SUPPORTING INFORMATION

Reversible switching of supramolecular morphology driven by an amphiphilic bistable [2]rotaxane

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Experimental Section

General Methods

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV-400 spectrometer. The electronic spray ionization (ESI) mass spectra were acquired on an LCT Premier XE mass spectrometer and the MALDI-TOF-MS was acquired on a AB Sciex 4800 plus TOF mass spectrometer. Dynamic light scattering (DLS) measurements were performed on the Delsat Nano C Particle Analyzer (Beckman Coulter, USA). Transmission electron microscopy (TEM) images were recorded on a JEOL-1400 (Jeol, Tokyo, Japan) transmission electron microscope. Samples were stained with the aqueous solution of sodium phosphotungestic acid 2% (w/v). The aggregates of compound **1-H** in water were prepared by dissolving the compound in water directly.

Materials

Chemicals were used as received from Adamas-beta®, Acros, Aldrich. All solvents were reagent grade and were dried and distilled prior to use according to standard procedures. The molecular structures were confirmed using ^{1}H NMR, ^{13}C NMR, HR ESI mass spectroscopy and MALDI-TOF-MS, respectively.

Synthesis

Compounds **3, 5, 6**, **7, 8** were synthesized according to previous reports [1, 2, 3, 4].

Synthesis of Compound 4

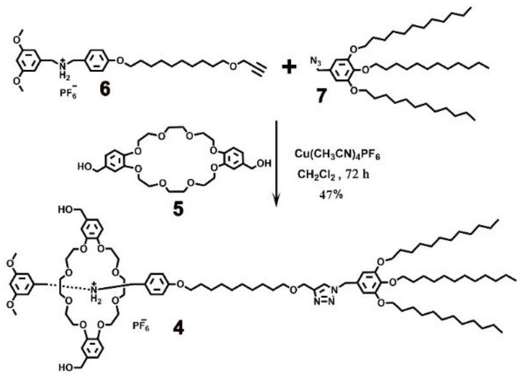


Figure S1. Preparation of compound **4**

Compound **4**: The mixture of compound **6** (0.5 g, 0.81 mmol) and crown ether **5** (0.62 g, 1.22 mmol) in dry

CH_2Cl_2 (10 mL) was stirred at room temperature for 30 minutes. Then compound **7** (1.12 g, 1.62 mmol) and $[Cu(CH_3CN)_4]PF_6$ (0.3 g, 0.81 mmol) were added to the solution, and the mixture was stirred for 72 hours under Ar atmosphere. After removal of the solvent, the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100/1) to give compound **4** (0.694 g, 47 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.55-7.42 (m, 3H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.82-6.76 (m, 4H), 6.69 (t, *J* = 8.8 Hz, 4H), 6.46 (s, 2H), 6.40-6.37 (m, 2H), 6.26-6.20 (m, 1H), 5.38 (s, 2H), 4.55-4.50 (m, 6H), 4.12-4.05 (m, 8H), 3.94 (t, *J* = 5.6 Hz, 2H), 3.92-3.88 (m, 6H), 3.85 (t, *J* = 6.8 Hz, 2H), 3.79-3.76 (m, 6H), 3.75-3.69 (m, 4H), 3.61 (s, 6H), 3.53-3.47 (m, 8H), 3.45-3.38 (m, 2H), 1.85-1.65 (m, 10H), 1.60-1.50 (m, 4H), 1.47-1.38 (m, 10H), 1.29-1.23 (m, 52H), 0.87 (t, *J* = 6.8 Hz, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 160.8, 159.5, 153.5, 147.3, 146.6, 138.4, 134.8, 134.0, 130.8, 123.4, 120.1, 114.6, 112.1, 111.7, 106.7, 106.6, 100.4, 73.5, 70.7, 70.6, 70.2, 69.2, 68.2, 68.1, 68.0, 64.7, 55.4, 52.2, 31.9, 30.3, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.1, 26.1, 26.0, 22.7, 14.1. HRMS (ESI) (m/z): $[M-PF_6]^+$ calcd for $C_{98}H_{157}N_4O_{17}$, 1663.1572; found, 1663.1624.

