Supporting Information

Water-Soluble Nanorods Self-Assembled *via* Pristine-C_{60} and Porphyrin Moieties

Maher Fathalla,[a] Shao-Chun Li,[b] Ulrike Diebold,[b]Alina Alb,[b] and Janarthanan Jayawickramarajah[a]*

[a] *Department of Chemistry, Tulane University, 2015 Percival Stern Hall, Louisiana 70118, USA.*
[b] *Department of Physics, Tulane University, 2001 Percival Stern Hall, Louisiana 70118, USA.*

General Experimental. All chemicals were purchased from Sigma-Aldrich or Acros Organics and solvents were purchased from Fischer Scientific. NMR spectra were recorded on Varian 400 MHz spectrometer using CD_3Cl as solvent, mass spectra were performed at the BioAnalytical Mass Spectrometry Facility at Georgia Institute of Technology. MALDI-TOF spectra were recorded on Bruker Autoflex3 Matrix Assisted Laser Desorption Ionization-Time of Flight Mass Spectrometer (MALDI-TOF MS), using 2,5-dihydroxybenzoic acid (DHB) or α-cyano-4-hydroxycinnamic acid as matrices. IR spectra were recorded on Thermo Electron Nicolet 8700 FT-IR spectrometer and UV-vis studies were undertaken using a Hewlett Packard 8452A Diode Array Spectrophotometer. TEM experiments were performed on a Joel 2011 Transmission Electron Microscope Instrument. SEM measurements were recorded on Hatchi S-4800 Scanning Electron Microscope (accelerating voltage=200 kV). STM experiments were carried out in an ultrahigh vacuum (UHV; base pressure ~1×10^{-10} mbar) chamber, with an Omicron STM operated at room temperature (RT). Thermogravimetric analyses (TGA) were performed on TGA 2950 instrument; samples (2 mg) were heated at 10^{o} C/min from room temperature to 700^{o}C under a nitrogen atmosphere. Melting points were recorded on MEL-

TEMP II (Laboratory Devices Inc., USA) instrument. Dynamic light scattering (DLS): Particle size was measured using a Brookhaven 90-Plus detector (l=670nm) operating at a scattering angle of 90°, at room temperature. Particle hydrodynamic diameter, D_h (the intensity-weighted average diameter) was determined based on the Stokes-Einstein relation for hydrodynamic radius derived from the intensity autocorrelation function,[1] expanded in terms of cumulants.[2] Note: the concentrations of the nanorods were prepared by matching the Soret band absorption of the nanorod solutions to those of separate solutions of monomer porphyrin **4** (i.e. assembly **6** concentrations noted in the text are the concentrations of porphyrin **4** within assembly **6**).

Synthesis of 3,5-dipropargyloxybenzaldehyde (1).

Propargyl bromide (1.3 mL, 12 mmol, 80% solution in toluene) was slowly added to a suspension of 3,5-dihydroxybenzaldehyde (700 mg, 5 mmol) and K_2CO_3 (2.07 g, 15 mmol) in 40 mL of acetone. The reaction mixture was then refluxed under argon for 6 hrs. After cooling to room temperature, water (100 mL) and dichloromethane (100 mL) were added to the reaction. Subsequently the organic layer was isolated and the aqueous layer was extracted a second time with another aliquot of dichloromethane (100 mL). The organic layers were combined and dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude residue was purified on a silica column, using petroleum ether/ethyl acetate (3/1) as the eluent, to afford **1** as yellow solid (1 gm, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.85 (s,1H), 7.06 (s,2H), 6.80 (s,1H), 4.67 (s,4H), 2.50 (s,2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 56.0, 76.1, 77.6, 108.6, 108.8, 138.2, 159.0 , 191.4. HR-MS (FAB): m/z= 215.0707 $(M+H)^+$, Calcd for $C_{13}H_{11}O_3$ (215.0708); m.p=55 °C.

Synthesis of 5,10,15,20-tetrakis(3,5-dipropargyloxyphenyl)porphyrin (2).

A solution of **1** (0.9 g, 4.2 mmol) in propionic acid (100 mL) was heated till reflux, upon which time freshly distilled pyrrole (0.3 mL, 4.2 mmol) was slowly added. The reaction mixture was maintained under reflux for 3 hr. Subsequently the propionic acid solvent was evaporated under reduced pressure and triethylamine (1 mL) was then added to the resultant residue. After complete evaporation of the solvent, the crude residue was purified on a silica column using dichloromethane as eluent to yield **2** as a purple solid (140 mg, 13%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.93 (s,8H), 7.50 (s,8H), 7.05 (s,4H), 4.84 (s,16H), 2.58 (s,8H), -2.89 (s,2H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ= 56.7, 76.7, 78.9, 102.7, 109.3, 109.4, 115.8, 119.9, 144.5, 157.3. MALDI TOF-MS: m/z= 1047.4 $(M+H)^+$, ESI: m/z = 1047.3 $(M+H)^+$. HR-MS (FAB) m/z= 1046.3309 (M^+), Calcd for $C_{68}H_{46}N_4O_8$ (1046.3316). UV-vis (CH_2Cl_2): 420 (ε 514 500 dm^3 mol^{-1} cm^{-1}), 514 (61 600), 550 (34 426), 588 (15 935), 644 (9790); m.p= 167-170 ^{o}C.

Synthesis of 5,10,15,20-tetrakis(3,5-dipropargyloxyphenyl)-Zn-porphyrin(3).

To a solution of **2** (120 mg, 0.114 mmol) in chloroform (30 mL), was added a solution of zinc acetate (0.20 g, 1.1 mmol) in methanol (3 mL). The mixture was stirred at room temperature for 3 hr and then was washed with water and dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure to give **3** as a purple solid quantitatively. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.02 (s,8H), 7.49 (s,8H), 7.04 (s,4H), 4.83 (s,16H), 2.58 (s,8H); ^{13}C NMR (100MHz, $CDCl_3$): δ= 56.4, 76.3, 78.6, 102.3, 107.9, 115.4, 120.6, 132.2, 144.9, 150.1, 156.8. MALDI TOF-MS: m/z= 1108.3 (M^+), ESI: (m/z 1131.2, M+Na)$^+$. HR-MS (FAB) m/z= 1108.2429 (M^+), Calcd for $C_{68}H_{44}N_4O_8Zn$ (1108.2451). UV-vis (CH_2Cl_2): 420 (ε 528 000 dm^{-3} mol^{-1} cm^{-1}), 548 (23 000), 582 (6315); m.p= 117-120°C.

