Supporting Information

Hetero Bis-Addition of Spiro-Acetalized or Cyclohexanone Ring to 58π Fullerene Impacts Solubility and Mobility Balance in Polymer Solar Cells

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Experimental.

Materials. Regioregular P3HT, fullerenes (C_{60}, ICMA and PCBM), and solvents were purchased from Aldrich Inc., Frontier Carbon Inc., and Kishida Chemical Inc., respectively, and were used as received. Methano[60]fullerene MCMA was prepared according to a known method. [S1,2]

Synthesis.

*Hetero Cyclohexanone-Fused Bis-Adducts: **CMCBA**, **CICBA**, and **CPCBM**.*

To a solution of MCMA, ICMA, and PCBM in *o*-dichlorobenzene (DCB) (100 mg, ca. 0.01 M), 1.5, 2.0, and 2.0 equivalent of 2-tri-methylsilyloxy-1,3-butadiene was added, respectively. The mixture was stirred and heated at 160 °C for 1.5 h. The mixture was poured and left on silica gel column chromatography for 12 h to decompose of the resulting [2+4] bis-adducts to cyclohexanone. Using chlorobenzene to toluene/ethyl acetate (AcOEt) (90/10) eluent gradient system, the first fraction was corrected and concentrated to afford **CCBA** as brown solid in 36, 57, 70% yields, respectively.

*Hetero Spiro-Acetalized Bis-Adducts: **SMCBA**, **SICBA**, and **SPCBM**.*

To a solution of **CMCBA**, **CICBA**, and **CPCBM** in DCB/tetrahydrofuran(THF)/1,2-ethylenediol (5/5/1 v/v/v) (50 mg, ca. 0.002 M), 20 equivalent of $TiCl_4$ was added. The mixture was stirred at 40 °C for 16 h and quenched by trimethylamine. The resulting mixture was extracted by 30 mL of toluene, washed by water and brine, and dried over using $MgSO_4$. The corrected organic layer was concentrated and the resulting crude was passed through a silica gel column chromatography with CS_2/AcOEt (97/3) as eluent to obtain **SMCBA**, **SICBA**, and **SPCBM** in 92, 90, and 85% yields, respectively.

*Homo Bis-Adducts of Cyclohexanone; **CCBA**.*

To a solution of C_{60} in DCB (500 mg, 0.014 M), 2.2 equivalent of 2-tri-methylsilyloxy-1,3-butadiene was added. The mixture was stirred and heated at reflux temperature. The mixture was poured and left on silica gel column chromatography for 12 h to decompose of the resulting [2+4] bis-adducts to cyclohexanone. Using chlorobenzene to toluene/ethyl acetate (AcOEt) eluent gradient system, the second fraction was corrected and concentrated to afford **CCBA** as brown solid in 38% yields.

Homo Spiro-Acetalized Bis-Adducts: ***SCBA***.

To a solution of **CCBA** in DCB/tetrahydrofuran(THF)/1,2-ethylenediol (5/5/1 v/v/v) (100 mg, 0.005 M), 20 equivalent of $TiCl_4$ was added. The mixture was stirred at 40 °C for 16 h and quenched by trimethylamine. The resulting mixture was extracted by 30 mL of toluene, washed by water and brine, and dried over using $MgSO_4$. The corrected organic layer was concentrated and the resulting crude was passed through a silica gel column chromatography with CS_2/AcOEt (95/5) as eluent to obtain **SCBA** in 92% yields.

Compound Data

Cyclohexanone C_{60} Bis Adducts: ***CCBA***

^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ=2.88-3.73 (m, 12H), 4.01-4.34 (m, 8H); ^{13}C NMR (150MHz, $CS_2/CDCl_3$) δ=36.92, 37.31, 37.36, 37.46, 38.96, 39.25, 39.31, 39.33, 50.75, 51.44, 51.65, 51.72, 52.09, 60.77, 60.78, 61.01, 61.20, 61.34, 61.58, 61.59, 61.95, 136.46, 136.53, 141.27, 141.40, 141.96, 141.99, 142.05, 142.08, 143.06, 143.12, 144.10, 144.22, 144.42, 144.44, 144.57, 144.60, 144.84, 144.86, 145.22, 145.23, 145.26, 145.27, 145.44, 145.82, 145.95, 145.99, 147.39, 147.43, 148.09, 148.11, 148.30, 148.33, 148.39, 149.25, 150.33, 153.15, 153.24, 153.31, 153.36, 153.43, 153.87, 153.97, 160.02, 160.03, 207.93, 208.06, 208.22; FAB MS, calculated for $C_{68}H_{12}O_2$ [M], 860.0832, found 860.0824.

Spiro-Acetalized 5-Membered Ring C_{60} Bis Adducts: ***SCBA***

^{1}H NMR (600MHz, $CS_2/CDCl_3$) δ=3.14-4.07 (m, 8H), 3.20 (m, 4H), 3.42 (m, 2H), 3.53 (m, 2H), 4.14(s, 2H); ^{13}C NMR (150MHz, $CS_2/CDCl_3$) δ=35.02, 35.05, 35.66, 35.72, 35.80, 35.84, 35.87, 35.88, 35.98, 36.10, 36.33, 36.44, 44.55, 44.64, 44.97, 44.98, 45.54, 45.63, 45.93, 46.25, 60.22, 60.35, 60.37, 60.75, 60.96, 62.18, 62.27, 62.33, 62.74, 62.88, 64.45, 64.48, 64.53, 64.57, 64.61, 64.62, 64.65, 64.69, 64.73, 109.34, 109.57, 109.60, 109.63, 109.76, 109.80, 125.28, 127.70, 128.20, 128.60, 128.99, 129.02, 129.75, 130.26, 132.63, 132.66, 134.36, 134.37, 134.68, 135.25, 135.27, 135.70, 135.72, 136.04, 137.91, 138.50, 138.84, 139.37, 139.59, 139.60, 139.79, 139.80, 139.82, 140.66, 140.70, 141.02, 140.10, 141.21, 141.23, 141.26, 141.45, 141.47, 141.50, 141.53, 141.56, 141.62, 142.63, 142.80, 142.84, 142.85, 143.70, 143.72, 143.77, 144.07, 144.13, 144.21, 144.24, 144.62, 144.89, 145.15, 145.26, 145.37, 145.40, 145.52, 145.60, 146.10, 146.97, 148.17, 148.19, 148.35, 148.37, 148.61, 148.70, 148.83, 149.16, 149.24, 149.34, 149.35, 149.42, 149.43, 156.03, 156.05, 157.00, 157.04, 157.13, 157.19, 158.02, 158.17, 158.25, 160.07, 160.15, 160.91, 161.15, 161.24, 161.90, 161.97; FAB MS, calculated for $C_{72}H_{20}O_4$ [M], 948.1352, found 948.1356.

Cyclohexanone MethanoC$_{60}$ Bis Adducts: ***CMCBA***

^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ=3.28 (s, 2H), 3.31-3.66 (m, 4H), 4.10 (s, 2H); ^{13}C NMR (150MHz, $CS_2/CDCl_3$) δ=24.22, 24.51, 26.12, 26.51, 28.23, 36.66, 37.26, 37.58, 37.69, 37.80, 38.06, 39.51, 39.58, 39.71, 51.02, 51.84, 52.12, 61.68, 61.95, 62.07, 62.23, 62.48, 62.72, 63.08, 6958, 69.69, 70.61, 70.79, 71.24, 127.44, 136.39, 139.48, 140.28, 141.78, 142.18, 142.62, 143.20, 143.42, 143.79, 144.04, 144.76, 144.96, 145.06, 145.28, 145.42, 147.24, 147.49, 148.43, 150.30, 150.38, 150.43, 151.88, 153.30, 155.01, 156.24, 207.37, 207.38, 207.42; FAB MS, calculated for $C_{65}H_8O$ [M], 804.0570, found 804.0577.

Spiro-Acetalized 5-Membered Ring MethanoC$_{60}$ Bis Adducts: ***SMCBA***

^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ=2.88-3.84 (m, 8H), 4.07-4.29 (m, 4H); ^{13}C NMR (150MHz, $CS_2/CDCl_3$) δ=24.44, 25.99, 26.38, 26.40, 28.19, 29.86, 35.45, 35.83, 35.99, 36.03, 36.07, 36.40, 36.63, 45.18, 45.66, 46.27, 46.66, 60. 69, 61.02, 61.54, 62.96, 63.44, 64.49, 64.51, 64.52, 64.54, 64.56, 64.62, 64.69, 70.36, 70.53, 70.62, 109.32, 109.52, 109.54, 109.68, 135.01, 139.20, 139.30, 140.34, 141.20, 141.92, 142.16, 142.64, 142.67, 142.91, 143.49, 143.76, 144.14, 144.97, 144.99, 145.02, 145.06, 145.46, 145.52, 146.92, 147.17, 147.81, 153.23, 155.89, 157.24, 157.37, 158.37, 158.39, 158.78; FAB MS, calculated for $C_{67}H_{12}O_2$ [M], 848.0832, found 848.0860.