Synthesis of Compound 2-H

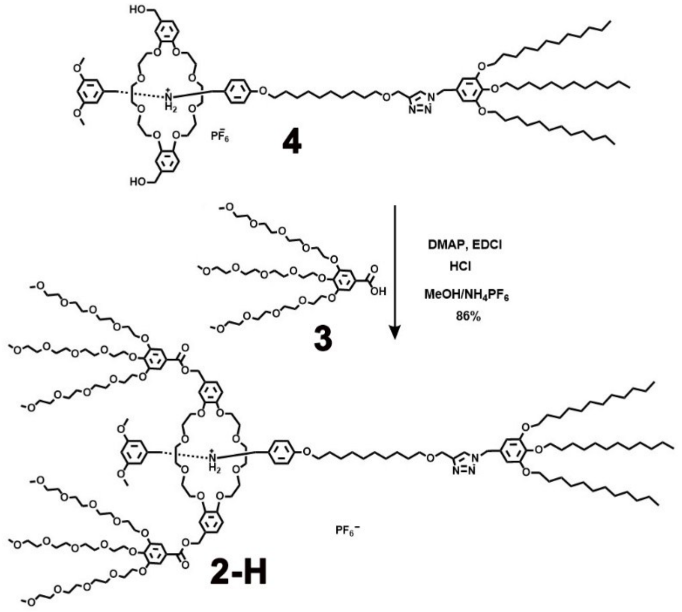


Figure S2. Preparation of compound **2-H**

To the mixture of compound **4** (0.86 g, 0.47 mmol) and compound **3** (0.77 g, 1.04 mmol) in dry CH_2Cl_2 (10 mL) was added DMAP (0.12 g, 0.98 mmol) and EDCI (0.73 g, 3.81 mmol) under stirring. The mixture was stirred overnight under Ar atmosphere, then dilute hydrochloric acid solution was added to the solution until the pH = 1. Next, the mixture was stirred for two hours and poured into 50 mL deionized water then the aqueous phase was extracted with CH_2Cl_2 (3 × 50 ml). The solvent was removed in vacuo to give a colorless liquid, which was dissolved in 20 mL methanol, followed by the addition of 5.0 mL saturated aqueous NH_4PF_6 solution. After the mixture was stirred overnight, it was poured into 50 mL deionized water and then extracted with CH_2Cl_2 (3 × 25 mL). The organic solvent was evaporated, and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100/1) to give compound **2-H** (1.3 g, 86 %) as a colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.58-7.48 (m, 2H), 7.47 (s, 1H), 7.27 (s, 4H), 7.25-7.21 (s, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.87 (s, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 7.2 Hz, 2H), 6.45 (s, 2H), 6.39 (s, 2H), 6.2 (s, 1H), 5.39 (s, 2H), 5.22 (s, 4H), 4.58 (s, 2H), 4.56-4.45 (m, 4H), 4.26-4.00 (m, 20H), 3.96-3.76 (m, 28H), 3.74 (s, 4H), 3.72-3.67 (m, 12H), 3.66-3.61 (m, 44H), 3.57 (s, 6H), 3.56-3.45 (m, 22H), 3.36 (s, 18H), 1.76-1.71 (m, 10H), 1.58-1.55 (m, 2H) 1.50-1.38 (m, 10H), 1.27-1.23 (m, 54H), 0.87 (t, *J* = 7.2 Hz, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 165.0, 159.9, 158.9, 152.5, 151.3, 146.5, 146.3, 144.7, 137.4, 132.8, 129.8, 128.9, 128.6, 128.5, 128.4, 123.8, 122.1, 121.3, 121.1, 113.5, 112.1, 111.5, 108.1, 105.8, 105.7, 99.0, 72.4, 71.4, 70.9, 70.0, 69.8, 69.6, 69.5, 69.4, 69.2, 68.6, 68.2, 67.9, 67.4, 67.2, 667.1, 65.5, 63.3, 60.0, 54.3, 53.4, 51.3, 30.9, 29.3, 28.7, 28.6, 28.5, 28.4, 28.3, 28.2, 26.2, 25.1, 25.0, 21.7, 13.1. MALDI-TOF-MS (m/z): $[M-PF_6]^+$ calcd for $C_{166}H_{273}N_4O_{49}$, 3107.9022; found, 3107.9216.

