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# Supporting Information

# Alkylated-$C_{60}$ Based Soft Materials: Regulation of Self-Assembly and Optoelectronic Property by Chain Branching

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## (A) Chemicals

### i) Alcohols

Branched alcohols 2-hexyl-1-decanol ($C_6C_{10}OH$), 2-octyl-1-dodecanol ($C_8C_{12}OH$), and 2-decyl-1-tetradecanol ($C_{10}C_{14}OH$) were purchased from Sigma-Aldrich. Hyperbranched alcohols FINE OXOCOL 180N ($F_{180}NOH$) and FINE OXOCOL 180 ($F_{180}OH$) were gifted by NISSAN CHEMICAL INDUSTRIES, LTD., Japan. All the alcohols are colorless liquids and were used as received.

### ii) Hydroxybenzaldehydes

3,4-Dihydroxybenzaldehyde, 2,5-dihydroxybenzaldehyde, 3,4,5-trihydroxybenzaldehyde and 2,4,6-trihydroxybenzaldehyde were purchased from Sigma-Aldrich. 3,5-Dihydroxybenzaldehyde and 4-hydroxybenzaldehyde were purchased from ACROS ORGANICS. Before use, they have been purified by column chromatography where necessary.

### iii) Others

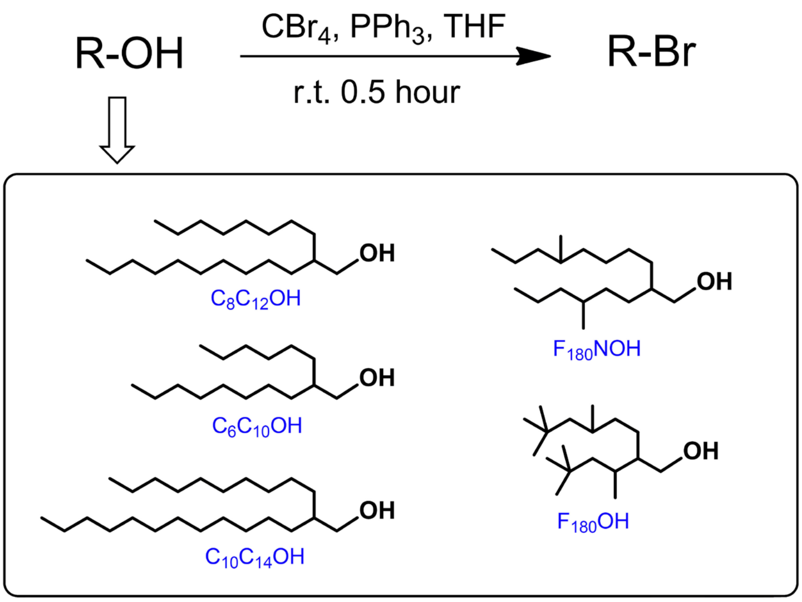
$C_{60}$ with a purity over 99.5%, sarcosine, carbon tetrabromide ($CBr_4$), triphenylphosphine ($PPh_3$) and sodium sulfate ($Na_2SO_4$) were purchased from Sigma-Aldrich. Potassium carbonate ($K_2CO_3$) and potassium iodide (KI) were purchased from Fluka and Alfa Aesar, respectively. Solvents for reactions including THF, DMF and monochlorobenzene are anhydrous and were purchased from Sigma-Aldrich. Solvents for column chromatography are of analytical grade. All of these substances or solvents were used as received unless stated differently.

## (B) Characterizations

NMR spectra were recorded on a Bruker DMX400. MALDI-TOF-MS spectra were recorded on a SHIMADZU AXIMA Confidence with a matrix of 2-(4-hydroxyphenylazo)-benzoic acid or trans-cinnamic acid. UV-vis spectra were measured on a Varian Cary 5000 spectrophotometer. FT-IR spectra were recorded on a Bruker EQUINOX 55/S spectrophotometer using a KBr pellet. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were carried out using a DSC 204 (Netzsch) under nitrogen with a scanning speed of 10 °C/min. Temperature-dependent XRD powder patterns were carried out using a RIGAKU RINT Ultima III X-ray diffractometer with monochromatic Cu Kα radiation ($\lambda = 0.15405$ nm). Small angle X-ray scattering (SAXS) measurement was carried out on a self-built setup (Rotating Anode Fr 591, Osmic mirror, MARCCD Detector) with Cu Kα radiation ($\lambda = 0.154$ nm). Electrochemical experiments were conducted in a classical three-electrode system using a Gamry Reference 600 Potentiostat/Galvanostat/ZRA Instrument. A glassy carbon electrode was used as working electrode and a Pt ring was used as auxiliary electrode, respectively. A Pt plate was used as the quasi-reference electrode and the $Fc^+/Fc$ couple was used as internal reference for the potential calibration. SEM samples were prepared by drop deposition of the precipitated objects from the suspension on a Si substrate and sputtered with Au in a JFC-1300 JEOL Automatic sputter coater, equipped with MTM-20 Thickness Controller. SEM images were recorded by means of a Philips XL30 electron microscope at an accelerating voltage of 3 kV. Rheological measurements were performed on a Thermo Haake model Rheostress I with a 1.0 mm parallel plate geometry at 25 °C. Evaluation of the solar energy conversion efficiency was carried out on a bulk heterojunction organic solar cell with a structure of ITO/PEDOT:PSS/active layer/Samarium/Aluminum. The light intensity used for device measurements is 80 mW/cm$^2$ and was corrected to match the AM 1.5 requirement of 100 mW/cm$^2$. Other details can be found elsewhere.[1]

## (C) Synthesis

i) Synthesis of alkyl bromide



**Typical synthetic procedure:** To a two-neck flask with a volume of 100 mL, triphenylphosphine ($PPh_3$, 7.87 g, 30 mmol) and carbon tetrabromide ($CBr_4$, 5.97 g, 18 mmol) were added. After removing air by repeated vacuum-argon cycles, 40 mL anhydrous THF was injected and the mixture was stirred at room temperature to make a homogeneous suspension. 15 mmol alkyl alcohol which was pre-dissolved in 10 mL anhydrous THF was then injected under stirring. The mixture was stirred for another 30 min at room temperature under argon. After the reaction was stopped, the mixture was filtered to remove insoluble solids. After THF was removed under reduced pressure, *n*-hexane was added and the mixture was filtered again. The filtrate was concentrated under reduced pressure and the resulting crude product was purified by column chromatography (silica gel 60, 0.063-0.200 mm) using *n*-hexane as an eluent. All the alkyl bromides obtained are colorless oil with good yield (> 90%).

The obtained results for **$C_8C_{12}Br$**[2], **$C_6C_{10}Br$**[3] and **F180NBr**[4] are consistent with those reported in the literatures.

**$C_8C_{12}Br$:** $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 3.55-3.35 (*d*, 2H, $J$ = 4.8 Hz), 1.66-1.52 (1 H), 1.46-1.15 (32H), 1.00-0.75 (*t*, 6H, $J$ = 13.6 Hz).

