Supplementary Material (ESI) for Chemical Communications

Functionalization of Hexakis Methanofullerene Malonate Crown-Ethers: Promising Octahedral Building Blocks for Molecular Networks

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Supplementary Information

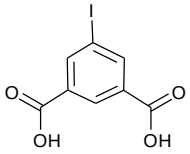
Experimental section

General

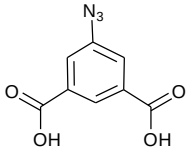
^{1}H and ^{13}C NMR spectra were recorded on a *Bruker*-AC-250, *Bruker* AM400 (400 MHz/100 MHz) or *Bruker* DRX500 (500 MHz/125 MHz) instrument using $CDCl_3$ or DMSO-d_6 as solvents. For assigning signal separation of ^{1}H NMR-spectra the following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet, hept = heptuplet, br = broad singlet. The coupling constant *J* was assigned in Hertz [Hz].

MS (EI) (electron impact mass spectrometry) and EI-HRMS: Finnigan MAT 90 (70 eV). The molecular fragments are quoted as the relation between mass and charge (m/z), the intensities as a percentage value relative to the intensity of the base signal (100%). The molecular ion obtains the abbreviation $[M]^{+}$. FAB spectra were recorded on a MAT 90 apparatus. MALDI TOF mass spectra were acquired on BRUKER BIFLEX IV using dihydroxylbenzoic acid as matrix with 50% acetonitrile and 0.1% TFA in H_2O. IR (infrared spectroscopy): FT-IR Bruker IFS 88. IR spectra of solids were recorded in KBr, and of oils as thin films on KBr. The deposit of the absorption band is given in wave numbers in cm^{-1}. The forms and intensities of the bands were characterized as follows: *m* = medium 40–70% T, *w* = weak 70–90% T, *vw* = very weak 90–100% T. Solvents and chemicals used for reactions were purchased from commercial suppliers. Solvents were dried under standard conditions; chemicals were used without further purification. All the reactions were performed in standard glassware. It is important to notice that absolute CH_2Cl_2 and *o*-dichlorobenzene over molecular sieves were used for the macrocyclization and Bingel steps respectively. All reactions were carried out under Ar in flame-dried glassware. Evaporation of solvents and concentration of reaction mixtures were performed *in vacuo* at 40 °C on a Heidolph rotary evaporator. Column chromatography was performed using *Macherey-Nagel* silica gel 60 (230–400 mesh) under flash conditions. For thin layer chromatography, aluminum foils layered with silica gel with fluorescence indicator (silica gel 60 F_{254}) produced by *Merck* were employed. The detection was carried out with an UV-lamp from Heraeus, model Fluotest. Seebach-reagent [Molybdo phosphoric acid (2.5 w%), Cer(IV)sulfate tetrahydrate (1.0 w%), H_2SO_4 conc. (6 w%), water (90.5 w%)] or $KMnO_4$ (0.5% in water) were used as dipping reagents. Elemental analyses were performed using an Elementar vario EL cube. Specific rotations $[\alpha]_D^{20}$ were determined using the *Perkin-Elmer* device Polarimeter 241.

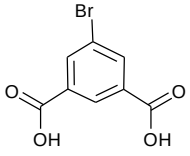
The reagents used for small scale reaction were used as an aliquot in the solvent used as the reaction media.



A solution of 5-aminoisophthalic acid (5.00 g, 27.6 mmol) in water (45 mL) / conc. HCl (10 mL) was cooled below 5 °C with an ice/NaCl bath. Upon slow addition of a $NaNO_2$ solution (1.79 g, 25.9 mmol) in water (20 mL) a pale yellow precipitate formed. After complete addition, the reaction mixture was stirred at 0–5 °C for additional 30 min. Then, an ice cold solution of I_2 (355 mg, 1.40 mmol) and KI (4.29 g, 25.8 mmol) in water (25 mL) was added dropwise to the previous solution while maintaining the temperature below 5 °C. The reaction mixture was stirred at room temperature for 90 min and was then refluxed for 1 h. Excess iodine was removed by adding an aqueous solution of $NaHSO_3$. Then, the reaction mixture was cooled down, filtered, washed with water and finally the expected compound was obtained by solving in acetone. The organic solution was concentrated and dried over night *in vacuo* at 50 °C. The expected 5-iodoisophthalic acid was isolated in 74% yield (5.54 g, 19.0 mmol) as a pale yellow solid. – ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.41 (s, 3H), 13.55 (br, 2H) ppm. – ^{13}C NMR (100 MHz, DMSO-d_6): δ = 94.7, 129.1, 133.1, 141.4, 165.2 ppm. – IR (capillary): ν = 3081 (m), 2650 (m), 2533 (m), 1850 (w), 1703 (m), 1598 (m), 1566 (m), 1439 (m), 1396 (m), 1271 (m), 1161 (w), 1115 (w), 997 (w), 941 (w), 903 (m), 806 (w), 751 (m), 699 (m) cm^{-1}. – MS (70 eV, EI), m/z (%): 293 ([M + 1]$^+$, 8), 292 ([M]$^+$, 100), 274 (13), 165 (6), 58 (12.5), 55 (5), 43 (42). – HRMS ($C_8H_5IO_4$): calc. 291.9227; found. 291.9229.

