

Supporting Information

Sequential copper catalyzed alkyne-azide and thiol-ene click reactions for the multiple functionalization of fullerene hexaadducts

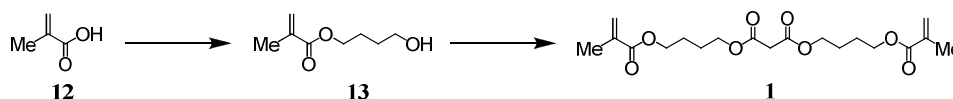
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Experimental section

General. Reagents and solvents were purchased as reagent grade and used without further purification. Compound **7**¹ was prepared according to a previously reported procedure. All reactions were performed in standard glassware under an inert Ar or N₂ atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10⁻² Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on glass sheets coated with silica gel 60 F₂₅₄ purchased from E. Merck, visualization by UV light. IR spectra (cm⁻¹) were measured on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AC 300 or AC 400 with solvent peaks as reference. MALDI-TOF-mass spectra were carried out on a Bruker BIFLEXTM matrix-assisted laser desorption time-of-flight mass spectrometer.

Preparation of compound **1**

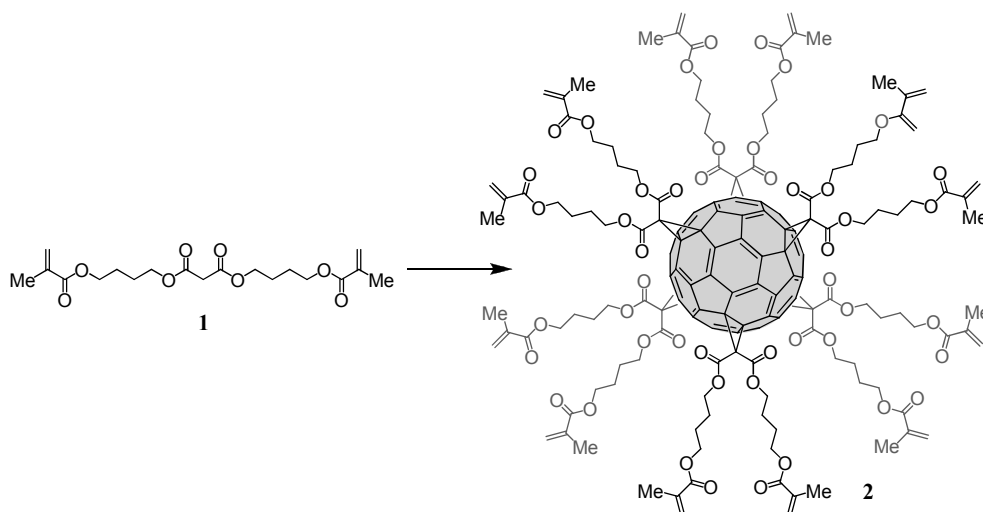


Compound 13. DCC (14.24 g, 69.69 mmol) was added to a solution of **12** (6 g, 69.69 mmol), 1,4-butanediol (9.32 mL, 104.54 mmol), HOBt (0.94 g, 6.97 mmol) and DMAP (1.70 g, 13.94 mmol) in CH₂Cl₂ (300 mL) at 0 °C under argon. The mixture was stirred for 48 h, filtered through a celite pad and concentrated. Column chromatography (SiO₂, CH₂Cl₂) yielded **13** (5.6 g, 51%) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz): 6.06 (dq, *J* = 4 and 1.5 Hz, 1H), 5.51 (dq, *J* = 4 and 1.5 Hz, 1H), 4.14 (t, *J* = 6 Hz, 2H), 3.63 (t, *J* = 6 Hz, 2H), 2.25 (s, 1H), 1.90 (m, 3H); ¹³C NMR (CDCl₃, 75 MHz): 167.5, 136.3, 125.3, 64.4, 62.1, 29.0, 25.0, 18.2.

¹ J. Iehl, R. Pereira de Freitas, B. Delavaux-Nicot and J.-F. Nierengarten, *Chem. Commun.* 2008, 2450.