Synthesis of octa-(permethylated-β-cyclodextrin)-Zn-porphyrin (4).

To a solution of **3** (120 mg, 0.108 mmol) and 6-azido-6-deoxy-permethyl-β-cyclodextrin[3] (1.85 g, 1.29 mmol; i.e., 1.5 eq. per each alkyne group on **3**) in THF (20 mL), was added sodium ascorbate (85 mg, 0.43 mmol). $CuSO_4$ (21 mg, 0.086 mmol) was dissolved in water (1mL) and was added to the reaction. The reaction vessel was then charged with argon, sealed, and left to stir at 40°C for 48hr. Subsequently, the solvents were removed *in vacuo* and the crude product was purified *via* flash chromatography using methylene chloride eluent to afford **4** as a purple solid. (0.9 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.99 (s,8H), 7.81 (s,8H), 7.47 (br s,8H), 7.04 (s,4H), 5.28 (s,16H), 5.23-5.00 (m,56H), 4.82 (m,8H), 4.06-3.14 (m, the rest of PMβ-CDs protons ca. 808H). MALDI TOF-MS: Calcd for $C_{564}H_{916}N_{28}O_{280}ZnNa$ (Theoretical = 12648.759) g/mol), Found=12650.771. UV-vis (CH_2Cl_2): 422 (ε 650 993 dm^{-3} mol^{-1} cm^{-1}), 548 (40 666), 598 (10 075); m.p= 160-163°C.

Preparation of assembly 6.

Assembly **6** was prepared by modification of a previously reported method that maximizes the solubility of fullerene as well as the formation of 2:1 β-CD-C_{60} interactions.[4] Specifically, assembly **6** was prepared by stirring a mixture of porphyrin **4** (63 mg, 0.005 mmol) and fullerene C_{60} (21 mg, 0.03 mmol) in 20 mL of toluene/DMF (4:6 (v:v)) solvent for three weeks at room temperature. After evaporating the solvents, the crude product was dissolved in water and purified by filtration through a fine pores sintered glass filter to remove insoluble fullerene. Subsequent evaporation of water from the filtrate afforded assembly **6** (50 mg).

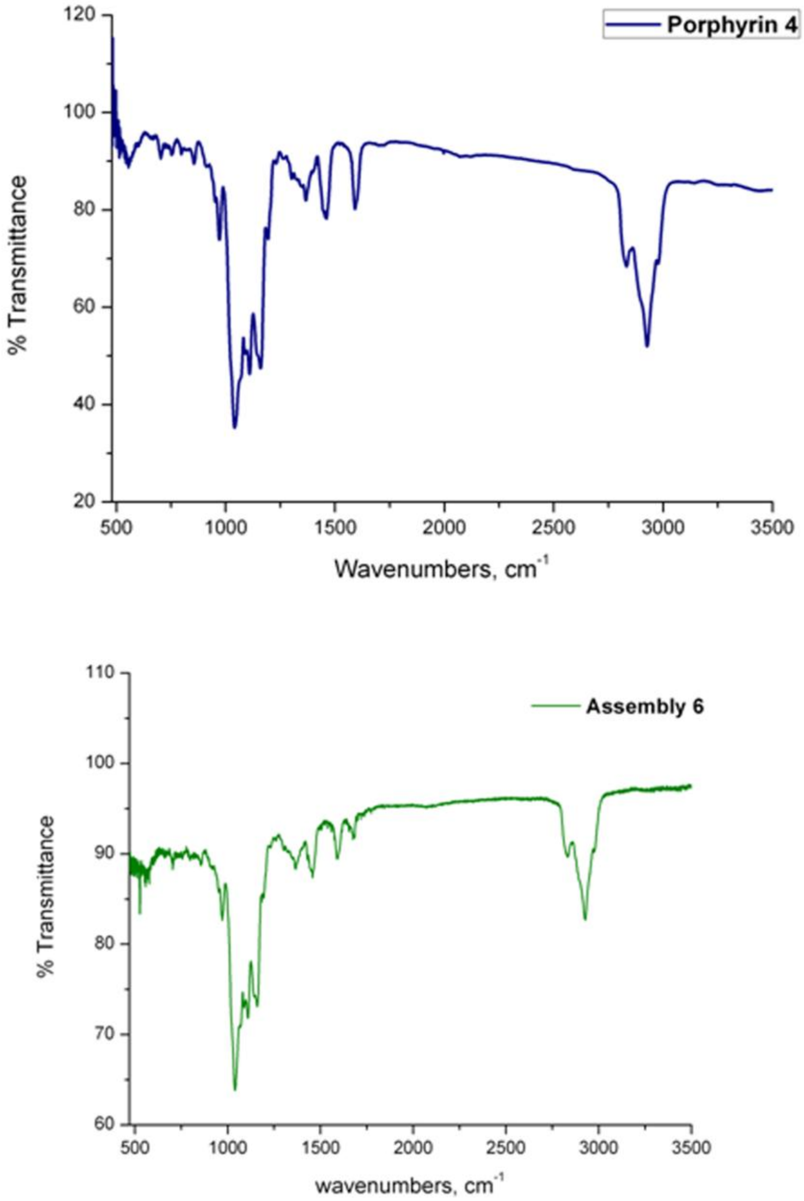

Figure S1. IR spectra of porphyrin **4** (top) and assembly **6** (bottom). Note the sharp peak at 527 cm^{-1} which is a characteristic fullerene vibrational mode.[5]

