Micelle vs vesicle formation controlled by distal functionalization of C_{60}-PEG conjugates

–supporting information–

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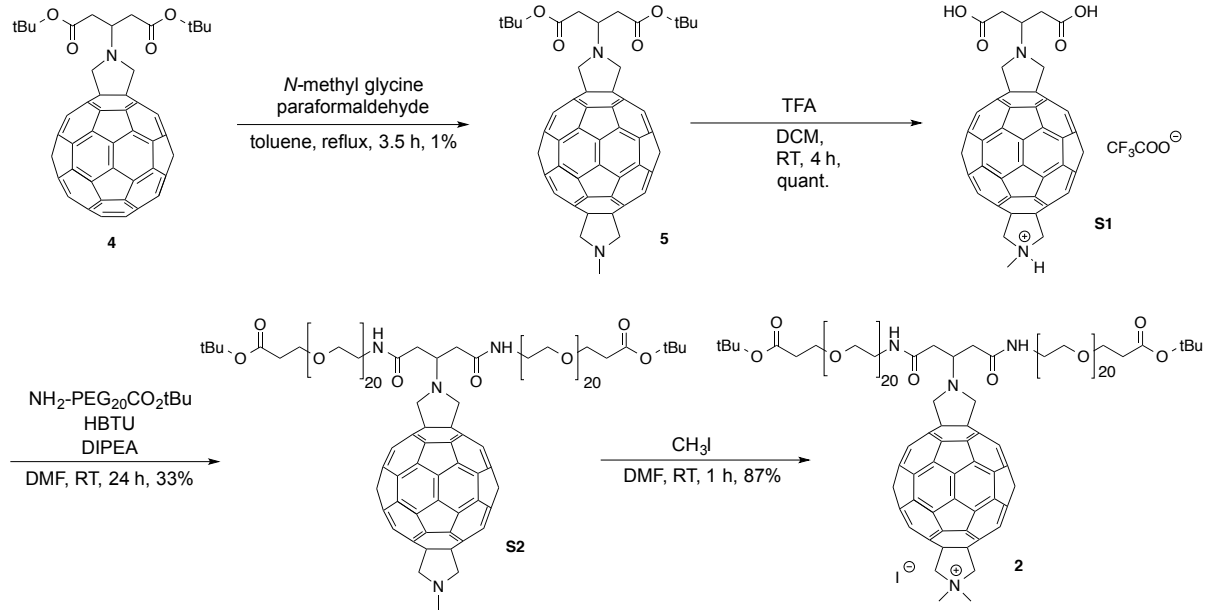
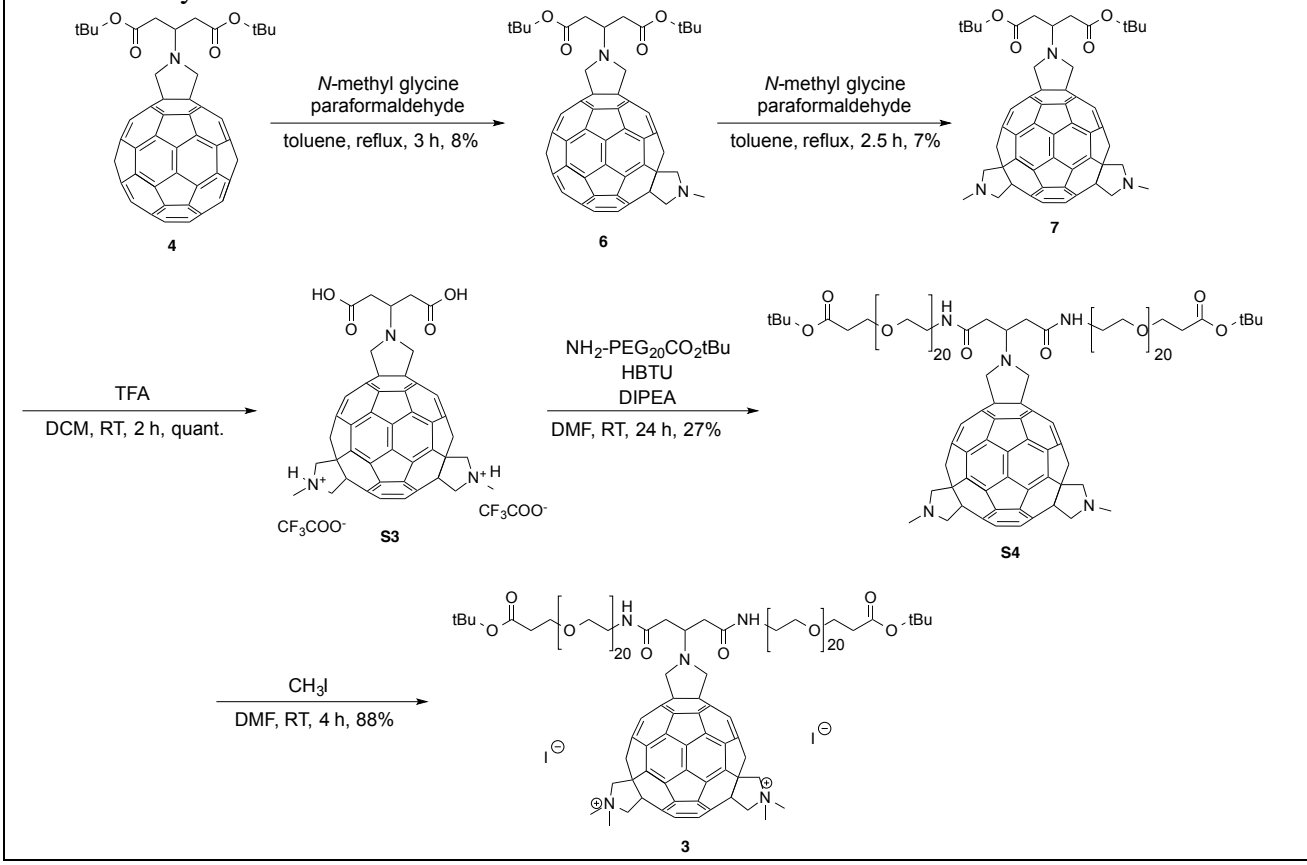
1. Synthesis of C_{60} – PEG_{20} derivatives 2 and 3

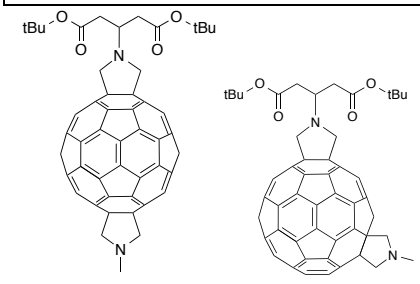
General. NMR spectra were recorded on Varian 300 spectrometer (Varian Inc., CA, USA), Bruker 400 spectrometer, and Bruker 600 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany). MALDI-TOF-MS (Bruker Daltonics GmbH, Bremen, *Germany*) and HRMS analyses were by Bruker Ultraflex II LRF200 MALDI-TOF with MALDI-FT ion spec Ultima and Bruker maXis ESI (Bruker Daltonics). FT- IR spectra were recorded on PerkinElmer Spectrum One FT-IR Spectrometer with Universal ATR Sampling Accessory (PerkinElmer Inc., Waltham, MA, USA). HPLC analyses were carried out by JASCO PU-2080 Plus HPLC pump, JASCO MD-2018 Plus detector, and ChromNAV Chromatography Data System (JASCO). All the solvents were purchased from Acros Organic (Thermo Fischer Scientific, Inc., Geel, Belgium). Dynamic light scattering was recorded on Zetasized Nano S (Malvern) using a glass cuvette. Column chromatography and analytical TLC were performed on SILICYCLE SilicaFlash® F60 (230 – 400 mesh) and silica gel 60 F254 TLC (Merck KGaA, Darmstadt, Germany), respectively.

Scheme 1. Synthesis of **2.**



Scheme 2. Synthesis of **3.**





Synthesis of 5 and 6. To a solution of compound **4** (2.11 g, 2.09 mmol) in toluene (650 mL), sarcosine (317 mg, 3.56 mmol, 1.7 equiv) and paraformaldehyde (189 mg, 6.28 mmol, 3.0 equiv) were added. The reaction mixture was sonicated for about 1.5 h and subsequently refluxed for 3 h. The solvent was removed *in vacuo* and the obtained crude mixture was purified by silica gel column chromatography. The monoadduct **4** (SM), *trans-1* **5**, and *trans-3* **6** were eluted with toluene, toluene - EtOAc 99 : 1, and 96 : 4, respectively. Additional purification of *trans-1* **5** was carried out by preparative HPLC (column: SHISEIDO Silica SG80, size: Φ 30 x 250 mm, solvent: toluene - EtOAc (99 : 1), flow rate: 10 mL/min, detection: 390 nm, rt of **5**: 20 min) to provide *trans*-1 bis-adduct **5** (25.0 mg, 0.024 mmol, 1%); IR (ATR) ν_{max} (cm^{-1}): 2963 (w), 2776 (w), 1724 (m), 1471 (w), 1453 (w), 1425 (w), 1390 (w), 1365 (w), 1340 (w), 1319 (w), 1258 (m), 1146 (m), 1087 (s), 1012 (s), 861 (w), 793 (s), 766 (m), 742 (m), 732 (m), 705 (m), 662 (w), 646 (w); ^{1}H NMR (400 MHz, in $CDCl_3$) δ 1.61 (s, 18H), 2.87 (dd, *J* = 6.5 Hz, 15.0 Hz, 2H), 3.07 (dd, *J* = 6.9, 15.0 Hz, 2H), 3.13 (s, 3H), 4.31 (q, *J* = 6.6 Hz, 1H), 4.65 (s, 4H), 4.77 (s, 4H); ^{13}C-NMR (100 MHz, in $CDCl_3$) δ 28.7, 38.8,

42.1, 54.9, 63.6, 70.5, 81.5, 171.5; carbon cage: 68.0, 69.3, 136.8, 137.04, 141.1, 142.7, 144.5, 145.6, 145.8, 146.5, 146.6, 148.0, 148.1, 153.8, 153.84; HRMS (MALDI$^+$, matrix: DCTB) *m/z* calcd. for $C_{78}H_{34}N_2O_4Na^+$: 1085.2411, found 1085.2413 ([M+Na]$^+$). Additional purification of *trans-3* **6** was carried out by preparative HPLC (column: SHISEIDO Silica SG80, size: Φ 30 x 250 mm, solvent: toluene - EtOAc (99 : 4), flow rate: 10 mL/min, detection: 390 nm, rt of **6**: 38 min), to provide *trans*-3 bis-adduct **6** (187 mg, 0.176 mmol, 8%); IR (ATR) ν_{max} (cm^{-1}): 2972 (w), 2936 (w), 2776 (w), 1722 (s), 1470 (w), 1454 (w), 1425 (w), 1389 (w), 1364 (m), 1339 (m), 1248 (m), 1136 (s), 1117 (s), 1092 (m), 1029 (m), 949 (w), 884 (w), 840 (w), 768 (m), 751 (m), 729 (m), 702 (w), 665 (w); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 18H), 2.69 (dd, *J* = 6.5, 1.2 Hz, 1H), 2.73 (dd, *J* = 6.5, 1.1 Hz, 1H), 2.94 – 2.85 (m, 5H), 4.04 - 4.17 (m, 4H), 4.26 (d, *J* = 8.8 Hz, 1H), 4.31 (d, *J* = 9.2 Hz, 1H), 4.44 – 4.36 (m, 2H), 4.51 (d, *J* = 8.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 28.4, 38.4, 41.8, 54.6, 62.5, 63.3, 69.0, 69.3, 81.2, 171.1; carbon cage: 69.5, 70.3, 70.6, 135.7, 135.9, 136.6, 136.8, 139.90, 139.94, 141.2, 141.39, 141.42, 141.6, 141.8, 142.0, 142.7, 143.76, 143.79, 144.1, 144.7, 144.8, 145.0, 145.1, 145.26, 145.32, 145.34, 145.36, 145.46, 145.49, 145.51, 146.8, 146.9, 148.4, 148.5, 148.96, 149.02, 149.09, 149.10, 149.2, 149.3, 155.1, 155.7, 155.8, 158.4; HRMS (MALDI$^+$, matrix: DCTB) *m/z* calcd. for $C_{78}H_{34}N_2O_4Na^+$: 1085.2411, found 1085.2412 [M+Na]$^+$.

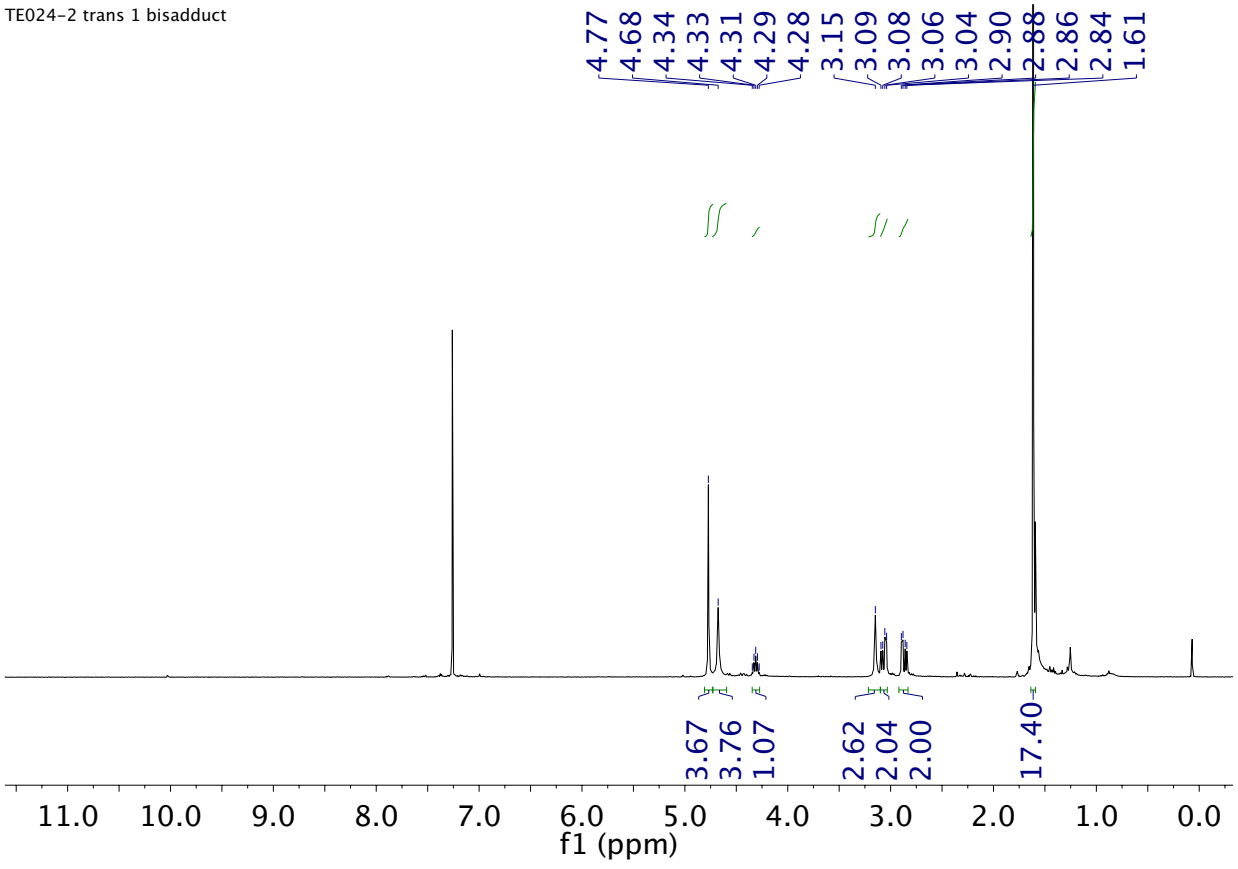


Figure S1. ^{1}H-NMR of **5** (400 MHz, in $CDCl_3$).

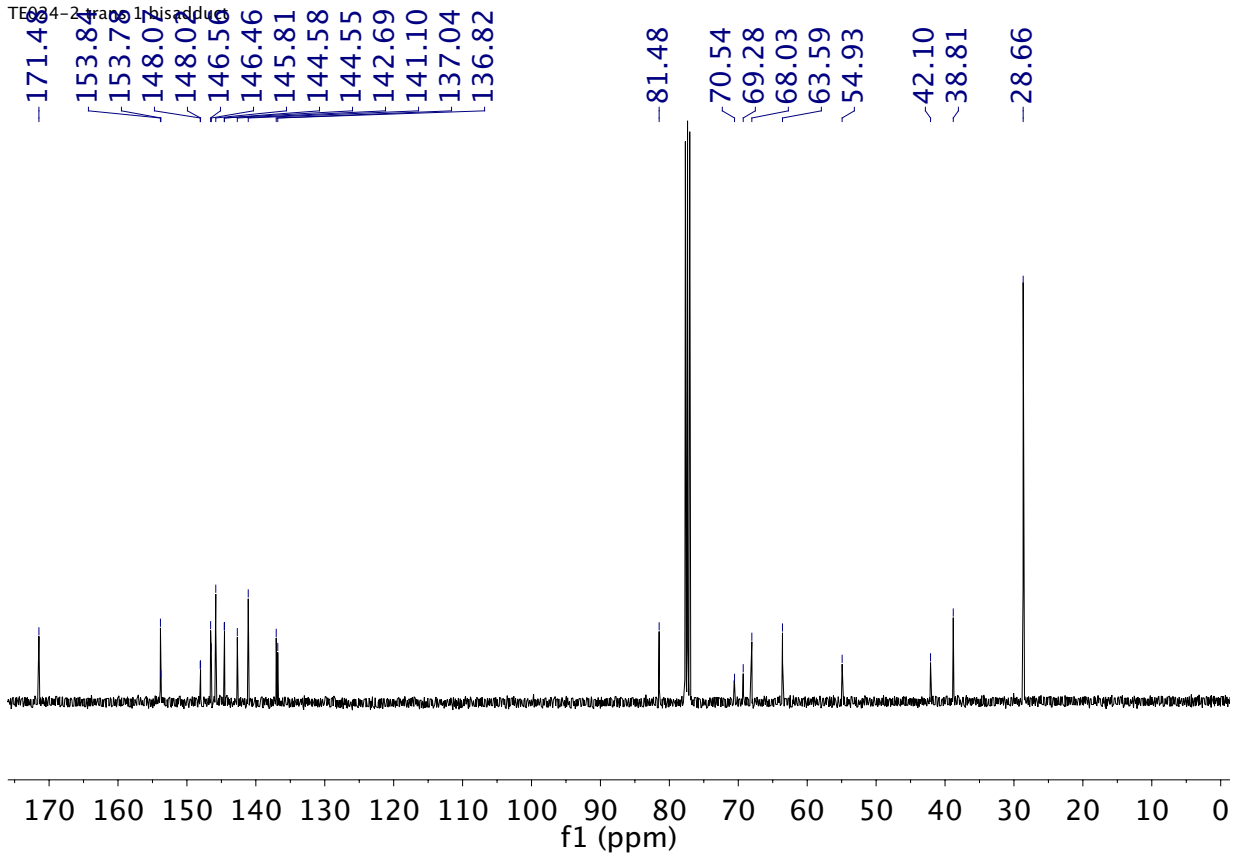


Figure S2. ^{13}C-NMR of **5** (100 MHz, in $CDCl_3$).