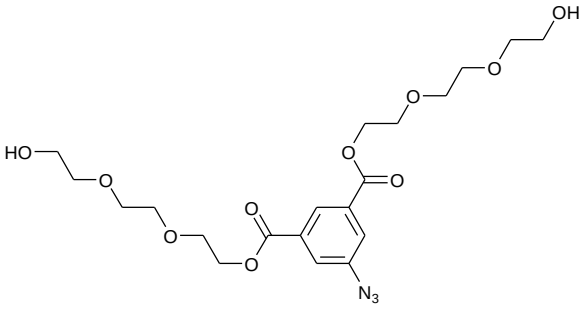


A solution of 5-aminoisophthalic acid (2.00 g, 11.0 mmol) in water (20 mL) / conc. HCl (4 mL) was cooled below 5 °C with an ice/NaCl bath. Upon addition of a solution of $NaNO_2$ (760 mg, 11.0 mmol) in water (10 mL) a pale yellow precipitate formed. After complete addition, the reaction mixture was stirred at 0–5 °C for additional 30 min. Then, an ice cold solution of NaN_3 (740 mg, 11.0 mmol) in water (5 mL) was added dropwise to the previous solution by maintaining the temperature below 5 °C. The reaction mixture was stirred at room temperature for 14 h, filtered, washed with water and dried *in vacuo* at 50 °C. The expected 5-azidoisophthalic acid was obtained in 85% yield (1.94 g, 9.37 mmol) as a white solid. – ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.73 (d, J = 1.2 Hz, 2H), 8.22 (t, J = 1.2 Hz, 1H); 13.44 (br, 2H) ppm. – ^{13}C NMR (100 MHz, DMSO-d_6): δ = 123.4, 126.1, 132.9, 140.5, 165.8 ppm. – IR (capillary): ν = 3554 (m), 3462 (w), 3099 (m), 2666 (w), 2121 (m), 1811 (vw), 1720 (m), 1682 (m), 1601 (m), 1465 (w), 1405 (w), 1289 (m), 1258 (w), 1220 (m), 1174 (w), 1118 (vw), 899 (w), 755 (w) cm^{-1}.– MS (70 eV, EI), m/z (%): 207 ([M]$^+$, 36), 179 (100), 123 (42), 89 (19), 77 (15), 63 (32), 45 (31). – HRMS ($C_8H_5N_3O_4$): calc. 207.0274; found 207.0280.

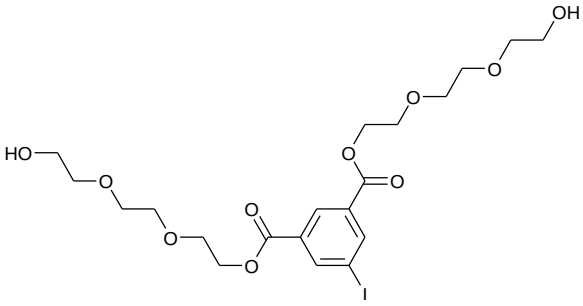


To a solution of isophthalic acid (10.0 g, 60.2 mmol) in conc. H_2SO_4 (30 mL) at 60 °C was added in 3 portions NBS (12.8 g, 71.9 mmol) over 45 min. After additional 90 min stirring, the mixture was poured into crushed ice (100 g). The precipitated solid was filtered, washed with water (60 mL) and dried over night *in vacuo*. Then, the crude solid was recrystallized from EtOAc, filtered and dried. The expected 5-bromoisophthalic acid was obtained in 96% yield (14.0 g, 57.0 mmol) as a white solid. – ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.22 (d, J = 1.5 Hz, 2H); 8.40 (t, J = 1.5 Hz, 1H), 9.94 (br, 2H) ppm. – ^{13}C NMR (100 MHz, DMSO-d_6): δ = 122.3, 129.2, 133.8, 136.1, 165.7 ppm. – IR (capillary): ν = 2998 (m), 2888 (m), 2641 (w), 2539 (w), 1701 (m), 1603 (w), 1571 (w), 1448 (w), 1400 (w), 1277 (m), 1245 (w), 1070 (w), 909 (m), 852 (w) cm^{-1}. – MS (70 eV, EI), m/z (%): 246 ([M]$^+$, 95), 244 ([M]$^+$, 100), 229 (53), 227 (55), 199 (14), 143 (11), 75 (13), 43 (23). – HRMS ($C_8H_5BrO_4$): calc. 243.9365; found 243.9368.

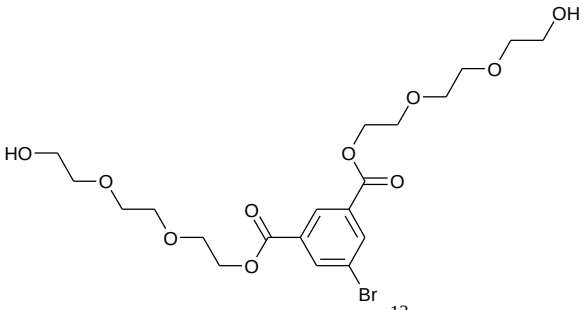
General procedure for the introduction of the triethyleneglycol chain. Cs_2CO_3 (1.00 eq.) and the 5-substituted-isophthalic acid (1.00 eq.) were dissolved in the minimum amount of water. The reaction mixture was stirred at room temperature until no more gas evolution was observed. Then, the reaction mixture was concentrated *in vacuo*, affording the dicesium salt as a white solid. 2-[2-(2-Methoxy)ethoxy]ethyl-*p*-toluenesulfonate (2.00 eq.) and dry DMF were added to the salt, and the mixture was stirred at 60 °C for 1–3 days. Volatiles were removed *in vacuo*, and the crude product was dissolved in CH_2Cl_2, leading to the precipitation of a white solid which was removed by filtration and washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure. The expected compounds were obtained as pure materials after purification on silica flash column chromatography as outlined.