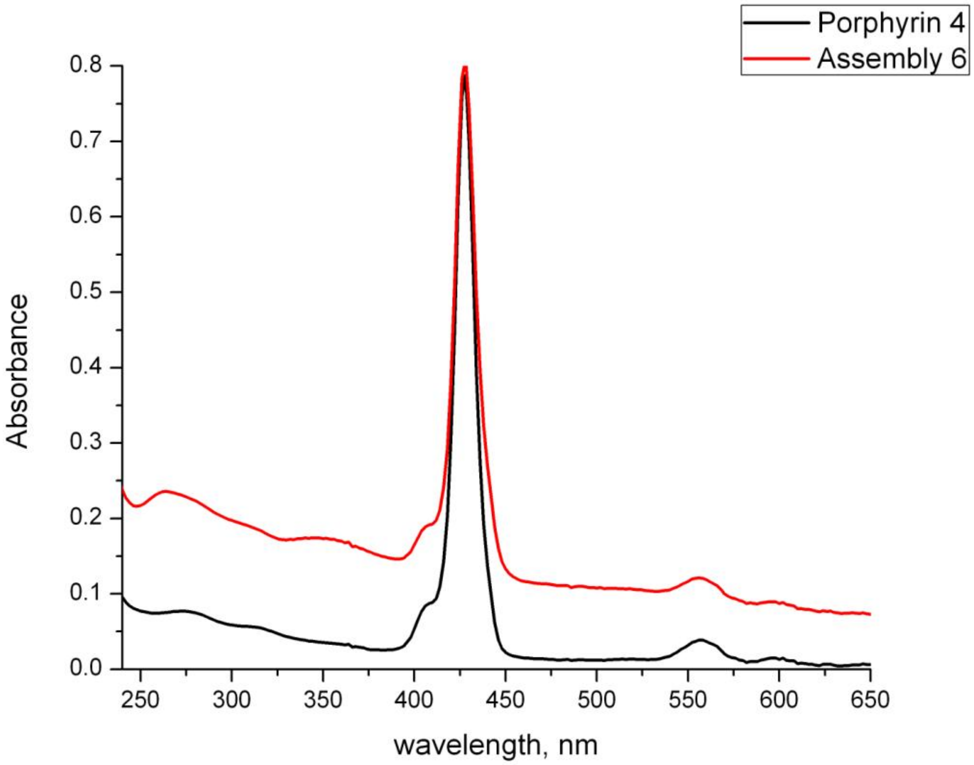

Figure S2. Electronic absorption spectra of porphyrin **4** (black line) and assembly **6** (red line) in water. Concentrations are 3×10^{-6} M.

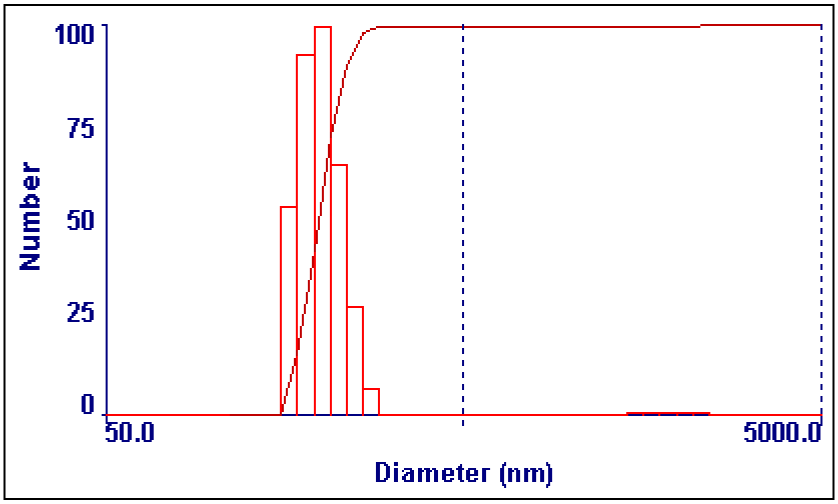

Figure S3. Multi-size distribution from dynamic light scattering measurements for assembly **6** (0.3×10^{-6} M) in water. The intensity-weighted average particle diameter was D_h=263nm and broad particle distribution was observed.