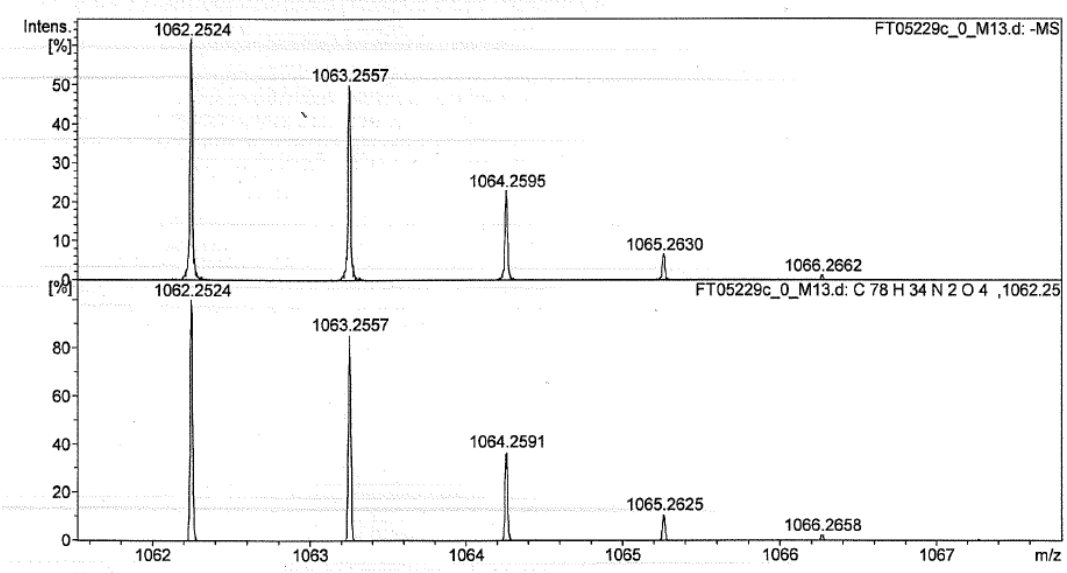


Figure S3. HRMS of **5** (MALDI$^+$, DCTB).

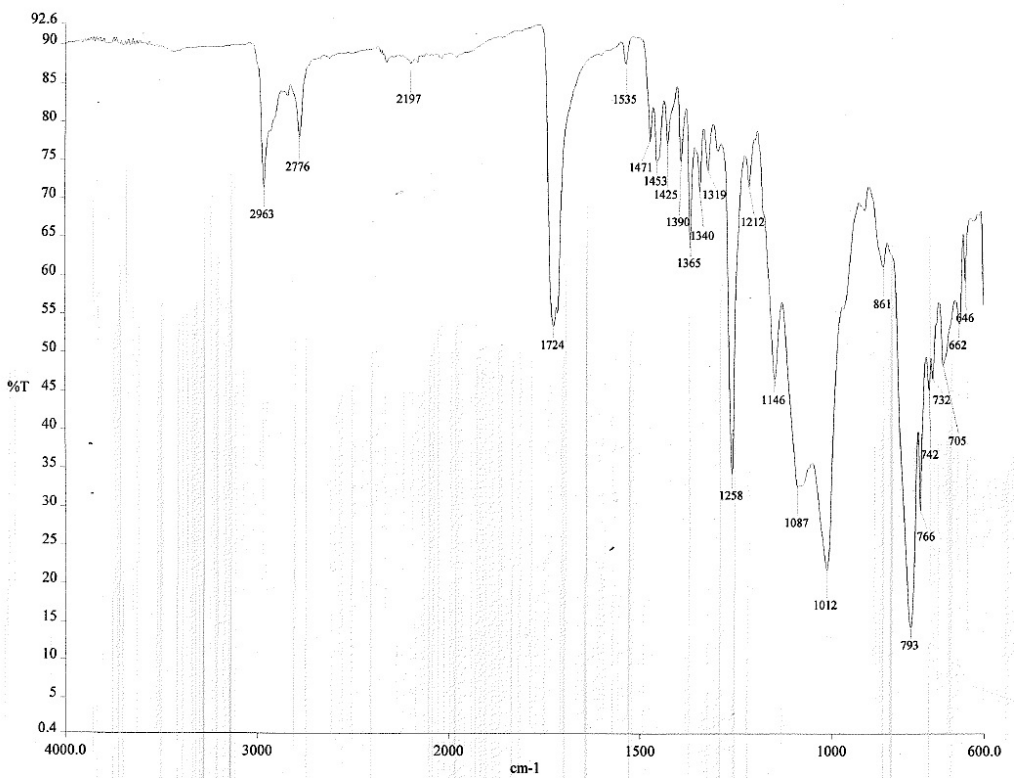


Figure S4. IR spectrum of **5.**

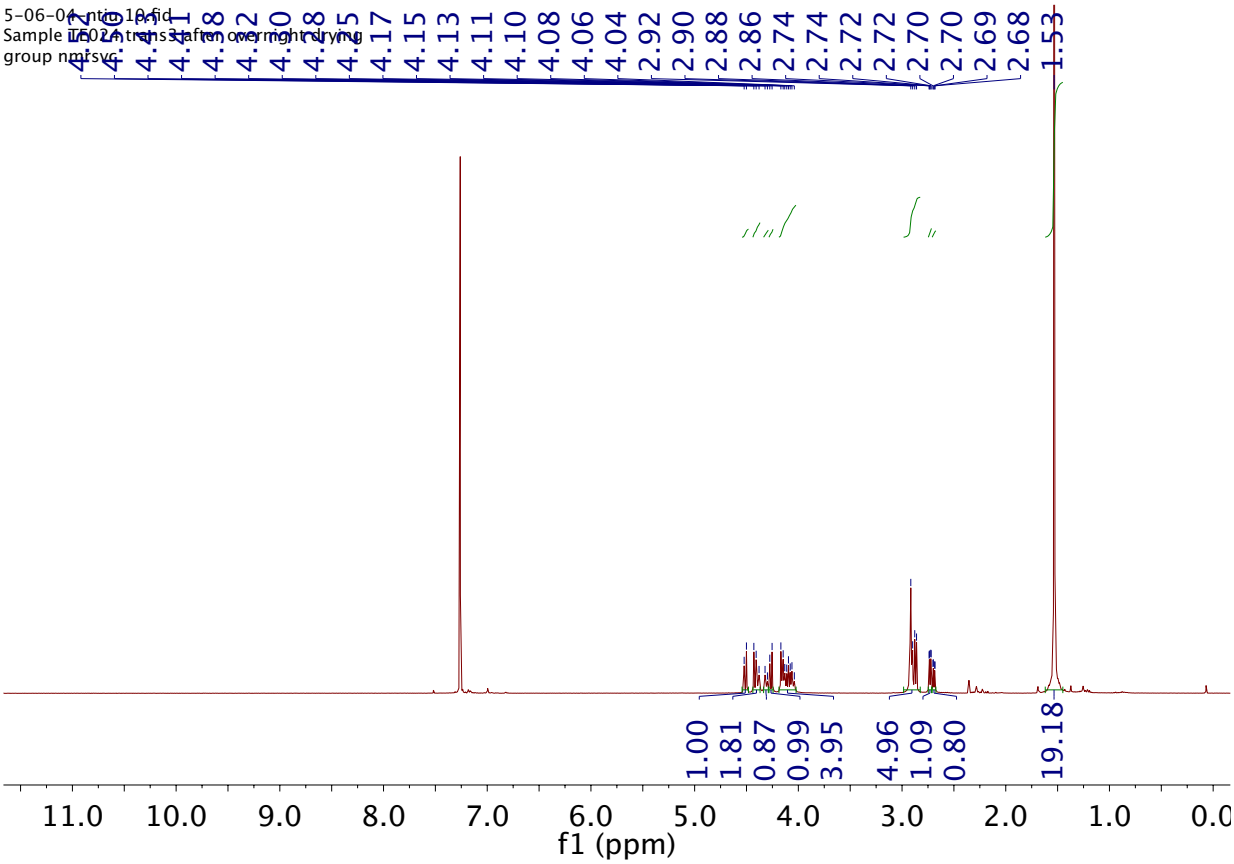


Figure S5. ^{1}H-NMR of **6** (400 MHz, in $CDCl_3$).

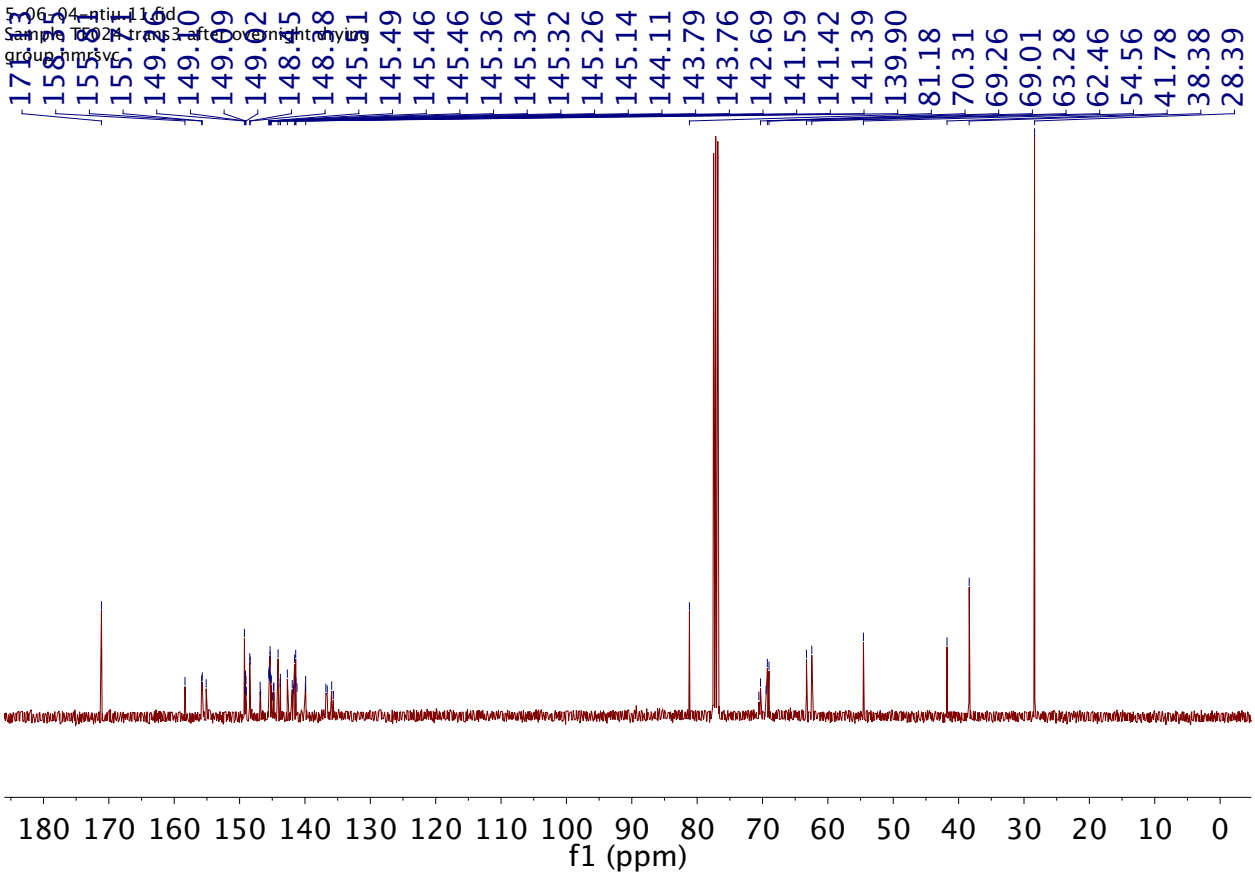


Figure S6. ^{13}C-NMR spectrum of **6** (100 MHz, in $CDCl_3$).

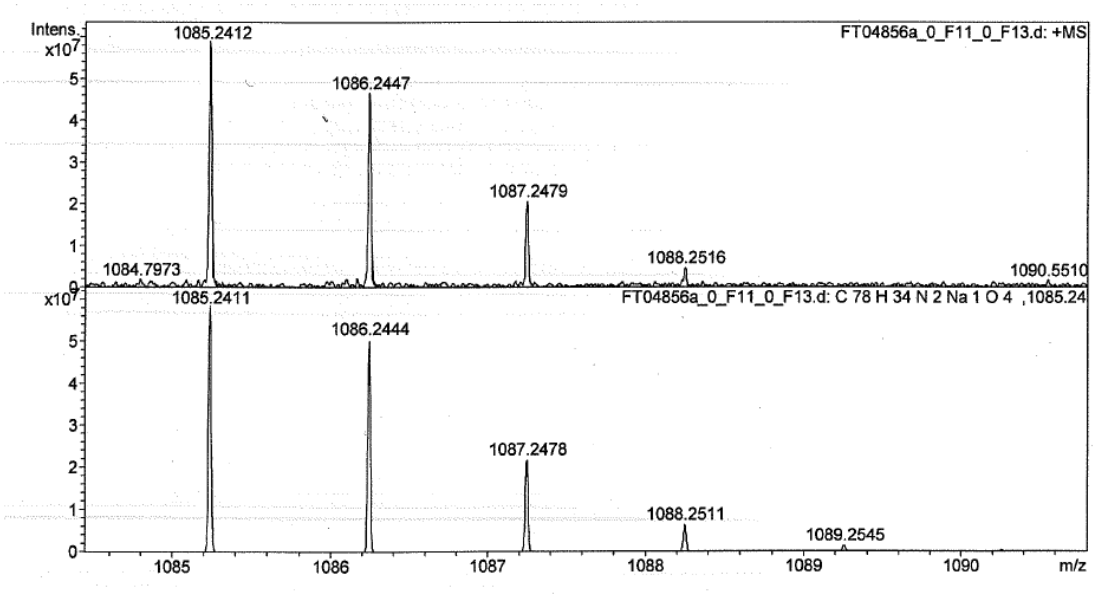


Figure S7. HRMS of **6** (MALDI$^+$, DCTB).

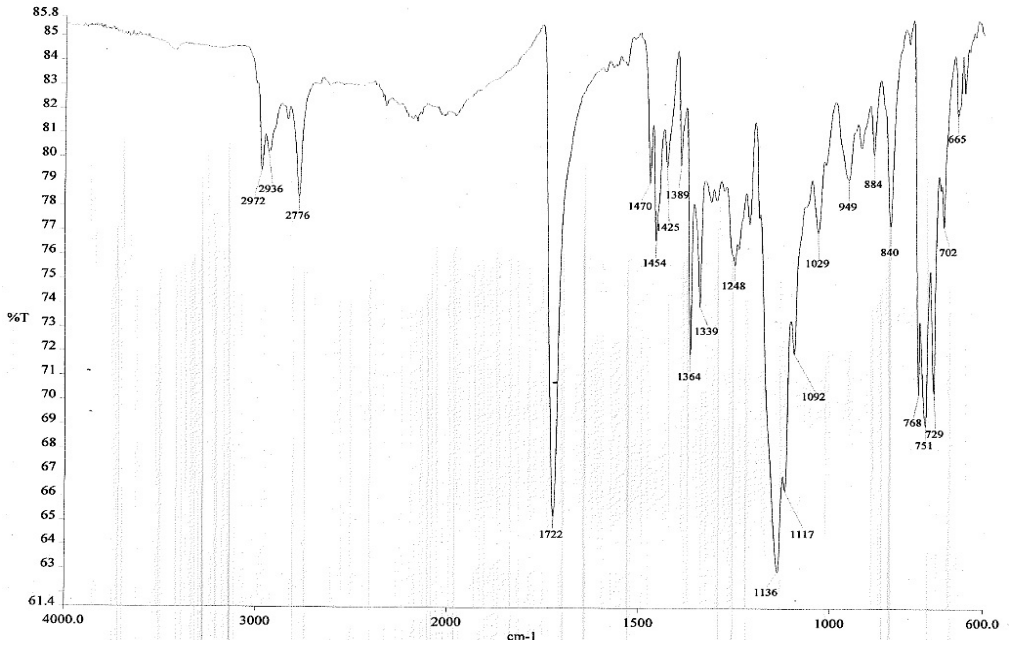
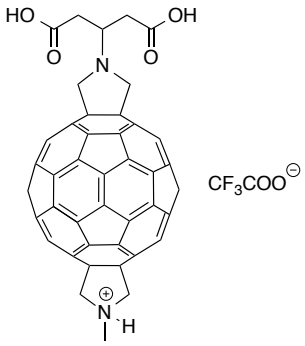


Figure S8. IR spectrum of **6.**



S1

Synthesis of S1. To a solution of **5** (14.0 mg, 13.2 μmol) in CH_2Cl_2 (3.5 mL), TFA (3.5 mL) was added dropwise. The solution was stirred at room temperature for 4 h. The solvents were removed by flushing nitrogen gas. The residue was washed with hexane and the product was dried under vacuum to provide **S1** (14 mg, 13.1 μmol, quant); IR (ATR) ν_{max} (cm^{-1}): 2924 (w), 1718 (m), 1619 (m), 1406 (w), 1135 (s), 894 (w), 834 (w), 795 (w), 766 (w), 719 (m), 623 (w); ^{1}H-NMR (400 MHz, DMF-d_7) δ 3.04 (dd, J = 15.4, 6.7 Hz, 2H), 3.33 (dd, J = 15.4, 6.7 Hz, 2H), 3.66 (s, 3H), 4.46 (q, J = 6.7 Hz, 1H), 4.97 (s, 4H), 5.54 (s, 4H); ^{13}C-NMR (100 MHz, DMF-d_7) δ 36.9, 40.3, 54.3, 62.8, 67.2, 173.5; carbon cage: 68.1, 68.2, 136.8, 136.9, 140.5, 140.7, 142.3, 143.9, 144.4, 145.32, 145.6, 146.1, 146.7, 147.76, 147.80, 152.4, 154.4; (MALDI$^-$, matrix: DCTB) *m/z* calcd. for $C_{70}H_{18}N_2O_4^-$: 950.1272, found 950.1273 $[M]^-$.

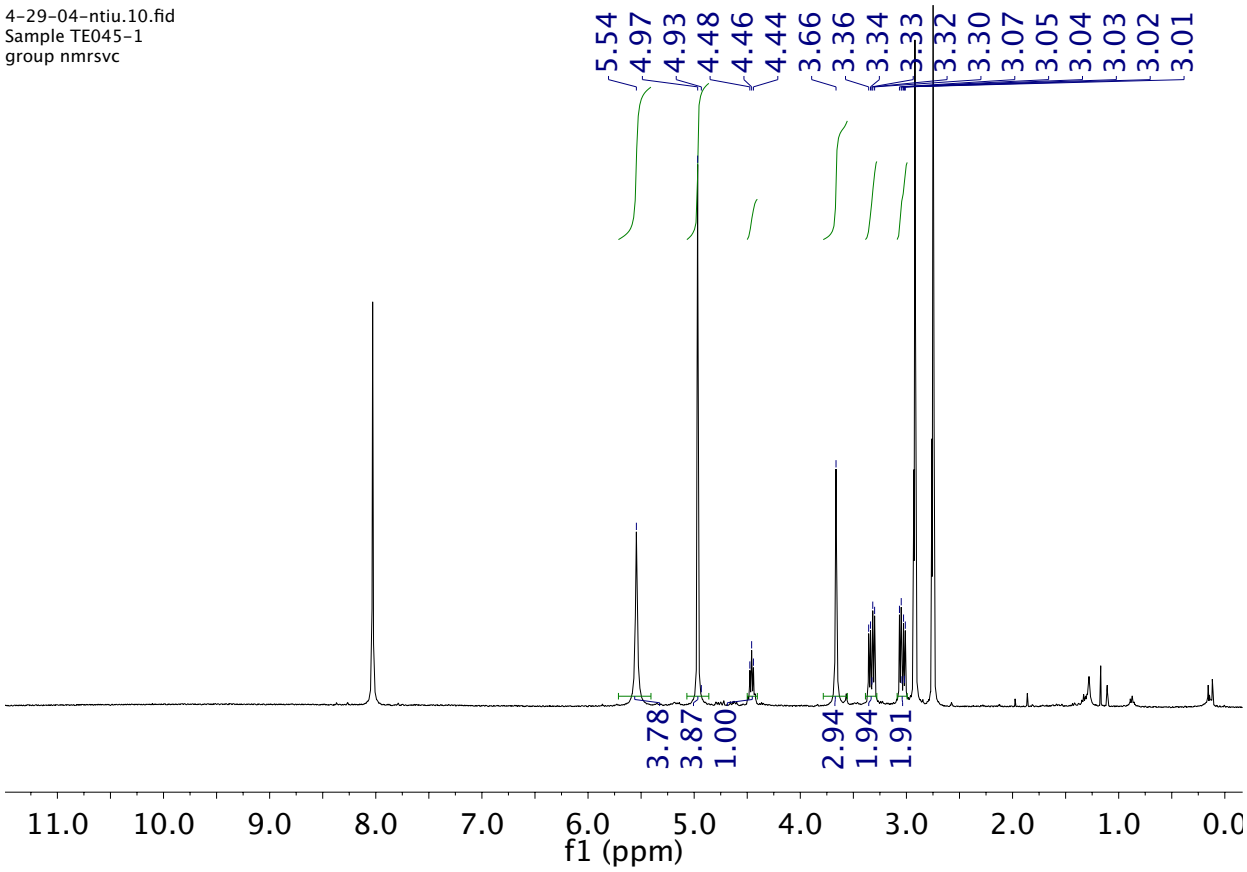


Figure S9. ^{1}H-NMR of **S1** (400 MHz, DMF-d_7).