Synthesis of Compound 1-H

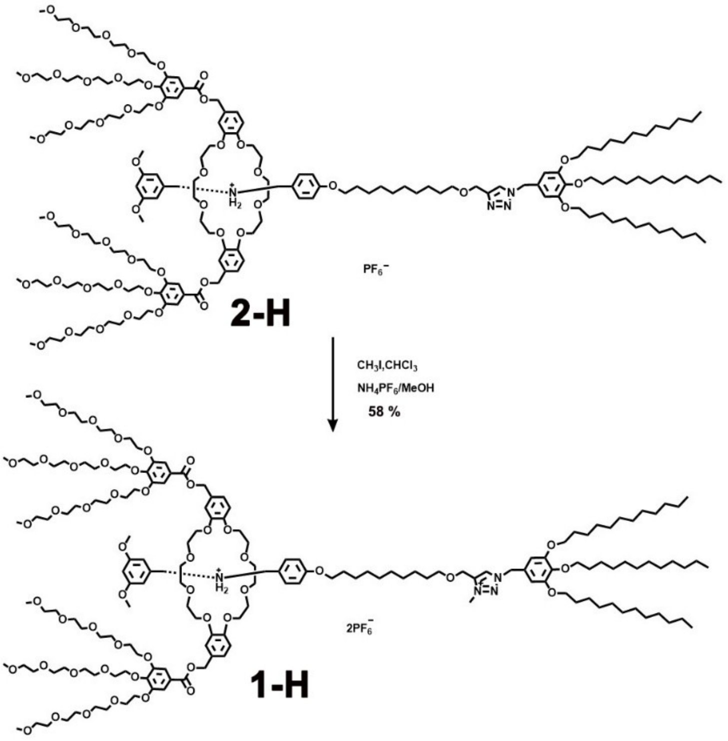


Figure S3. Preparation of compound **1-H**

The solution of compound **2-H** (0.33 g, 0.10 mmol) in CH_3I (5.0 mL) and $CHCl_3$ (1.0 mL) was stirred at 40 °C for 72 hours. The reaction mixture was cooled to room temperature, and the solvent was evaporated in vacuo. The residue was dissolved in methanol (10 mL), followed by the addition of 5.0 mL saturated NH_4PF_6 aqueous solution. After the mixture was stirred overnight, the mixture was washed by deionized water (25 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The solvent was evaporated, and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 100/1) to give compound **1-H** (0.20 g, 58 %) as a colorless viscous liquid. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.21 (s, 1H), 7.48 (s, 2H), 7.26 (s, 4H), 7.19 (d, *J* = 7.2 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 2H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 7.6 Hz, 2H), 6.64 (s, 2H), 6.36 (s, 2H), 6.17 (s, 1H), 5.49 (s, 2H), 5.19 (s, 4H), 4.62 (s, 2H), 4.53-4.43 (m, 4H), 4.23 (s, 3H), 4.20-4.10 (m, 20H), 3.97-3.87 (m, 8H), 3.85-3.79 (m, 12H), 3.76-3.72 (m, 8H), 3.70-3.64 (m, 16H), 3.61-3.58 (m, 44H), 3.53 (s, 6H), 3.52-3.46 (m, 22H), 3.31 (s, 18H), 1.85-1.62 (m, 10H), 1.55-1.49 (m, 2H), 1.48-1.36 (m, 10H), 1.25-1.18 (m, 54H), 0.83 (t, *J* = 6.8 Hz, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 165.7, 160.8, 159.8, 153.8, 151.8, 147.5, 147.4, 140.8, 139.1, 134.0, 130.8, 129.3, 128.6, 126.1, 125.5, 123.0, 122.1, 114.5, 113.1, 112.4, 108.4, 107.8, 106.6, 100.3, 73.4, 72.4, 71.9, 71.6, 71.5, 70.6, 70.2, 70.1, 70.0, 69.9, 69.8, 69.6, 69.2, 69.0, 68.3, 68.1, 68.0, 66.7, 60.0, 58.9, 58.3, 57.9, 55.2, 52.3, 38.4, 31.9, 30.4, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 26.1, 25.9, 25.8, 22.7, 18.4, 14.1. HRMS (ESI) (m/z): $[M-2PF_6]^{2+}$ calcd for $C_{167}H_{276}N_4O_{49}/2$, 1561.4625; found, 1561.4648.