Cyclohexanone Indene C$_{60}$ Bis Adducts: ***CICBA***

^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ=2.35 (s, 2H), 2.59-4.36 (m, 4H), 4.50-4.64 (m, 2H), 4.82-5.28 (m, 2H) 7.17-7.91 (m, 4H); ^{13}C NMR (150MHz, $CS_2/CDCl_3$) δ=30.93, 36.19, 36.69, 37.30, 37.47, 39.09, 39.44, 39.60, 45.27, 45.99, 46.06, 46.30, 46.38, 47.05, 51.20, 51.75, 52.08, 52.46, 52.46, 52.60, 57.04, 57.15, 57.32, 57.68, 57.91, 58.10, 58.28, 58.92, 60.79, 60.84, 61.11, 61.20, 61.45, 61.64, 61.81, 62.10, 62.26, 73.96, 74.13, 74.47, 74.57, 74.60, 74.72, 135.96, 136.60, 136.69, 136.88, 136.96, 137.71, 137.80, 138.83, 138.99, 139.01, 139.46, 138.89, 141.20, 141.26, 141.60, 141.90, 142.15, 142.60, 142.80, 143.78, 143.88, 143.99, 144.57, 144.89, 144.98, 145.10, 145.26, 145.34, 145.40, 145.49, 145.59, 145.73, 145.89, 146.04, 146.14, 146.40, 146.55, 146.79, 146.90, 147.41, 147.70, 147.98, 148.09, 148.23, 148.57, 149.00, 149.07, 149.13, 149.33, 149.36, 153.44, 153.55, 153.79, 154.16, 154.24, 154.49, 154.76, 154.94, 155.02, 155.16, 155.31, 155.92, 156.03, 156.09, 156.13, 156.20, 157.24, 157.28, 157.45, 158.25, 158.36, 159.11, 159.74, 209.47, 209.52, 209.60, 209.63, 209.69, 209.74, 209.81; FAB MS, calculated for $C_{73}H_{14}O$ [M], 906.1014, found 906.1014.

Spiro-Acetalized 5-Membered Ring Indene C_{60} Bis Adducts: ***SICBA***

^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ=2.35 (s, 2H), 2.58-3.70 (m, 4H), 4.07-4.29 (m, 4H), 4.50-4.62 (m, 2H), 4.83-5.27 (m, 2H) 7.19-7.93 (m, 4H); ^{13}C NMR (150MHz, $CS_2/CDCl_3$) δ=29.22, 35.13, 35.67, 35.80, 35.82, 35.85, 36.46, 36.49, 46.06, 46.28, 46.37, 57.05, 57.11, 57.17, 57.57, 57.98, 58.13, 58.21, 61.05, 62.77, 62.97, 64.45, 64.54, 64.56, 64.61, 64.65, 64.71, 64.74, 73.93, 74.37, 74.49, 74.60, 74.62, 109.28, 109.34, 109.41, 109.42, 109.54, 109.57, 109.62, 109.64, 109.66, 109.70, 109.77, 109.80, 109.83, 123.71, 123.88, 123.93, 123.96, 124.00, 124.10, 124.16, 126.70, 127.05, 127.15, 127.19, 127.28, 127.50, 127.71, 129.01, 134.32, 134.83, 136.32, 136.75, 137.67, 137.90, 139.08, 139.56, 139.84, 140.41, 140.78, 141.16, 141.59, 141.66, 142.69, 142.71, 143.66, 144.17, 144.54, 144.75, 144.96, 145.05, 145.10, 145.13, 145.16, 145.21, 145.23, 145.26, 145.36, 145.51, 145.58, 145.88, 145.91, 146.10, 146.18, 146.27, 146.83, 148.03, 148.89, 148.94, 149.04, 150.12, 150.99, 153.17, 153.33, 154.11, 154.62, 154.69, 154.82, 155.05, 156.00, 156.23, 156.42, 157.03, 157.23, 157.37, 158.04, 158.09, 159.26, 159.91, 160.81, 161.13, 161.80; FAB MS, calculated for $C_{75}H_{18}O_2$ [M], 950.1301, found 950.1306.

Cyclohexanone Phenyl C_{60} Butylic Acid Methyl Ester: ***CPCBM***

^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ=1.94-2.74 (m, 10H), 3.57-3.78 (m, 5H), 7.34-8.28 (m, 5H); ^{13}C NMR (150MHz, $CS_2/CDCl_3$) δ=22.09, 22.32, 32.80, 33.54, 33.74, 33.77, 33.83, 33.84, 33.87, 33.92, 34.12, 37.49, 37.62, 39.50, 47.63, 47.72, 49.88, 50.42, 51.59, 51.62, 51.71, 51.79, 52.19, 52.57, 53.05, 61.83, 62.39, 62.42, 63.19, 77.92, 78.62, 78.75, 79.12, 79.32, 127.71, 128.06, 128.20, 128.23, 128.35, 130.53, 132.03, 132.39, 132.56, 136.79, 137.36, 138.10, 139.90, 141.70, 141.88, 142.34, 143.20, 143.49, 144.08, 144.20, 144.32, 144.83, 144.95, 145.03, 145.06, 145.23, 145.44, 145.50, 145.63, 145.66, 145.70, 145.83, 146.90, 147.13, 147.58, 147.86, 148.21, 148.29, 149.16, 149.67, 151.14, 152.54, 154.17, 154.56, 156.06, 156.19, 156.24, 156.44, 173.32, 173.35, 173.37, 173.39, 173.44, 173.52, 173.65, 209.48, 209.53, 209.60, 209.67, 209.70; FAB MS, calculated for $C_{76}H_{20}O_3$ [M], 980.1407, found 980.1403.

Spiro-Acetalized 5-Membered Ring Phenyl C_{60} Butylic Acid Methyl Ester: ***SPCBM***

^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ=1.94-3.77 (m, 15H), 4.12-4.29 (m, 4H), 7.33-8.30 (m, 5H); ^{13}C NMR (150MHz, $CS_2/CDCl_3$) δ=22.11, 2.17, 22.22, 22.32, 22.53, 33.53, 33.73, 33.78, 33.82, 33.86, 33.88, 33.94, 34.14, 35.64, 35.90, 45.20, 46.32, 50.15, 50.22, 51.56, 51.59, 51.62, 51.66, 51.68, 61.12, 61.64, 62.89, 63.07, 63.56, 64.32, 64.55, 64.59, 64.64, 64.69, 64.71, 79.09, 79.15, 79.23, 79.32, 109.54, 109.57, 109.63, 109.66, 109.67, 109.69, 109.71, 109.76, 109.79, 109.81, 109.84, 109.86, 127.71, 127.94, 127.98, 128.14, 128.21, 128.30, 128.32, 128.66, 130.53, 131.44, 131.86, 131.91, 132.04, 132.39, 137.27, 137.86, 139.72, 141.48, 141.77, 141.98, 142.18, 142.21, 142.50, 143.03, 143.08, 143.94, 144.24, 144.43, 144.71, 144.84, 145.08, 145.13, 145.20, 145.33, 145.44, 145.53, 145.62, 146.04, 146.18, 146.37, 146.46, 147.06, 147.29, 147.37, 147.49, 147.58, 147.69, 147.74, 148.20, 148.23, 148.37, 148.43, 149.30, 150.23, 151.18, 152.26, 153.55, 155.43, 156.58, 157.06, 157.32, 157.38, 158.07, 158.12, 158.32, 158.41, 159.10, 159.65, 161.08, 173.38, 173.41, 173.45, 173.46, 173.52, 173.55, 173.68; FAB MS, calculated for $C_{78}H_{24}O_4$ [M], 1024.1669, found 1024.1667.

Supporting Tables.

Table S1. Reduction potentials of fullerene bisadducts in DCB.

Compound	E^1_{red} / V [a]	E^2_{red} / V [a]	E^3_{red} / V [a]	LUMO / eV [b]
C_{60}	-1.09	-1.46	-1.91	-3.71
CCBA	-1.27	-1.65	-	-3.53
SCBA	-1.36	-1.72	-	-3.44
MCMA	-1.19	-1.52	-2.00	-3.61
CMCMA	-1.28	-1.63	-	-3.52
SMCMA	-1.32	-1.68	-	-3.48
ICMA	-1.21	-1.57	-	-3.59
CICBA	-1.30	-1.68	-	-3.50
SICBA	-1.36	-1.71	-	-3.44
PCBM	-1.19	-1.54	-2.04	-3.61
CPCBM	-1.27	-1.64	-	-3.53
SPCBM	-1.31	-1.67	-	-3.49
ICBA	-1.36	-1.71	-	-3.44

[a] Reduction potentials E_{red} = 0.5 (E^{ox}_p + E^{red}_p) were measured versus Ag/AgCl reference electrode and standardized to Fc/Fc^+ couple E_{Fc/Fc^+} = +0.224 V versus Ag/Ag^+ (DCB) in 0.1 mM DCB with 0.1 M $^nBu_4PF_6$ as supporting electrolyte. Scan rate was 100 mV/s. [b] Calculated from E_1 using LUMO level = $-e$ (E^1_{red} + 4.8).