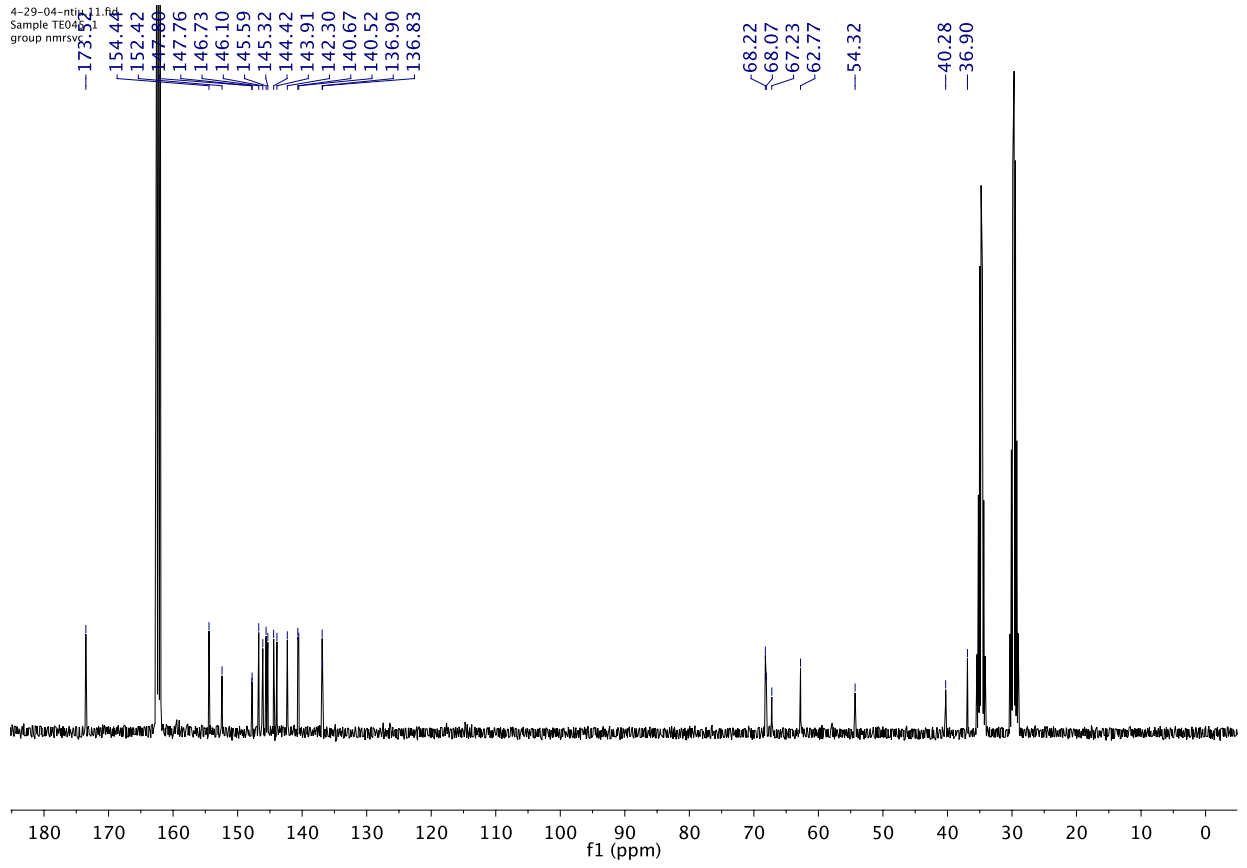


Figure S10. ^{13}C-NMR of **S1** (100 MHz, DMF-d_7).

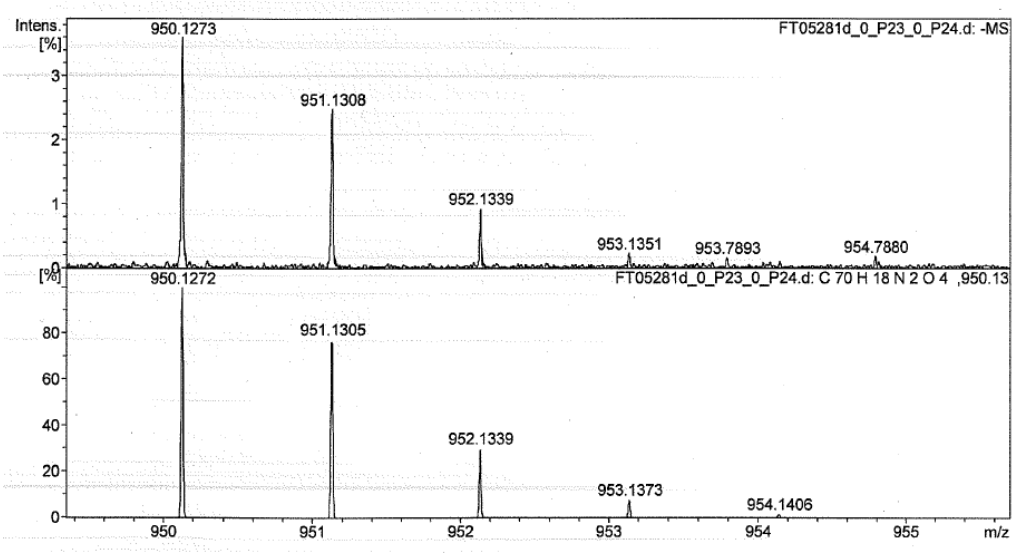


Figure S11. HRMS of **S1** (MALDI$^-$, DCTB).

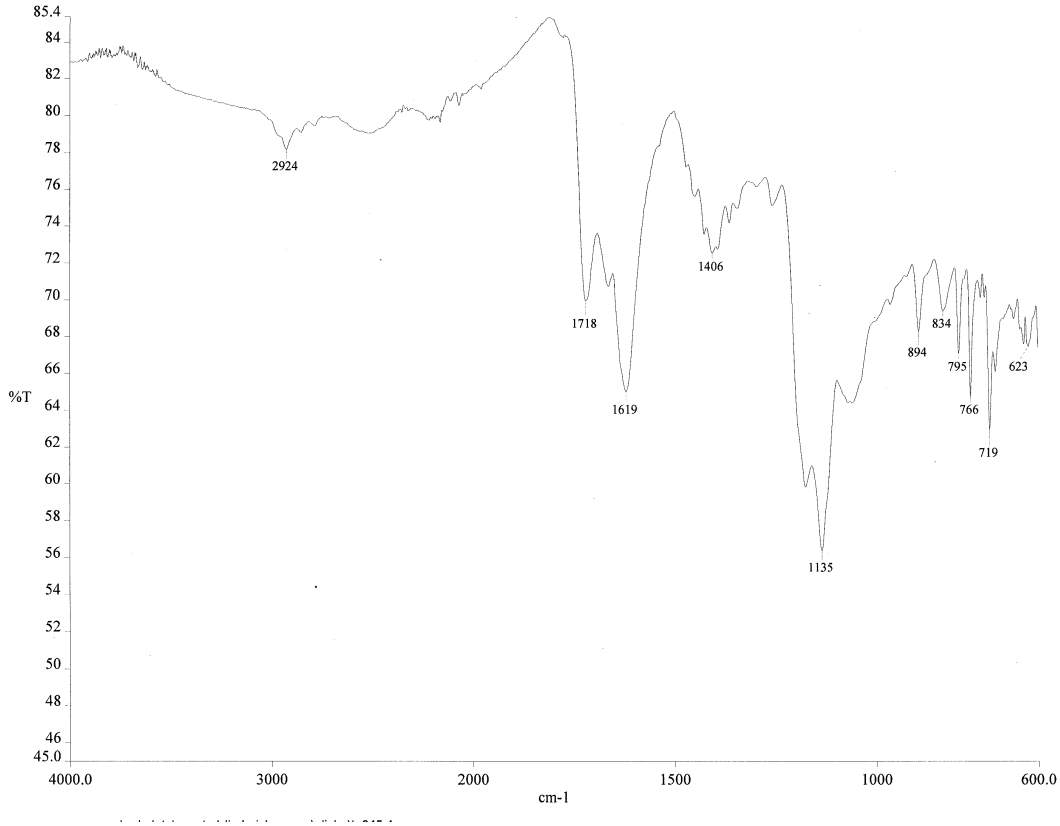
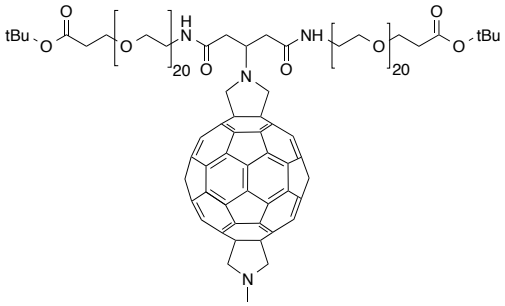


Figure S12. IR spectrum of **S1.**



S2

Synthesis of S2. To a solution of **S1** (15.0 mg, 14.1 μmol) in distilled DMF (1.25 mL), HBTU (CHEM-IMPEX international, 8.0 equiv, 42.7 mg, 112.8 μmol), Amino-dPEG$_{20}$-^{t}Bu ester (Quanta Biodesign, 3.0 eq., 43.4 mg, 42.3 μmol), DIPEA (10 equiv, 18.5 mg, 141 μmol) were added. Reaction mixture was stirred 24 h at room temperature. The solvent was removed under vacuum and subsequently water was added. The crude mixture was purified by HPLC (column: Phenomenex C4 Φ10 x 250 mm, solvent: isocratic CH_3CN/H_2O 45:55, flow rate: 3 mL/min, detection: 370 nm, retention time of **S2**: 15.0 min) and collected fraction was freeze-dried to provide a brown sticky solid **S2** (13.8 mg, 4.7 μmol, 33%); IR (ATR) ν_{max} (cm^{-1}): 3300 (w), 2868 (m), 1725 (w), 1669 (m), 1547 (w), 1453 (w), 1349 (w), 1294 (w), 1248 (w), 1200 (w), 1094 (s), 946 (m), 843 (m), 798 (w), 767 (w), 719 (w), 678 (w); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 18H), 2.51, (t, J = 6.4 Hz, 4H), 3.61 – 3.69 (m, 160 H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 28.2, 29.9, 36.4, 67.0, 70.2 - 70.4, 80.7, 171.14, 171.15, carbon cage: 136.6, 136.7, 140.9, 142.5, 144.4, 145.6, 146.2, 146.3, 147.8, 153.3, 153.5; HRMS (MALDI^{+}, matrix: DCTB) *m/z* calcd. for $C_{164}H_{204}N_4O_{46}Na^{+}$: 2988.3639, found 2988.3642 $[M+Na]^{+}$.

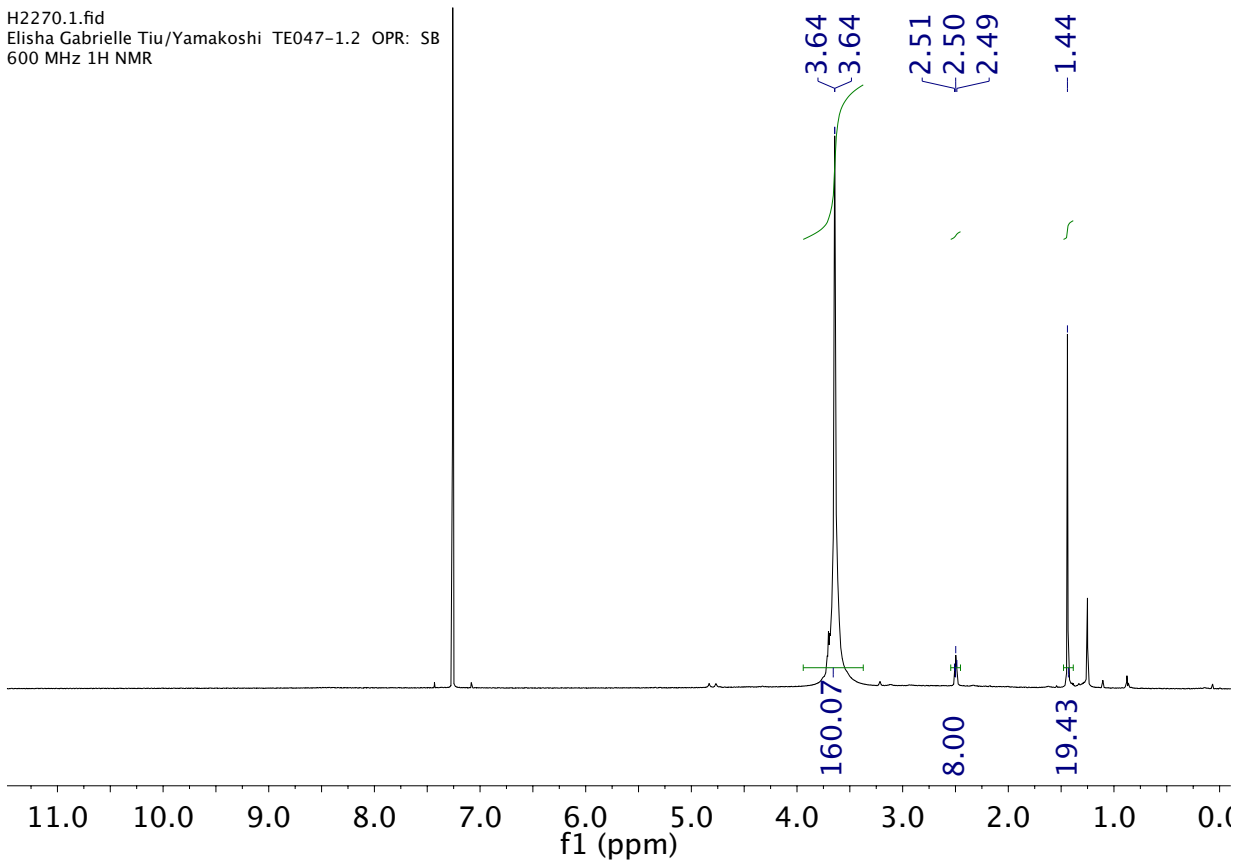


Figure S13. ^{1}H NMR of **S2** (400 MHz, in $CDCl_3$).

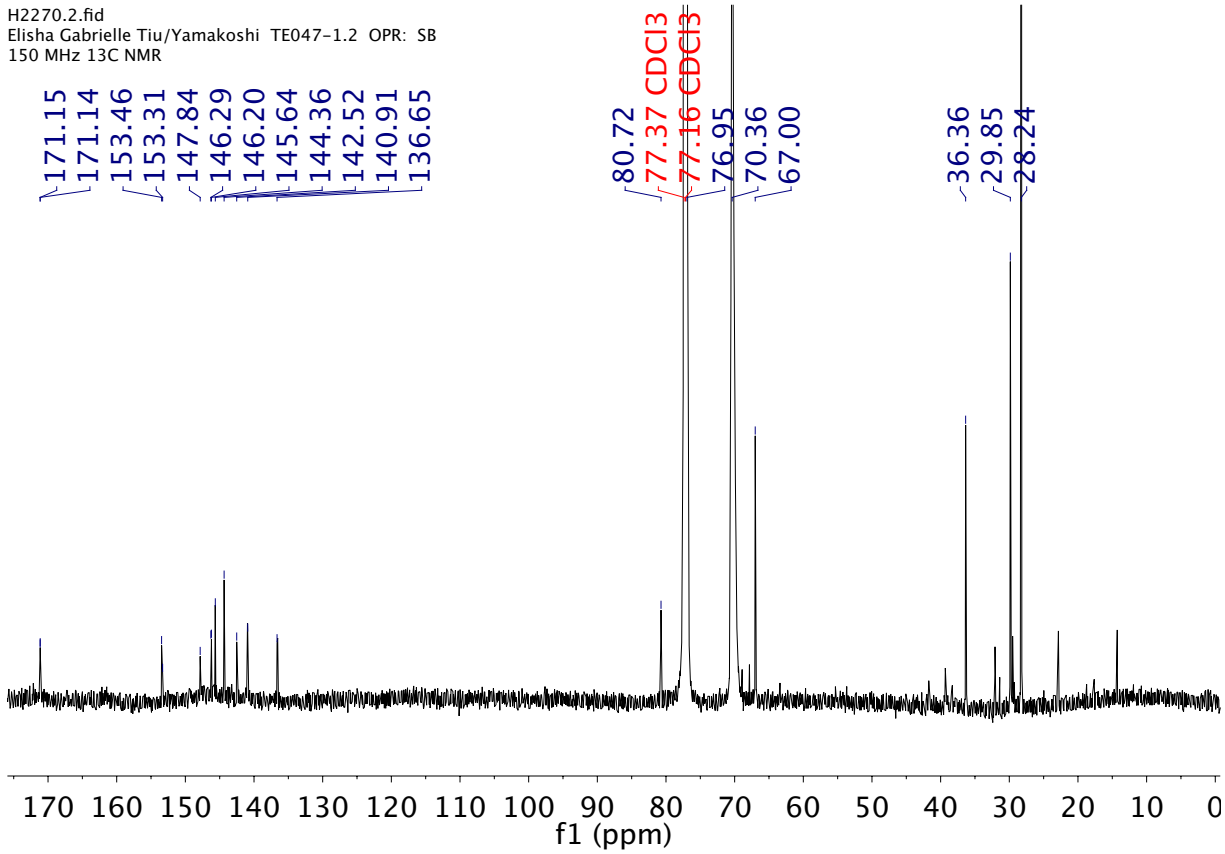


Figure S14. ^{13}C NMR of **S2** (150 MHz, in $CDCl_3$).

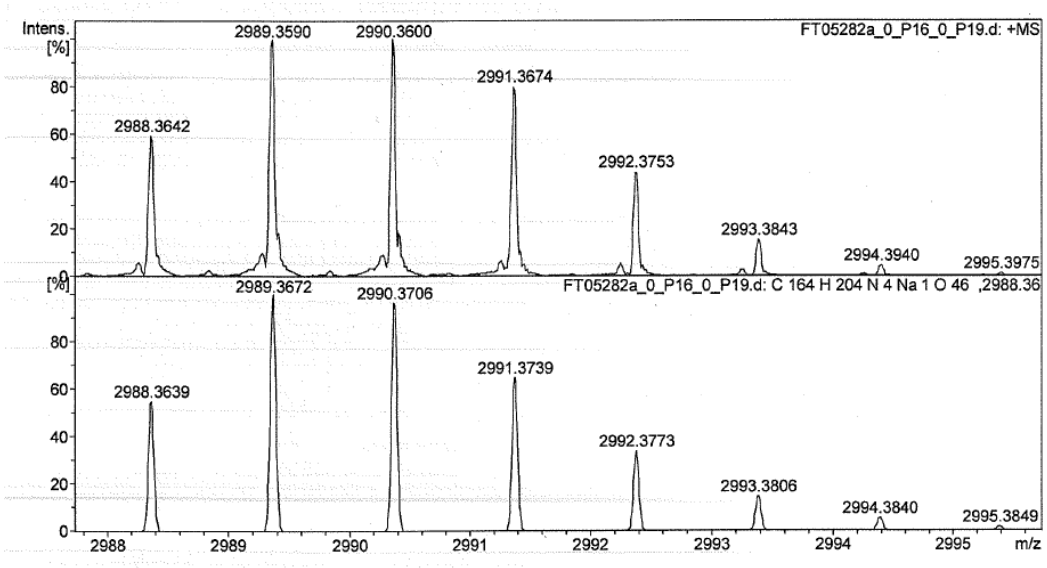


Figure S15. HRMS of **S2** (MALDI$^+$, DCTB).