CMC Measurement

Surface tension was measured at 25 °C by tensiometer DCAT21 (Dataphysics, Germany) using a Wilhelmy small platinum plate of ca. 4 cm perimeter. The plate was first rinsed with deionized water and then heated to red before each measurement. The surface tension of deionized water was measured (72 ± 0.2 mN/m) at the beginning to check the instrument. Surface tension was measured three times and plotted as a function of concentration. The turning points in the plot are indicated in Figure S4.

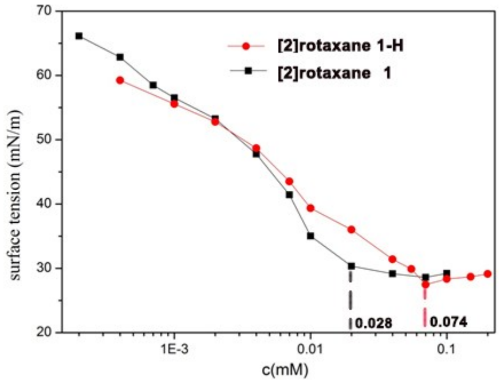


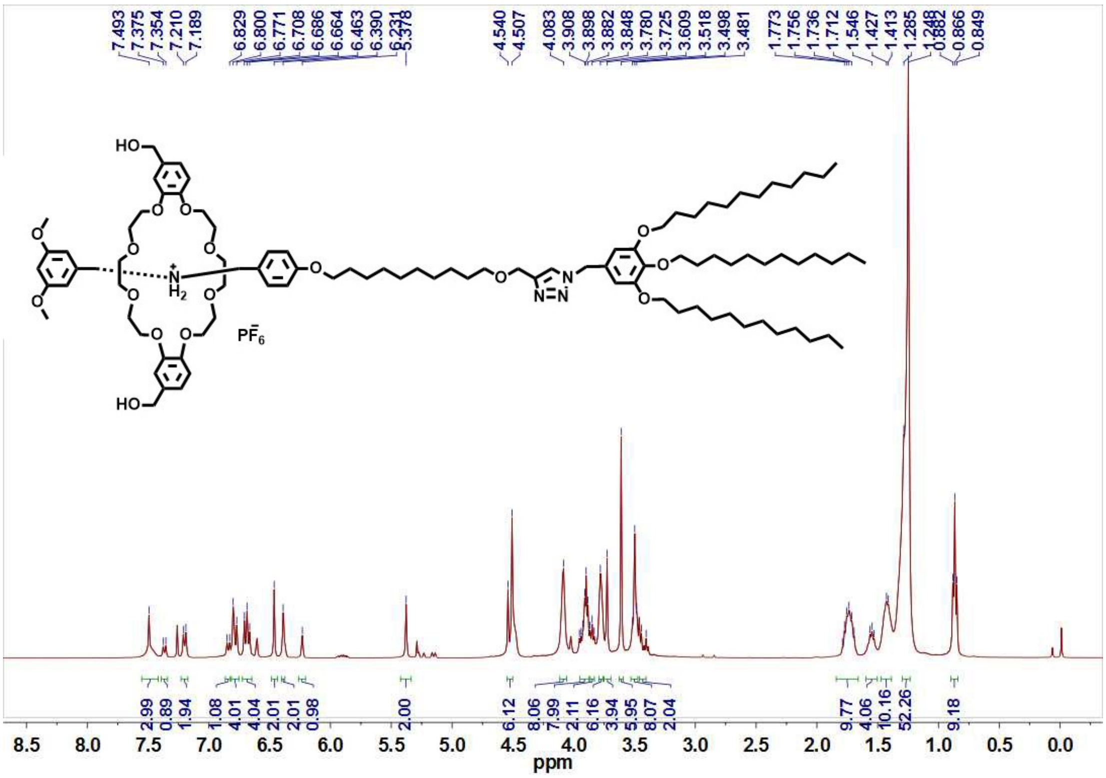
Figure S4. The CMC of [2]rotaxane **1-H** and its intermediate compound **1**

Reference:

1. F. Wang, W.-G. Wang, X.-J. Wang, H.-Y. Wang, C.-H. Tung, L.-Z. Wu, *Angew. Chem. Int. Ed.* 2011, **50**, 3193.
2. H. Zhang, J. Hu, D.-H. Qu, *Org. Lett.* 2012, **14***,* 2334.
3. V. Percec, M. Peterca, P. A. Heiney, S. D. Hudson, *J. Am. Chem. Soc.* 2011, **133**, 12197.
4. T. Fujihara, T. Yoshikawa, M. Satou, H. Ohta, J. Terao, Y. Tsuji, *Chem. Commun.* 2015, **51**, 17382.