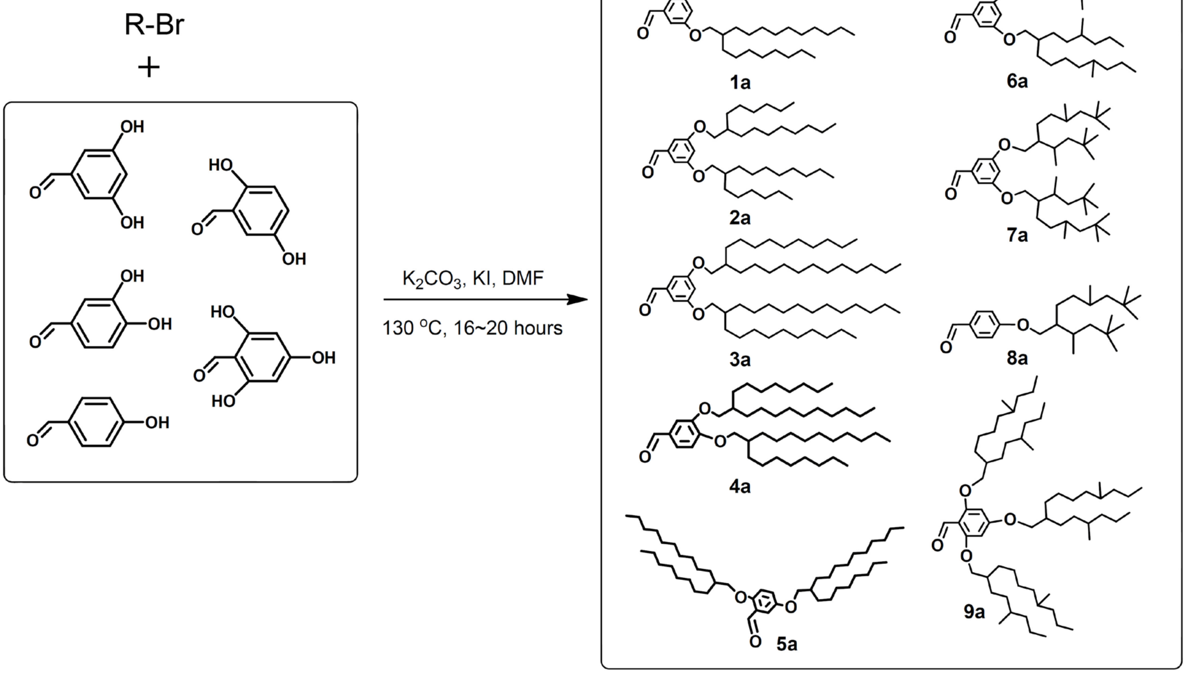
**$C_6C_{10}Br$:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.55-3.35 (*d*, 2H, *J* = 4.8 Hz), 1.66-1.52 (1 H), 1.46-1.15 (24H), 1.00-0.75 (*t*, 6H, *J* = 13.2 Hz).

**$C_{10}C_{14}Br$:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.55-3.35 (*d*, 2H, *J* = 4.8 Hz), 1.66-1.52 (1 H), 1.46-1.15 (40H), 1.00-0.75 (*t*, 6H, *J* = 12.8 Hz). IR (ATR): 2945 2921, 2852, 1465, 1377, 1233, 761, 721, 653, 622 cm$^{-1}$.

**F180NBr:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.70-3.16 (*m*, 2H), 2.10-0.55 (*m*, 35 H). IR (ATR): 2958, 2926, 2872, 2858, 1462, 1379, 1250, 1144, 658, 624 cm$^{-1}$.

**F180Br:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.56-3.26 (*m*, 2H), 2.20-1.66 (*m*, 1 H), 1.60-0.70 (*m*, 34H). IR (ATR): 2954, 2903, 2867, 1476, 1393, 1378, 1364, 1245, 1200, 673 cm$^{-1}$.

ii) Synthesis of alkyloxybenzaldehyde



**Typical synthetic procedure:** To a 250 mL two-neck flask, 2.5 mmol hydroxy-substituted benzaldehyde, $K_2CO_3$ (1.04 g, 7.5 mmol), and KI (25 mg) were added. After removing air by repeated vacuum-argon cycles, 50 mL anhydrous DMF was injected and the mixture was stirred at room temperature to make a homogeneous suspension. Alkyl bromide which was pre-dissolved in 10 mL anhydrous DMF was then injected under stirring. The molar ratio of alkyl bromide to the hydroxy group on benzaldehyde was set at 1.5:1. The mixture was stirred at 120 ˚C for 16-18 hours. After the reaction was stopped and the mixture was cooled to room temperature, water and $CHCl_3$ were added. The organic layer was separated and the water layer was extracted with $CHCl_3$ twice. The organic layers were combined, washed with brine three times and dried over $Na_2SO_4$. The solvent was removed under reduced pressure and the resulting crude product was purified by column chromatography (silica gel 60, 0.063-0.200 mm) using $CHCl_3$/*n*-hexane mixture as an eluent. The volume ratio of $CHCl_3$ to *n*-hexane was adjusted according to each molecule. The yields given below are based on hydroxy-substituted benzaldehyde conversion.

The obtained results for **1a** and **6a** are consistent with those reported in the literature.[4]

**1a** (78.6%)**:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.90 (*s*, 1H, -CHO), 7.03-6.95 (*d*, 2H, *J* = 2.0 Hz), 6.74-6.66 (*t*, 1H, *J* = 4.4 Hz), 3.97-3.75 (*d*, 4H, *J* = 5.6 Hz), 1.85-1.70 (*m*, 2H), 1.60-1.10 (*m*, 64H), 1.00-0.75 (*t*, 12H, *J* = 13.6Hz).

**2a** (47.9%)**:** $^1$H NMR (400 MHz, $CDCl_3$)$\delta$ 9.90 (*s*, 1H, -CHO), 7.03-6.95 (*d*, 2H, *J* = 2.4 Hz), 6.74-6.65 (*t*, 1H, *J* = 4.4 Hz), 4.00-3.72 (*d*, 4H, *J* = 5.6 Hz), 1.85-1.70 (*m*, 2H), 1.60-1.10 (*m*, 48H), 1.00-0.75 (*m*, 12H). MALDI-TOF-MS $[M+H]^+$ calcd: 587.5, found: 587.8. IR (ATR): 2954, 2922, 2853, 1702, 1592, 1451, 1380, 1349, 1316, 1295, 1166, 1055, 843, 722, 676 cm$^{-1}$.

**3a:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.90 (*s*, 1H, -CHO), 7.03-6.95 (*d*, 2H, *J* = 2.4 Hz), 6.74-6.66 (*t*, 1H, *J* = 4.8 Hz), 3.97-3.75 (*d*, 4H, *J* = 5.6 Hz), 1.85-1.70 (*m*, 2H), 1.60-1.10 (*m*, 80H), 1.00-0.75 (*t*, 12H, *J* = 13.6Hz). MALDI-TOF-MS $[M+H]^+$ calcd: 811.8, found: 812.7. IR (ATR): 2953, 2920, 2852, 1703, 1592, 1454, 1380, 1349, 1316, 1295, 1166, 1055, 844, 759, 721, 676 cm$^{-1}$.