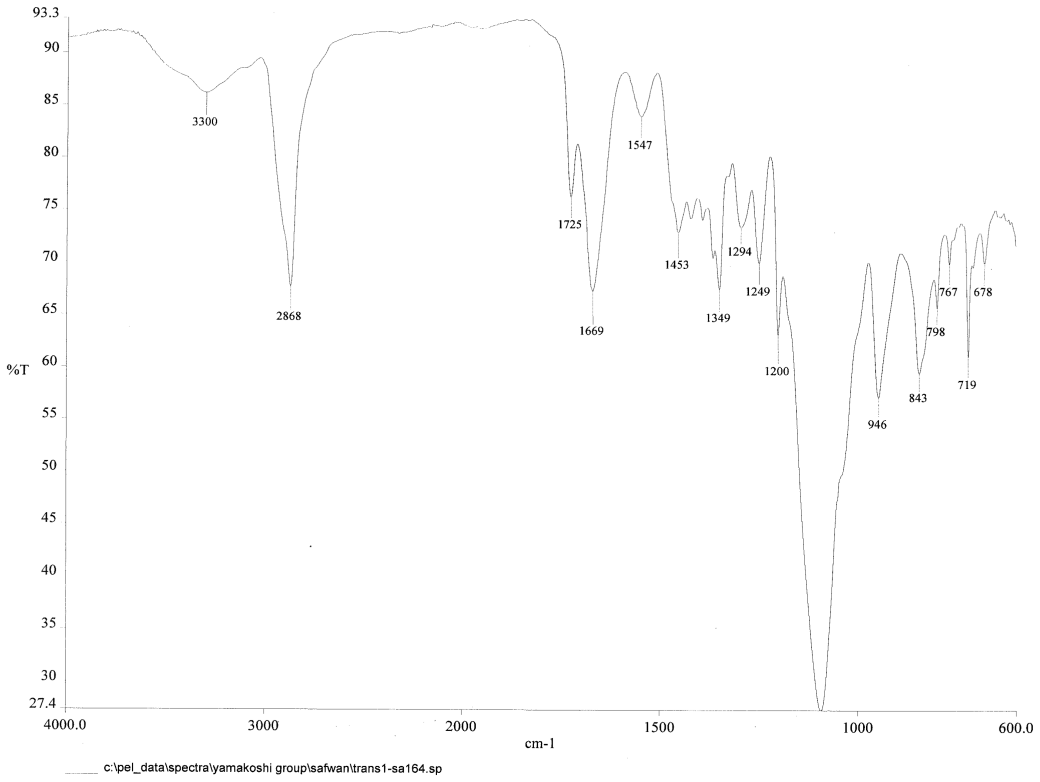
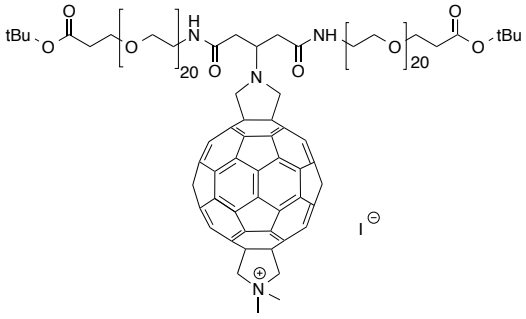


Figure S16. IR spectrum of **S2**.



2

Synthesis of 2. To a solution of **S2** (13.8 mg, 4.7 μmol) in dry DMF (0.5 mL) CH_3I (0.5 mL, 8.0 mmol, excess equiv) was added. The reaction mixture was stirred at room temperature for 1 h. The solvent was removed by rotary evaporator, the residue was washed with hexane and diethyl ether, and the product was dried under vacuum to give **2** as a brown sticky solid (12.7 mg, 4.1 μmol, 87%); IR (ATR) ν_{max} (cm^{-1}): 3430 (w), 2921 (m), 1721 (m), 1663 (m), 1454 (w), 1350 (w), 1248 (w), 1090 (s), 947 (m), 842 (m), 766 (w), 720 (w); ^{1}H NMR (600 MHz, DMF-d_7) δ 1.43 (s, 18H), 2.47 (t, J = 6.2 Hz, 4H), 2.78 (s, 3H), 2.81 (m, 8H), 2.95 (s, 3H), 3.52 - 3.64 (m, 160H). ^{13}C NMR (151 MHz, DMF-d_7) δ 28.6, 37.2, 40.2, 53.6, 63.5, 67.7, 71.4, 80.8, 171.7, 172.4; carbon cage: 110.5, 110.6, 120.4, 121.8, 125.4, 128.4, 129.0, 129.3, 137.4, 137.8, 141.3, 141.6, 143.3, 144.5, 145.4, 146.2, 146.5, 146.7, 147.7, 148.6, 148.8, 152.4, 155.8. HRMS (MALDI$^+$, matrix: DCTB) m/z calcd. for $C_{165}H_{207}N_4O_{46}^+$: 2980.3976, found 2980.3970 $[M–I]^+$.

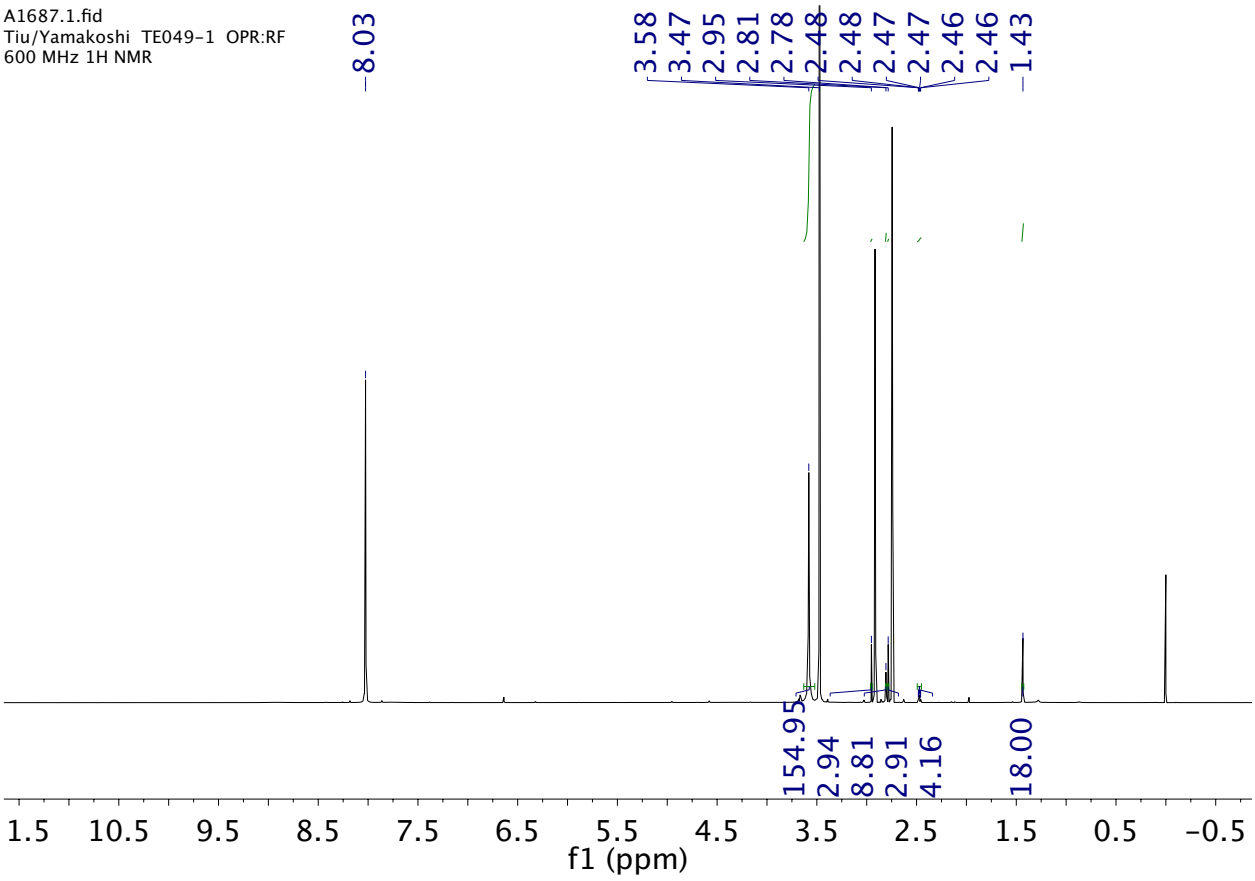


Figure S17. ^{1}H-NMR of **2** (600 MHz, in DMF-d_7).

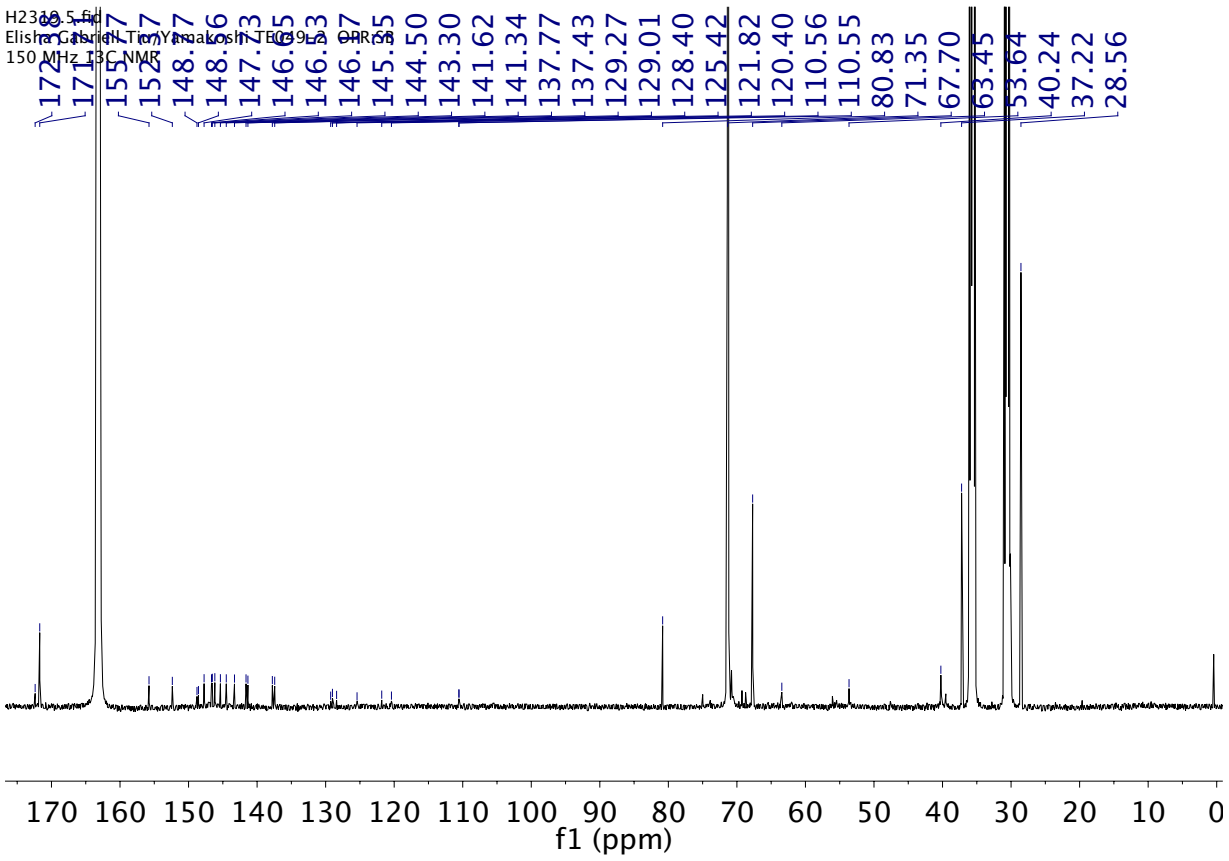


Figure S18. ^{13}C NMR of **2** (150 MHz, in DMF-d_7)**.**

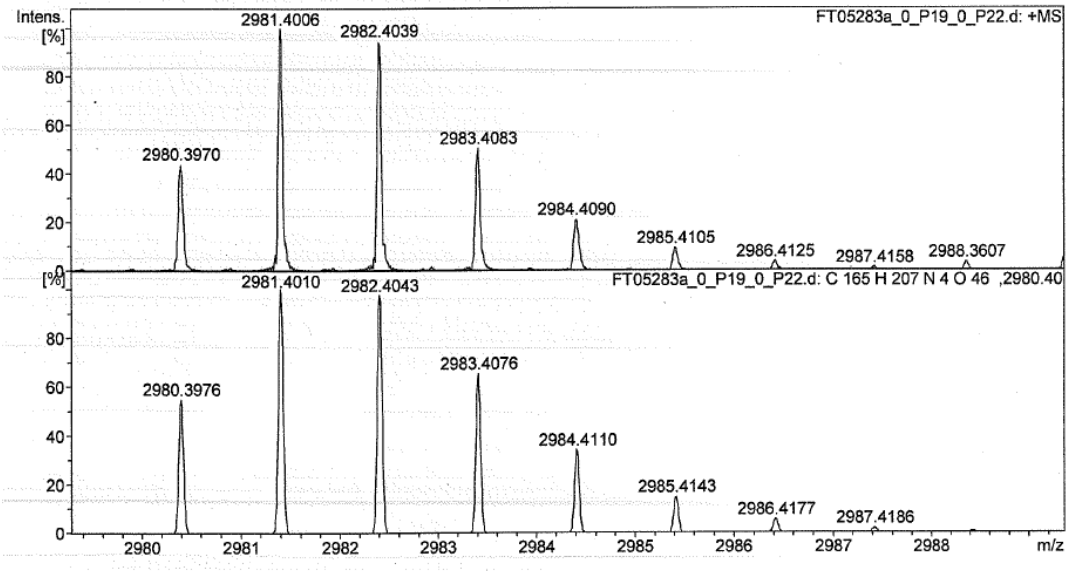


Figure S19. HRMS of **2** (MALDI$^+$, DCTB)**.**

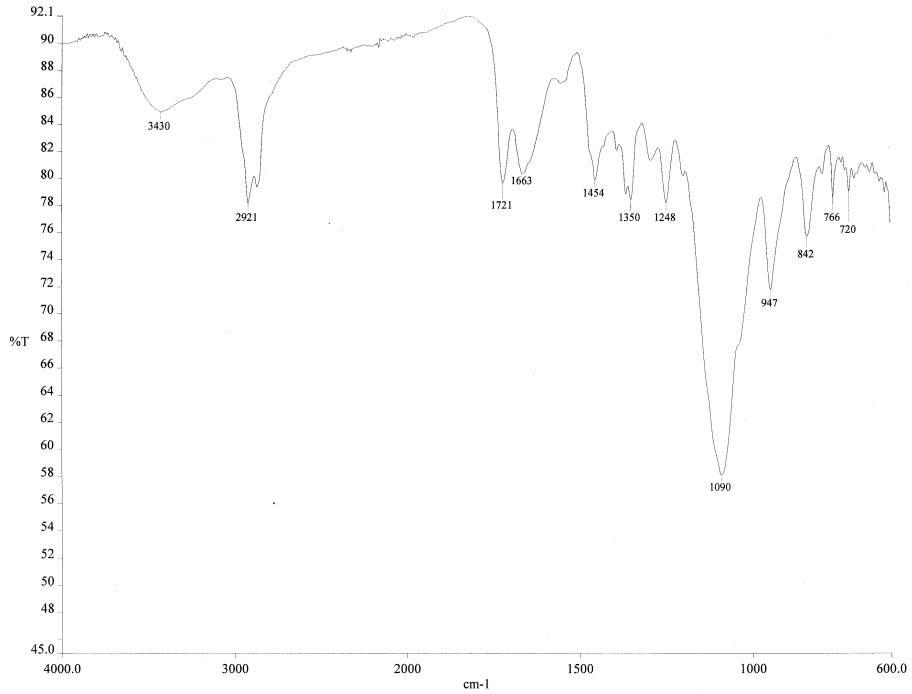
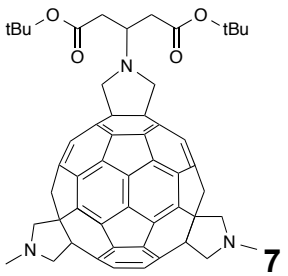


Figure S20. IR spectrum of **2**.



7

Synthesis of 7. To a solution of *trans-3* **6** (109 mg, 103 μmol) in toluene (46 mL), sarcosine (1.4 equiv, 12.8 mg, 144 μmol) and paraformaldehyde (2.6 equiv, 8 mg, 267 μmol) were added. The mixture was sonicated for 30 min and the reaction mixture was refluxed for 2.5 h. The solvent was removed *in vacuo* and the crude mixture was subjected to a plug of SiO_2 eluted with toluene - EtOAc

(93:7). The solvent was removed and the residue was purified by a preparative HPLC (column: SHISEIDO Silica SG80 (Φ30 x 250 mm), solvent: toluene - EtOAc (93:7), flow rate: 10 mL/min, detection: 390 nm). The solvent was removed to give *trans-3 trans-3 trans-3* **7** (8 mg, 7.14 μmol, 7%); IR (ATR) ν_{max} (cm^{-1}): 2968 (w), 2936 (w), 2777 (w), 1724 (m), 1471 (w), 1446 (w), 1388 (w), 1364 (w), 1335 (w), 1255 (w), 1137 (m), 1026 (w), 904 (w), 839 (w), 764 (w), 728 (w); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.50 (s, 18H), 2.64 (dd, *J* = 6.5 Hz, 15.0 Hz, 2H), 2.80 (dd, *J* = 6.9, 15.0 Hz, 2H), 2.81 (s, 6H), 3.98 (q, *J* = 6.6 Hz, 1H), 4.02 (s, 8H), 4.14 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 28.4, 38.3, 41.7, 54.5, 62.4, 69.8, 81.1, 171.1; carbon cage: 68.4, 69.5, 125.4, 128.4, 129.2, 140.4, 140.5, 140.7, 141.8, 142.0, 143.11, 143.15, 144.7, 144.8, 148.8, 148.9, 149.0, 149.44, 149.46, 149.51, 152.4, 156.0, 156.1, 158.5, 158.6, 158.7; HRMS (MALDI$^+$, matrix: DCTB) *m/z* calcd. For $C_{81}H_{41}N_3O_4Na^+$:1142.2989, found 1142.2987 ($[M+Na]^+$).