^{1}H NMR, ^{13}C NMR and Mass spectra

Compound 4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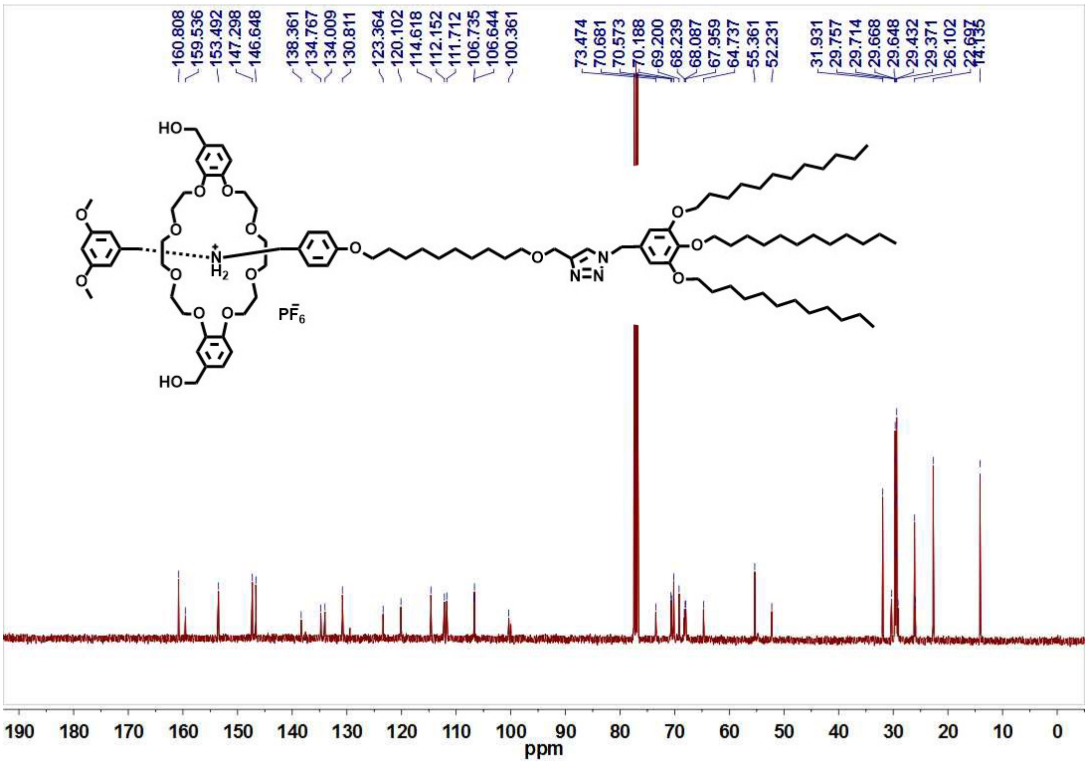
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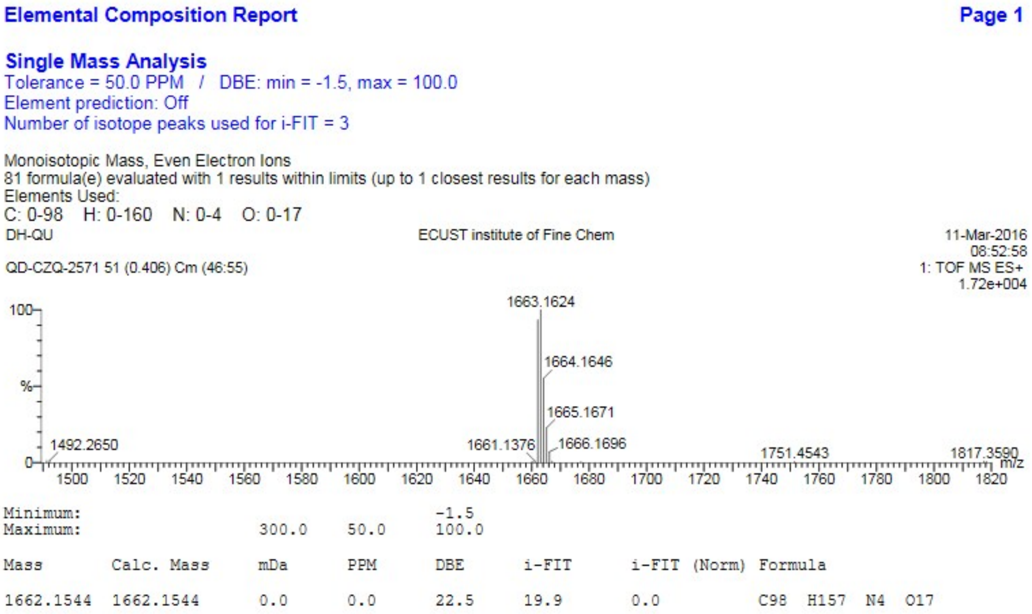