Supporting Figures.

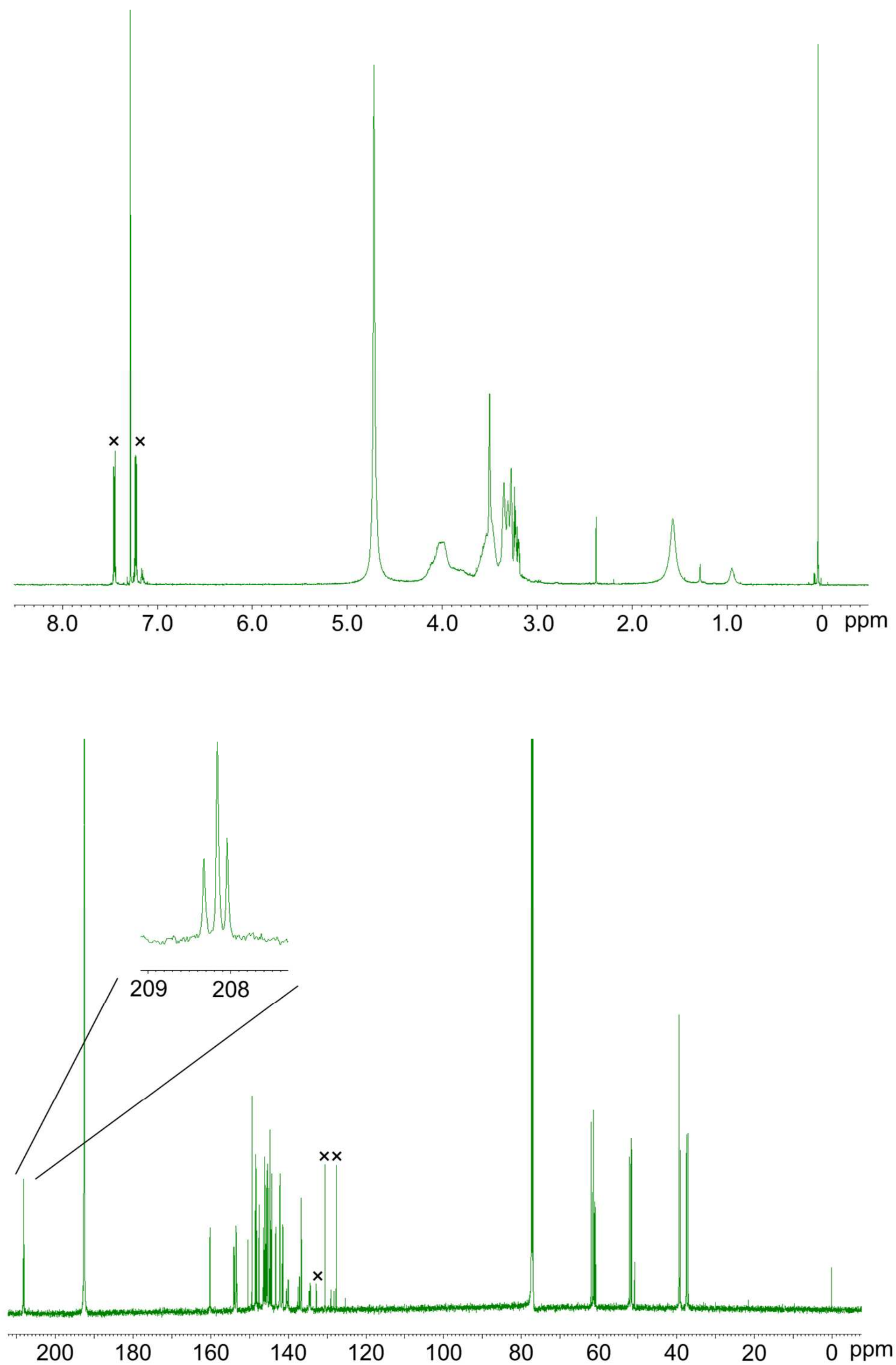
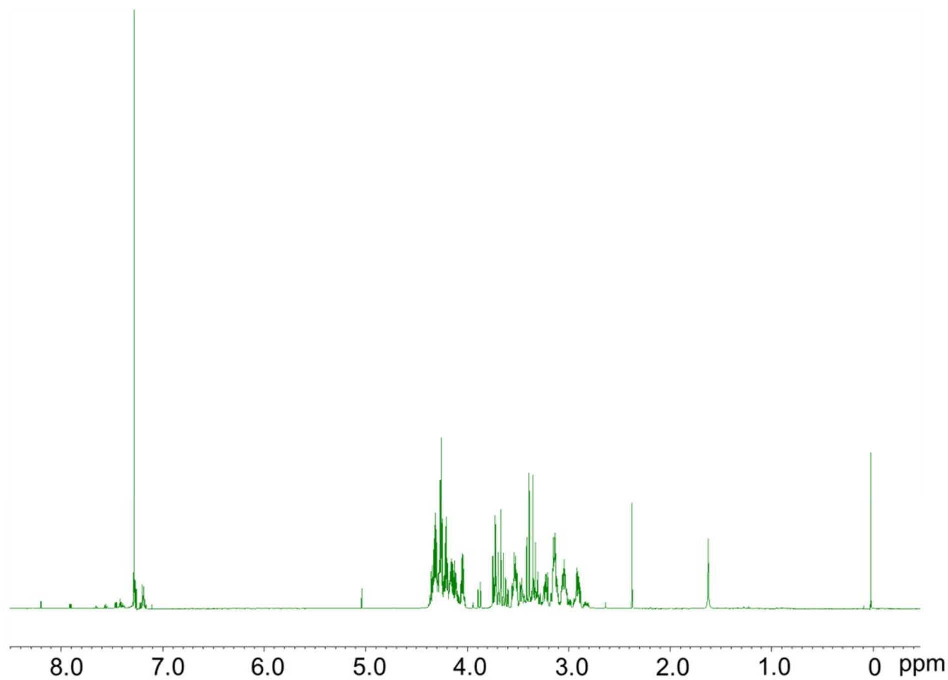


Figure S1. ^{1}H (upper) and ^{13}C NMR spectra (lower) of **CCBA**.



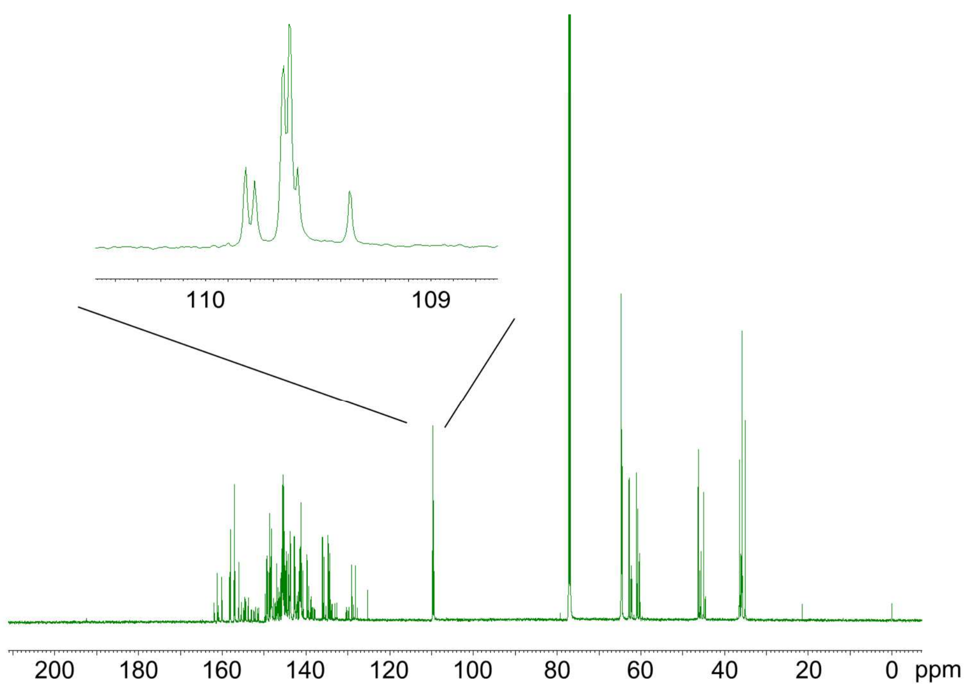


Figure S2. ^{1}H (upper) and ^{13}C NMR spectra (lower) of **SCBA**.