**4a** (92.6%)**:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.83 (*s*, 1H, -CHO), 7.45-7.32 (*m*, 2H), 6.99-6.85 (*d*, 1H, *J* = 8 Hz), 4.05-3.77 (*q*, 4H, *J* = 8.4 Hz), 1.94-1.74 (*m*, 2H), 1.60-1.15 (*m*, 64H), 1.00-0.75 (*t*, 12H, *J* = 13.6Hz). MALDI-TOF-MS $[M+H]^+$ calcd: 699.7, found: 699.8, $M+Na^+$ calcd: 721.7, found: 721.4. IR (ATR): 2954, 2921, 2852, 1691, 1584, 1510, 1465, 1435, 1267, 1237, 1164, 1131, 1021, 802, 757, 721, 655 cm$^{-1}$.

**5a** (73.2%)**:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.48 (*s*, 1H, -CHO), 7.33-7.29 (*d*, 1H, *J* = 3.2 Hz), 7.15-7.08 (*m*, 1H), 6.95-6.88 (*d*, 1H, *J* = 9.2 Hz), 3.94-3.88 (*d*, 2H, *J* = 5.6 Hz), 3.84-3.77 (*d*, 2H, *J* = 5.6 Hz), 1.86-1.69 (*m*, 2H), 1.60-1.15 (*m*, 64H), 1.00-0.75 (*t*, 12H, *J* = 13.6Hz). MALDI-TOF-MS $[M]^+$ calcd: 698.7, found: 698.4. IR (ATR): 2953, 2921, 2852, 1684, 1494, 1465, 1385, 1274, 1215, 1161, 1032, 812, 749, 721 cm$^{-1}$.

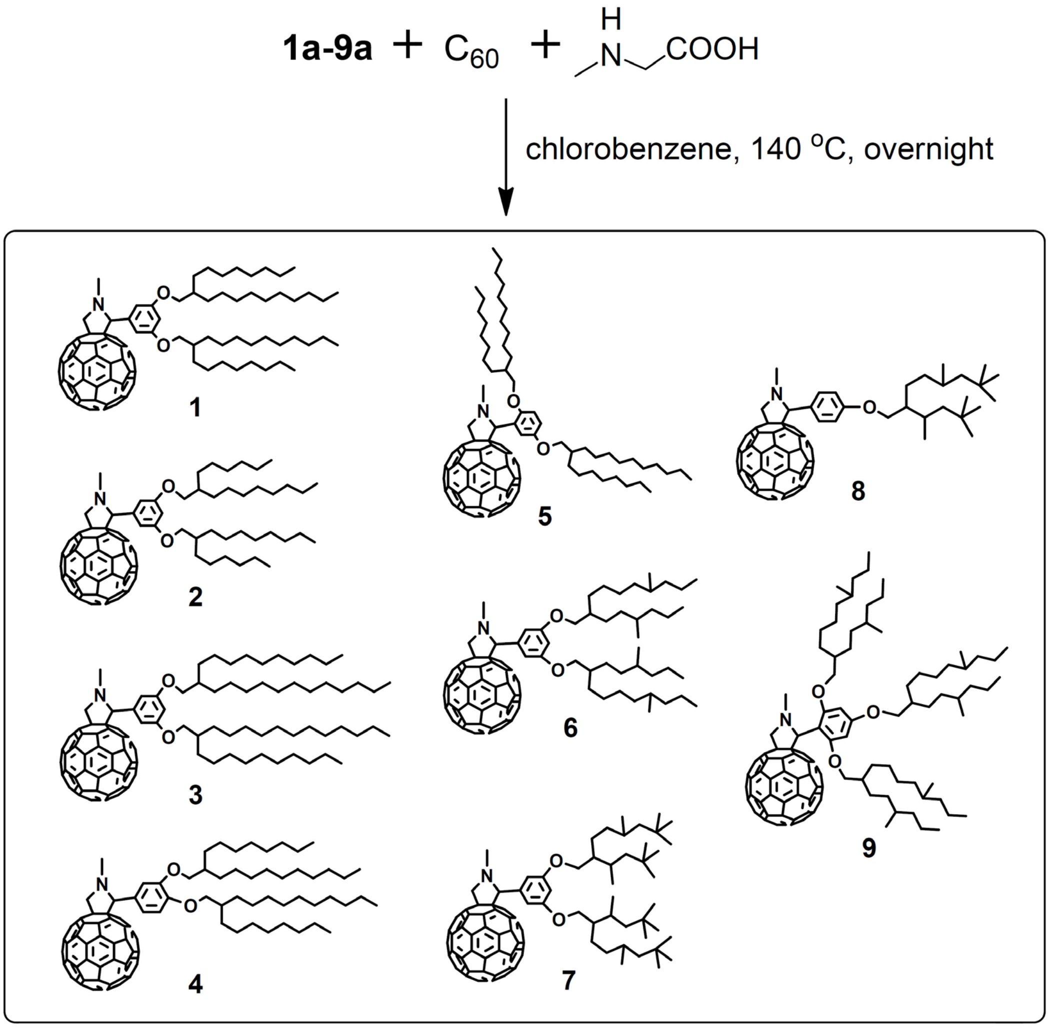
**6a:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.90 (*s*, 1H, -CHO), 6.99 (*s*, 2H), 6.70 (*s*, 1H), 4.2-3.4 (*m*, 4H), 2.0-0.6 (*m*, 70H).

**7a:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.91 (*s*, 1H, -CHO), 7.07-6.92 (*d*, 2H, *J* = 2 Hz), 6.77-6.62 (*t*, 1H, *J* = 4.4 Hz), 4.15-3.60 (*m*, 4H), 2.0-0.5 (*m*, 70H). MALDI-TOF-MS $[M]^+$ calcd: 642.6, found: 642.0. IR (ATR): 2952, 2904, 2867, 1702, 1604, 1592, 1465, 1451, 1381, 1363, 1295, 1164, 1055, 845, 759, 676 cm$^{-1}$.

**8a** (91.0%)**:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.88 (*s*, 1H, -CHO), 7.90-7.76 (*d*, 2H, *J* = 8.8 Hz), 7.07-6.88 (*d*, 2H, *J* = 8.8 Hz), 4.02-3.72 (*m*, 2H), 1.95-0.70 (*m*, 35H). MALDI-TOF-MS $[M+H]^+$ calcd: 375.3, found: 376.4. IR (ATR): 2951, 2902, 2866, 1694, 1600, 1577, 1509, 1467, 1363, 1310, 1255, 1214, 1157, 11015, 858, 830, 651, 618 cm$^{-1}$.