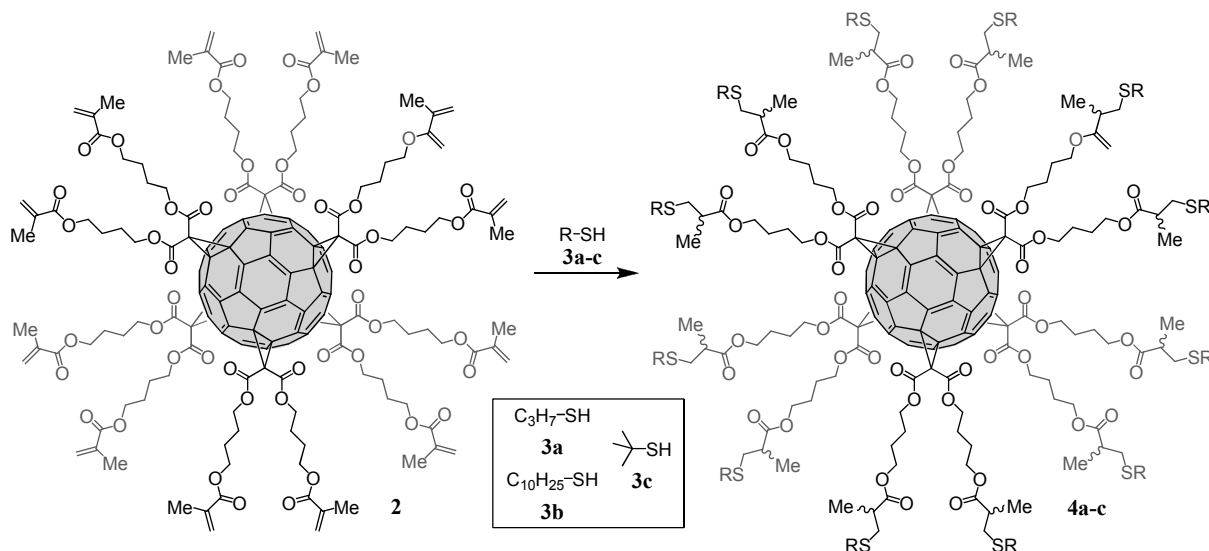
Compound 1. Malonyl dichloride (0.62 mL, 6.32 mmol) was added to a solution of **13** (2 g, 12.64 mmol) and pyridine (1.02 mL, 12.64 mmol) in CH₂Cl₂ (100 mL) at 0°C. After 1 h, the mixture was allowed to warm up to room temperature, then stirred for 18 h, filtered, and evaporated. Column chromatography (SiO₂, CH₂Cl₂/AcOEt 9:1) gave **1** (2.17 g, 89%) as a pale yellow oil. IR (neat): 1740 (C=O), 1714 (C=O), 1637 (C=C); ¹H NMR (CDCl₃, 300 MHz): 6.05 (m, 2H), 5.51 (m, 2H), 4.14 (m, 8H), 3.34 (s, 2H), 1.89 (m, 6H), 1.71 (m, 8H); ¹³C NMR (CDCl₃, 75 MHz): 167.2, 166.3, 136.2, 125.3, 64.9, 63.9, 41.3, 25.1(x2), 18.1.

Preparation of compound 2



Compound 2. CBr₄ (12.64 g, 38.13 mmol), **1** (1.46 g, 3.81 mmol), and DBU (1.14 mL, 7.63 mmol) were added successively to a solution of C₆₀ (0.27 g, 0.375 mmol) in ODCB (80 mL). The mixture was stirred for 72 h and evaporated. Column chromatography (SiO₂, CH₂Cl₂/AcOEt 8:2) gave **2** (0.47 g, 41%) as an orange glassy product. IR (neat): 1742 (C=O), 1713 (C=O), 1636 (C=C); UV/Vis (CH₂Cl₂): 245 (93500), 269 (68600), 283 (70000), 318 (sh, 42600), 338 (sh, 31100); ¹H NMR (CDCl₃, 300 MHz): 6.03 (m, 12H), 5.50 (m, 12H), 4.26 (t, *J* = 6 Hz, 24H), 4.10 (t, *J* = 6 Hz, 24H), 1.87 (m, 36H), 1.73 (m, 48H); ¹³C NMR (CDCl₃, 75 MHz): 167.0, 163.4, 145.6, 140.9, 136.1, 125.3, 68.9, 66.2, 63.6, 45.1, 25.1(x2), 18.1; MALDI-TOF-MS: 3015 (M⁺, calcd. for C₁₇₄H₁₅₆O₄₈: 3015.12).