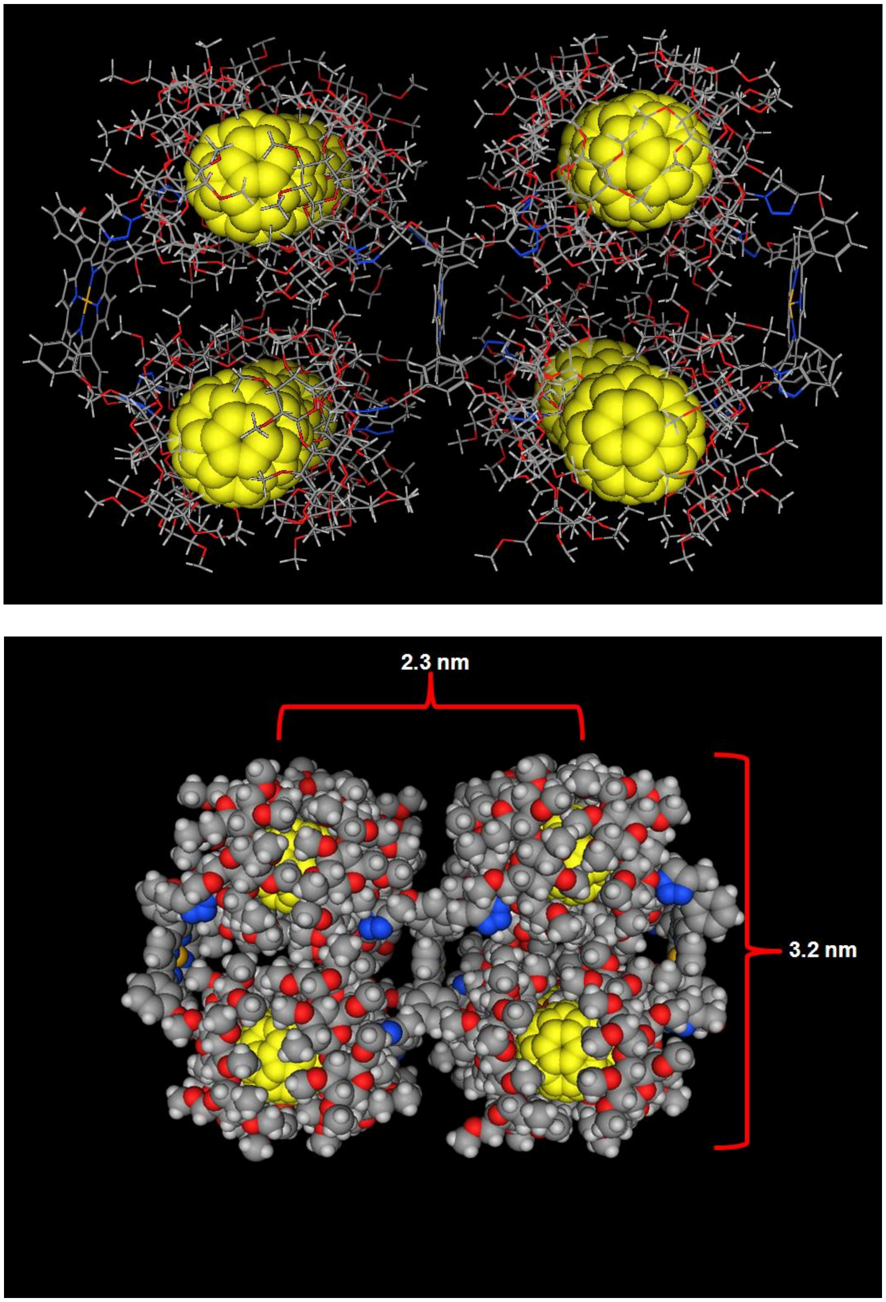

Figure S4. A representative illustration of assembly **6** made up of three molecules of porphyrin **4** encasing a total of eight fullerenes (shown in yellow). Note: the PMβ-CD arms projecting on the outside faces of the two flanking molecules of **4** have been omitted for clarity. This model was energy minimized (AMBER94 forcefield) using the MOE software. The periodicity and the height are close (albeit slightly larger) to the values observed by STM measurements (cf. Figure 3 in the main text).

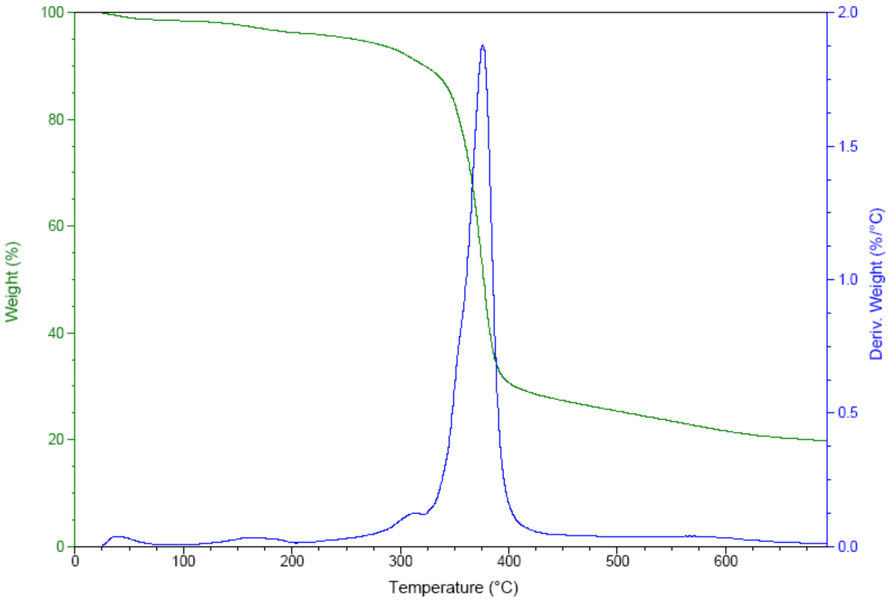

Figure S5. Thermogravimetric curve for porphyrin **4**.

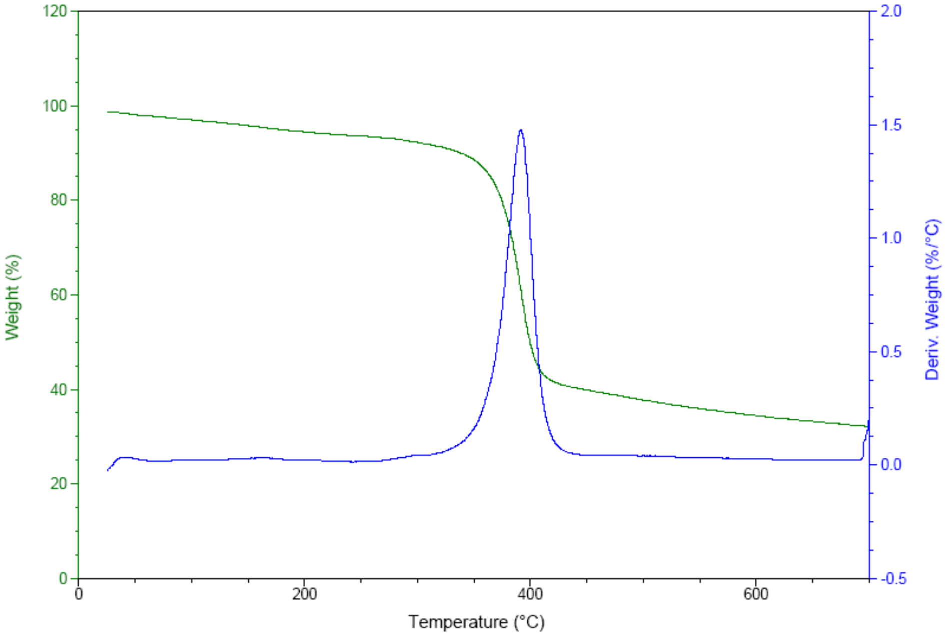

Figure S6. Thermogravimetric curve for assembly **6**.