Elemental Composition Report Page 1

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Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
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Elements Used:
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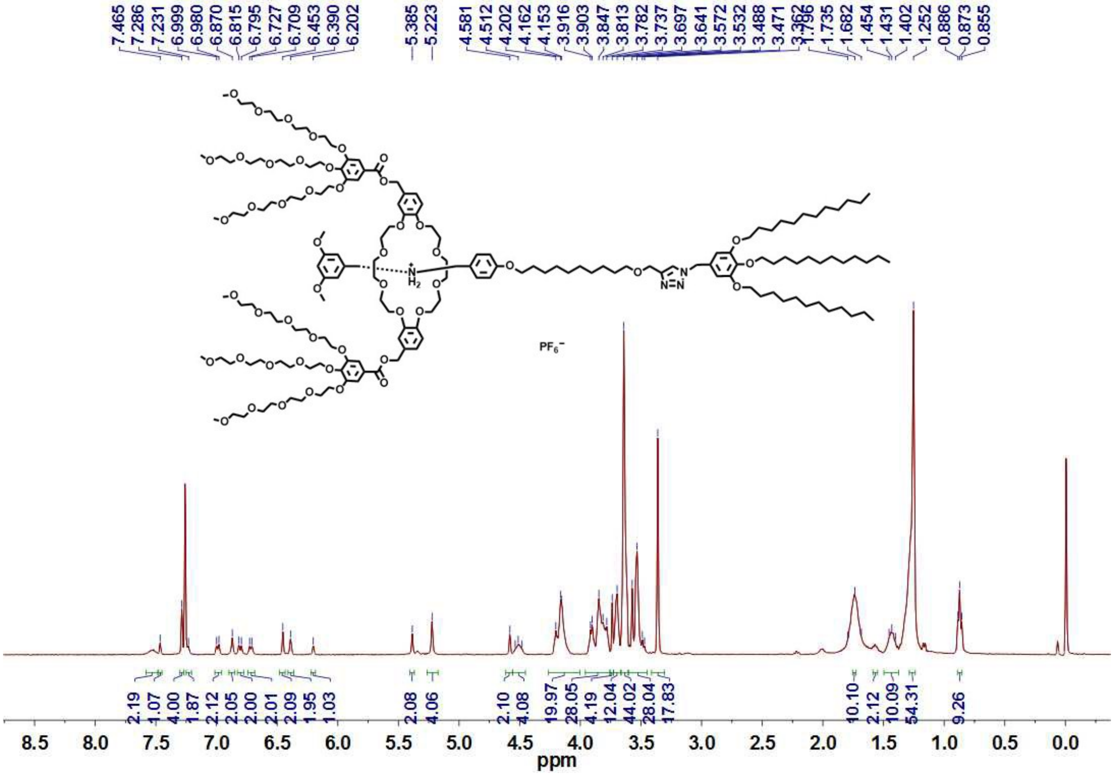
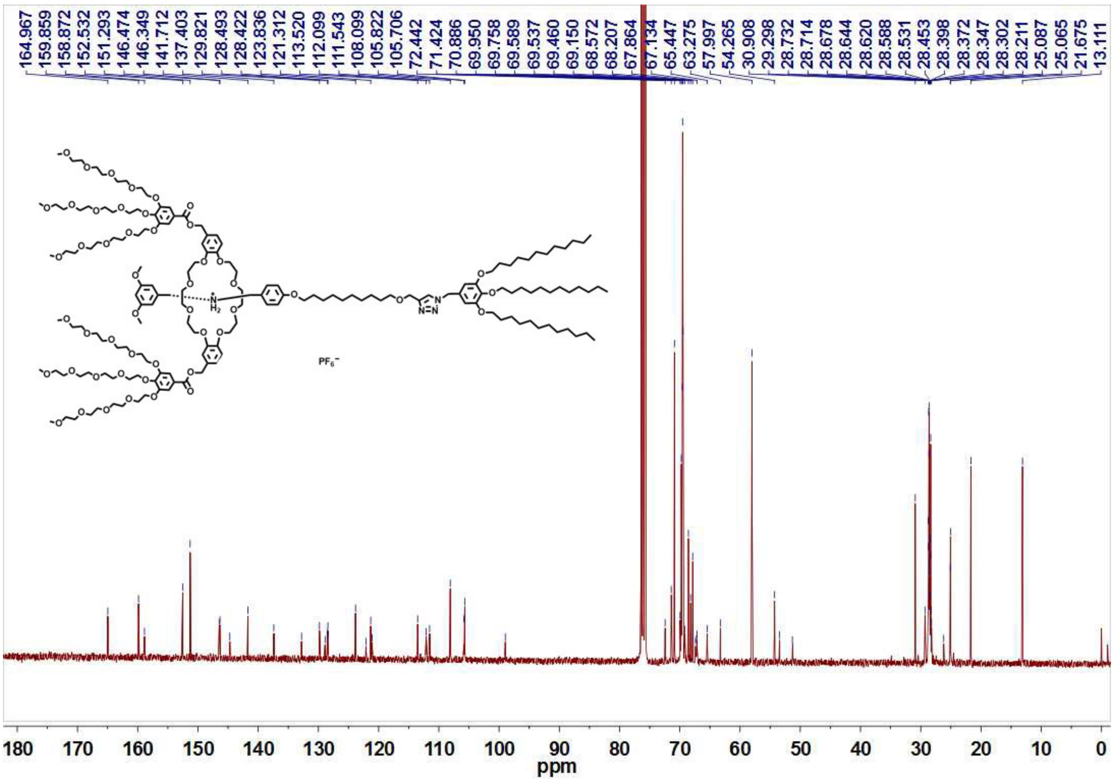
Compound 2-H