Preparation of compounds 4a-c



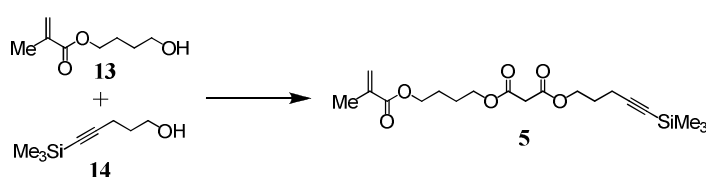
General procedure. AIBN (3 equiv.) was added to a mixture of **2** (1 equiv.) and the appropriate thiol (20 equiv.) in carefully degassed benzene. The resulting mixture was stirred for 1 h at 80°C. The mixture was then diluted with a small amount of CH_2Cl_2 and the product precipitated by addition of cyclohexane and filtered. The product was then purified as outlined in the following text.

Compound 4a. This compound was prepared from **2** (158 mg, 0.052 mmol), **3a** (80 mg, 1.04 mmol), AIBN (26 mg, 0.16 mmol) in benzene (5 mL). Column chromatography (SiO_2 , CH_2Cl_2 containing 0.5% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **4a** (104 mg, 51%) as a red glassy product. IR (neat): 1728 (C=O); UV/Vis (CH_2Cl_2): 245 (115200), 269 (80200), 282 (77400), 320 (sh, 44500), 338 (sh, 33900); ^1H NMR (CDCl_3 , 300 MHz): 4.30 (m, 24H), 4.12 (m, 24H), 2.81 (m, 12H), 2.67 (m, 12H), 2.57 (m, 12H), 2.49 (t, $J = 7$ Hz, 24H), 1.77 (m, 48H), 1.58 (q, $J = 7$ Hz, 24H), 1.25 (d, $J = 7$ Hz, 36H), 0.97 (t, $J = 7$ Hz, 36H); ^{13}C NMR (CDCl_3 , 75 MHz): 175.0, 174.3, 163.5 (several peaks), 145.9 (several peaks), 140.9 (several peaks), 69.3 (several peaks), 64.2 (several peaks), 63.6 (several peaks), 45.2 (several peaks), 40.2, 32.7, 31.8, 25.0 (several peaks), 22.8, 16.8, 13.3 (several peaks); MALDI-TOF-MS: 3929 (M^+ , calcd. for $\text{C}_{210}\text{H}_{252}\text{O}_{48}\text{S}_{12}$: 3929.0).

Compound 4b. This compound was prepared from **2** (133 mg, 0.04 mmol), **3b** (154 mg, 0.88 mmol), AIBN (22 mg, 0.13 mmol) in benzene (3 mL). Column chromatography (SiO₂, CH₂Cl₂ containing 1% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH₂Cl₂) gave **4b** (79 mg, 35%) as a red glassy product. IR (neat): 1728 (C=O); UV/Vis (CH₂Cl₂): 246 (116200), 269 (88100), 283 (84300), 325 (sh, 48500), 337 (sh, 39600); ¹H NMR (CDCl₃, 300 MHz): 4.29 (m, 24H), 4.12 (m, 24H), 2.77 (m, 12H), 2.68 (m, 12H), 2.56 (m, 12H), 2.49 (t, *J* = 7 Hz, 24H), 1.76 (m, 48H), 1.53 (m, 24H), 1.24 (m, 216H), 0.86 (t, *J* = 7 Hz, 36H); ¹³C NMR (CDCl₃, 75 MHz): 176.2 (several peaks), 175.0, 174.4, 163.6 (several peaks), 145.9 (several peaks), 140.9 (several peaks), 69.0 (several peaks), 64.3 (several peaks), 63.7 (several peaks), 45.2 (several peaks), 40.2, 32.7, 31.8, 29.8, 29.6, 29.5, 29.3, 29.25, 29.2, 28.8, 25.0 (several peaks), 16.9, 14.0; MALDI-TOF-MS: 5107 (M⁺, calcd. for C₂₉₄H₄₂₀O₄₈S₁₂: 5107.26).