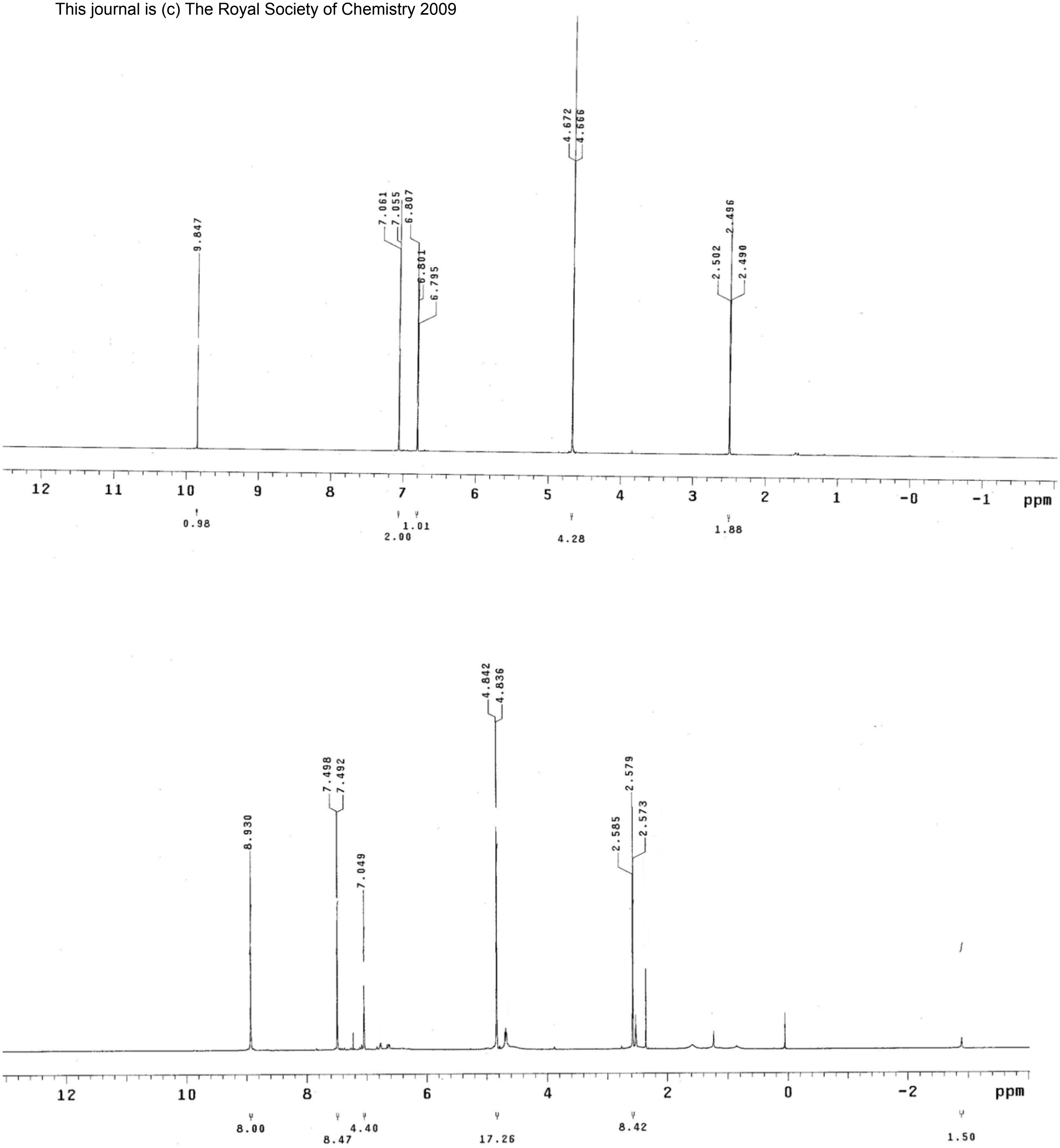

Figure S7: ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of aldehyde **1** (top), and porphyrin **2** (bottom).