This compound was prepared from 5-azidoisophthalic acid (1.91 g, 9.22 mmol), Cs_2CO_3 (3.00 g, 9.22 mmol), 2-[2-(2-methoxy)ethoxy]ethyl-*p*-toluenesulfonate (5.61 g, 18.4 mmol) in dry DMF (50 mL). Column chromatography (EtOAc/EtOH, 90/10 to 80/20) yielded the expected bis{2-[2-(2-hydroxyethoxy)ethoxy]ethyl} 5-azidoisophthalate in 90% yield (3.90 g, 8.27 mmol) as yellow oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.62 (t, *J* = 6 Hz, 2H), 3.61–3.63 (m, 4H), 3.68–3.74 (m, 12H), 3.85–3.87 (m, 4H); 4.52–4.55 (m, 4H), 7.90 (d, *J* = 1.5 Hz, 2H), 8.48 (t, *J* = 1.5 Hz, 1H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.7, 64.6, 69.0, 70.3, 70.7, 72.5, 124.2, 127.0, 132.2, 141.2, 164.9 ppm. – IR : ν = 3432 (w), 2873 (w), 2119 (m), 1726 (m), 1595 (w), 1453 (w), 1325 (m), 1239 (m), 1121 (m), 1068 (w), 939 (w), 890 (w), 754 (w), 722 (w) cm^{-1}. – MS (FAB, NBA), m/z: 472 $[M + H]^+$, 494 $[M + Na]^+$. – $C_{20}H_{29}N_3O_{10}$: calc. C 50.95, H 6.20, N 8.91; found C 50.61, H 6.31, N 8.58. – HRMS $[M + H]^+$ ($C_{20}H_{30}N_3O_{10}$): calc. 472.1925; found 472.1931.



This compound was prepared from 5-iodoisophthalic acid (5.23 g, 17.9 mmol), Cs_2CO_3 (5.84 g, 17.9 mmol), 2-[2-(2-methoxy)ethoxy]ethyl-*p*-toluenesulfonate (10.9 g, 35.8 mmol) in dry DMF (150 mL). Column chromatography (EtOAc/EtOH, 90/10 to 80/20). The expected bis{2-[2-(2-hydroxyethoxy)ethoxy]ethyl} 5-iodoisophthalate was obtained in 95% yield (9.43 g, 16.9 mmol) as yellow oil. - ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.81 (t, *J* = 6.0 Hz, 2H), 3.58–3.60 (m, 4H), 3.67–3.70 (m, 12H), 3.81–3.84 (m, 4H), 4.48–4.51 (m, 4H), 8.54 (d, *J* = 1.5 Hz, 2H), 8.63 (t, *J* = 1.5 Hz, 1H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.7, 64.6, 68.9, 70.3, 70.7, 72.5, 93.4, 130.0, 132.0, 142.6, 164.3 ppm. – IR (capillary): ν = 3428 (m), 3072 (vw), 2872 (m), 1726 (m), 1598 (w), 1568 (w), 1437 (m), 1352 (m), 1297 (m), 1240 (m), 1123 (m), 1069 (m), 936 (w), 750 (w) cm^{-1}. – MS (FAB, NBA), m/z: 557 $[M + H]^+$, 579 $[M + Na]^+$. – $C_{20}H_{29}IO_{10}$: calc. C 43.18, H 5.25; found C 43.07, H 5.38. – HRMS $[M + H]^+$ ($C_{20}H_{30}IO_{10}$): calc. 557.0878; found 557.0883.



This compound was prepared from 5-bromoisophthalic acid (3.00 g, 12.3 mmol), Cs_2CO_3 (4.02 g, 12.3 mmol), 2-[2-(2-methoxy)ethoxy]ethyl-*p*-toluenesulfonate (7.51 g, 24.7 mmol) in dry DMF (120 mL). Column chromatography (EtOAc/EtOH, 90/10). The expected bis{2-[2-(2-hydroxyethoxy)ethoxy]ethyl} 5-bromoisophthalate was obtained in 65% yield (4.07 g, 8.02 mmol) as yellow oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (br, 2H), 3.62–3.64 (m, 4H), 3.69–3.75 (m, 12H), 3.85–3.88 (m, 4H), 4.53–4.55 (m, 4H), 8.39 (d, *J* = 1.5 Hz, 2H), 8.65 (t, *J* = 1.5 Hz, 1H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.7, 64.6, 69.1, 70.4, 70.7, 72.6, 122.6, 129.4, 132.2, 136.8, 164.5 ppm. – $C_{20}H_{29}BrO_{10}$: calc. C 47.16, H 5.74; found C 47.04, H 5.68. – HRMS $[M + H]^+$ ($C_{20}H_{30}BrO_{10}$): calc. 509.1016; found 509.1022.

General procedure for the macrocyclization step. A suspension of $NaHCO_3$ (2.00 eq.) in dry CH_2Cl_2 was prepared in a flame-dried flask and was stirred under argon. To this solution, the appropriate diester (1.00 eq.) in dry CH_2Cl_2 and malonyl dichloride (1.13 eq.) in dry CH_2Cl_2 were slowly added through two separate dropping funnels over a period of 3 h. The reaction mixture was then stirred at room temperature for additional 12 h. The mixture was washed with water (3 × 200 mL), the organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The expected compounds were obtained as pure materials after purification on silica flash column chromatography as outlined.