**9a:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.39 (*s*, 1H, -CHO), 6.01 (*s*, 2H), 3.72-4.11 (*m*, 6H), 1.96 (*s*, 3H), 1.26-1.52 (*m*, 60H), 1.75-1.04 (*m*, 6H), 0.79-0.89 (*m*, 36H). MALDI-TOF-MS $[M+Na]^+$ calcd: 933.9, found: 934.7. IR (ATR): 2956, 2923, 2871, 2857, 1682, 1598, 1573, 1461, 1415, 1378, 1331, 1224, 1171, 1118, 1051, 812, 756, 728 cm$^{-1}$

iii) Synthesis of alkylated fullerenes



**Typical synthetic procedure:** To a 1 L two-neck flask, $C_{60}$ (0.54 g, 0.75 mmol) and sarcosine (0.2227 g, 2.5 mmol) were added. After removing air by repeated vacuum-argon cycles, 450 mL anhydrous monochlorobenzene was injected and the mixture was stirred at ~ 80 °C until the $C_{60}$ dissolved completely. Then 0.5 mmol alkyloxybenzaldehyde which was pre-dissolved in 50 mL anhydrous monochlorobenzene was injected and the mixture was refluxed under dark for 16-18 hours. After the reaction was stopped and the mixture was cooled to room temperature, unreacted sarcosine was filtered off and the solvent was removed under reduced pressure. The crude product was first subjected to column chromatography (silica gel 60, 0.063-0.200 mm) using $CHCl_3$ as an eluent to remove most of the unreacted $C_{60}$. The solution was collected and the solvent was removed under reduced pressure. The crude product was then subjected to GPC (Bio-Beads ® S-X1 Beads, 200-400 mesh) twice using toluene as an eluent affording the final pure mono-substituted alkylated fullerene. The yields given below are based on $C_{60}$ conversion.

**1** (34.0%)**:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.2-6.6 (*br*, 2H), 6.44-6.36 (*t*, 1H, *J* = 4.4 Hz), 5.03-4.93 (*d*, 1H, *J* = 9.6 Hz), 4.82 (*s*, 1 H), 4.29-4.16 (*d*, 1H, *J* = 9.6 Hz), 4.0-3.6 (*m*, 4H), 2.85 (*s*, 3H), 1.82-1.65 (*m*, 2H), 1.50-1.10 (*m*, 64H), 1.0-0.75 (*m*, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 156.14, 154.12,153.87, 153.50, 147.30, 147.12, 146.47, 146.30, 146.24, 146.21, 146.10, 146.07, 145.94, 145.93, 145.78, 145.53, 145.50, 145.48, 145.32, 145.26, 145.24, 145.21, 145.14, 144.68, 144.66, 144.37, 143.14, 142.95, 142.67, 142.56, 142.21, 142.14, 142.12, 142.02, 141.87, 141.79, 141.67, 141.57, 140.17, 140.10, 139.70, 139.57, 138.91, 136.61, 136.30, 135.78, 102.05, 83.80, 71.21, 70.04, 69.05, 40.14, 37.90, 31.94, 31.39, 30.09, 29.72, 29.69, 29.66, 29.38, 26.90, 26.87, 22.71, 14.15. MALDI-TOF-MS calcd $[M-H]^+$: 1445.70, found: 1445.52. Elemental analysis calcd: C 90.48%; H 6.34%; N 0.97%, found: C 90.51%; H 6.34%; N 0.98%. IR (ATR): 2952, 2922, 2851, 2777, 1593, 1458, 1356, 1332, 1294, 1160, 1056, 1032, 898, 850, 831 cm$^{-1}$.

**2** (45.9%)**:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.2-6.6 (*br*, 2H), 6.47-6.33 (*t*, 1H, *J* = 4.4 Hz), 5.05-4.90 (*d*, 1H, *J* = 9.6 Hz), 4.82 (s, 1 H), 4.32-4.16 (d, 1H, J = 9.2 Hz), 4.0-3.6 (m, 4H), 2.85 (s, 3H), 1.82-1.64 (m, 2H), 1.50-1.05 (*m*, 48H), 1.0-0.75 (*m*, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 156.14, 154.12, 153.86, 153.50, 147.29, 147.12, 146.47, 146.30, 146.24, 146.21, 146.13, 146.10, 146.07, 145.94, 145.92, 145.78, 145.52, 145.50, 145.48, 145.31, 145.26, 145.21, 145.14, 144.66, 144.36, 143.14, 142.95, 142.67, 142.56, 142.21, 142.14, 142.12, 142.01 141.87, 141.78, 141.67, 141.57, 140.17, 140.10, 139.70, 139.57, 138.91, 136.61, 136.30, 135.79, 102.04, 83.79, 71.19, 70.03, 69.05, 40.14, 37.91, 31.93, 31.90, 31.40, 30.08, 29.74, 29.65, 29.37, 26.90, 26.86, 26.82, 22.70, 14.16. MALDI-TOF-MS calcd $[M-H]^+$: 1333.58, found: 1333.48. Elemental analysis calcd: C 90.89%; H 5.66%; N 1.05%, found: C 90.88%; H 5.69%; N 1.05%. IR (ATR): 2952, 2922, 2851, 2776, 1593, 1458, 1356, 1332, 1294, 1160, 1056, 1032, 898, 850, 831 cm$^{-1}$.

**3** (47%)**:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.14-6.56 (*br*, 2H), 6.45-6.36 (*m*, 1H), 5.02-4.93 (*d*, 1H, *J* = 9.2 Hz), 4.82 (*s*, 1H), 4.29-4.20 (*d*, 1H, *J* = 9.6 Hz), 3.94-3.68 (*m*, 4H), 2.85 (*s*, 3H), 1.80-1.64 (*m*, 2H), 1.48-1.00 (*m*, 80H), 1.00-0.75 (*m*, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 156.15, 154.12, 153.88, 153.50, 147.30, 147.13, 146.47, 146.30, 146.25, 146.22, 146.14, 146.10, 146.08, 145.95, 145.93, 145.78, 145.53, 145.50, 145.48, 145.32, 145.26, 145.25, 145.22, 145.15, 144.68, 144.67, 144.38, 144.37, 143.15, 142.96, 142.68, 142.56, 142.22, 142.15, 142.13, 142.02, 141.88, 141.79, 141.68, 141.58, 136.62, 136.30, 135.79, 129.02, 128.21, 125.29, 102.08, 71.22, 70.06, 69.06, 40.14, 37.91, 31.95, 31.41, 30.11, 29.74, 29.70, 29.39, 26.92, 26.88, 22.72, 14.15. MALDI-TOF-MS calcd $[M-H]^+$: 1557.83, found: 1557.91. IR (ATR): 2952, 2922, 2851, 2779, 1593, 1462, 1332, 1294, 1163, 1056, 1029, 898, 853, 831 cm$^{-1}$.