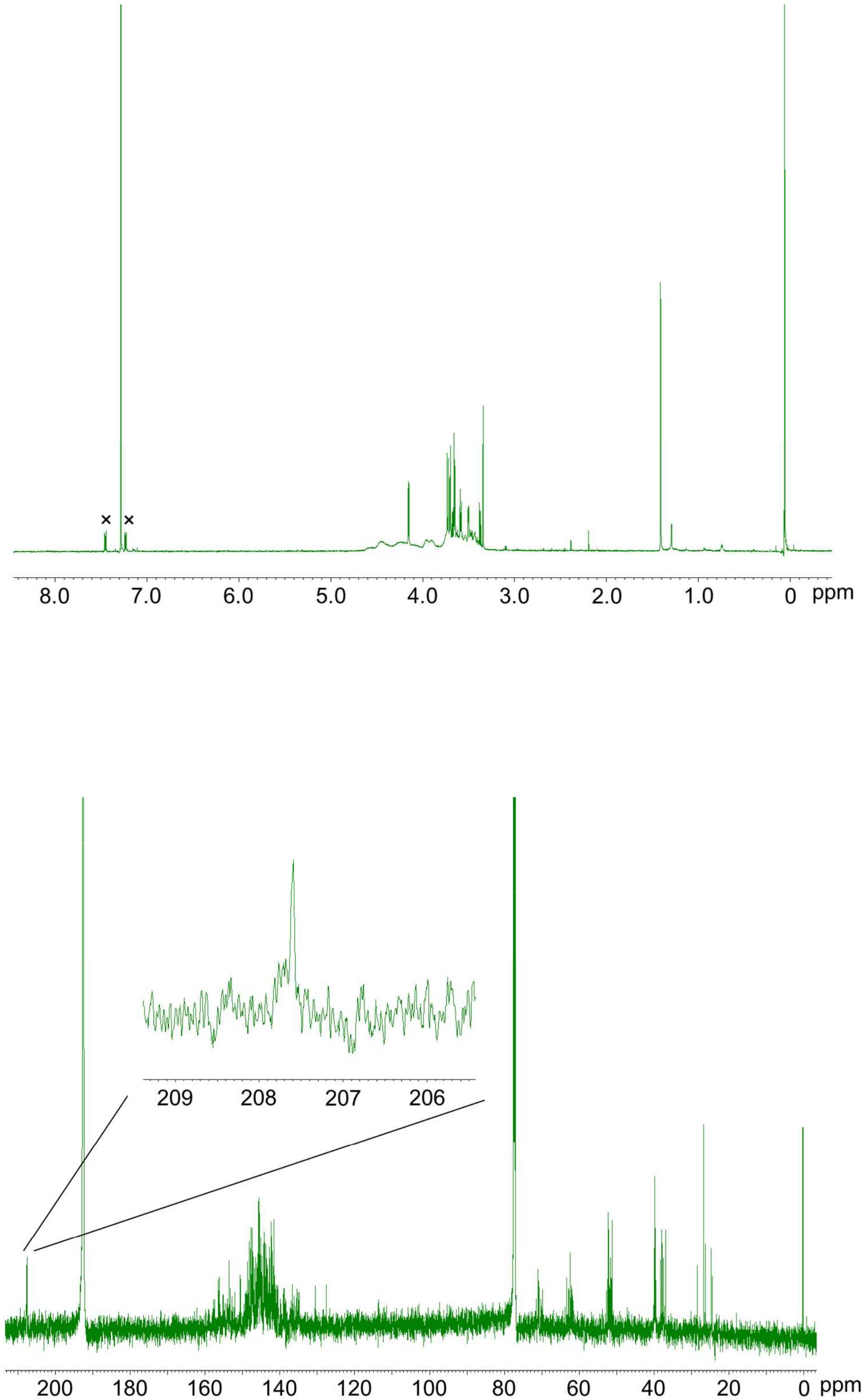
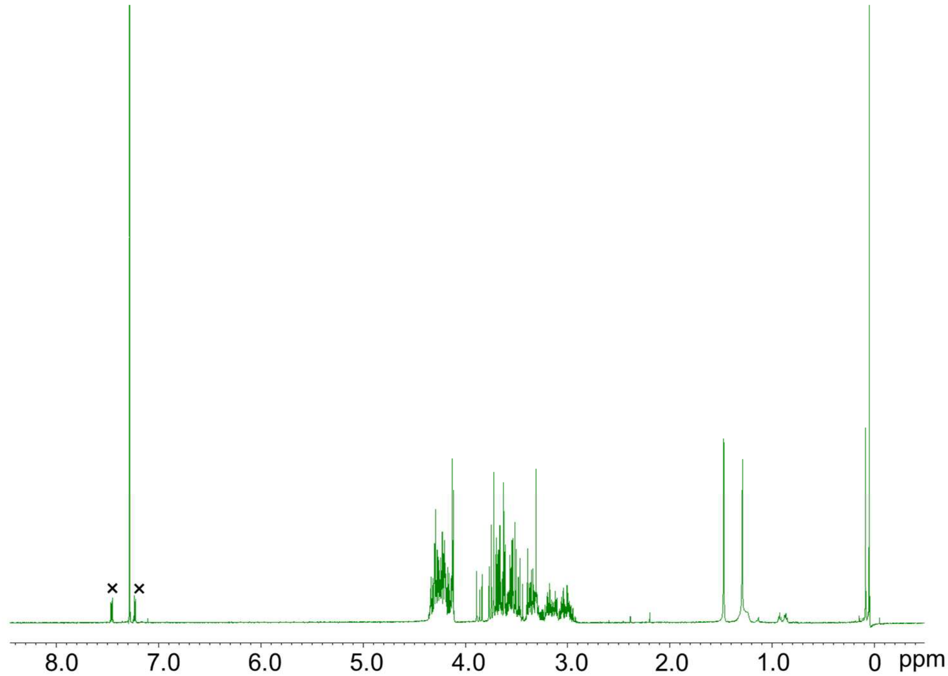


Figure S3. ^{1}H (upper) and ^{13}C NMR spectra (lower) of **CMCBA**.



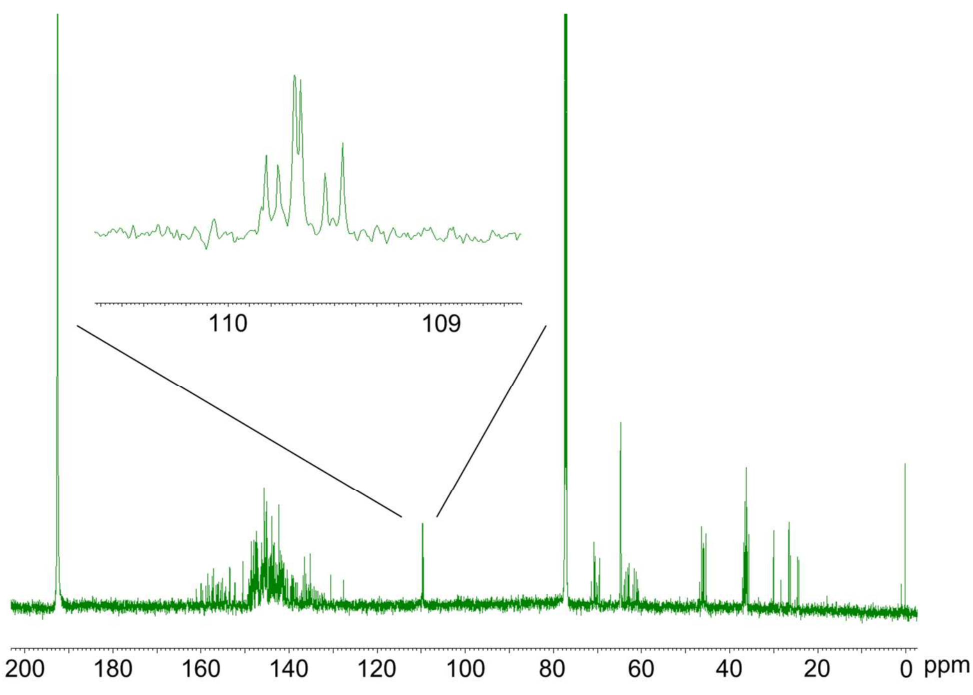
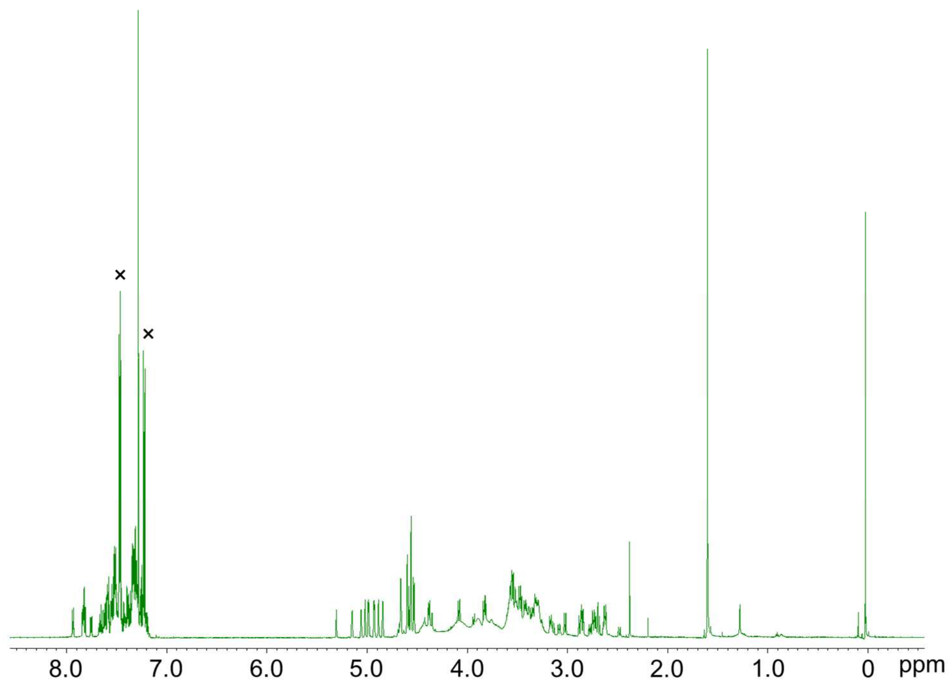