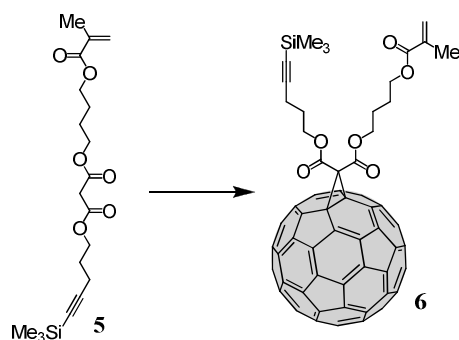
Compound 4c. This compound was prepared from **2** (200 mg, 0.06 mmol), **3c** (120 mg, 1.33 mmol), AIBN (33 mg, 0.2 mmol) in benzene (5 mL). Column chromatography (SiO₂, CH₂Cl₂ containing 1% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH₂Cl₂) gave **4c** (140 mg, 52%) as a red glassy product. IR (neat): 1726 (C=O); UV/Vis (CH₂Cl₂): 245 (91200), 269 (69300), 283 (65100), 322 (sh, 38700), 339 (sh, 29400); ¹H NMR (CDCl₃, 300 MHz): 4.28 (m, 24H), 4.11 (m, 24H), 2.79 (m, 12H), 2.59 (m, 24H), 1.75 (m, 48H), 1.28 (m, 108H), 1.24 (m, 36H); ¹³C NMR (CDCl₃, 75 MHz): ¹³C NMR (CDCl₃, 75 MHz): 176.3 (several peaks), 175.0, 163.4 (several peaks), 146.0 (several peaks), 140.8 (several peaks), 68.9 (several peaks), 66.4 (several peaks), 63.6 (several peaks), 45.2 (several peaks), 40.3, 31.6, 30.8, 30.7, 25.1 (several peaks), 17.1; MALDI-TOF-MS: 4097 (M⁺, calcd. for C₂₂₂H₂₇₆O₄₈S₁₂: 4097.32).

Preparation of compound 5.



Compound 5. Malonyl dichloride (0.92 mL, 9.48 mmol) was added to a solution of **13** (1.5 g, 9.48 mmol), **14** (1.48 g, 9.48 mmol) and pyridine (1.53 mL, 18.96 mmol) in CH₂Cl₂ (150 mL) at 0°C. After 1 h, the mixture was allowed to warm up to room temperature, then stirred for 16 h, filtered, and evaporated. Column chromatography (SiO₂, CH₂Cl₂/Hexane 9:1) gave **5** (1.35 g, 37%) as a colorless oil. IR (neat): 2175 (C≡C), 1742 (C=O), 1713 (C=O), 1636 (C=C); ¹H NMR (CDCl₃, 300 MHz): 6.07 (dq, *J* = 4 and 1.5 Hz, 1H), 5.53 (dq, *J* = 4 and 1.5 Hz, 1H), 4.21 (t, *J* = 6 Hz, 2H), 4.16 (m, 4H), 3.35 (s, 2H), 2.29 (t, *J* = 6 Hz, 2H), 1.91 (m, 3H), 1.83 (t, *J* = 6 Hz, 2H), 1.74 (m, 4H), 0.11 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz): 167.2, 166.4, 166.3, 136.3, 125.3, 105.3, 85.4, 64.9, 64.1, 63.9, 41.4, 27.5, 25.2, 25.1, 18.2, 16.4, 0.0.