**4** (32.2%)**:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.60-7.25 (*br*, 1H), 7.0-6.7 (*d*, 1H, *J* = 7.6 Hz), 5.04-4.91 (*d*, 1H, *J* = 9.2 Hz), 4.85 (*s*, 1H), 4.31-4.15 (*d*, 1H, *J* = 9.2 Hz), 4.10-3.60 (*m*, 4H), 2.81 (*s*, 3H), 1.86-1.64 (*m*, 2H), 1.60-1.00 (*m*, 64H), 0.96-0.75 (*m*, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 156.30, 154.18, 154.04, 153.69, 149.66, 147.32, 147.29, 146.97, 146.52, 146.34, 146.31, 146.25, 146.21, 146.14, 146.09, 145.95, 145.93, 145.79, 145.54, 145.51, 145.46, 145.34, 145.29, 145.27, 145.24, 145.15, 144.69, 144.67, 144.40, 144.39, 143.15, 142.98, 142.68, 142.58, 142.57, 142.54, 142.26, 142.25, 142.16, 142.14, 142.12, 142.06, 142.03, 141.90, 141.83, 141.69, 141.56, 141.16, 141.11, 139.81, 139.68, 136.58, 136.45, 135.81, 135.77, 129.12, 83.52, 72.21, 71.98, 70.02, 68.99, 40.07, 38.25, 38.12, 31.97, 31.94, 31.42, 30.18, 30.12, 29.80, 29.74, 29.69, 29.44, 29.41, 29.39, 27.00, 22.72, 22.70, 14.16, 14.13. MALDI-TOF-MS calcd $[M-H]^+$: 1445.70, found: 1445.64. Elemental analysis calcd: C 90.48%; H 6.34%; N 0.97%, found: C 90.43%; H 6.40%; N 0.96%. IR (ATR): 2952, 2922, 2851, 2775, 1515, 1462, 1430, 1377, 1334, 1263, 1227, 1179, 1132, 1029 cm$^{-1}$.

**5** (44.4%)**:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.64-7.40 (*m*, 1H), 6.92-6.65 (*m*, 2H), 6.52 (*s*, 1H), 5.05-4.88 (*d*, 1H, *J* = 9.2 Hz), 4.35-4.15 (*d*, 1H, *J* = 9.6 Hz), 4.00-3.60 (*m*, 4H), 2.81 (*s*, 3H), 1.80-1.65 (*m*, 1H), 1.65-1.52 (*m*, 1H), 1.50-1.00 (*m*, 64H), 1.00-0.75 (*m*, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 156.73, 155.11, 154.43, 153.93, 153.74, 152.11, 147.28, 146.82, 146.73, 146.24, 146.20, 146.16, 146.06, 145.91, 145.75, 145.57, 145.52, 145.29, 145.22, 145.16, 145.12, 145.08, 144.60, 144.55, 144.40, 144.33, 143.04, 142.93, 142.60, 142.53, 142.51, 142.28, 142.27, 142.23, 142.18, 142.15, 142.09, 142.06, 141.95, 141.78, 141.71, 141.67, 141.59, 140.13, 140.09, 139.54, 136.58, 136.27, 136.07, 134.68, 126.14, 115.93, 115.90, 112.90, 75.80, 72.11, 71.56, 71.56, 71.54, 70.01, 69.30, 53.40, 40.20, 38.23, 37.95, 32.00, 31.95, 31.39, 30.19, 30.12, 29.89, 29.83, 29.74, 29.70, 29.49, 29.45, 29.39, 27.21, 26.92, 26.89, 22.72, 14.16. MALDI-TOF-MS calcd $[M]^+$: 1446.71, found: 1447.20. IR (ATR): 2952, 2922, 2850, 2779, 1496, 1462, 1430, 1332, 1203, 1032 $cm^{-1}$.

**6** (48.3%)**:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.20-6.50 (*br*, 2H), 6.40 (*s*, 1H), 5.04-4.89 (*d*, 1H, *J* = 9.6 Hz), 4.83 (*s*, 1H), 4.31-4.15 (*d*, 1H, *J* = 9.2 Hz), 3.80 (*s*, 4H), 2.84 (*s*, 3H), 1.95-0.50 (*m*, 70H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 156.14, 154.14, 253.87, 153.52, 147.30, 147.11, 146.47, 146.31, 146.26, 146.22, 146.14, 146.12, 146.08, 145.95, 145.93, 145.79, 145.53, 145.51, 145.49, 145.32, 145.26, 145.15, 144.68, 144.37, 143.14, 142.96, 142.68, 142.57, 142.22, 142.15, 142.12, 142.02, 141.89, 141.80, 141.68, 141.59, 140.18, 140.10, 139.72, 139.58, 138.93, 136.62, 136.31, 135.79, 102.03, 83.83, 70.05, 69.07, 40.13, 39.51, 38.58, 37.99, 37.46, 37.28, 37.01, 36.81, 36.66, 36.26, 35.95, 35.51, 34.37, 33.56, 32.71, 31.92, 31.76, 31.63, 30.89, 30.44, 30.24, 29.52, 29.35, 29.26, 28.99, 27.53, 27.12, 26.74, 25.86, 25.58, 24.33, 23.17, 23.06, 22.69, 20.09, 19.74, 19.25, 19.04, 16.87, 16.58, 16.00, 15.23, 14.73, 14.41, 14.21, 14.06, 12.36, 12.27, 11.44, 11.27, 10.94. MALDI-TOF-MS calcd [M-H]+: 1389.64, found: 1390.01. Elemental analysis calcd: C 90.68%; H 6.02%; N 1.01%, found: C 90.72%; H 6.04%; N 1.01%. IR (ATR): 2955, 2922, 2869, 2851, 2778, 1593, 1458, 1377, 1332, 1294, 1164, 1056, 1029, 898, 853, 831 $cm^{-1}$.