Figure S4. ^{1}H (upper) and ^{13}C NMR spectra (lower) of **SMCBA**.



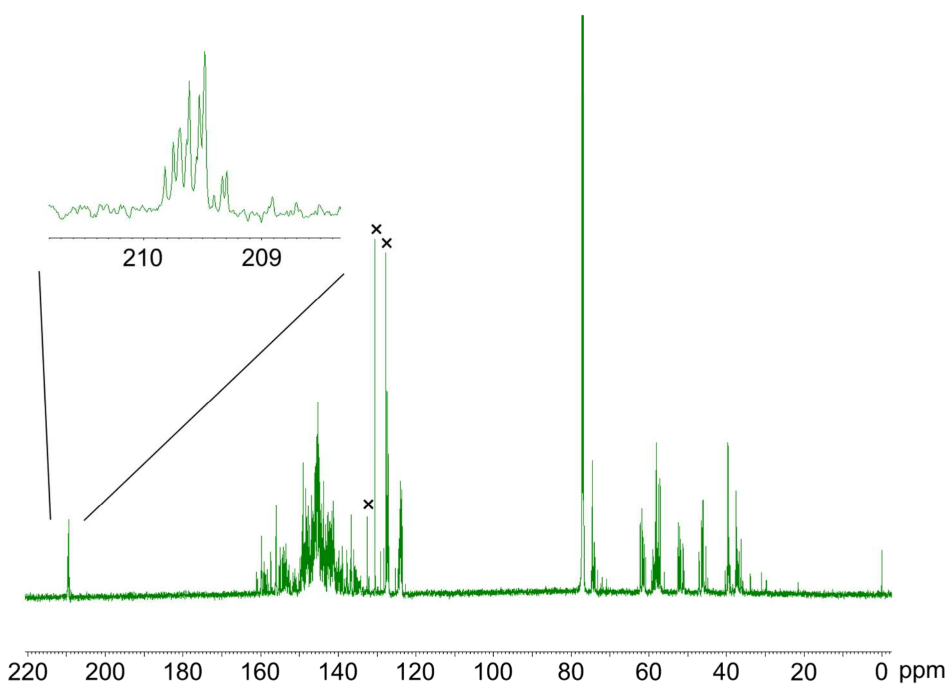


Figure S5. ^{1}H (upper) and ^{13}C NMR spectra (lower) of **CICBA**

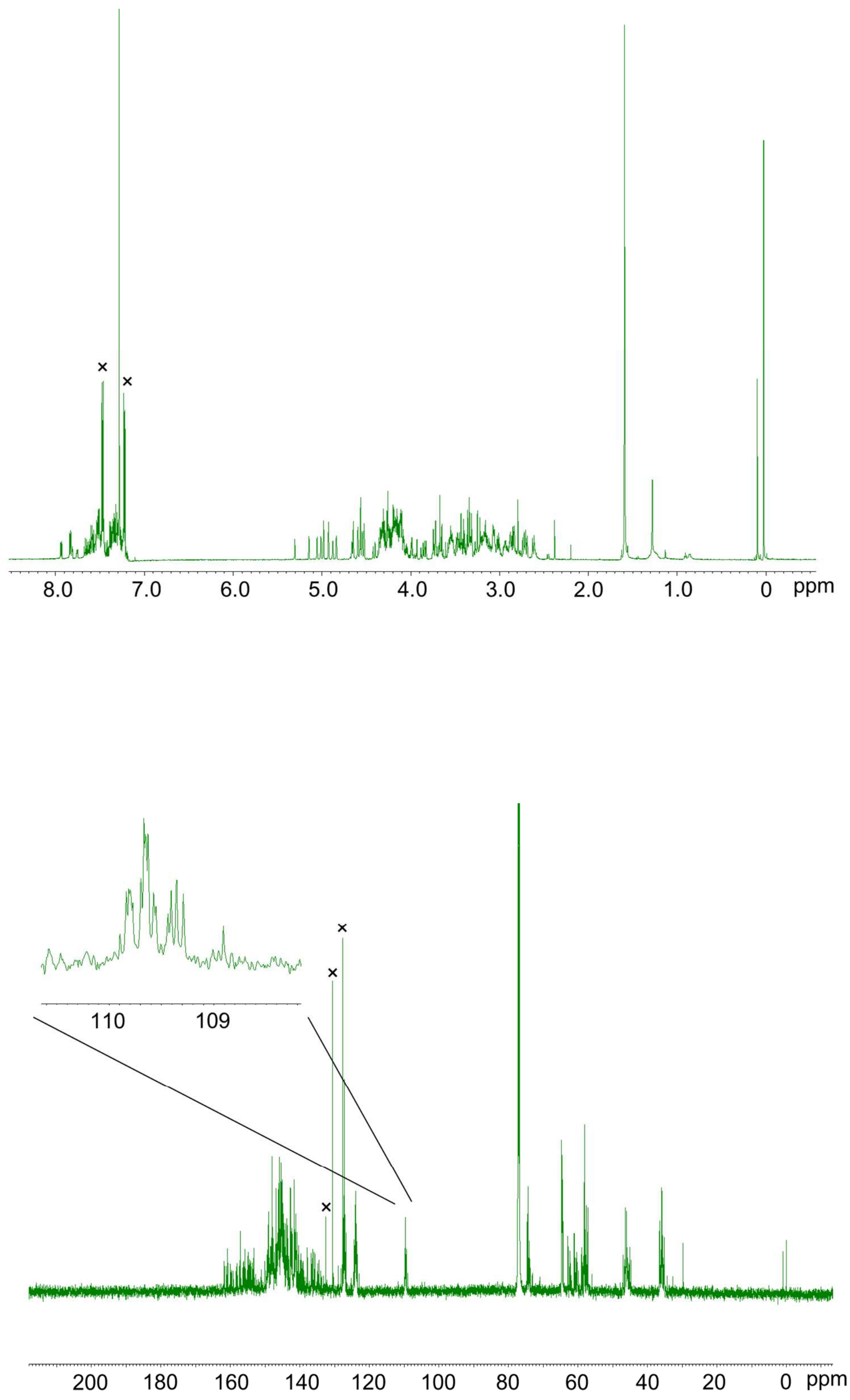


Figure S6. ^{1}H (upper) and ^{13}C NMR spectra (lower) of **SICBA**.