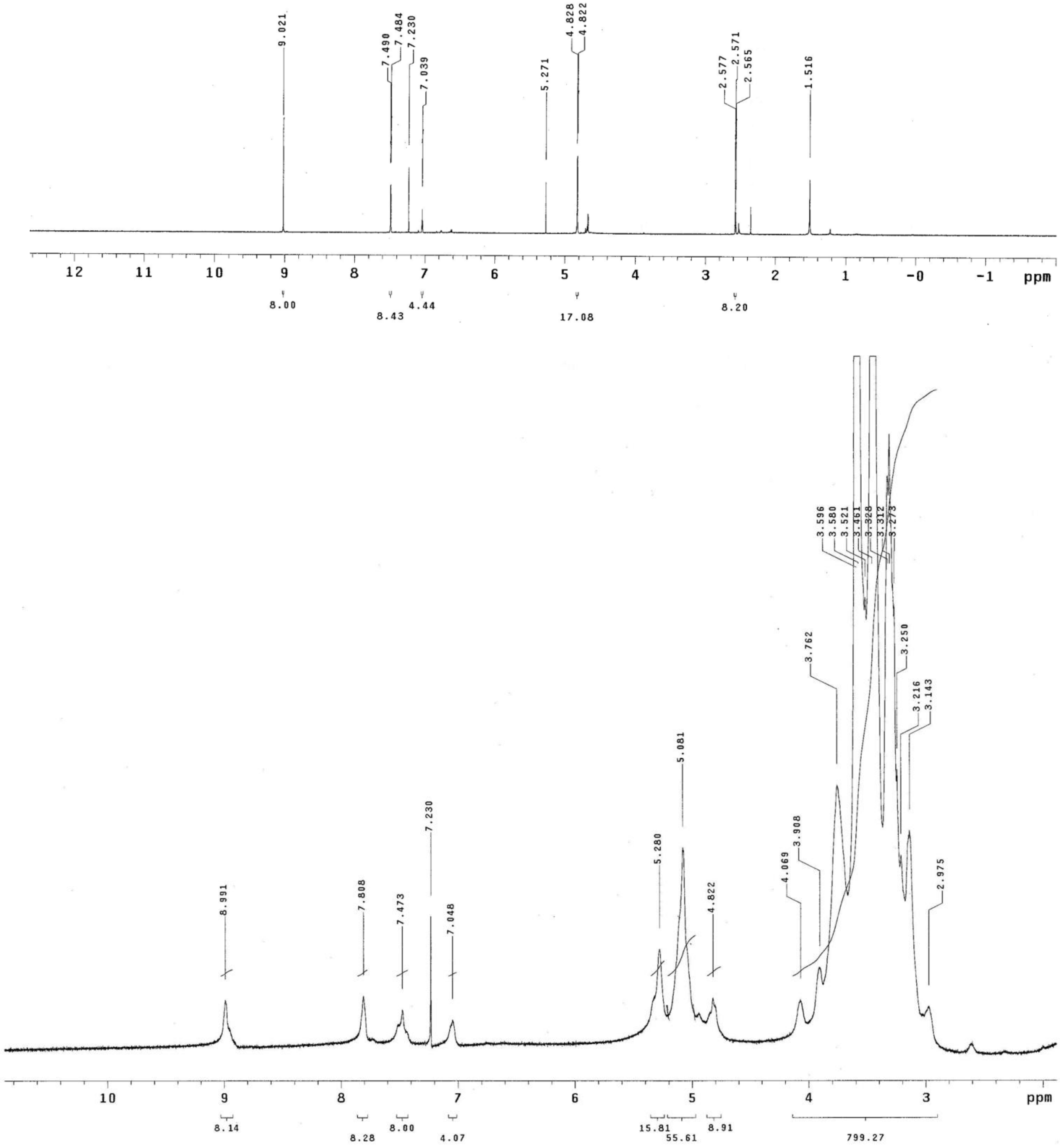

Figure S8: ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of porphyrin **3** (top), and porphyrin **4** (bottom). Note that the integrations of the triazole protons (at 7.81 ppm) and that for β-pyrrole protons (at 8.99 ppm) are equal confirming the formation of eight triazole rings from the click reaction. In addition, the integrations of the CD protons implied the formation of octa-CD substituted porphyrin (i.e., porphyrin **4**).

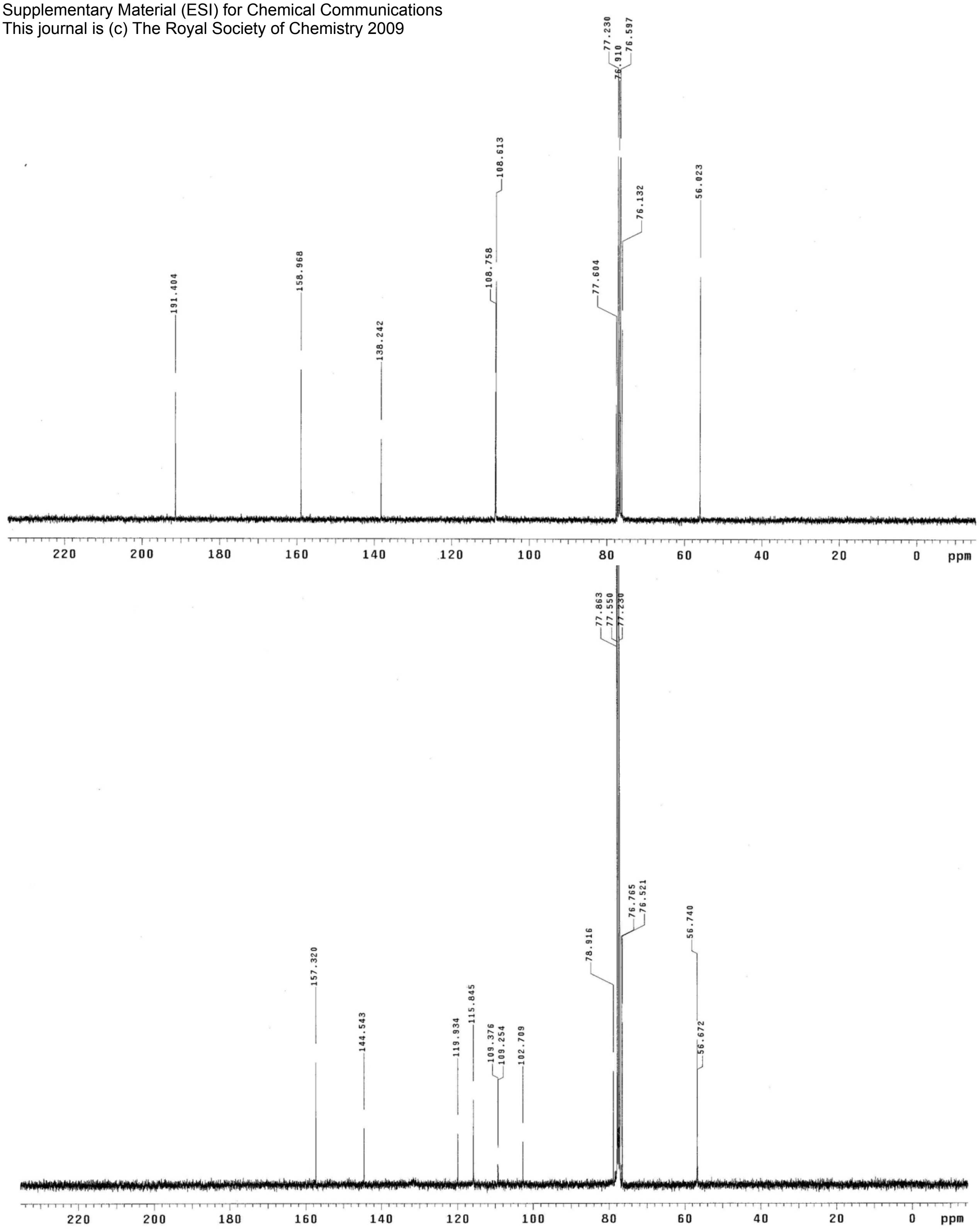

Figure S9. ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of aldehyde **1** (top), and porphyrin **2** (bottom).

