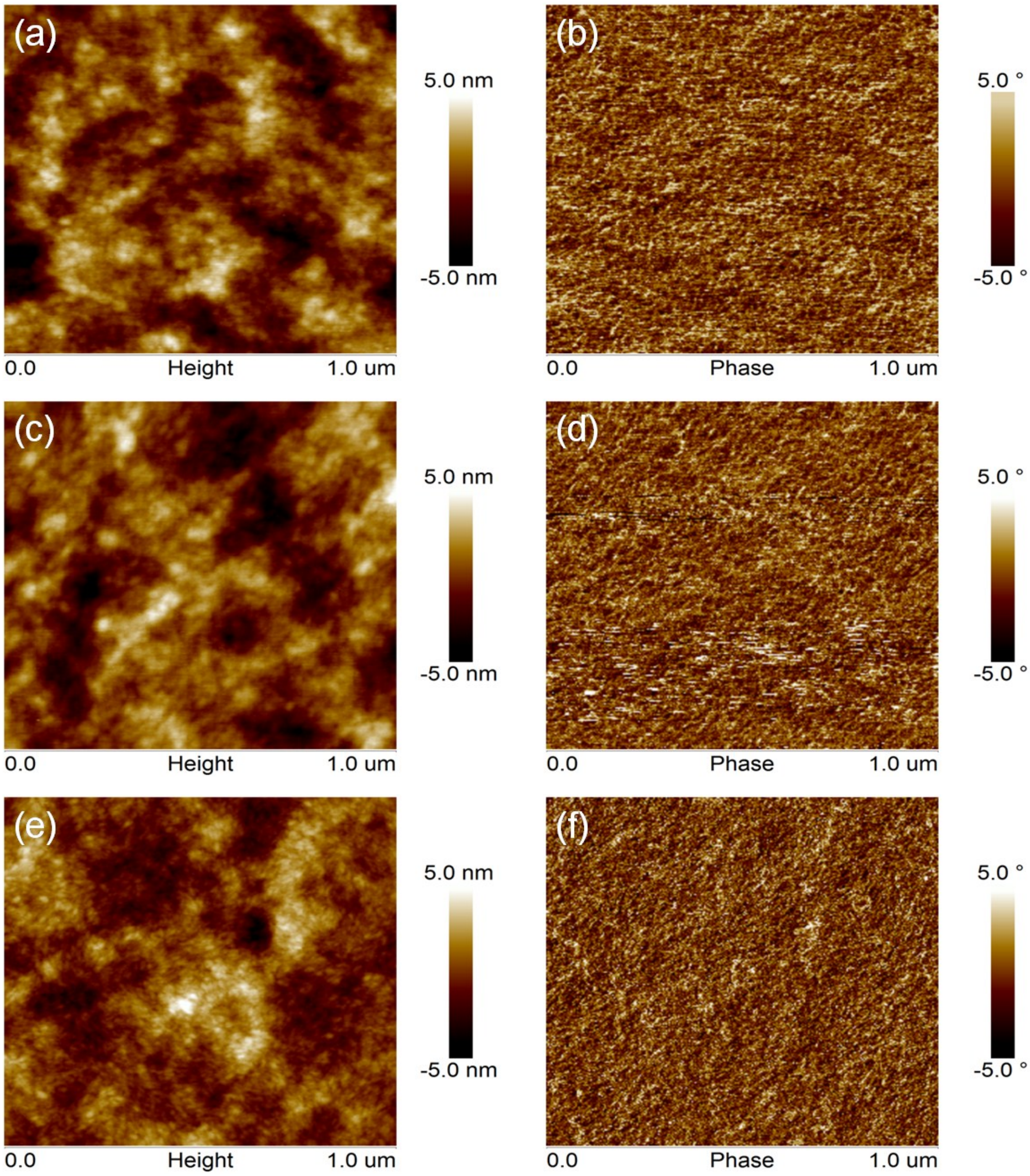


Figure S32. AFM height (left) and phase (right) images for the blend films. (a) and (b), PBDTTT-C-T:$PC_{61}BM$ blend; (c) and (d), PBDTTT-C-T:*e*-PPMF blend; (e) and (f), PBDTTT-C-T:*m*-PPMF blend.

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