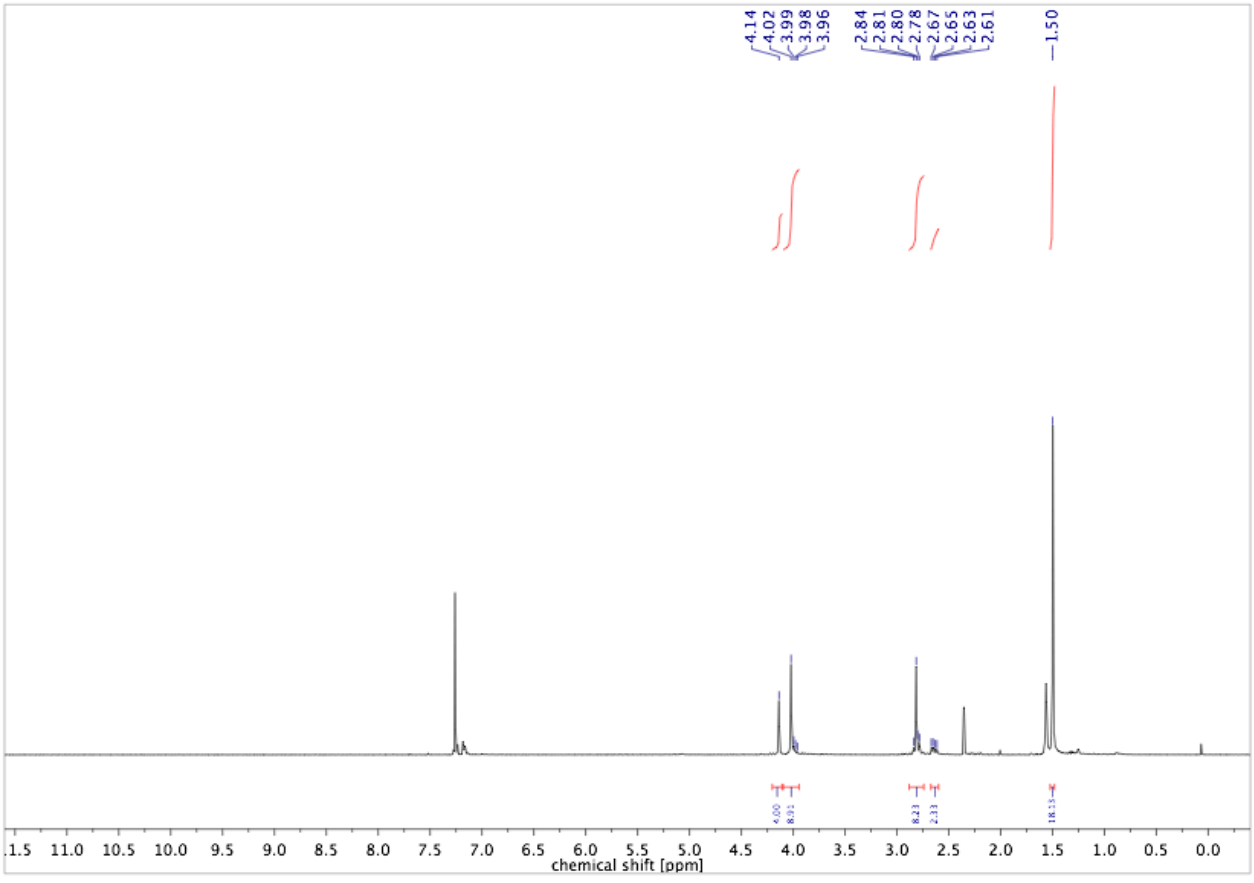


Figure S21. ^{1}H-NMR of **7** (400 MHz, in $CDCl_3$).

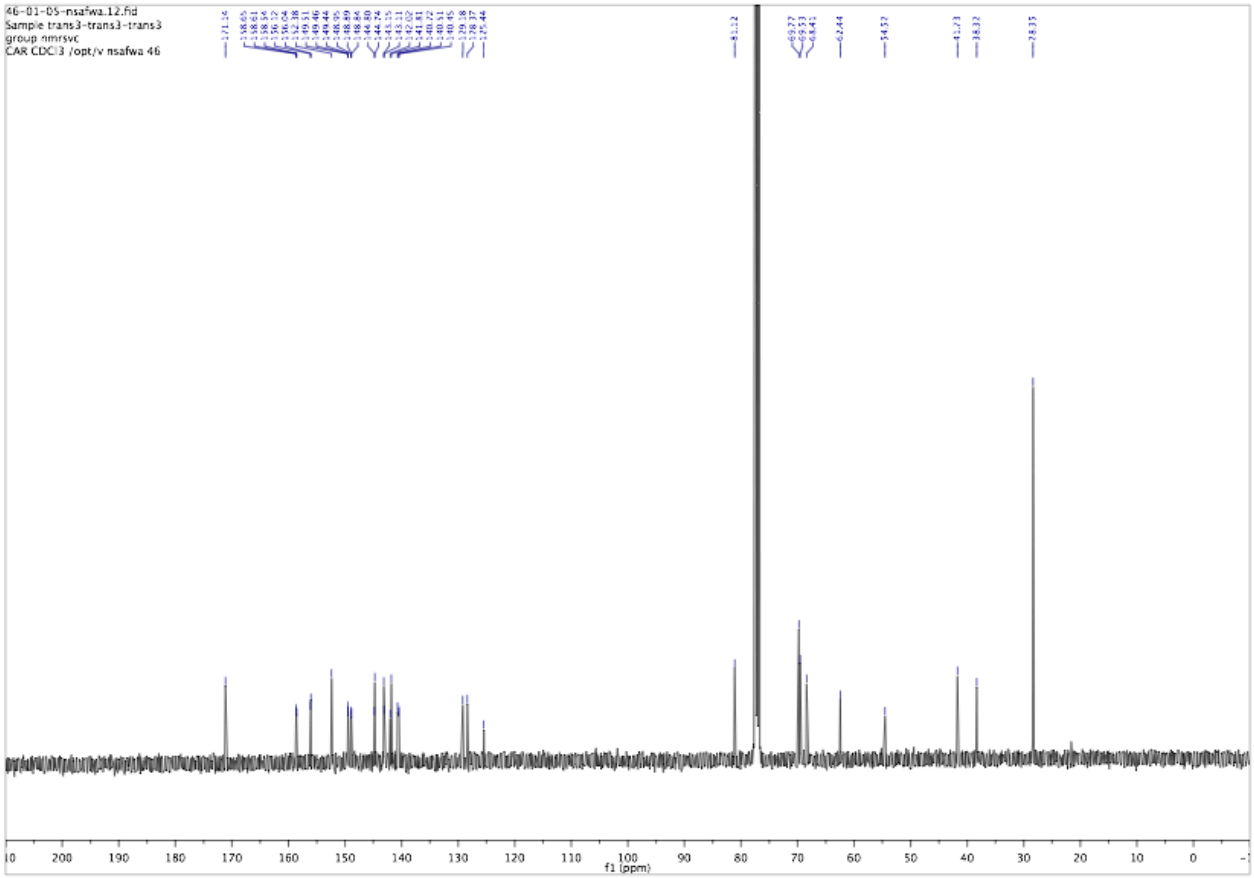


Figure S22. ^{13}C-NMR of **7** (101 MHz, in $CDCl_3$)**.**

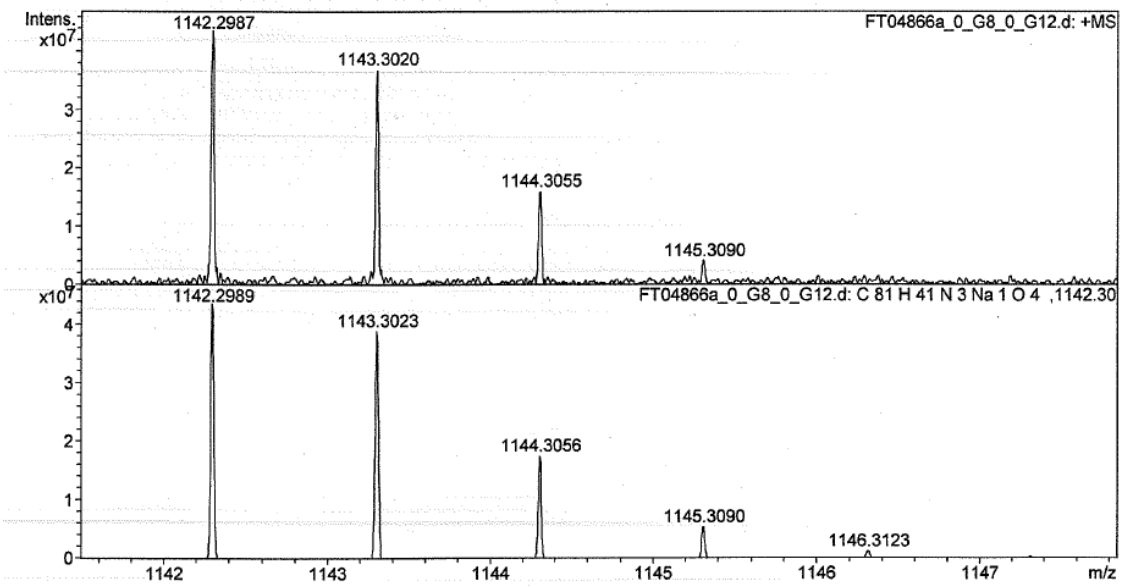


Figure S23. HRMS of **7** (MALDI$^+$, DCTB).

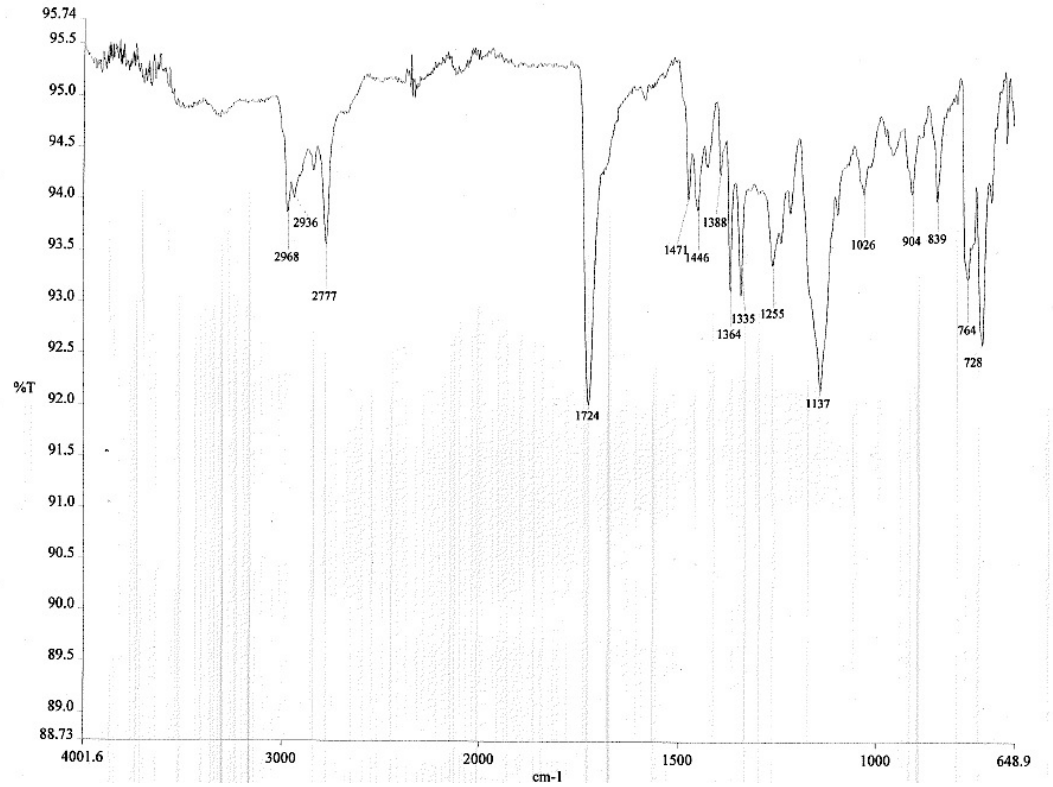
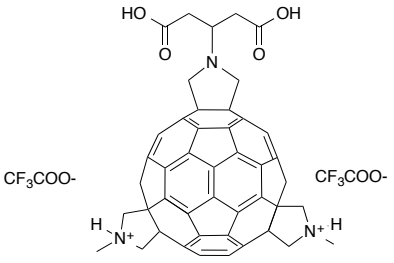


Figure S24. IR spectrum of **7.**



S3.

Synthesis of S3. To a solution of **7** (8.8 mg, 7.9 μmol) in CH_2Cl_2 (2 mL), TFA (2 mL) was added dropwise. The reaction mixture was stirred at room temperature for 2 h. The solvent and reagent were removed by flushing nitrogen, and obtained residue was washed with hexane and subsequently dried under vacuum to give **S3** (8 mg, 7.9 μmol, quant); IR (ATR) ν_{max} (cm^{-1}): 2925 (w), 2800 (w), 1667 (s), 1469 (w), 1414 (w), 1172 (s), 1123 (s), 1058 (m), 1019 (m), 963 (m), 947 (m), 828 (m), 796 (m), 771 (m), 718 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81 (dd, *J* = 15.4, 6.6 Hz, 2H), 3.06 (dd, *J* = 15.3, 6.9 Hz, 2H), 3.23 (s, 6H), 4.13 (q, *J* = 6.6 Hz, 1H), 4.33 (s, 4H), 4.71 (s, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 36.7, 40.3, 54.2, 62.0, 173.5; carbon cage: 67.0, 69.1, 140.6, 140.8, 140.9, 142.0, 142.2, 142.3, 142.8, 142.9, 143.1, 144.5, 144.6, 144.8, 148.6, 148.7, 149.1, 149.4, 149.5, 149.9, 152.3, 152.4, 157.0, 159.2, 159.5; HRMS (MALDI$^+$, matrix: DCTB) *m/z* calcd. for $C_{73}H_{26}N_3O_4^+$:1008.1918, found 1008.1922 ([M+H]$^+$)

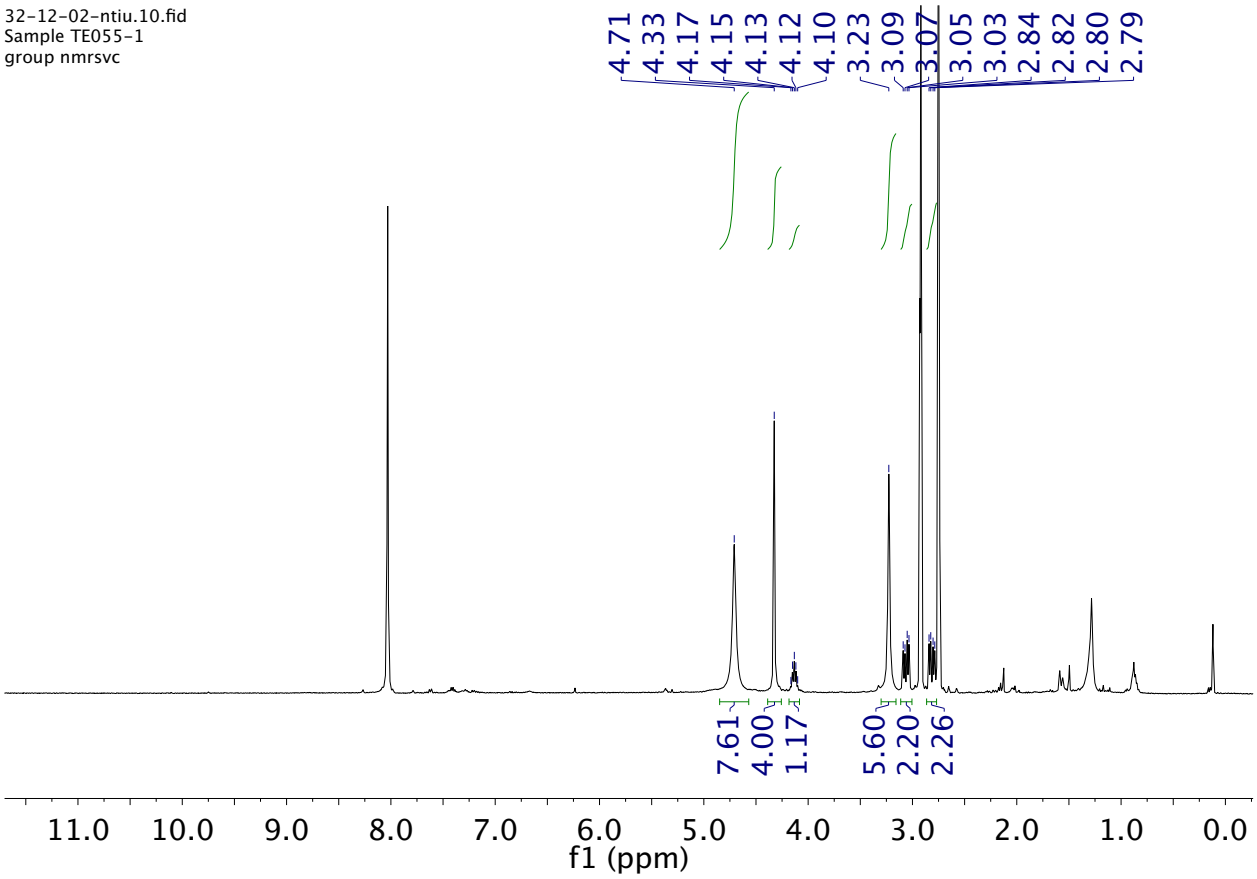


Figure S25. ^{1}H-NMR of **S3** (400 MHz, in $CDCl_3$).