Compound 1a was prepared according to a literature known procedure.[1]

Compound 1b. This compound was prepared from bis{2-[2-(2-hydroxyethoxy)ethoxy]ethyl} 5-azidoisophthalate (3.90 g, 8.27 mmol) in dry CH_2Cl_2 (270 mL), $NaHCO_3$ (1.39 g, 16.5 mmol) in dry CH_2Cl_2 (530 mL), malonyl

dichloride (1.32 g, 9.35 mmol) in dry CH_2Cl_2 (270 mL). After column chromatography (EtOAc), compound **1b** was obtained in 57% yield (2.52 g, 4.68 mmol) as a white solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.36 (s, 2H), 3.69–3.73 (m, 12H), 3.85–3.88 (m, 4H), 4.25–4.28 (m, 4H), 4.53–4.55 (m, 4H), 7.91 (d, *J* = 1.5 Hz, 2H), 8.45 (t, *J* = 1.5 Hz, 1H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.3, 64.7, 64.9, 68.9, 69.1, 70.6, 70.9, 124.3, 126.7, 132.3, 141.4, 164.9, 166.3 ppm. – IR (capillary): ν = 2952 (m), 2872 (m), 2120 (m), 1728 (m), 1604 (w), 1454 (m), 1326 (m), 1238 (m), 1140 (m), 1040 (m), 953 (m), 868 (w), 755 (w) cm^{-1}. – MS (FAB, NBA), m/z: 540 $[M+1]^+$, 562 $[M+ Na]^+$. – HRMS $[M + H]^+$ ($C_{23}H_{30}N_3O_{12}$): calc. 540.1824; found 540.1829.

Compound 1c. This compound was prepared from bis{2-[2-(2-hydroxyethoxy)ethoxy]ethyl} 5-iodoisophthalate (2.23 g, 4.00 mmol) in dry CH_2Cl_2 (130 mL), $NaHCO_3$ (1.39 g, 16.5 mmol) in dry CH_2Cl_2 (260 mL), malonyl dichloride (1.32 g, 9.35 mmol) in dry CH_2Cl_2 (130 mL). After column chromatography (EtOAc), compound **1c** was obtained in 48% yield (1.20 g, 1.92 mmol) as a white solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.36 (s, 2H), 3.67–3.73 (m, 12H), 3.85–3.87 (m, 4H), 4.25–4.27 (m, 4H), 4.52–4.54 (m, 4H), 8.58 (d, *J* = 1.5 Hz, 2H), 8.64 (t, *J* = 1.5 Hz, 1H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.3, 64.6, 64.9, 68.9, 69.0, 70.6, 70.8, 93.5, 129.7, 132.1, 142.6, 164.2, 166.3 ppm. – IR (capillary): ν = 3072 (w), 2965 (w), 2894 (m), 1728 (m), 1476 (w), 1413 (w), 1342 (w), 1302 (m), 1253 (m), 1229 (m), 1148 (w), 1110 (m), 1064 (w), 1021 (m), 977 (w), 948 (w), 924 (w), 891 (w), 860 (w) cm^{-1}. – MS (FAB, NBA), m/z: 625 $[M + H]^+$, 647 $[M + Na]^+$. – $C_{23}H_{29}IO_{12}$: calc. C 44.24, H 4.68; found C 44.21, H 4.69. – HRMS $[M + H]^+$ ($C_{23}H_{30}IO_{12}$): calc. 625.0776; found 625.0781.

Compound 1d. This compound was prepared from bis{2-[2-(2-hydroxyethoxy)ethoxy]ethyl} 5-bromoisophthalate (2.26 g, 4.44 mmol) in dry CH_2Cl_2 (150 mL), $NaHCO_3$ (776 mg, 9.24 mmol) in dry CH_2Cl_2 (200 mL), malonyl dichloride (707 mg, 5.01 mmol) in dry CH_2Cl_2 (150 mL). After column chromatography (EtOAc), compound **1d** was obtained in 52% yield (1.34 g, 2.32 mmol) as a white solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.36 (s, 2H); 3.67–3.87 (m, 12H); 3.85–3.87 (m, 4H); 4.25–4.27 (m, 4H); 4.53–4.55 (m, 4H); 8.39 (d, *J* = 1.5 Hz, 2H); 8.61 (t, *J* = 1.5 Hz, 1H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 41.2, 64.6, 64.9, 68.9, 69.1, 70.6, 70.8, 122.7, 129.1, 132.3, 136.8, 164.4, 166.3 ppm. – IR (capillary): ν = 3076 (w), 2960 (w), 2895 (m), 1728 (m), 1579 (vw), 1476 (w), 1445 (m), 1414 (w), 1378 (m), 1355 (m), 1342 (w), 1307 (w), 1254 (m), 1230 (m), 1146 (w), 1110 (w), 1065 (w), 1049 (w), 1021 (w), 977 (w), 947 (w), 925 (w), 860 (w), 811 (m), 750 (m), 726 (w) cm^{-1}. – MS (FAB, NBA), m/z : 577.1 $[M]^+$, 579.1 $[M + 2]^+$. – $C_{23}H_{29}BrO_{12}$: calc. C 47.85, H 5.06; found C 47.72, H 4.98. – HRMS $[M + H]^+$ ($C_{23}H_{30}BrO_{12}$): calc. 577.0915; found 577.0919.

General procedure for the preparation of hexakis fullerene derivatives. CBr_4 (100 eq.), the appropriate malonate (10.0 eq.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 20.0 eq.) were successively added to a fullerene C_{60} solution (1.00 eq.) in dry *o*-dichlorobenzene (*o*–DCB). The resulting reaction mixture was stirred under argon for 72 h at room temperature. The crude reaction mixture was then directly purified by flash column chromatography as outlined.