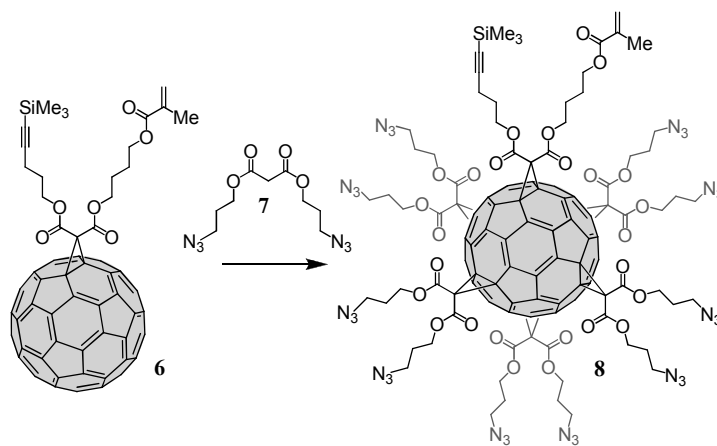
Preparation of compound 6.



Compound 6. DBU (1.27 mL, 8.49 mmol) was added to a stirred solution of C₆₀ (2.45 g, 3.39 mmol), I₂ (1.3 g, 5.09 mmol) and **5** (1.3 g, 3.39 mmol) in toluene (2.45 L) at room temperature. The resulting solution was stirred for 12 h, then filtered through a short plug of SiO₂ (CH₂Cl₂) and evaporated. Column chromatography (SiO₂, CH₂Cl₂/Hexane 6/4) gave **5** (1.87 g, 50%) as a dark red glassy product. IR (neat): 2174 (C≡C), 1742 (C=O), 1713 (C=O), 1636 (C=C); UV/Vis (CH₂Cl₂): 257 (123000), 227 (95400), 327 (36300), 360 (sh, 11000), 393 (3700), 414 (sh, 1700), 426 (1900); ¹H NMR (CDCl₃, 300 MHz): 6.12 (m, 1H), 5.57 (m, 1H), 4.59 (t, *J* = 6 Hz, 2H), 4.55 (t, *J* = 6 Hz, 2H), 4.23 (t, *J* = 6 Hz, 2H), 2.43 (t, *J* = 6 Hz, 2H), 2.05 (q, *J* = 6 Hz, 2H), 1.95 (m, 3H), 1.90 (m, 4H), 0.16 (s, 9H); ¹³C NMR (CDCl₃, 75

MHz): 167.3, 163.5(x2), 145.3, 145.2(x2), 145.1(x2), 144.9, 144.7, 144.6, 143.9, 143.1, 143.0(x2), 142.2, 141.9, 141.8, 141.0, 139.0(x2), 136.3, 125.6, 105.0, 86.0, 71.5, 66.8, 65.8, 63.9, 52.1, 27.6, 25.4, 25.3, 18.3, 16.6, 0.1; MALDI-TOF-MS: 1101 (M^+ , calcd. for $C_{79}H_{28}O_6Si$: 1101.17).

Preparation of compound 8.



Compound 8. CBr_4 (15.05 g, 45.4 mmol), **7** (1.22 g, 4.54 mmol), and DBU (1.36 mL, 9.08 mmol) were added successively to a solution of **6** (0.5 g, 0.45 mmol) in ODCB (90 mL). The mixture was stirred for 72 h and evaporated. Column chromatography (SiO_2 , CH_2Cl_2) gave **8** (0.62 g, 57%) as an orange glassy product. IR (neat): 2174 ($C\equiv C$), 2094 (N_3), 1742 ($C=O$), 1713 ($C=O$), 1636 ($C=C$); 1H NMR ($CDCl_3$, 300 MHz): 6.08 (m, 1H), 5.55 (m, 1H), 4.35 (m, 24H), 4.16 (t, $J = 6$ Hz, 2H), 3.38 (t, $J = 6$ Hz, 20H), 2.30 (t, $J = 6$ Hz, 2H), 1.95 (m, 27H), 1.81 (q, $J = 6$ Hz, 2H), 0.12 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): 166.7, 163.0 (several peaks), 161.5, 145.3 (several peaks), 140.6 (several peaks), 135.8, 125.0, 104.7, 85.2, 68.6, 66.1, 65.2, 63.7, 63.4 (several peaks), 62.6, 59.1, 47.9, 47.4 (several peaks), 47.1, 44.8, 31.1, 30.4, 27.5 (several peaks), 24.8, 24.7, 17.8, 16.0, -0.4.