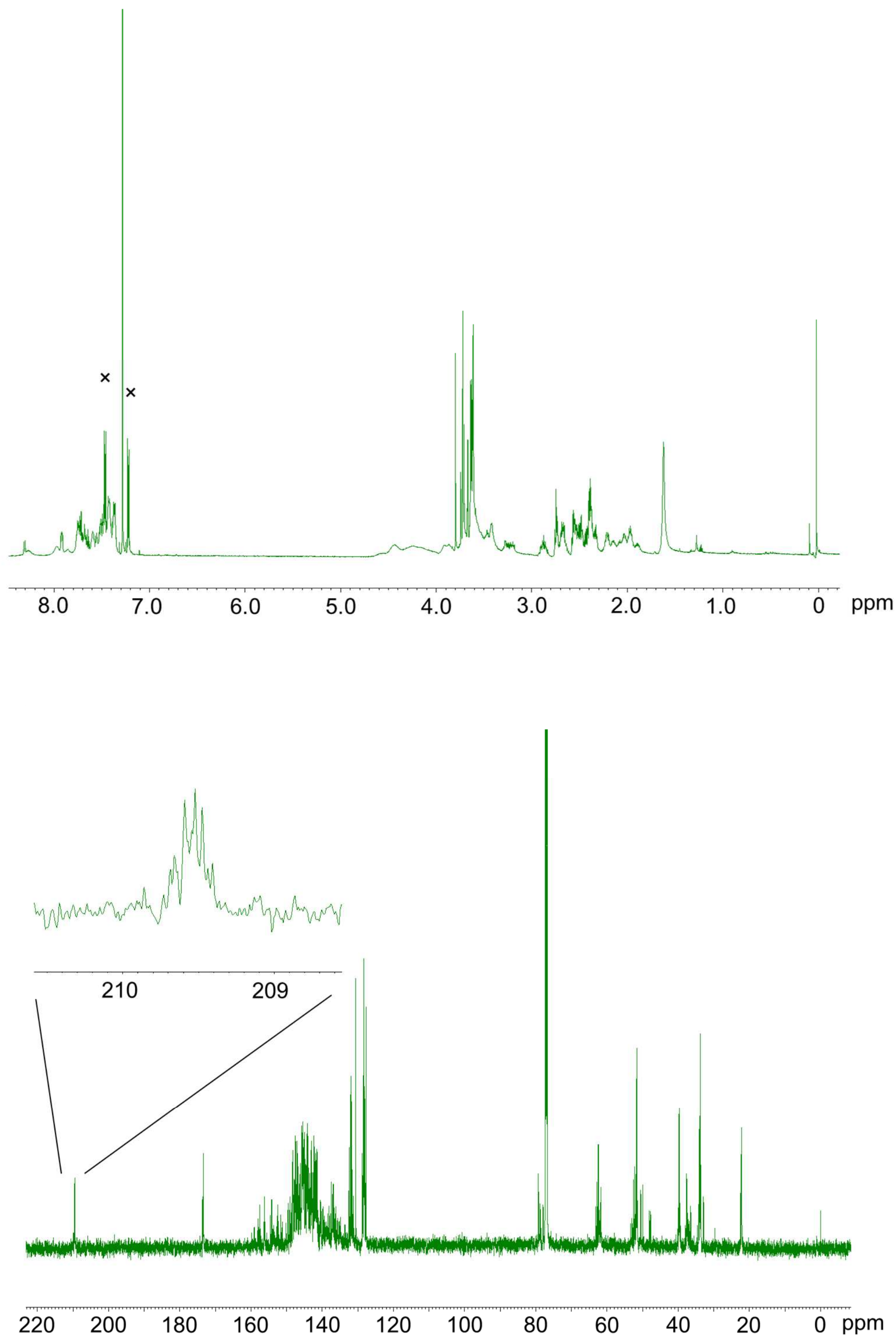


Figure S7. ^{1}H (upper) and ^{13}C NMR spectra (lower) of **CPCBM**.

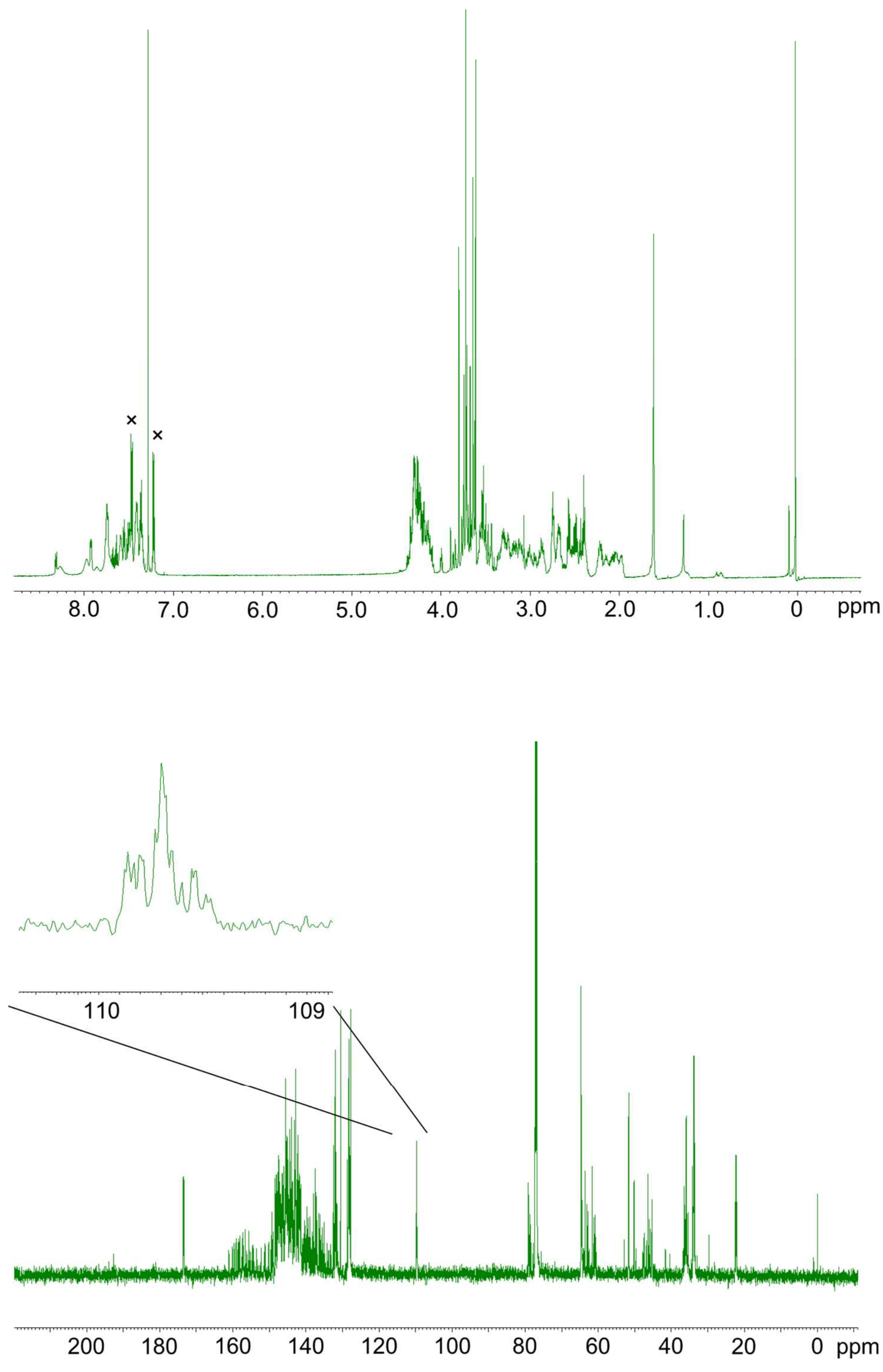
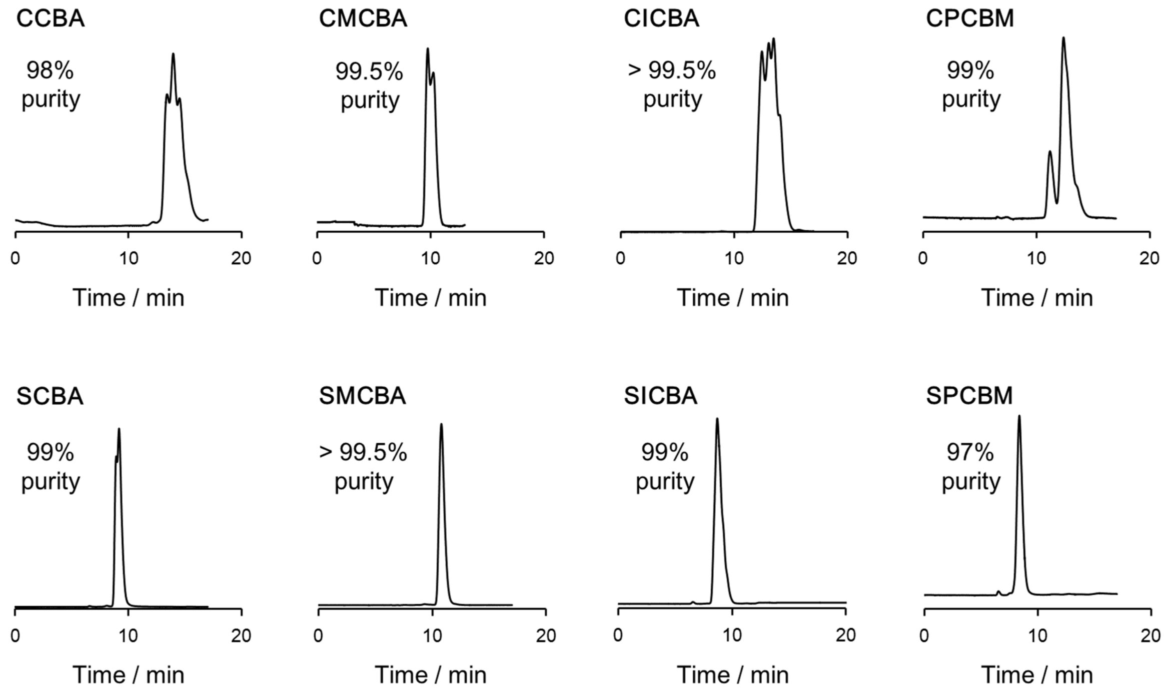


Figure S8. ^{1}H (upper) and ^{13}C NMR spectra (lower) of **SPCBM**.