Compound 2a. This compound was prepared from CBr_4 (1.34 g, 4.00 mmol), pyridine macrocycle **1a**[1] (200 mg, 400 μmol) in *o*–DCB (2 mL) and DBU (122 mg, 800 μmol) in *o*–DCB (2 mL) which were successively added to a fullerene C_{60} solution (28.8 mg, 40.0 μmol) in *o*–DCB (20 mL). After column chromatography (toluene/EtOH, 90/10 to 75/25), compound **2a** was obtained in 55% yield (82.0 mg, 22.1 μmol) as a glassy red solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.58–3.78 (m, 108H), 4.31–4.33 (m, 24H), 4.47–4.49 (m, 24H), 8.75 (s, 6H), 9.34 (br, 12H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.1, 64.9, 65.9, 68.7, 69.0, 69.1, 70.6, 70.8, 125.8, 137.4, 140.9, 145.8, 154.7, 163.4, 164.3 ppm. – IR: ν = 3062 (vw), 2924 (m), 2857 (m), 1727 (m), 1600 (w), 1577 (w), 1529 (vw), 1450 (m), 1311 (w), 1238 (m), 1105 (m), 1027 (w), 938 (m), 863 (m), 746 (w) cm^{-1}. – MALDI-TOF-MS: 3725 ($[M + Na]^+$, calc. for $C_{192}H_{162}N_6O_{72}Na$: 3725.90).

Compound 2b. This compound was prepared from CBr_4 (6.50 g, 19.6 mmol), **1b** (1.00 g, 1.85 mmol) in *o*–DCB (20 mL) and DBU (597 mg, 3.92 mmol) in *o*–DCB (20 mL) which were successively added to a fullerene C_{60} solution (141 mg, 196 μmol) in *o*–DCB (80 mL). After column chromatography (toluene/EtOAc/EtOH, 75/20/5 to 75/17/8), the expected compound **2b** was obtained in 23% yield (180 mg, 45.6 μmol) as a glassy orange solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67–3.87 (m, 96H), 4.01–4.22 (m, 24H), 4.52–4.55 (m, 24H), 7.91 (d, *J* = 1.5 Hz, 12H), 8.41 (t, *J* = 1.5 Hz, 6H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.1, 64.9, 65.9, 68.7, 68.9, 69.1, 70.5, 70.9, 124.4, 126.4, 132.3, 140.9, 141.4, 145.8, 163.5, 164.9 ppm. – IR: ν = 2952 (w), 2870 (w), 2118 (m), 1725

(m), 1603 (w), 1452 (w), 1325 (m), 1234 (m), 1140 (m), 1033 (w), 947 (w), 863 (w), 755 (w), 715 (w) cm^{-1}. – $C_{198}H_{162}N_{18}O_{72}$: calc. C 60.27, H 4.14, N 6.39; found C 60.10, H 4.35, N 5.91.

Compound 2c. This compound was prepared from CBr_4 (6.70 g, 20.2 mmol), **1c** (1.26 g, 2.02 mmol) in *o*–DCB (20 mL) and DBU (615 mg, 4.04 mmol) in *o*–DCB (20 mL) which were successively added to a fullerene C_{60} solution (145 mg, 202 μmol) in *o*–DCB (80 mL). After column chromatography (toluene/EtOAc/EtOH, 75/20/5 to 75/19/6), compound **2c** was obtained in 30% yield (270 mg, 60.6 μmol) as a glassy orange solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.66–3.86 (m, 96H), 4.39–4.40 (m, 24H), 4.51–4.54 (m, 24H), 8.58–8.60 (m, 18H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.1, 64.9, 65.9, 68.7, 68.9, 69.1, 70.5, 70.8, 93.6, 129.3, 132.1, 140.9, 142.8, 145.8, 163.4, 164.2 ppm. – IR: ν = 3076 (vw), 2951 (w), 2869 (w), 1725 (m), 1569 (vw), 1440 (w), 1365 (w), 1298 (w), 1234 (m), 1126 (w), 1033 (w), 942 (w), 908 (w), 865 (w), 751 (w), 713 (w) cm^{-1}. – MALDI-TOF-MS: 4452 ($[M]^+$, calc. for $C_{198}H_{162}I_6O_{72}$: 4452.32) – $C_{198}H_{162}I_6O_{72}$: calc. C 53.38, H 3.67; found. C 53.04, H 3.85.

Compound 2d. This compound was prepared from CBr_4 (6.29 g, 19.0 mmol), **1d** (1.16 g, 2.02 mmol) in *o*–DCB (20 mL) and DBU (614 mg, 4.04 mmol) in *o*–DCB (20 mL) which were successively added to a fullerene C_{60} solution (145 mg, 202 μmol) in *o*–DCB (80 mL). After column chromatography (toluene/EtOAc/EtOH 75/21/4 to 75/20/5), compound **2d** was obtained in 31% yield (260 mg, 62.3 μmol) as a glassy orange solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67–3.87 (m, 96H), 4.40–4.42 (m, 24H), 4.53–4.55 (m, 24H), 8.40 (d, *J* = 1.5 Hz, 12H), 8.58 (t, *J* = 1.5 Hz, 6H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.1, 65.0, 65.9, 68.7, 68.9, 69.0, 69.1, 70.5, 70.8, 125.8, 137.4, 140.9, 145.8, 154.7, 163.5, 164.3 ppm. – IR: ν = 3073 (vw), 2870 (w), 1726 (m), 1576 (vw), 1440 (vw), 1354 (vw), 1300 (w), 1234 (w), 1123 (w), 1030 (vw), 937 (vw), 866 (vw), 752 (w), 728 (w) cm^{-1}. – MALDI-TOF-MS: 4187 $[M + Na]^+$, calc. for $C_{198}H_{162}Br_6O_{72}Na$: 4187.40).