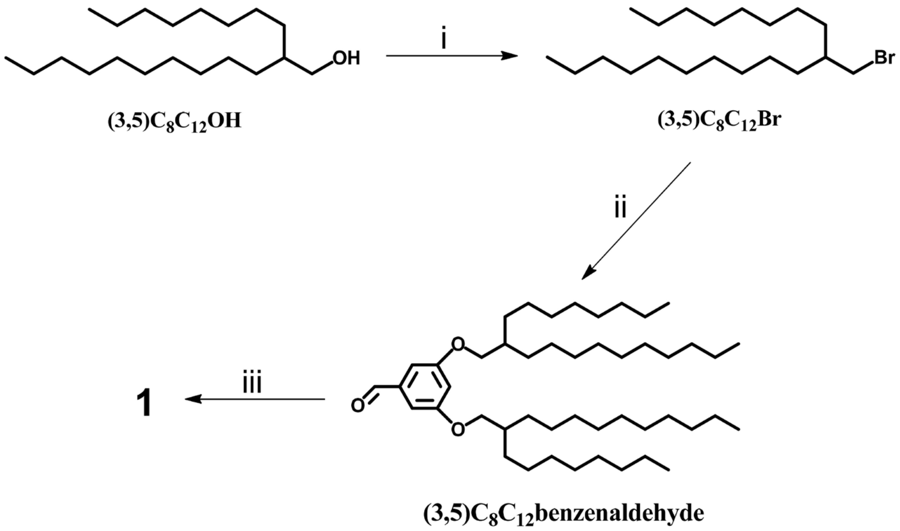
**7** (43.6%)**:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.20-6.50 (*br*, 2H), 6.40 (*s*, 1H), 5.04-4.89 (*d*, 1H, *J* = 9.2 Hz), 4.84 (*s*, 1H), 4.32-4.15 (*d*, 1H, *J* = 9.6 Hz), 4.10-3.60 (*m*, 4H), 2.85 (*s*, 3H), 1.90-1.70 (*m*, 2H), 1.70-1.50 (*m*, 2H), 1.50-0.65 (*m*, 66H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 156.13, 154.13, 153.91, 153.50, 147.29, 147.13, 146.46, 146.31, 146.27, 146.21, 146.14, 146.11, 146.07, 145.94, 145.92, 145.78, 145.52, 145.50, 145.48, 145.33, 145.25, 145.14, 144.68, 144.65, 144.37, 143.16, 142.96, 142.67, 142.56, 142.21, 142.14, 142.11, 142.02, 141.92, 141.80, 141.67, 141.59, 140.17, 140.10, 139.74, 139.58, 138.89, 136.62, 136.28, 135.78, 102.11, 83.77, 70.04, 69.75, 69.30, 69.24, 69.05, 51.43, 51.39, 51.34, 51.29, 51.21, 48.60, 48.56, 48.52, 48.05, 47.85, 45.24, 45.11, 45.07, 45.04, 40.13, 38.16, 38.11, 38.02, 37.95, 31.24, 31.22, 31.19, 31.05, 30.89, 30.13, 30.09, 30.00, 29.92, 29.82, 29.73, 29.70, 29.49, 29.43, 29.38, 29.33, 27.35, 27.29, 26.09, 25.97, 25.22, 22.82, 22.79, 22.69, 22.64, 19.53, 19.48, 19.31, 19.24, 18.77, 18.67, 18.64. MALDI-TOF-MS calcd [M-H]+: 1389.64, found: 1390.01. Elemental analysis calcd: C 90.68%; H 6.02%; N 1.01%, found: C 90.52%; H 5.80%; N 1.04%. IR (ATR): 2953, 2901, 2864, 2844, 2778, 1593, 1462, 1363, 1332, 1294, 1246, 1160, 1056, 1029, 898, 853, 831 cm$^{-1}$.

**8** (31.2%)**:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.90-7.50 (*br*, 2H), 7.10-6.86 (*m*, 2H), 5.08-4.93 (*d*, 1H, *J* = 9.6 Hz), 4.88 (*s*, 1H), 4.34-4.18 (*d*, 1H, *J* = 9.2 Hz), 4.00-3.70 (*m*, 2H), 2.90-2.70 (*m*, 3H), 2.00-1.74 (*m*, 1H), 1.74-0.70 (*m*, 34H). MALDI-TOF-MS calcd [M]+: 1121.37, found: 1121.21. Elemental analysis calcd: C 93.11%; H 4.22%; N 1.25%, found: C 93.06%; H 4.24%; N 1.29%. IR (ATR): 2950, 2901, 2863, 2778, 1610, 1510, 1465, 1427, 1363, 1332, 1301, 1247, 1172, 1125, 1108, 1032, 831 cm$^{-1}$.

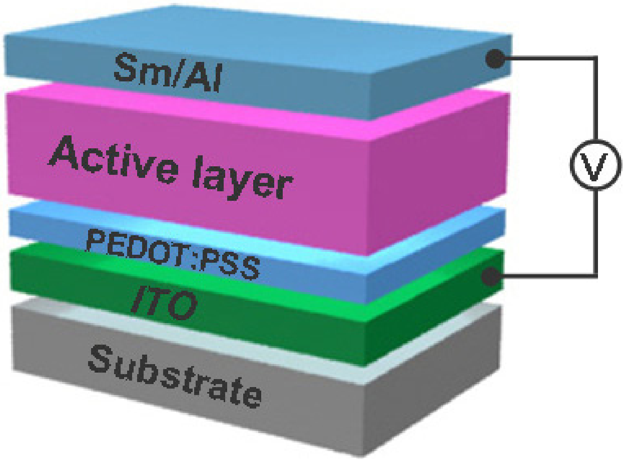
**9:** $^1$H NMR (400 MHz, $CDCl_3$), $\delta$ 6.09 (*s*, 2H), 5.60 (*s*, 1H), 4.82-4.84 (*d*, 1H, *J* = 7.6 Hz), 4.01-4.03 (*d*, 1H, *J* = 7.6 Hz), 3.62-3.91 (*m*, 6H), 2.66 (*s*, 3H), 1.89 (*s*, 3H), 1.16-1.52 (*m*, 60H), 1.00-1.14 (*m*, 6H), 0.79-0.89 (*m*, 36H, $CH_3$). MALDI-TOF-MS calcd [M-H]$^+$: 1657.92, found: 1657.92. UV-vis in *n*-hexane; $\lambda_{max}$ [nm], ($\varepsilon$ [L·cm$^{-1}$·mol$^{-1}$]): 211 (148854); 244 (88718); 255 (shoulder, 94796); 315 (33165); 430 (4019). IR (ATR): 2955, 2923, 2869, 2855, 2766, 1604, 1462, 1377, 1329, 1217, 1165, 1113, 810 cm$^{-1}$.

## (d) Additional data

i) Schemes



**Scheme S1.** Synthetic route for a typical alkylated $C_{60}$ derivative **1** bearing swallow-tail typed, branched aliphatic chains. Reagents and conditions: i) $CBr_4$, $PPh_3$, THF, r.t., 0.5 h. ii) $K_2CO_3$, KI, DMF, 130 °C, 16 h. iii) sarcosine, $C_{60}$, monochlorobenzene, 140 °C, overnight.