Figrue S9. Purity of fullerene bis-adduct analyzed by HPLC using COSMOSIL Buckyprep column.

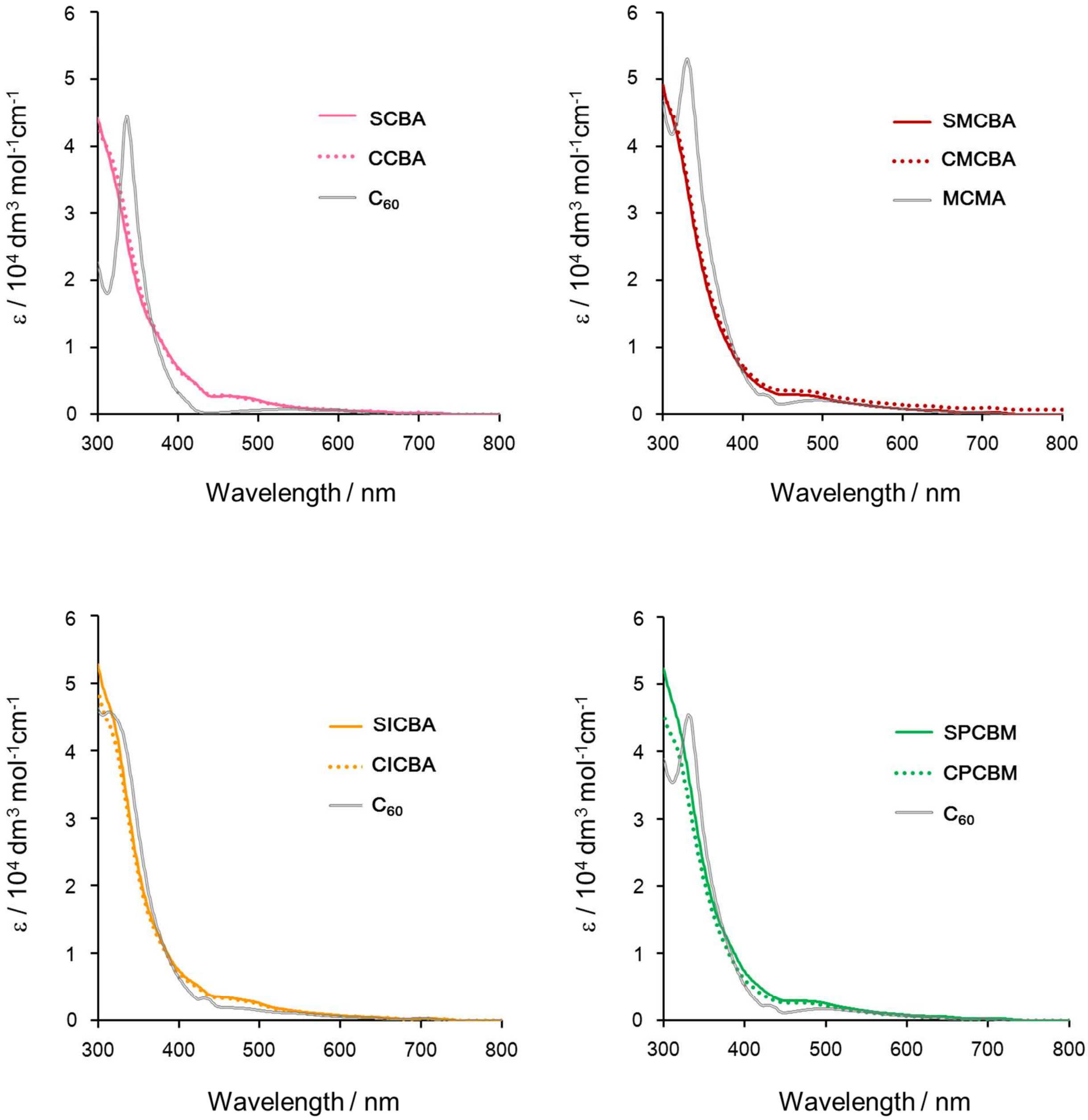


Figure S10. UV-Vis spectrum of fullerene bisadduct in toluene (2×10^{-5} mol dm^{-3}).

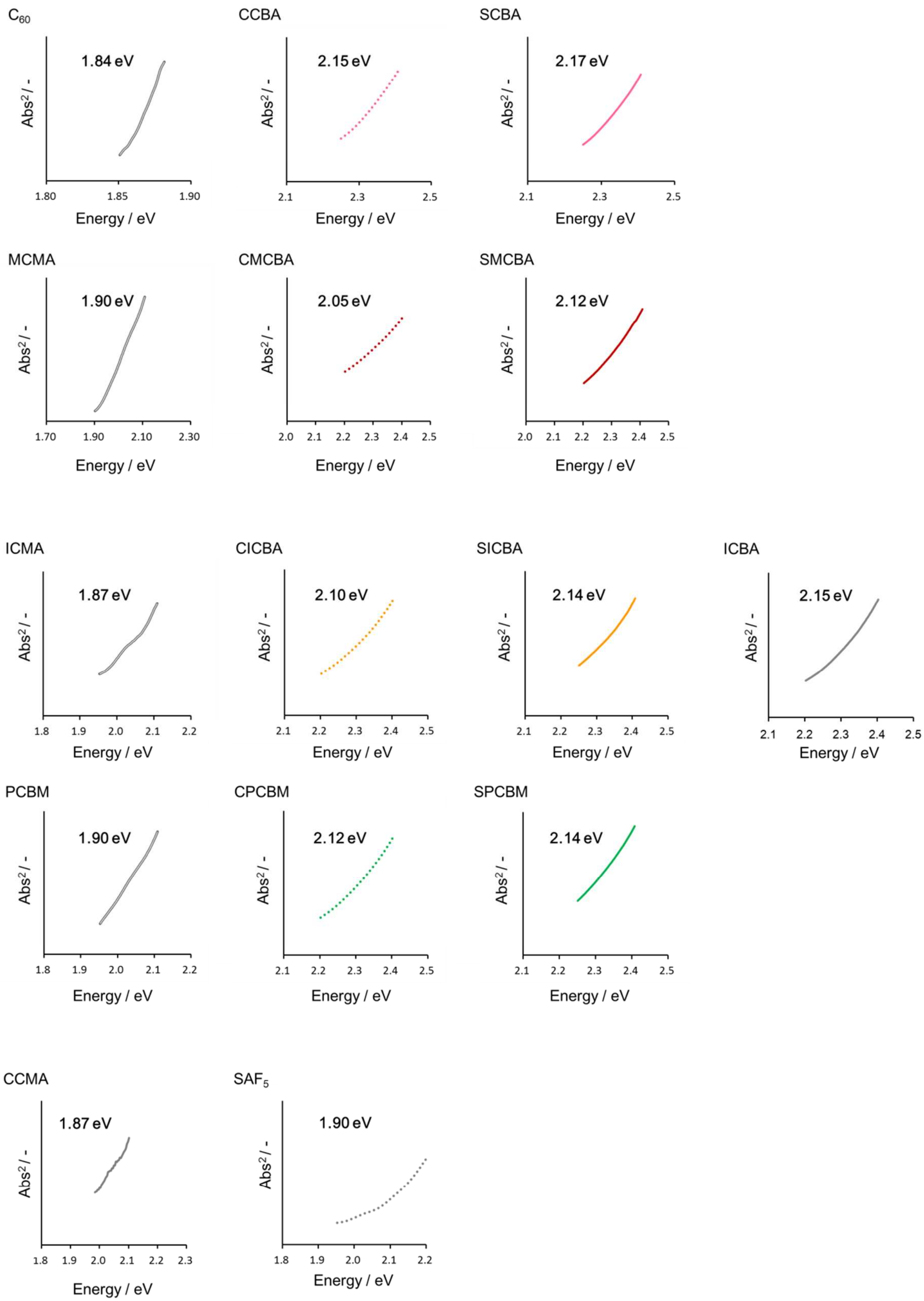


Figure S11. Optical bandgap estimated from absorption edge of fullerene bisadduct in toluene (2×10^{-5} mol dm^{-3}).