General procedure for the Click reactions. Azide **2b** (40.0 mg, 10.0 μmol) and the terminal alkyne (7.00 eq., 70.0 μmol) were dissolved in CH_2Cl_2 (500 μL). To this solution were added $CuSO_4 \cdot 5H_2O$ (250 μg, 0.10 eq., 1.00 μmol) and sodium ascorbate (60.0 μg, 0.30 eq., 3.00 μmol) and water (500 μL). The resulting biphasic reaction mixture was vigorously stirred under argon until TLC analysis (toluene/EtOAc/EtOH 75/19/6) indicated no more starting material (generally after 12 h). The crude mixture was diluted with CH_2Cl_2 (50 mL) and extracted with water (2 × 50 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was then purified by silica flash column chromatography as outlined.

Compound 3a. This compound was prepared from **2b** (40.0 mg, 10.0 μmol) and phenylacetylene (7.15 mg, 70.0 μmol). After column chromatography (toluene/EtOAc/EtOH 75/15/10), compound **3a** was obtained in 78% yield (35.0 mg, 7.80 μmol) as a glassy orange solid. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.59–3.79 (m, 96H); 4.30–4.31 (m, 24H); 4.48–4.49 (m, 24H), 7.33–7.39 (m, 18H), 7.85 (d, *J* = 7.1 Hz, 12H), 8.31 (s, 6H), 8.60–8.64 (m, 18H) ppm. – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 45.1, 65.2, 66.0, 68.8, 69.0, 69.1, 70.6, 70.9, 117.6, 125.9, 128.2, 128.7, 129.1, 129.8, 129.9, 132.5, 137.6, 141.0, 145.8, 148.9, 163.5, 164.6 ppm. – IR: ν = 2868 (w), 1727 (m), 1604 (w), 1481 (w), 1458 (w), 1408 (w), 1353 (w), 1310 (w), 1240 (m), 1125 (m), 1049 (w), 908 (w), 862 (w) cm^{-1}.

Compound 3b. This compound was prepared from **2b** (40.0 mg,10.0 μmol) and 2-methyl-3-butyn-1-ol (6.00 mg, 70.0 μmol). After column chromatography (toluene/EtOH 60/40), the expected compound **3b** was obtained in 63% yield (28.0 mg, 6.30 μmol) as an orange solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.61 (s, 36H), 2.81 (br, 6H), 3.58–3.78 (m, 96H), 4.30–4.32 (m, 24H), 4.46–4.48 (m, 24H), 8.03 (s, 6H), 8.56–8.59 (m, 18H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.5, 45.1, 65.1, 66.0, 68.6, 68.8, 69.0, 69.1, 70.6, 70.9, 117.8, 125.4, 129.7, 132.4, 137.7, 141.0, 145.8, 157.0, 163.5, 164.6 ppm. – IR: ν = 3434(w), 3149 (w), 2923 (m), 1727 (m), 1605 (w), 1559 (vw), 1456 (m), 1366 (w), 1302 (m), 1238 (m), 1124 (m), 1051 (w), 909 (w), 855 (w), 757 (m) cm^{-1}. – MALDI-TOF-MS: 4471 $([M + Na + H]^{2+}$, calc. for $C_{228}H_{211}N_{18}O_{78}Na$: 4471.29).

Compound 3c. This compound was prepared from **2b** (40.0 mg, 10.0 μmol) and (*R*)-(+)-3-butyn-2-ol (5.00 mg, 70.0 μmol). After column chromatography (CH_2Cl_2/EtOH 88/12), the expected compound **3c** was obtained in 41% yield (18.0 mg, 4.10 μmol) as a red solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (m, 6H), 1.68 (d, *J* = 6.5 Hz, 18H), 3.68–3.87 (m, 96H), 4.39–4.57 (m, 48H), 5.20 (m, 6H), 8.17 (s, 6H), 8.65 (d, *J* = 1.5 Hz, 12H), 8.67 (t, *J* = 1.5 Hz, 6H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.1, 65.1, 66.1, 68.7, 68.9, 69.1, 70.5, 70.6, 77.2, 125.3, 129.7, 132.4, 137.6, 140.9, 143.8, 145.7, 163.4, 164.5 ppm. – IR: ν = 3429 (w), 3145 (vw), 3096 (vw), 2952 (w),

2872 (w), 2116 (vw), 1727 (m), 1605 (w), 1558 (vw), 1483 (w), 1456 (vw), 1354 (w), 1307 (w), 1238 (m) 1120 (w), 1045 (w) cm^{-1}. – MALDI-TOF-MS: 4386 ($[M + Na]^+$, calc. for $C_{222}H_{198}N_{18}O_{78}Na$: 4386.19). $[\alpha]_D^{20}$ = + 4.1° (8 mg / 2 mL, $CHCl_3$)

General procedure for the Heck cross-coupling reactions. A mixture of $NaHCO_3$ (15.0 eq.), NBu_4HSO_4 (6.00 eq.), and crushed 4Å molecular sieves was prepared in dry DMF in a flame-dried Schlenk flask under argon. The resulting mixture was stirred for 15 min. Then, fullerene derivative **2c** (1.00 eq.) together with the appropriate alkene (12.0 eq.) were added to this solution. The resulting reaction mixture was stirred for 15 min before $Pd(OAc)_2$ (30 mol%) was added. Then, the reaction mixture was heated at 80 °C for 10 h under argon. The reaction mixture was cooled down, diluted with CH_2Cl_2 (ca. 50 mL) and washed with water (2 x 50 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting products were purified by silica flash column chromatography as outlined.