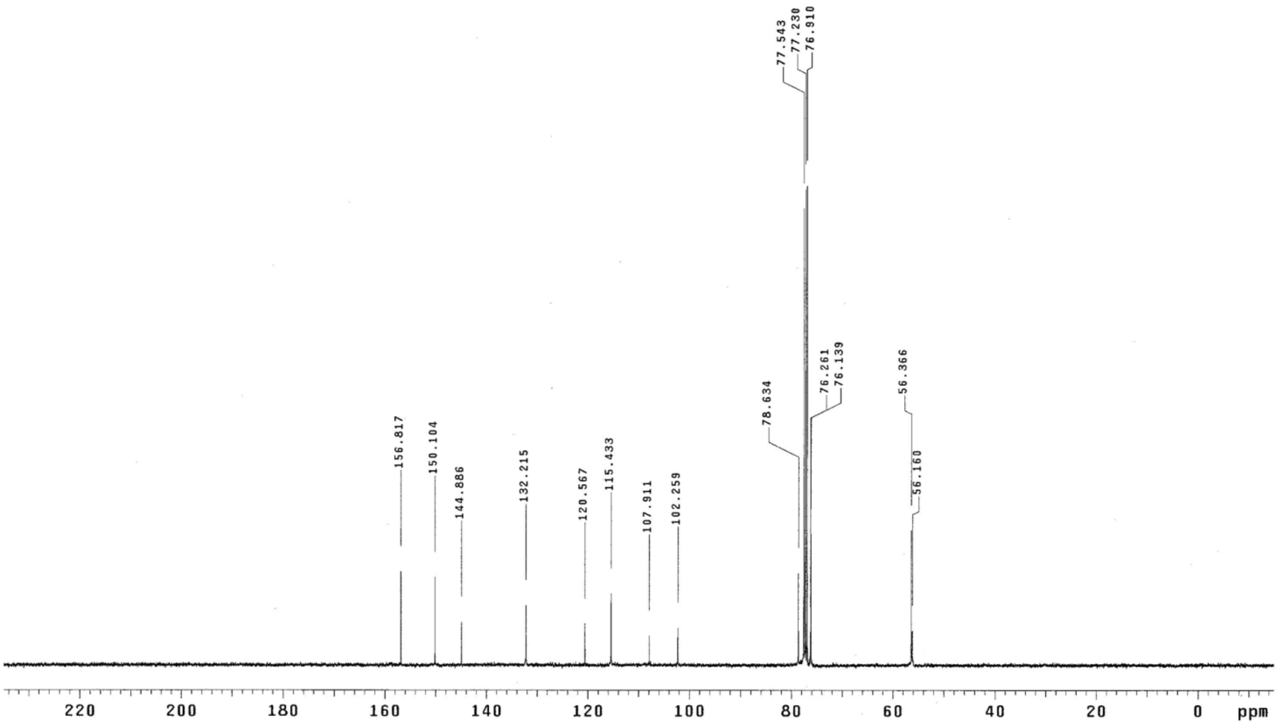

Figure S10. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of porphyrin **3**.

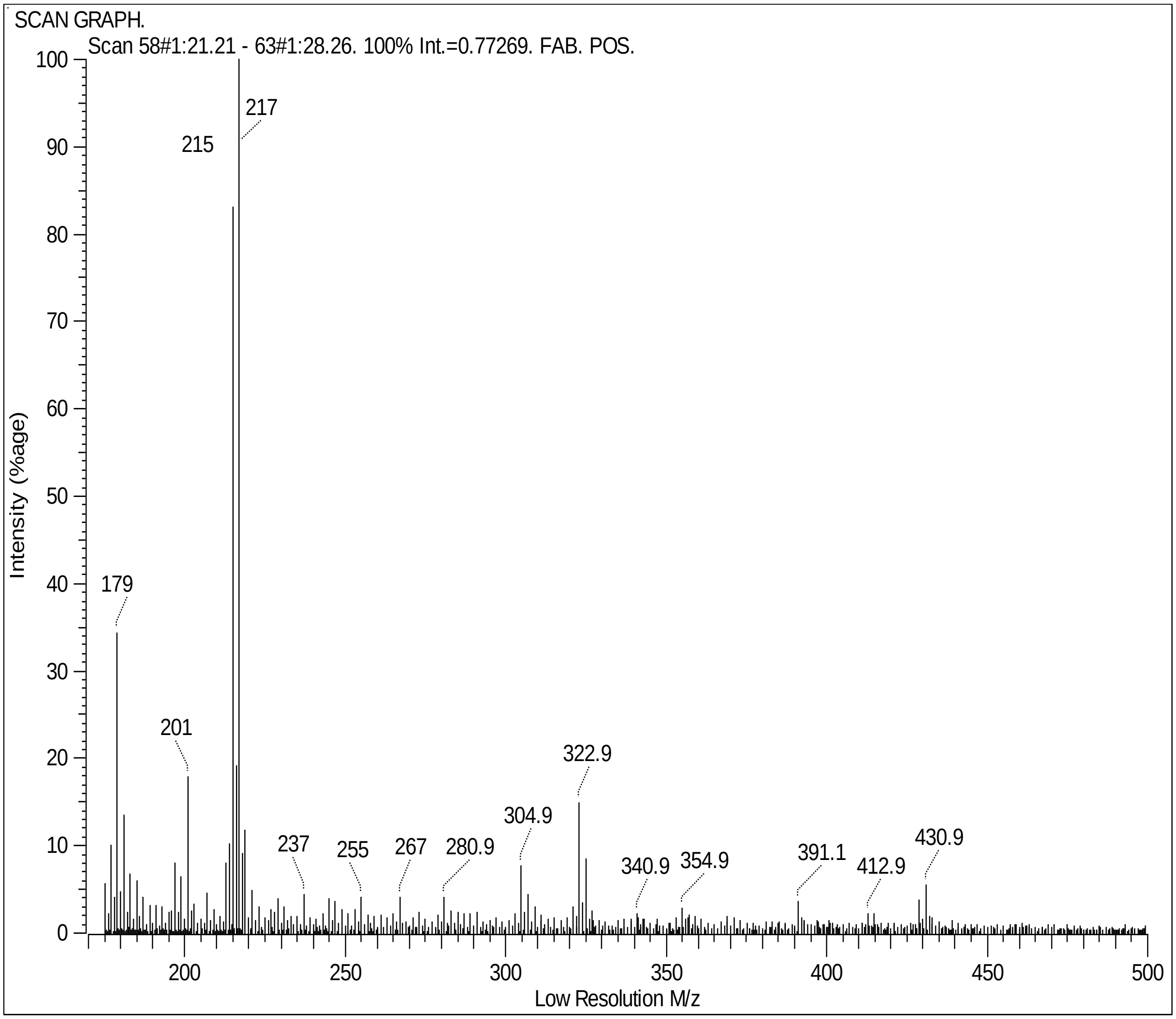

Figure S11. FAB-MS spectrum of aldehyde **1**.