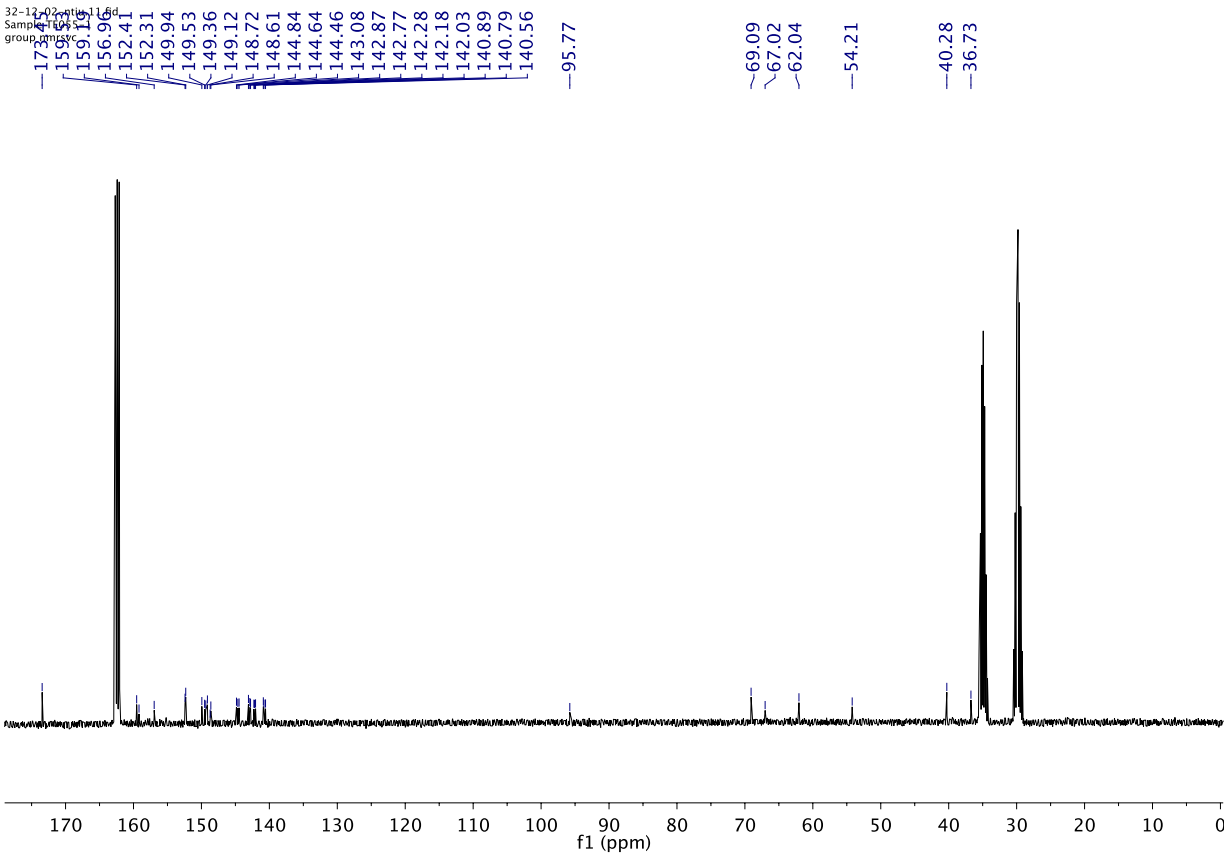


Figure S26. ^{13}C-NMR of **S3** (101 MHz, $CDCl_3$)**.**

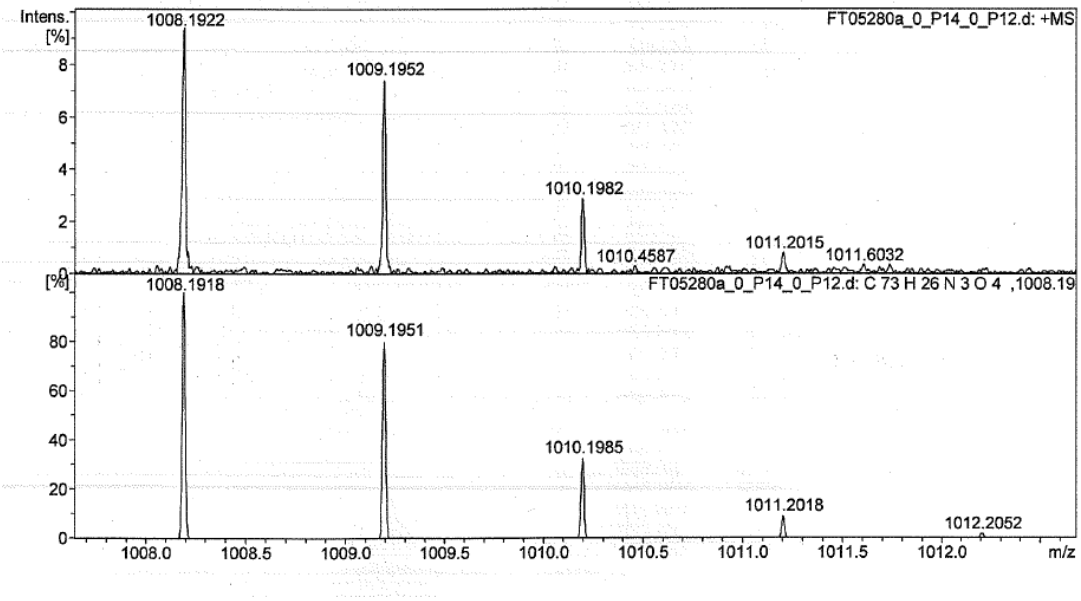


Figure S27. HRMS of **S3** (MALDI$^+$, matrix: DCTB)**.**

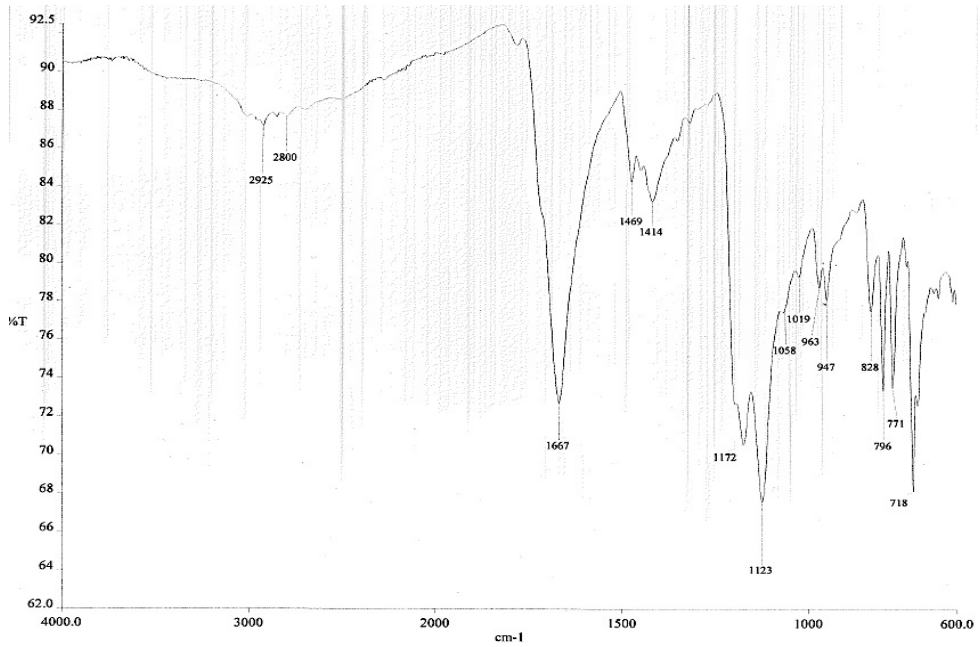
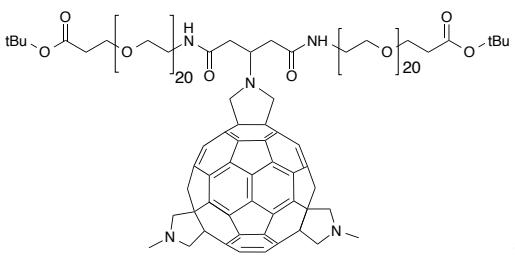


Figure S28. IR spectrum of **S3.**



S4.

Synthesis of S4. To a solution of **S3** (3.7 mg, 3.0 μmol) in DMF (distilled, 0.28 mL), HBTU (8.2 equiv, 9.3 mg, 24.5 μmol), Amino-dPEG$_{20}$-^{t}Bu ester (3.1 equiv, 9.6 mg, 9.3 μmol), DIPEA (14 equiv, 5.6 mg, 7.5 μL, 43 μmol) were added and reaction mixture was 24 h at room temperature. The solvent was removed under vacuum and water (2.5 mL) was added. The crude mixture was purified by HPLC (column: Phenomenex C4 Φ10 x 250 mm, solvent: CH_3CN-H_2O (5 : 95 to 88 : 12 (5 min), 88 : 12 to 95 : 5 (11 min), 95 : 5 to 5 : 95 (3 min)), flow rate: 3 mL/min, detection: 370 nm, retention time of **S4**: 9 min) the collected fraction was freeze-dried to provide a sticky red material **S4** (2.4 mg, 0.81 μmol, 27%); IR (ATR) ν_{max} (cm^{-1}): 3210 (m), 2879 (w), 1678 (s), 1469 (m), 1427 (m), 1348 (m), 1197 (s), 1128 (s), 949 (w), 831 (w), 799 (m), 720 (m), 674 (w), 647 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 18H), 2.49 (t, J = 6.6 Hz, 4H), 3.63 (m, 160H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 28.2, 36.4, 40.0, 45.1, 67.0, 70.7, 80.6, 171.0; carbon cage: 68.3 70.5, 115.0, 117.9, 140.8, 141.9, 142.8, 143.0, 143.9, 144.4, 144.5, 148.2, 148.8, 149.01, 149.05, 149.15, 149.2, 149.6, 152.4, 152.5, 161.2, 161.5, 161.9, 163.1; HRMS (MALDI^{+}, DCTB) *m/z* calcd. for $C_{167}H_{211}N_5O_{46}Na^{+}$: 3045.42, found: 3045.42 ([M+Na]$^{+}$.)

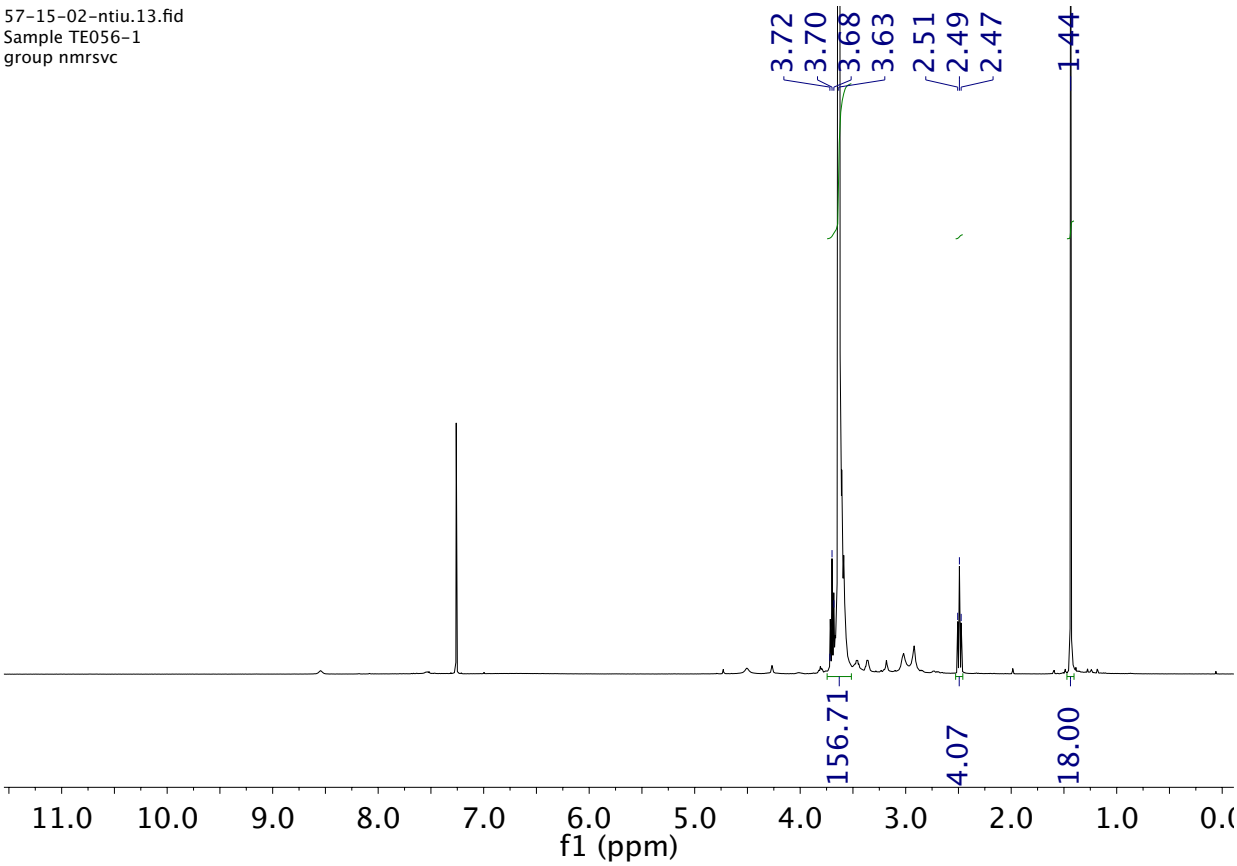


Figure S29. ^{1}H-NMR of **S4** (400 MHz, in $CDCl_3$).

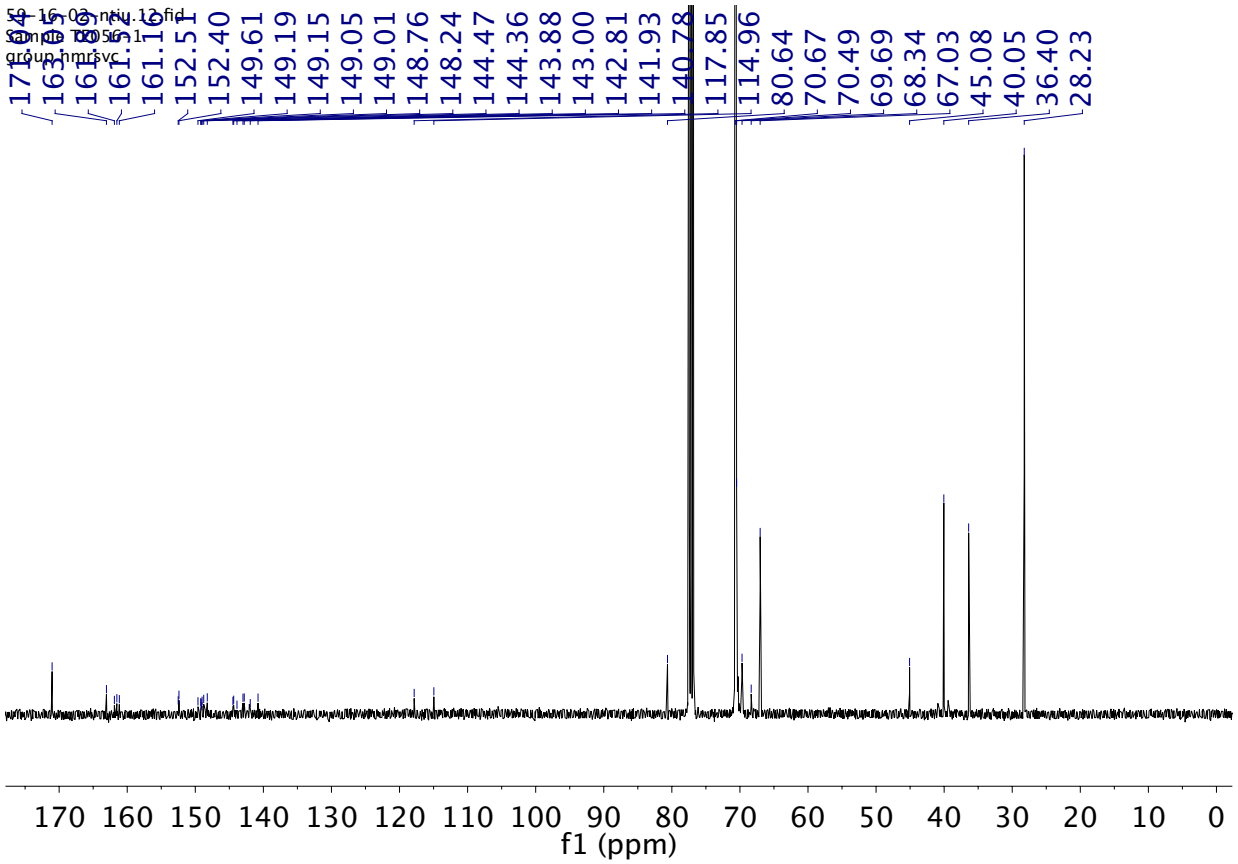


Figure S30. ^{13}C NMR of **S4** (100 MHz, in $CDCl_3$).

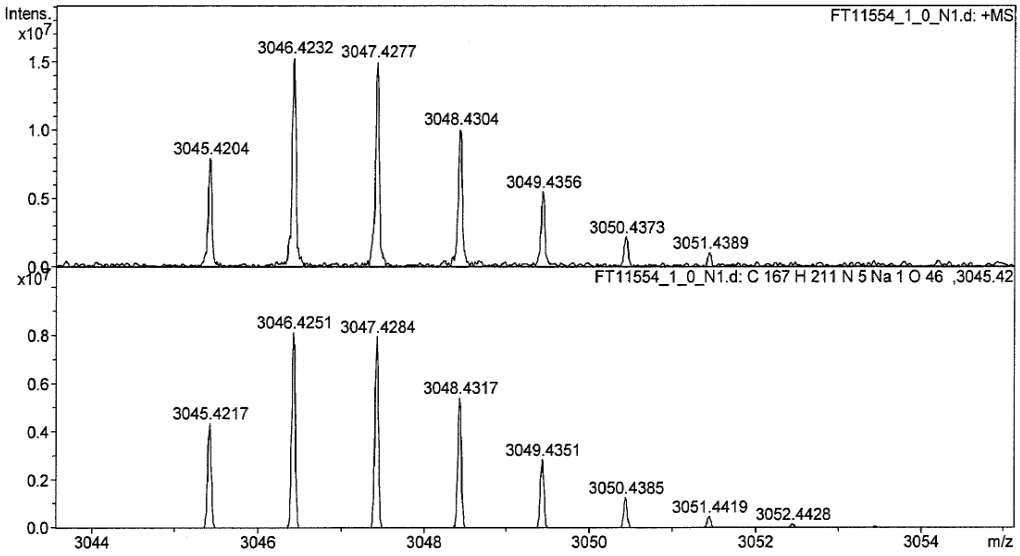


Figure S31. HRMS of **S4** (MALDI$^+$, DCTB).

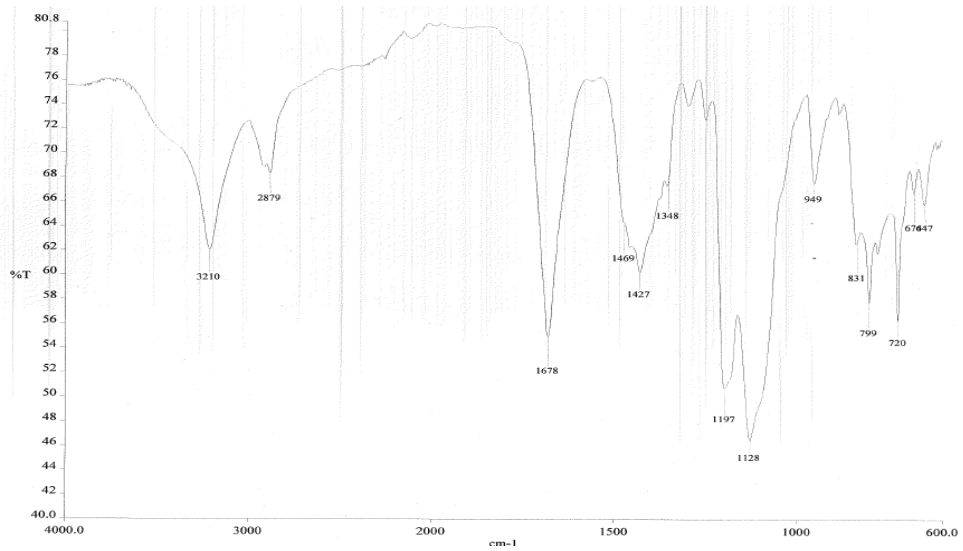
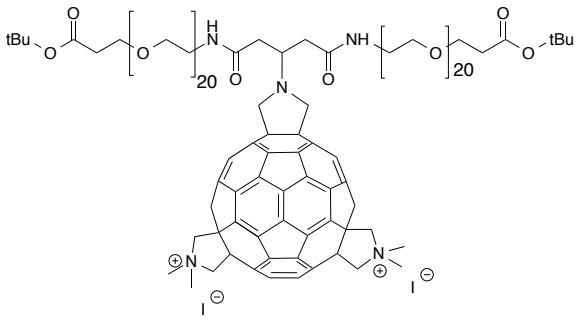


Figure S32. IR spectrum of **S4.**



3

Synthesis of 3. To a solution of **S4** (2.5 mg, 0.8 μmol) in dry DMF (1.0 mL) CH_3I (1.0 mL) was added. The reaction mixture was stirred at room temperature for 4 h. Subsequently the solvent and reagent were removed by rotary evaporator, and the residue was washed with hexane and diethyl ether and the product was dried under vacuum to give a red material **3** (2.5 mg, 0.7 μmol, 88%); IR (ATR) ν_{max} (cm^{-1}): 2873 (m), 1725 (w), 1266 (w), 1101 (s), 949 (w), 730 (m); ^{1}H NMR (300 MHz, DMF-d_7) δ 1.44 (s, 18H), 2.47 (t, J = 6.2 Hz, 4H), 2.87 (t, J = 5.2 Hz, 8H), 3.08 (s, 12H), 3.58 (m, 160H); ^{13}C NMR (150 MHz, DMF-d_7) δ 28.6, 37.2, 40.1, 40.5, 45.8, 53.6, 67.7, 67.9, 69.0, 70.2, 70.3, 70.7, 71.12, 71.17, 71.2, 71.3, 71.4, 73.8, 80.8, 171.7, 172.14; carbon cage: 141.2, 141.7, 141.9, 142.7, 143.00, 143.03, 143.21, 143.23, 143.7, 144.6, 148.7, 148.8, 150.1, 151.0, 153.1, 153.4, 154.2, 154.7, 156.4, 157.2, 158.4, 160.6; HRMS (MALDI$^+$, matrix: CCA) *m/z* calculated for $C_{169}H_{217}O_{46}N_5^+$: 3053.4868, found: 3053.4867 ($[M+H]^+$).