Compound 4a. This compound was prepared from **2c** (30.0 mg, 6.70 μmol), *tert*-butyl acrylate (9.22 mg, 72.0 μmol), $Pd(OAc)_2$ (60.0 μg, 2.60 μmol), $NaHCO_3$ (7.60 mg, 90.0 μmol), NBu_4HSO_4 (12.2 mg, 36.0 μmol) and molecular sieves (14.4 mg) in dry DMF (2 mL). After column chromatography (toluene/EtOAc/EtOH, 75/20/5 to 75/19/6), compound **4a** was obtained in 94% yield (28.0 mg, 6.29 μmol) as a red solid.– ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.60 (s, 54H), 3.74–3.92 (m, 96H), 4.46–4.47 (m, 24H), 4.58–4.59 (m, 24H), 6.58 (d, *J* = 16.0 Hz, 6H), 7.67 (d, *J* = 16.0 Hz, 6H), 8.44 (d, *J* = 1.5 Hz, 12H), 8.67 (t, *J* = 1.5 Hz, 6H) ppm. – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 28.2, 45.1, 64.9, 65.9, 68.7, 69.0, 69.2, 70.5, 70.8, 81.0, 123.0, 131.0, 131,3, 133.2, 135.8, 140.9, 141.0, 145.8, 163.5, 165.2, 165.6 ppm. – IR: ν = 2869 (w), 1725 (m), 1641 (w), 1452 (w), 1367 (w), 1334 (w), 1235 (m), 1151 (m), 1036 (w), 980 (w), 865 (w), 755 (w), 716 (w), 667 (w) cm^{-1}. – MALDI-TOF-MS: 4455 ($[M + 2H]^{2+}$, calc. for $C_{240}H_{230}O_{84}$: 4455.37).

Compound 4b. This compound was prepared from **2c** (30.0 mg, 6.70 μmol), but-3-en-2-one (9.22 mg, 72.0 μmol), $Pd(OAc)_2$ (60.0 μg, 2.60 μmol), $NaHCO_3$ (7.60 mg, 90.0 μmol), NBu_4HSO_4 (12.2 mg, 36.0 μmol) and molecular sieves (14.4 mg) in dry DMF (2 mL). After column chromatography (toluene/EtOAc/EtOH, 75/20/5 to 75/15/10), the expected compound **4b** was obtained in 80% yield (22.0 mg, 5.30 μmol) as a red solid. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.38 (s, 18H), 3.68–3.88 (m, 96H), 4.41–4.43 (m, 24H), 4.55–4.56 (m, 24H), 6.89 (d, *J* = 16.3 Hz, 6H), 7.59 (d, *J* = 16.3 Hz, 6H), 8.49 (d, *J* = 1.5 Hz, 12H), 8.66 (t, *J* = 1.5 Hz, 6H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.0, 45.1, 65.0, 66.0, 68.8, 69.0, 69.2, 70.6, 70.9, 129.1, 131.4, 131.5, 133.4, 135.6, 140.6, 141.0, 145.8, 163.5, 165.2, 197.7 ppm. – IR: ν = 2870 (m), 1721 (m), 1672 (w), 1616 (w), 1440 (w), 1358 (w), 1330 (w), 1233 (m), 1123 (w), 1036 (w), 983 (w), 865 (w), 752 (m), 715 (w) cm^{-1}. – MALDI-TOF-MS: 4107 ($[M + 2H]^{2+}$, calc. for $C_{222}H_{194}O_{78}$: 4107.12).

General procedure for the Sonogashira cross-coupling reactions. The fullerene derivative **2c** (44.5 mg, 10.0 μmol), CuI (2.30 mg, 12.0 μmol) and $PdCl_2(PPh_3)_2$ (4.20 mg, 6.00 μmol) were put in a flame-dried Schlenk flask under an argon atmosphere, which was then evacuated three times (*vacuo*-argon). THF (1.50 mL) and dichloromethane (1.00 mL) were added to the previous mixture and the resulting mixture was stirred under argon. Then the terminal alkyne derivative (120 μmol) was added to the mixture in CH_2Cl_2 (500 μL). Et_3N (200 μL) was added *via* a syringe and the resulting reaction mixture was stirred at room temperature for 24 h under argon. The solution was diluted with CH_2Cl_2 (50 mL) and washed with water (2 × 50 mL), the organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by silica flash chromatography as outlined.

Compound 5a. This compound was prepared from **2c** (44.5 mg, 10.0 μmol) and 2-methyl-3-butyn-1-ol (10.1 mg, 120 μmol). After column chromatography (toluene/EtOH 4/1), the expected compound **5a** was obtained in 83% yield (35.0 mg, 8.30 μmol) as a red solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.64 (s, 36H), 3.66–3.86 (m, 96H), 4.40–4.54 (m, 48H), 8.29 (d, *J* = 1.5 Hz, 12H), 8.58 (t, *J* = 1.5 Hz, 6H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.1, 45.1, 64.9, 65.4, 65.9, 68.7, 68.9, 69.2, 70.5, 70.8, 80.1, 96.1, 124.0, 129.6, 130.8, 136.9, 140.9, 145.8, 163.4, 165.1 ppm. – IR: ν = 3430 (w), 2870 (w), 1726 (m), 1598 (w), 1440 (w), 1324 (w), 1234 (w), 1183 (w), 1122 (w), 1334 (m), 950 (w), 913 (w) cm^{-1}. – MALDI-TOF-MS: 4213 ($[M + H + Na]^{2+}$, calc. for $C_{228}H_{205}O_{78}Na$: 4213.19).