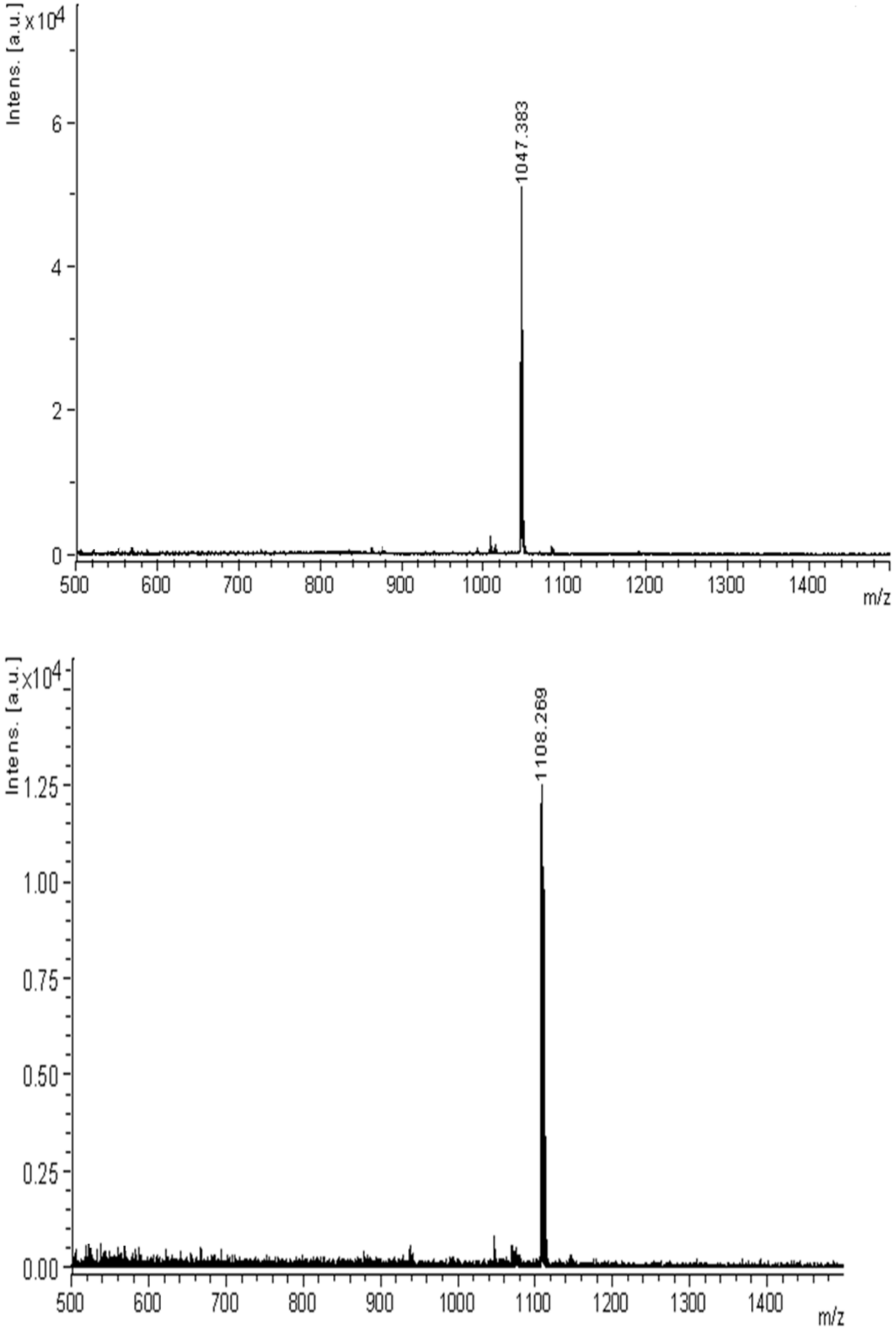

Figure S12. MALDI TOF-MS (α-cyano-4-hydroxycinnamic acid matrix) spectra of porphyrin **2** (top), and porphyrin **3** (bottom).

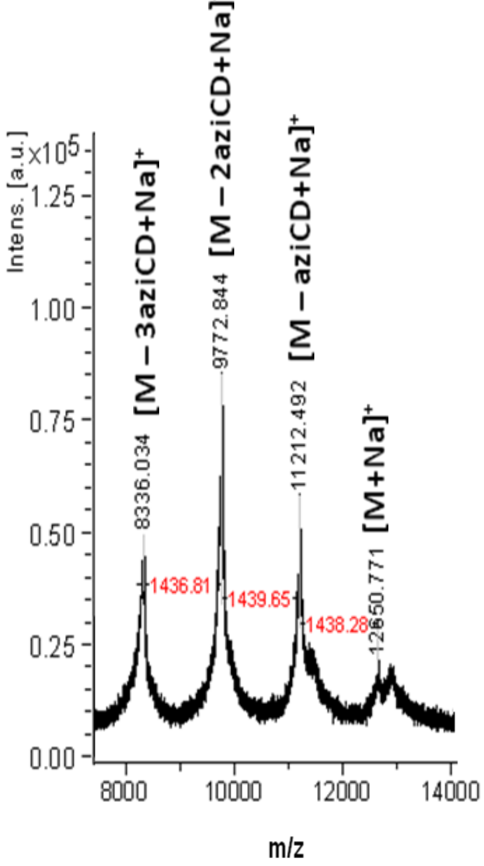

Figure S13. MALDI TOF-MS (DHB matrix) spectrum of porphyrin **4** (in the 7500-14000 Da region). The spectrum shows the parent peak at 12650.8 Da as well as fragmentation products ascribed to the sequential loss of the azido permethyl-β-cyclodextrin units.

References.

1- B. Berne and R. Pecora. *Dynamic Light Scattering,* John Wiley & Sons, N.Y. **1976**.

2- D. E. Koppel, *J. Chem. Phys*., 1972, **11**, 4814.

3- C. Hocquelet, J. Blu, C.K. Jankowski, S. Arseneau, D. Buisson and L. Mauclaire, *Tetrahedron*, 2004, **62**, 11963.

4- C. N. Murthy and K. E. Geckeler, *Chem. Commun.,* 2001, 1194.

5- Y. Liu, P. Liang, Y. Chen, Y.-M. Zhang, J.-Y. Zheng and H. Yue, *Macromolecules,* 2005, **38**, 9095.