**Scheme S2.** Illustration of the bulk heterojuction solar cell construction in this study.

ii) Figures

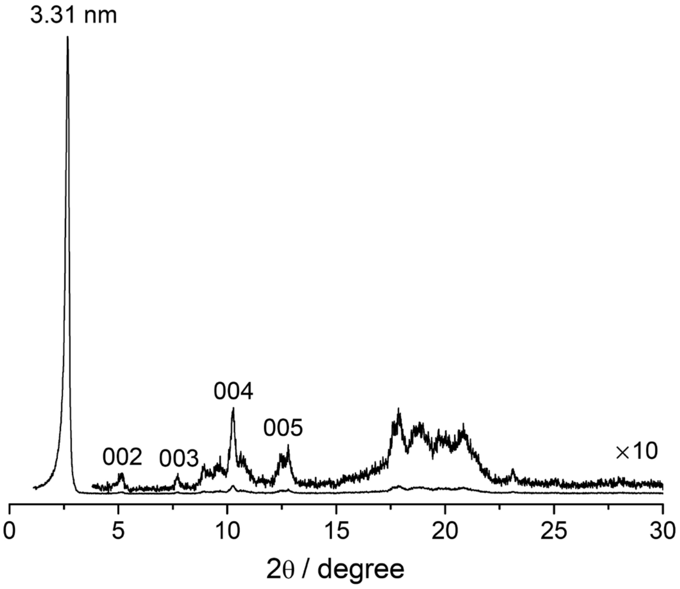


**Figure S1.** XRD of **2** at 140 °C cooling from the isotropic phase at a speed of 0.1 °C/min.

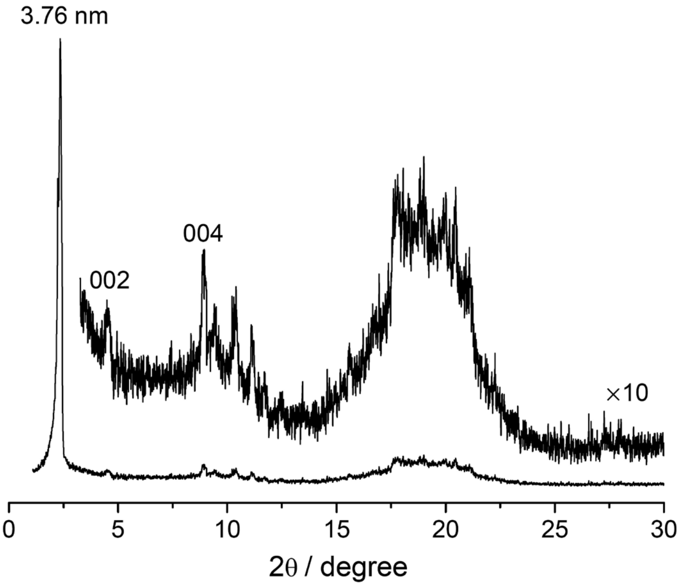


**Figure S2.** XRD of **4** at 190 °C cooling from the isotropic phase at a speed of 0.1 °C/min.

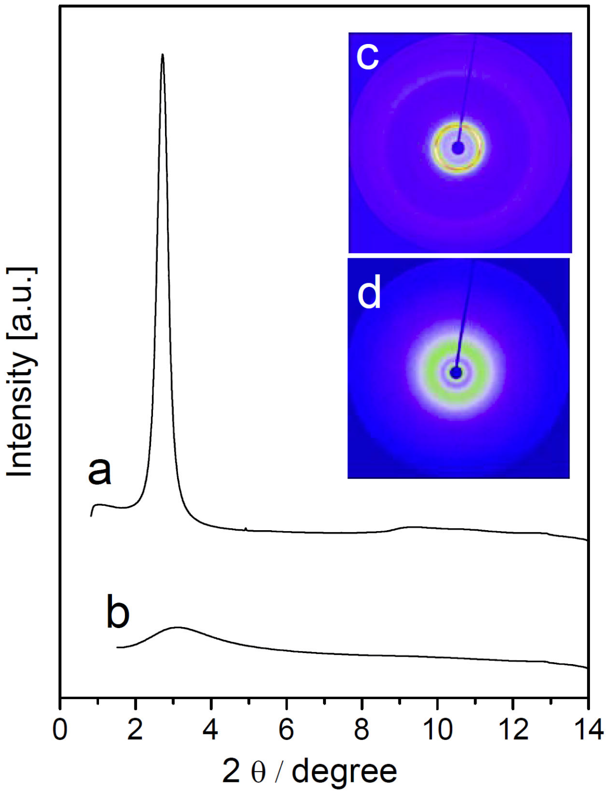


**Figure S3.** XRD scattering peaks (a, b) and corresponding two-dimensional diffraction pattern (c, d) of **6** (a, c) and **7** (b, d) at room temperature.