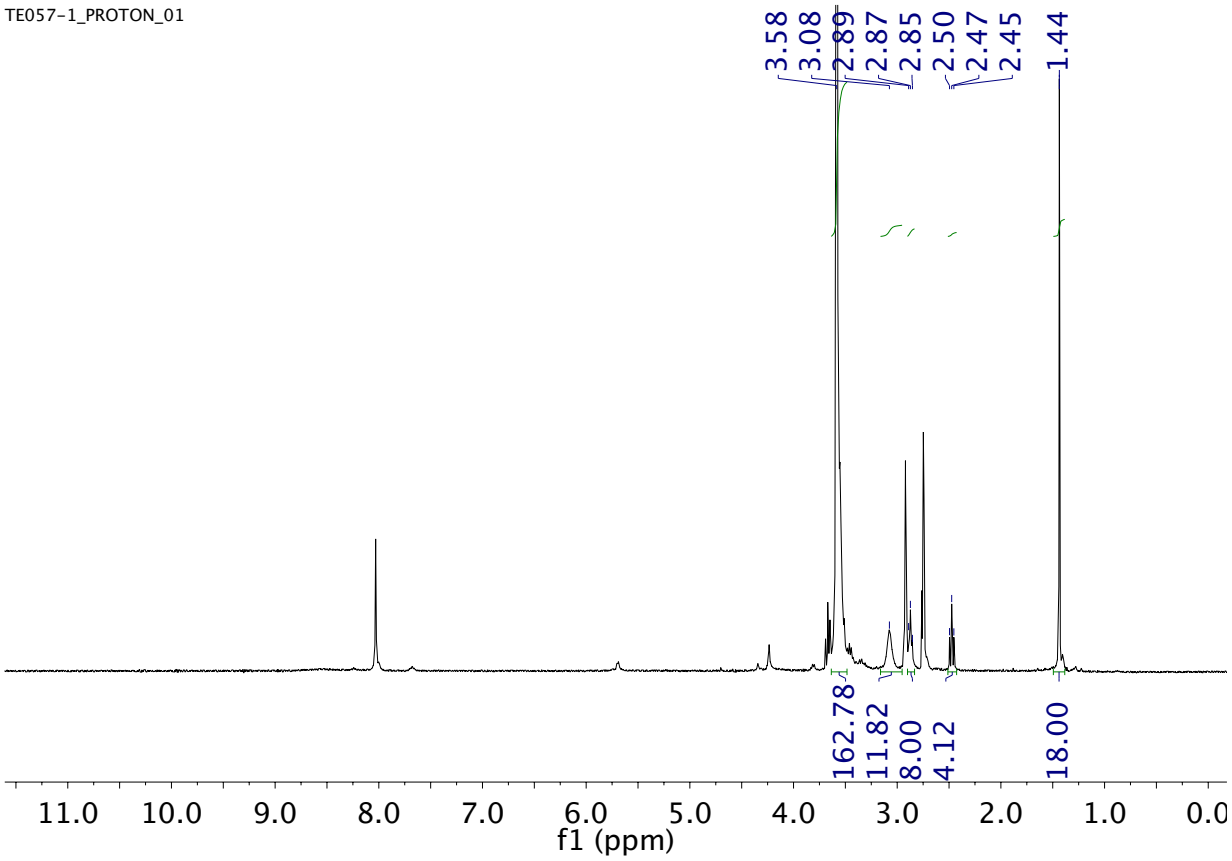


Figure S33. ^{1}H NMR of **3** (300 MHz, DMF-d_7).

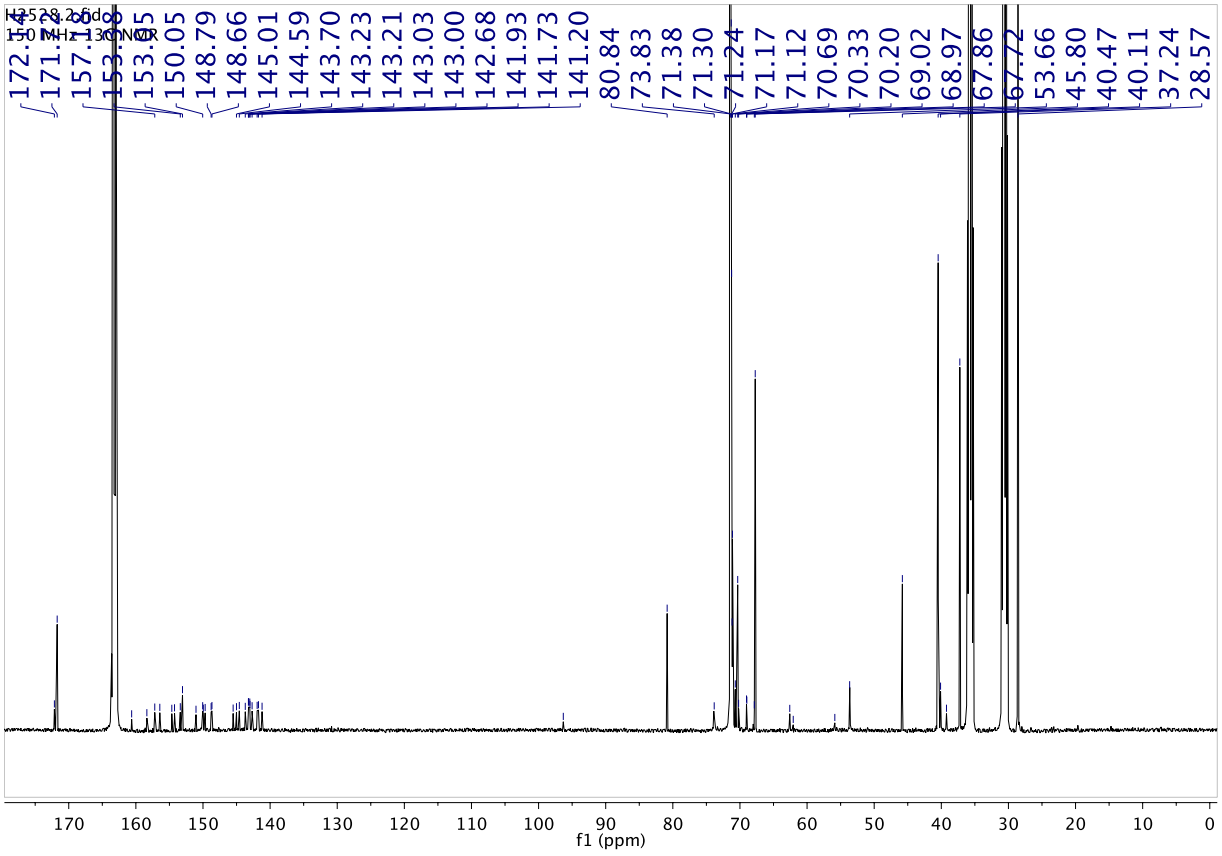


Figure S34. ^{13}C NMR of **3** (150 MHz, in DMF-d_7).

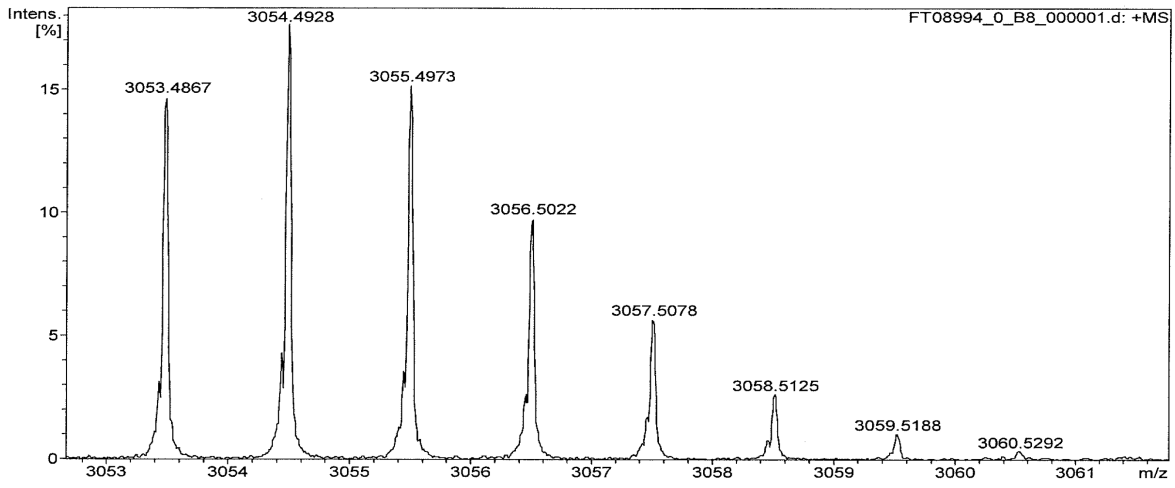


Figure S35. HRMS of **3** (MALDI$^+$, CCA).

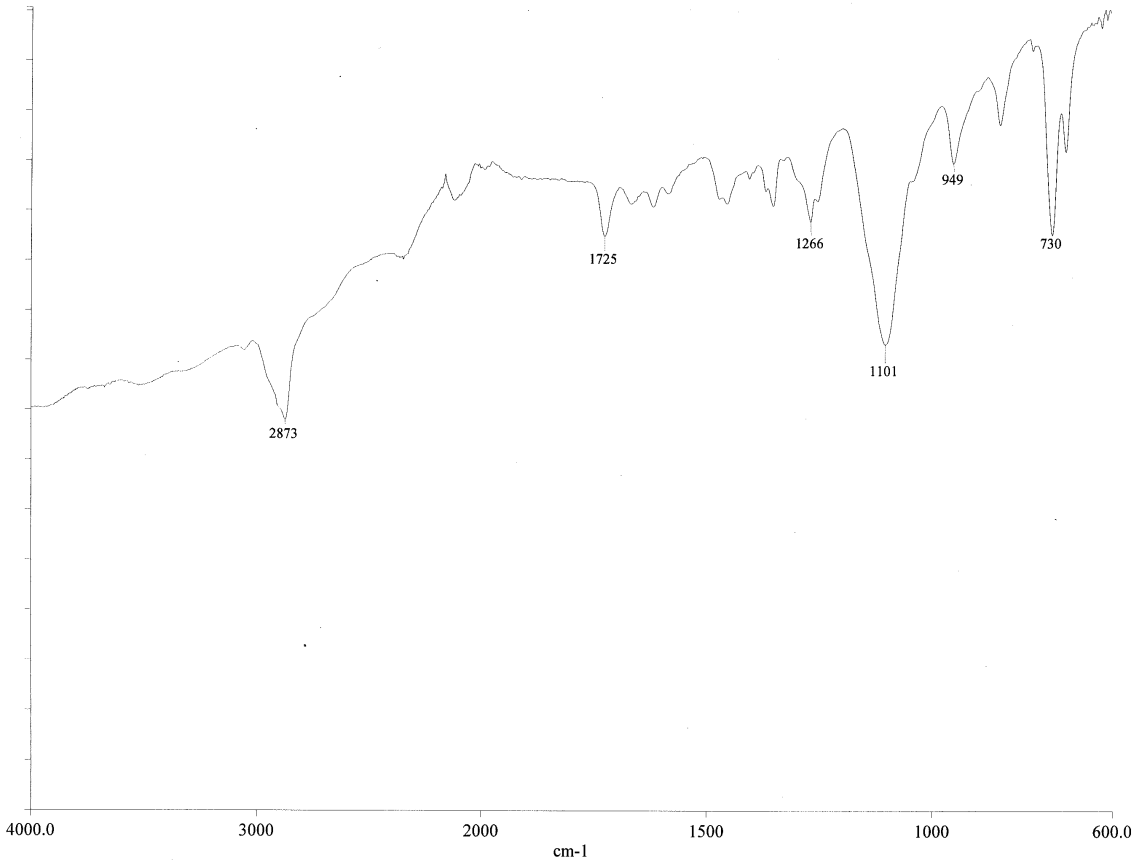


Figure S36. IR spectrum of **3.**

2.Characterization of 1-3.

2.1 Surface tension measurement

The interfacial tensions of the aqueous solutions of **1**, **2**, and **3** in a series of concentrations ($1x10^{-3}$ M to $3x10^{-7}$ M) were measured by pendant drop device (DSA100, Krüss GmbH, Germany). A water/air interface was produced at the tip of an inverted J-shaped, stainless steel needle (diameter 1.451 mm). A drop shape analysis system subsequently imaged with a CCD camera as a function of time was used to carry out the measurements. The droplet profile was detected automatically using the analysis software package DSA3 (Krüss). The Laplace–Young equation was fitted to the profile to obtain the interfacial tension as a function of time.

2.2 Dynamic Light Scattering (DLS)

Aqueous solutions of **1**, **2**, and **3** at 1 mM concentration were prepared and measured. Dynamic light scattering measurements were performed using Zetasizer Nano (Malvern, Malvern Worsc, U.K.) and a glass cuvette. Z-averages of the radii [nm] obtained for compounds **1**, **2** and **3** are summarized in Table I.

Table SI. Z-average (radius) of compounds **1-3**

Temperature	Z-average [nm]		
	Compound **1**	Compound **2**	Compound **3**
5 °C	5.67	37.06	85.48
10 °C	5.48	37.16	83.38
20 °C	5.38	36.91	81.78
30 °C	5.73	41.50	78.73
40 °C	6.20	3384.5	87.62
50 °C	14.09	3666.67	140.37
60 °C	666.67	2722.33	144.18
70 °C	687.17	2031.33	137.10
80 °C	648.5	2353.83	140.38

In addition, DLS measurements of compound **1-3** in aqueous solution were carried out before and after repeated thermal treatment. After initial DLS measurement at 20 °C, each aqueous solution was heated up to 80 °C and subjected again to DLS measurement. Subsequently, the each sample was cooled down to 20 °C and again heated up to 80 ºC. This cycle was repeated for three times and DLS data were shown in Figure S37.

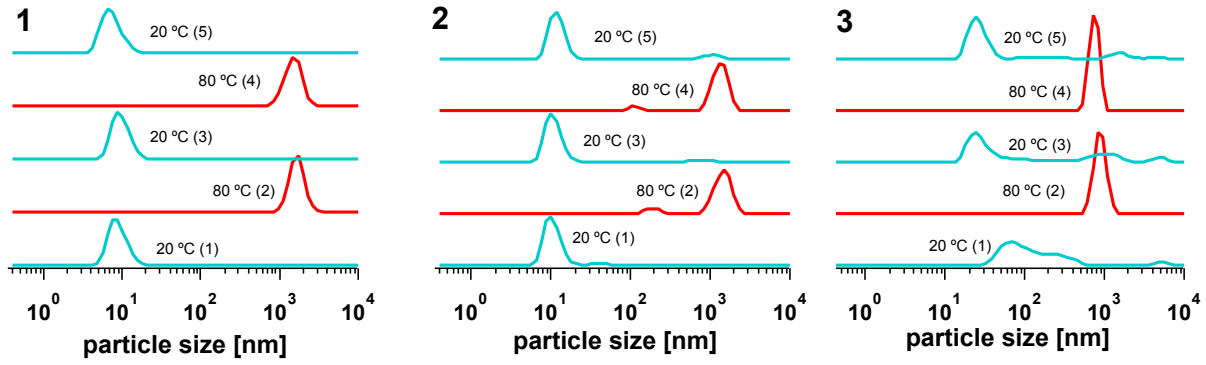


Figure S37. The effect of repeated thermal treatment of compounds **1**-**3** in aqueous solution (1 mM) by DLS analyses. The DLS of each sample was measured at lower (20 °C) and higher (80 °C) temperatures for three repeated cycles.

2.3 Scanning Transmission Electron Microscopy (STEM)

The morphological and elemental distribution analyses of assemblies in different states were carried out by transmission electron microscopy (TEM) on a FEI Talos F200X (FEI Coorporate, Hillsboro, OR, USA) instrument operated at 200kV in both, TEM and STEM, scanning transmission electron microscopy, modes. An atomic number sensitive, high angle annular dark field (HAADF) detector was used for STEM imaging. The elemental content analyses were carried out in an STEM mode with a probe size of about 0.8 nm by employing a SuperX EDX system consisting of 4 SDD detectors and used in the hypermap and line profile modes. Specimen preparation for TEM/STEM studies was performed immediately prior a TEM session. A drop of a particle suspension was placed on a graphene (monolayer) covered conventional Ni-grid. After that the suspension was left to dry out in air or in vacuum (10^{-2} mbar) for about an hour. The later yielded considerably reduced contamination rate during scanning in STEM. Samples were prepared in ca. 3 mM aqueous solution.

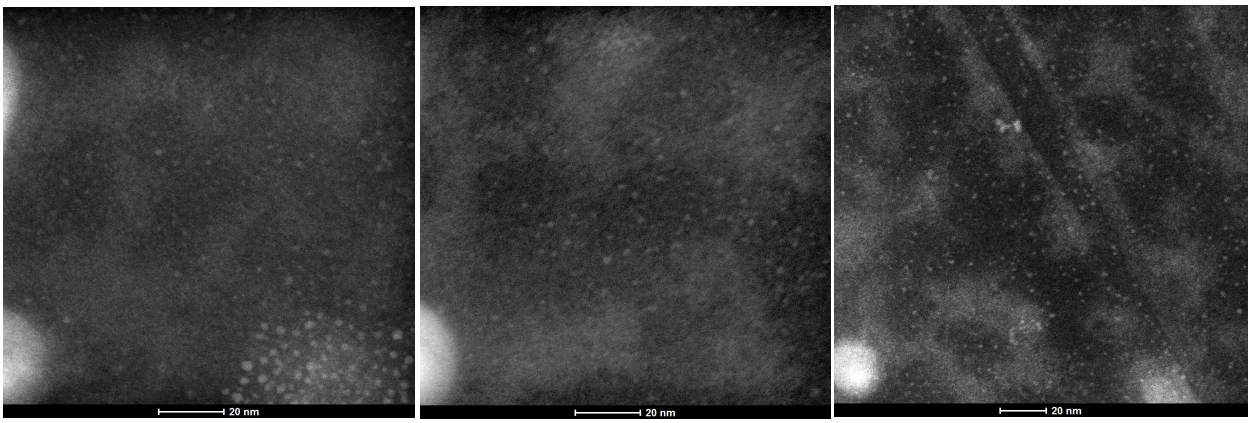


Figure S38. STEM images of **1** at 3 mM concentration. Sample was air-dried before measurement.

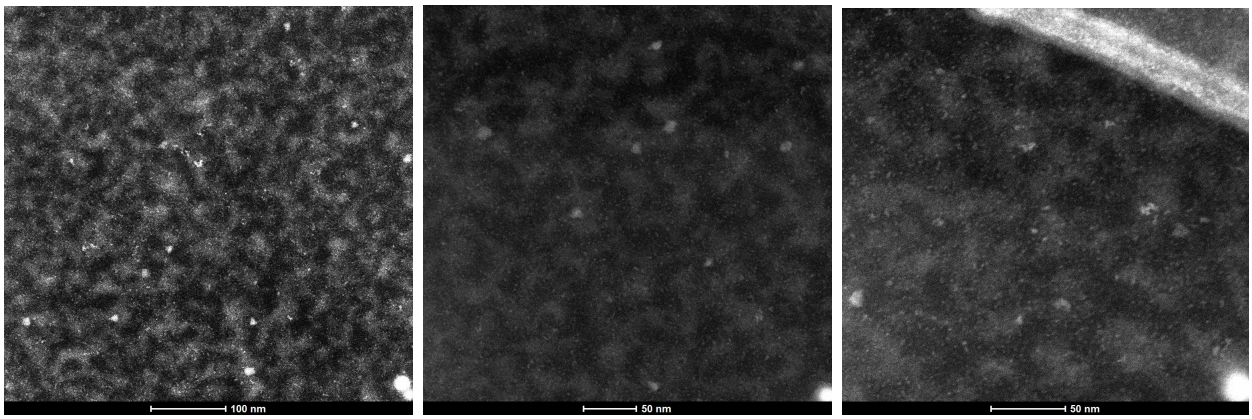


Figure S39. STEM images of **1** at 3 mM concentration. Sample was vacuum-dried before measurement.