Compound 5b. This compound was prepared from **2c** (44.5 mg, 10.0 μmol) and 4-ethynylbenzonitrile (15.3 mg, 120 μmol). After column chromatography (toluene/EtOAc/EtOH, 75/19/6), compound **5b** was obtained in 78% yield (35.0 mg, 7.80 μmol) as a red solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.68–3.88 (m, 96H), 4.41–4.42 (m, 24H), 4.54–4.56 (m, 24H), 7.64 (d, *J* = 8.6 Hz, 12H), 7.69 (d, *J* = 8.6 Hz, 12H), 8.42 (d, *J* = 1.5 Hz, 12H), 8.64 (t, *J* = 1.5 Hz, 6H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.1, 64.9, 65.9, 68.7, 68.9, 69.2, 70.6, 70.8, 81.4, 89.5, 91.3, 112.1, 118.3, 123.5, 125.3, 129.6, 131.1, 132.1, 132.5, 137.1, 140.9, 145.8, 163.5, 164.8 ppm. – IR: ν = 3066 (w), 2951 (m), 2871 (m), 2227 (m), 1927 (vw), 1725 (m), 1603 (w), 1502 (w), 1440 (w), 1379 (w), 1338 (w), 1267 (w), 1234 (m), 1119 (m), 1032 (w), 957 (w), 915 (w) cm^{-1}. – MALDI-TOF-MS: 4471 ($[M + H + Na]^{2+}$, calc. for $C_{252}H_{187}N_6O_{72}Na$: 4471.10).

General procedure for the Suzuki cross-coupling reactions. The fullerene derivative **2c** (1.00 eq.) was dissolved in anhydrous DMF and the boronic acid derivative (12.0 eq.), $PdCl_2(PPh_3)_2$ (36 mol%) and Na_2CO_3 (15.0 eq.) were added to this solution. The reaction mixture was stirred under argon at 110 °C for 10 h, during which time the reaction color turned gradually from red to brown. Then, the reaction mixture was cooled down and diluted with CH_2Cl_2 (50 mL). The organic layer was washed with water (2 × 50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The desired products were purified by silica flash column chromatography as outlined.

Compound 6a. This compound was prepared from **2c** (22.0 mg, 5.00 μmol), 4-methoxyphenylboronic acid (10.0 mg, 65.8 μmol), $PdCl_2(PPh_3)_2$ (1.26 mg, 1.80 μmol) and Na_2CO_3 (7.90 mg, 75.0 μmol) in dry DMF (2 mL). After column chromatography (toluene/EtOAc/EtOH, 75/17/8), the expected compound **6a** was obtained in 74% yield (16.0 mg, 3.70 μmol) as a red solid. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.70–3.88 (m, 114H), 4.44–4.45 (m, 24H), 4.55–4.57 (m, 24H), 7.02 (d, *J* = 8.8 Hz, 12H), 7.63 (d, *J* = 8.8 Hz, 12H), 8.48 (d, *J* = 1.5 Hz, 12H), 8.58 (t, *J* = 1.5 Hz, 6H) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 45.1, 55.4, 64.8, 65.9, 68.7, 69.0, 69.3, 70.6, 70.8, 114.5, 128.2, 128.3, 131.0, 131.3, 132.1, 141.0, 141.6, 145.8, 159.9, 163.5, 165.9 ppm. – IR: ν = 2868 (w), 1721 (m), 1609 (w), 1577 (w), 1517 (w), 1440 (w), 1332 (w), 1254 (m), 1182 (w), 1122 (w), 1071 (w), 1030 (w), 914 (w), 832(w), 757 (m) cm^{-1}. – MALDI-TOF-MS: 4336 ($[M + 3H]^{3+}$, calc. for $C_{240}H_{207}O_{78}$: 4336.22).

Compound 6b. This compound was prepared from **2c** (44.0 mg, 10.0 μmol), 4-(isopropoxycarbonyl)phenylboronic acid (25.0 mg, 120 μmol), $PdCl_2(PPh_3)_2$ (3.30 mg, 3.60 μmol) and Na_2CO_3 (16.0 mg, 150 μmol) in dry DMF (4 mL). After column chromatography (toluene/EtOAc/EtOH, 75/20/5 to 75/17/8), the expected compound **6b** was obtained in 47% yield (20.0 mg, 4.20 μmol) as a red solid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (d, *J* = 6.3 Hz, 36H), 3.61-3.81 (m, 96H), 4.35–4.37 (m, 24H), 4.47–4.49 (m, 24H), 5.22 (hept, *J* = 6.3 Hz, 6H), 7.65 (d, *J* = 8.3 Hz, 12H); 8.02 (d, *J* = 8.3 Hz, 12H); 8.45 (d, *J* = 1.5 Hz, 12H); 8.58 (t, *J* = 1.5 Hz, 6H) ppm. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.0, 45.1, 64.9, 65.9, 68.6, 68.7, 69.0, 69.2, 70.6, 70.8, 127.1, 129.5, 130.5, 130.7, 131.3, 132.1, 132.8, 141.0, 143.0, 145.9, 163.5, 165.6, 165.7 ppm. – IR: ν = 2870 (w), 1721 (m), 1609 (w), 1448 (w), 1332 (m), 1248 (m), 1103 (m), 1069 (w), 1041 (w), 918 (w), 858 (w), 752 (w) cm^{-1}. – MALDI-TOF-MS: 4694 ($[M + 3H + Na]^{4+}$, calc. for $C_{258}H_{230}O_{84}Na$: 4694.36).

Reference:

[1] Possamai, G. *et al.* Rhenium(I) and ruthenium(II) complexes with a crown-linked methanofullerene ligand: synthesis, electrochemistry and photophysical characterization. *Photochem. Photobiol. Sci.* **5**, 1154–1164 (2006).