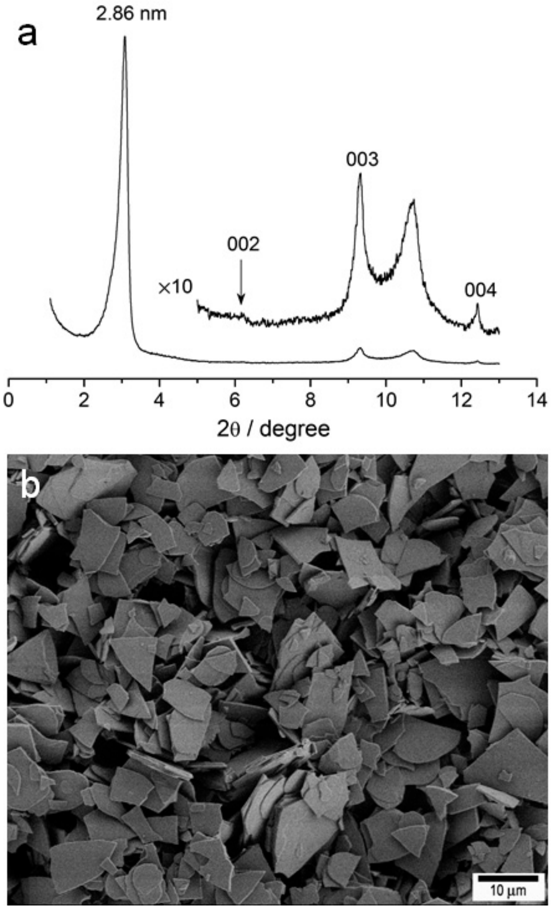


**Figure S4.** XRD result (a) and typical SEM image (b) of **8** precipitated from $CH_3OH/CH_2Cl_2$.

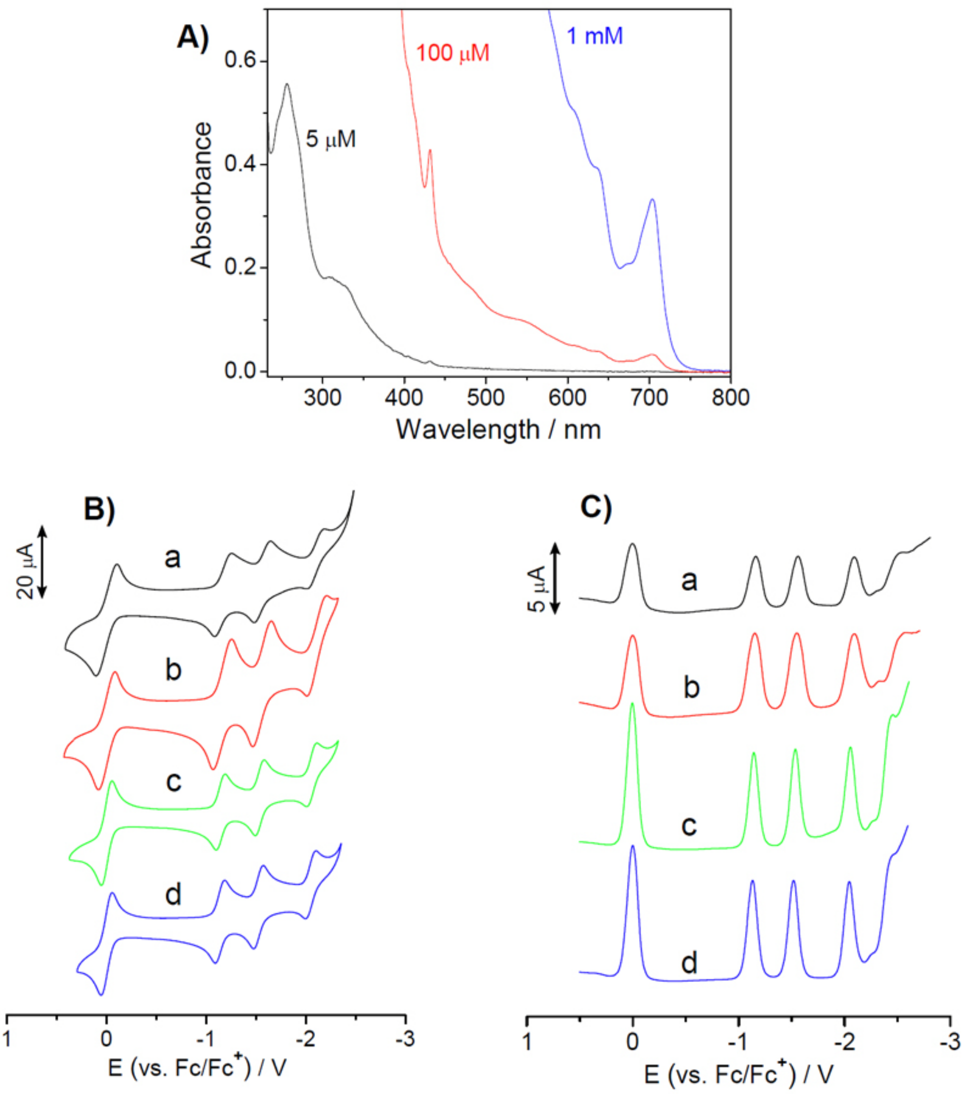


**Figure S5.** A) UV-vis absorption spectra of **1** recorded in $CH_2Cl_2$. Different concentrations were used to highlight the peaks with varying molar absorption coefficients. B) Cyclic and C) differential pulse voltammetries of selected derivatives (**1**, **3**, **6** and **8**) in $CH_2Cl_2$ at room temperature. The solution contains 0.5 mM ferrocene as internal reference and 0.1 M $TBABF_4$ as supporting electrolyte. Curves a-d correspond to the molecule **1**, **3**, **6** and **8**, respectively. The concentration of **3** is 1 mM while others are fixed at 0.5 mM. The scan rate in CV (B) is 0.1 V/s. DPV (C) was carried out with a scan rate of 25 mV/s and a pulse amplitude of 50 mV.

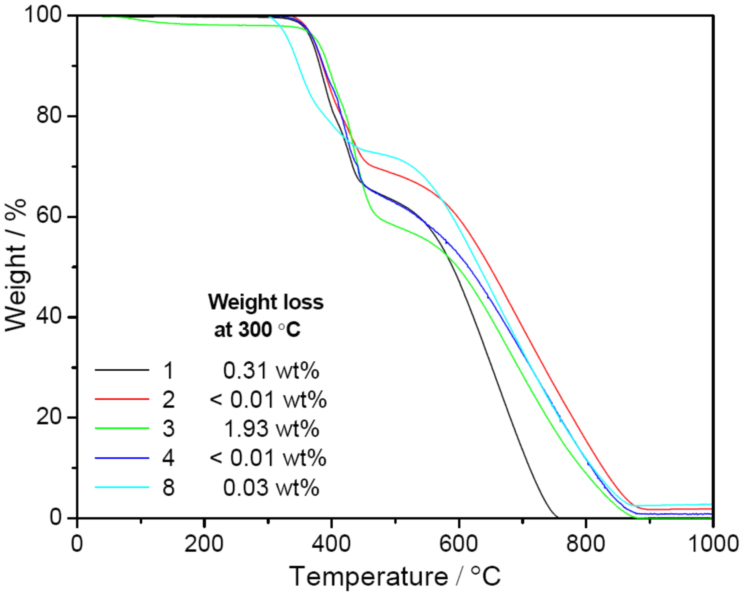


**Figure S6.** Typical results of thermogravimetric analysis (TGA) on selected alkylated $C_{60}$ derivatives bearing branched alkyl chains.

iii) Tables

**Table S1.** Molar absorption coefficients ($L\cdot cm^{-1}\cdot mol^{-1}$) of the main peaks of selected alkylated $C_{60}$ derivatives.

| **Compound** | **256.5 ± 0.5 nm (sharp)** | **300-320 nm (broad)**[a] | **432.5 ± 0.5 nm (sharp)** | **703.5 ± 0.5 nm (sharp)** | $\varepsilon_{256.5}/\varepsilon_{432.5}$[b] |
|---|---|---|---|---|---|
| **1** | 111528 | 35462 | 4302.6 | 333.6 | 25.9 |
| **2** | 117420 | 37722 | 4481.9 | 337.4 | 26.2 |
| **3** | 115322 | 37292 | 4311.1 | 327.9 | 26.8 |
| **4** | 111840 | 36226 | 4147.9 | 338.9 | 27.0 |
| **5** | 137714 | 46656 | 3933.5 | 349.7 | 35.0 |
| **6** | 139288 | 44280 | 4907.1 | 362.4 | 28.4 |
| **7** | 121526 | 38548 | 4935.2 | 378.0 | 24.6 |
| **8** | 157352 | 49976 | 5278.5 | 464.8 | 29.8 |

[a] Molar absorption coefficients were calculated according to the absorptions at 317 ± 0.5 nm.

[b] Subtle variations in $\varepsilon_{256.5}/\varepsilon_{432.5}$ between different molecules could be caused by the intramolecular interaction between the $C_{60}$ moiety and the substituted phenyl group.

**Table S2.** Redox potentials of the selected alkylated $C_{60}$ derivatives. Data for the first, second and third redox potentials (denoted as I, II and III, respectively) are $E_{1/2}$ values obtained from CV while those for the fourth redox potential (denoted as IV) are peak positions derived from DPV ($E$p).

| Compound | Potential vs. $Fc/Fc^+$ (V) | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| **1** | -1.172 | -1.565 | -2.100 | -2.568 (sharp) |
| **2** | -1.165 | -1.551 | -2.075 | -2.472 (shoulder) |
| **3** | -1.164 | -1.560 | -2.111 | -2.618 (shoulder) |
| **4** | -1.137 | -1.524 | -2.045 | -2.518 (sharp) |
| **5** | -1.168 | -1.574 | -2.123 | -2.670 (shoulder) |
| **6** | -1.147 | -1.537 | -2.060 | -2.457 (sharp) |
| **7** | -1.146 | -1.541 | -2.062 | -2.457 (shoulder) |
| **8** | -1.137 | -1.523 | -2.050 | -2.449 (shoulder) |

## Reference

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