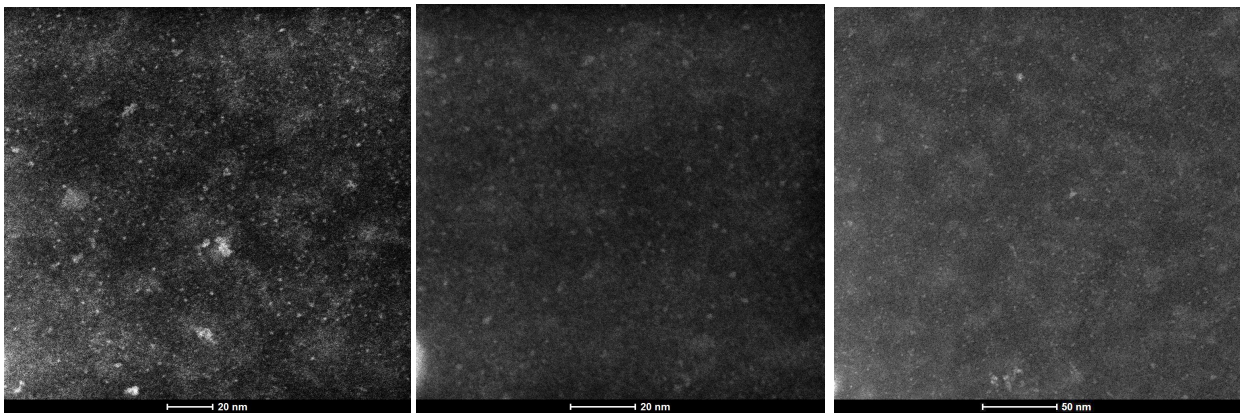


Figure S40. STEM images of **2** at 3 mM concentration. Sample was air-dried before measurement.

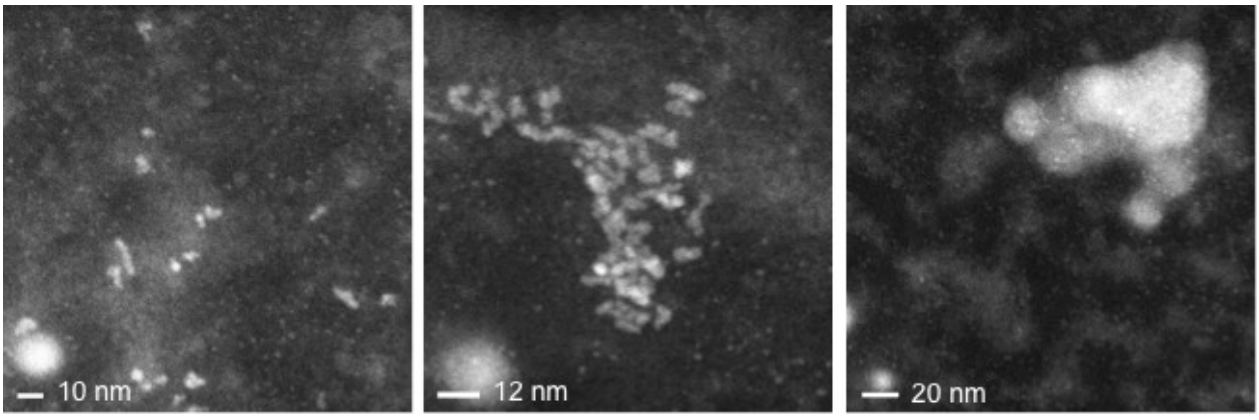


Figure S41. STEM images of **2** at 3 mM concentration. Sample was vacuum-dried before measurement.

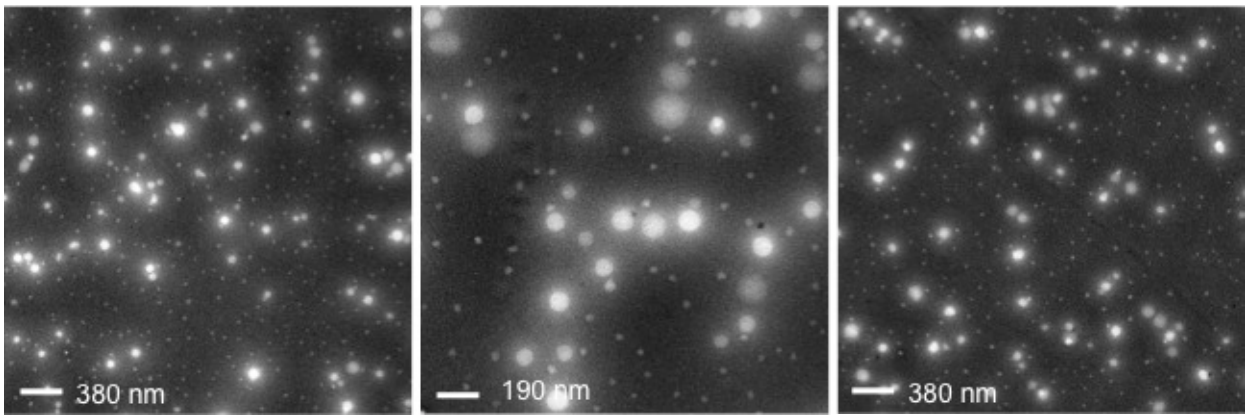


Figure S42. STEM images of **3** at 3 mM concentration. Sample was air-dried before measurement.

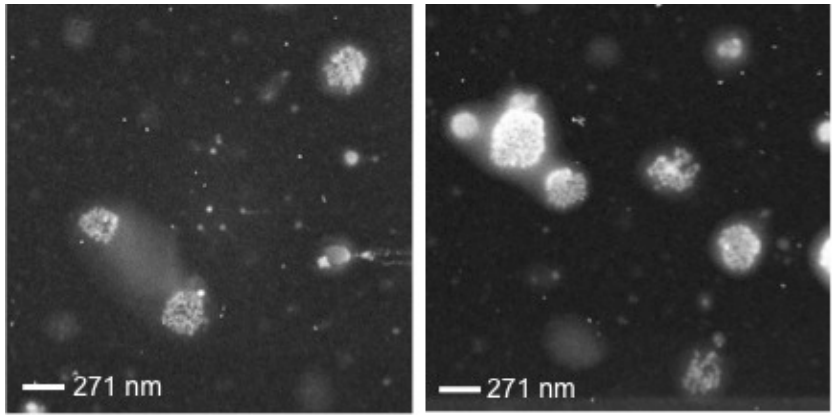


Figure S43. STEM images of **3** at 3 mM concentration. Sample was vacuum-dried before measurement.

2.4 Repeated thermal treatment of aqueous solution 1-3 detected by OD_{800}

Each aqueous solution of **1, 2, or 3** (1 mM) or $CH_3CONH\text{-}EG_n\text{-}CO^tBu$ (2 mM) as treated under thermal condition (from 20 ºC to 80 ºC) repeatedly while OD_{800} was measured for each time.

2.5 ROS generation from 1-3 under photoirradiation

2.5.1 Superoxide radical anion ($O_2\bullet^-$)

The 5-(Diethoxyphosphoryl)-5-methyl-1-pyrrolidine-*N*-oxide (DEPMPO) was used as a spin trapping agent for the detection of superoxide. Aqueous solution (0.5 mM) of **1**, **2** or **3** (40 μL), 5 mM of DETAPAC in 250 mM phosphate buffer (20 μL), water (8 μL), 625 mM DEPMPO in DMSO (22 μL), 100 mM NADH (10 μL) were mixed well and were collected in a capillary. Each

sample was placed inside an ESR tube and was irradiated with a 200-W lamp, then was subjected to ESR measurement.

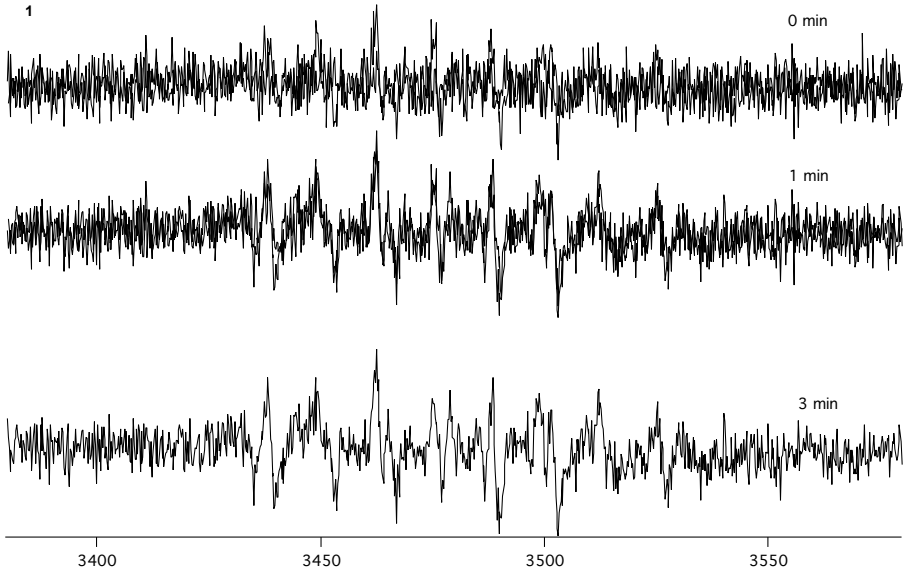


Figure S44. X-band ESR spectra of DEPMPO adduct with superoxide generated in aqueous solution of **1** under 0 min (top), 1 min (middle), and 3 min (bottom) light irradiation. Experimental conditions used: temperature 296 K, microwave frequency 9.790 GHz, microwave power 10 mW, receiver gain 5.0 x10^4, modulation amplitude 1.00 G, modulation frequency 100 kHz, sweep time 84 sec.

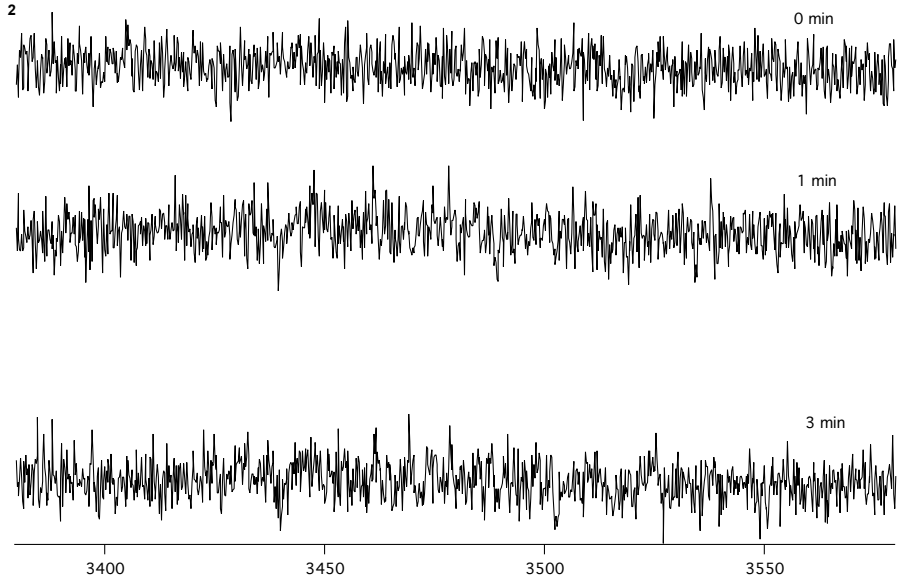


Figure S45. X-band ESR spectra of DEPMPO adduct with superoxide generated in aqueous solution of **2** under 0 min (top), 1 min (middle), and 3 min (bottom) light irradiation. Experimental conditions used: temperature 296 K, microwave frequency 9.790 GHz, microwave power 10 mW, receiver gain 5.0 x10^4, modulation amplitude 1.00 G, modulation frequency 100 kHz, sweep time 84 sec.

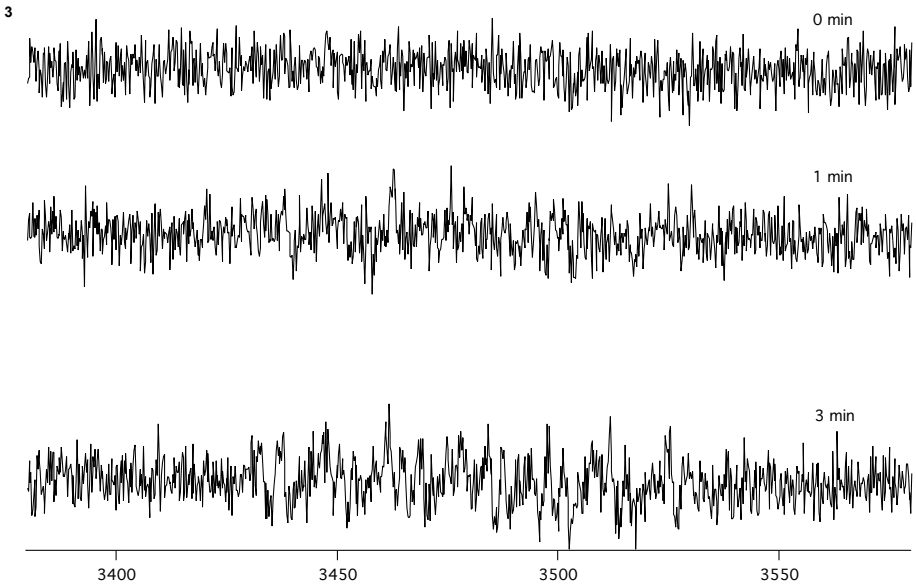


Figure S46. X-band ESR spectra of DEPMPO adduct with superoxide generated in aqueous solution of **3** under 0 min (top), 1 min (middle), and 3 min (bottom) light irradiation. Experimental conditions used: temperature 296 K, microwave frequency 9.790 GHz, microwave power 10 mW, receiver gain 5.0 x10^4, modulation amplitude 1.00 G, modulation frequency 100 kHz, sweep time 84 sec.

2.5.2 Singlet Oxygen (1O2)

Singlet oxygen was detected using 2,2,6,6-tetramethyl-4-piperidone (4-oxo-TEMP) as a spin trapping agent. Aqueous solutions (0.5 mM) of fullerene materials **1**, **2** or **3** (40 μL), 250 mM phosphate buffer (20 μL), water (32 μL), 1 M 4-oxo-TEMP (8 μL) were mixed well and were collected in a capillary. The filled capillary was placed inside an ESR tube and was irradiated with a 200-W lamp. Each sample was placed inside an ESR tube and was irradiated with a 200-W lamp, then was subjected to ESR measurement.

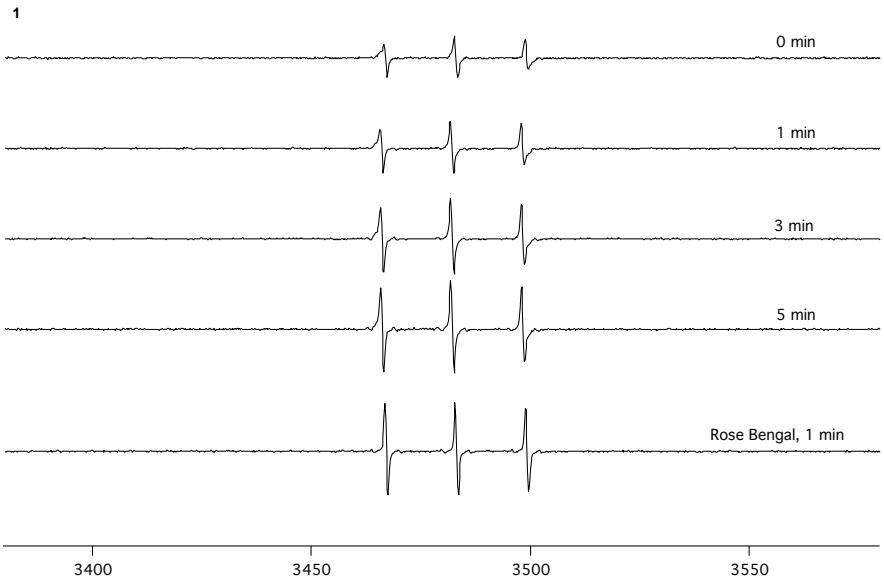


Figure S47. X-band ESR spectra of 4-oxo-TEMPO adduct with singlet oxygen generated in aqueous solution of **1** under 0 min (top), 1 min (second), 3 min (third), and 5 min (fourth) light irradiation. Rose Bengal was irradiated in 1 min as reference. Experimental conditions used: temperature 296 K, microwave frequency 9.790 GHz, microwave power 10 mW, receiver gain 5.0 x10^4, modulation amplitude 1.00 G, modulation frequency 100 kHz, sweep time 84 sec.

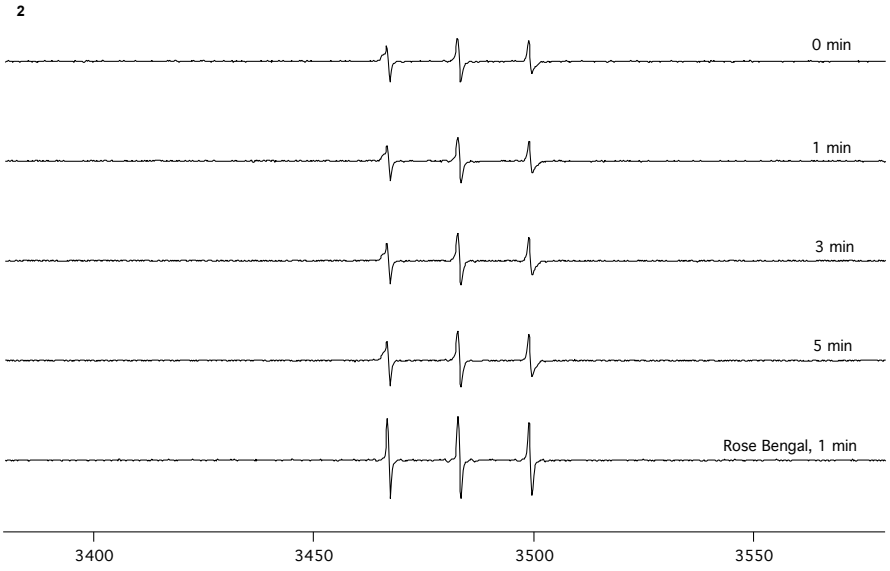


Figure S48. X-band ESR spectra of 4-oxo-TEMPO adduct with singlet oxygen generated in aqueous solution of **2** under 0 min (top), 1 min (second), 3 min (third), and 5 min (fourth) of light irradiation. Rose Bengal was irradiated in 1 min as reference. Experimental conditions used: temperature 296 K, microwave frequency 9.790 GHz, microwave power 10 mW, receiver gain 5.0 x10^4, modulation amplitude 1.00 G, modulation frequency 100 kHz, sweep time 84 sec.

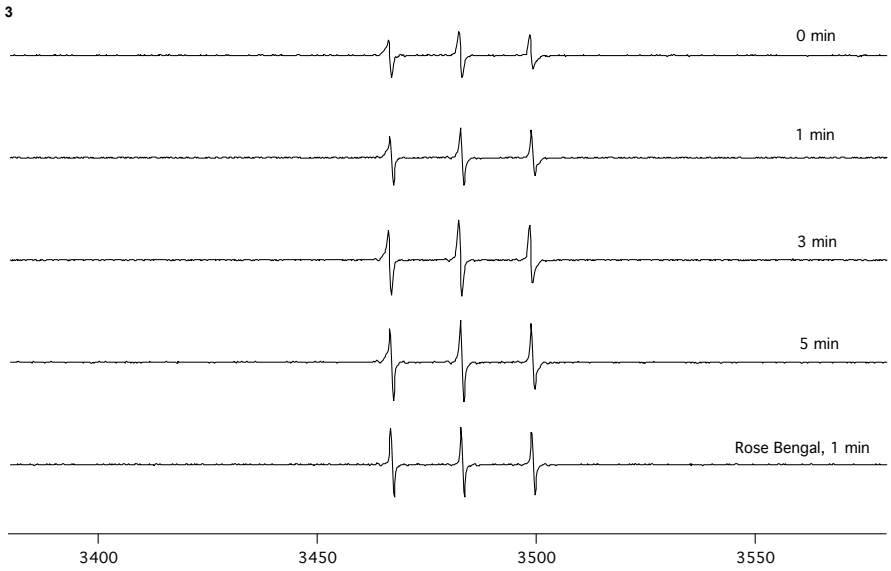


Figure S49. X-band ESR spectra of 4-oxo-TEMPO adduct with singlet oxygen generated in aqueous solution of **3** under 0 min (top), 1 min (second), 3 min (third), and 5 min (fourth) light irradiation. Rose Bengal was irradiated in 1 min as reference. Experimental conditions used: temperature 296 K, microwave frequency 9.790 GHz, microwave power 10 mW, receiver gain 5.0 x10^4, modulation amplitude 1.00 G, modulation frequency 100 kHz, sweep time 84 sec.