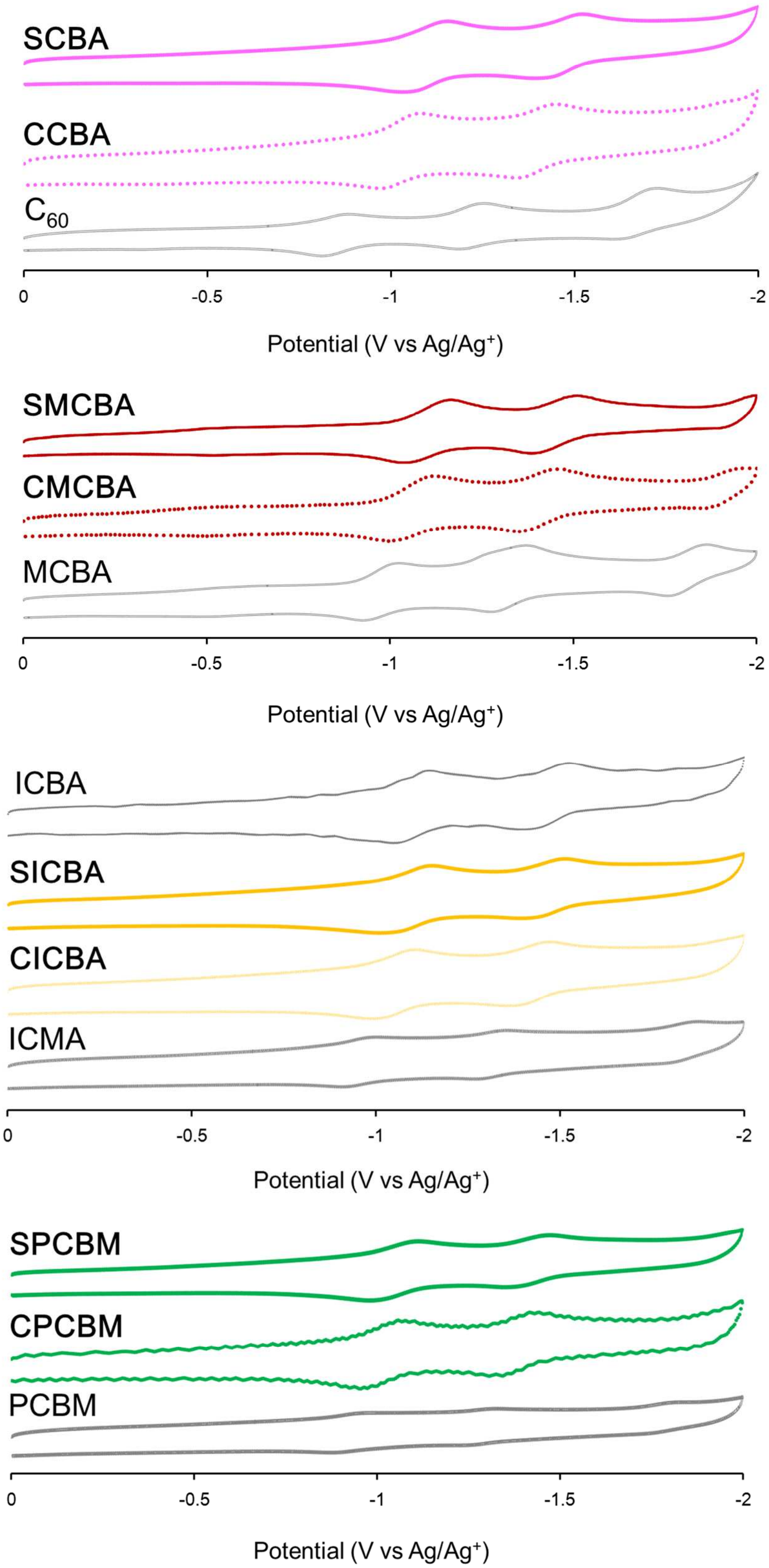


Figure S12. Cyclic voltammgram of fullerene bis-adducts in DCB.

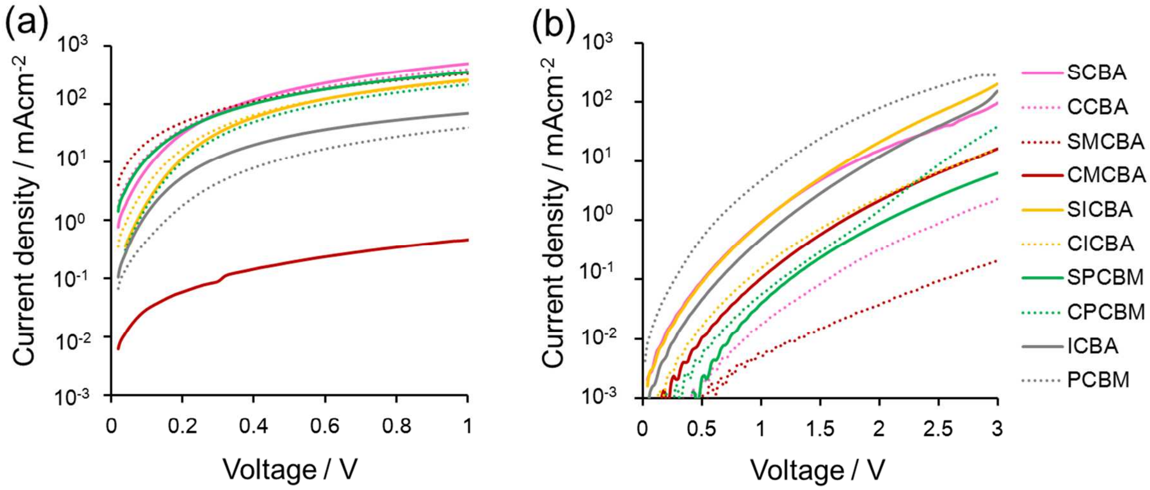


Figure S13. SCLC *J-V* curves of P3HT:fullerenes (1:0.6 in wt% for SMCBA and 1:1 for the others) under dark conditions using optimized device condition. (a) Hole- and (b) electron-only devices.

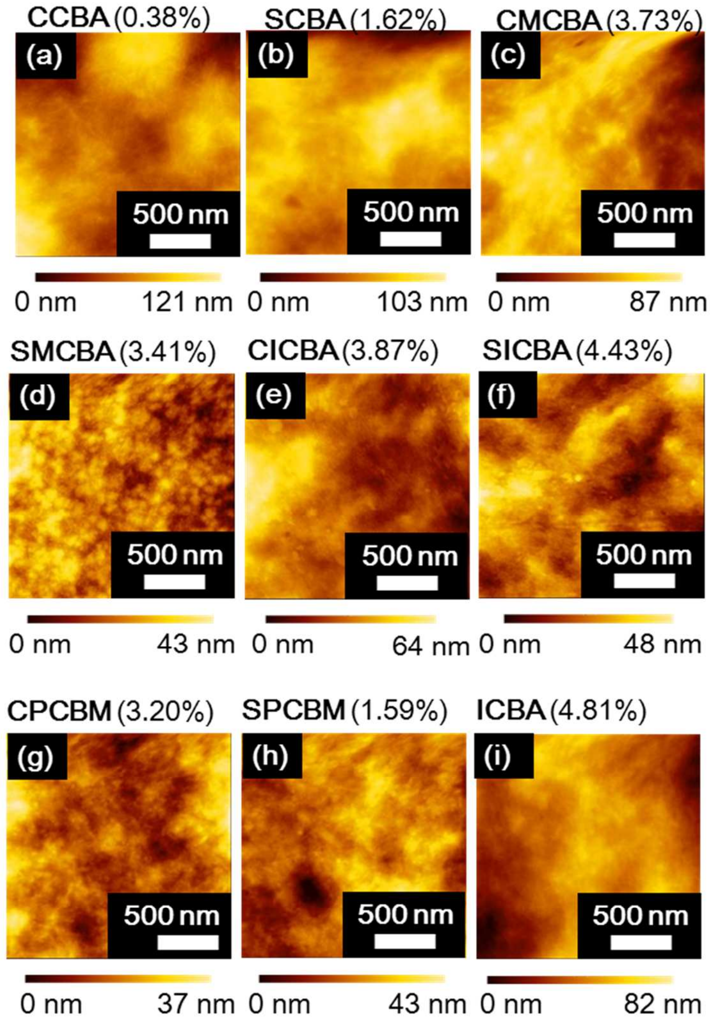


Figure S14. AFM topography images of P3HT:fullerene films at the OPV optimal condition. Images are observed for P3HT films blended with (a) CCBA, (b) SCBA, (c) CMCBA, (d) SMCBA, (e) CICBA, (f) SICBA, (g) CPCBM, (h) SPCBM, and (i) ICBA, respectively. The values in the brackets are the best PCE (Table 2). The image size is 2×2 μm^2.

Supporting References.

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