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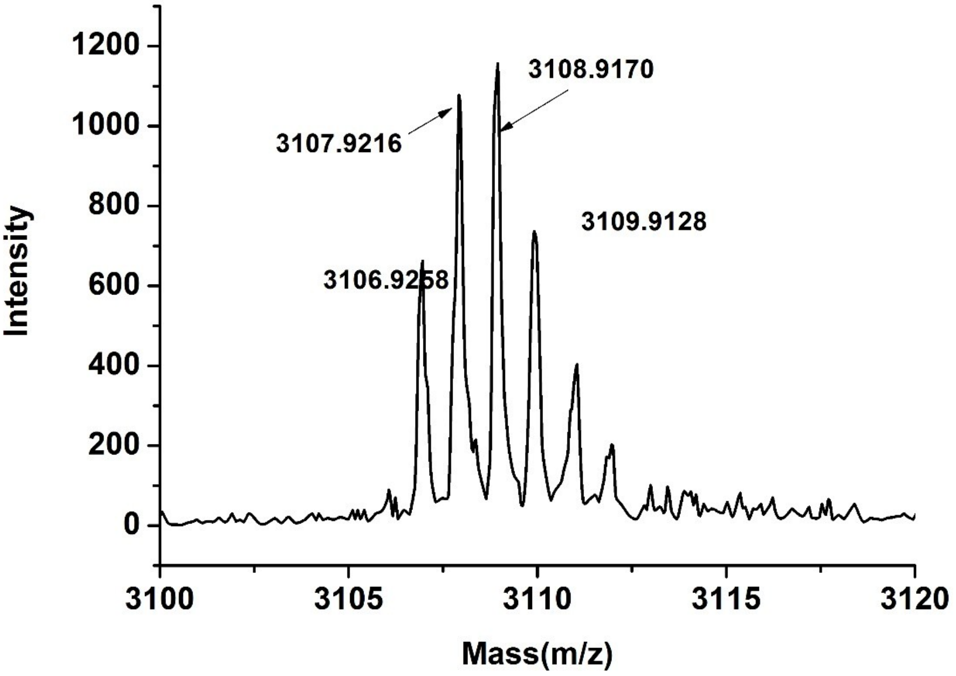
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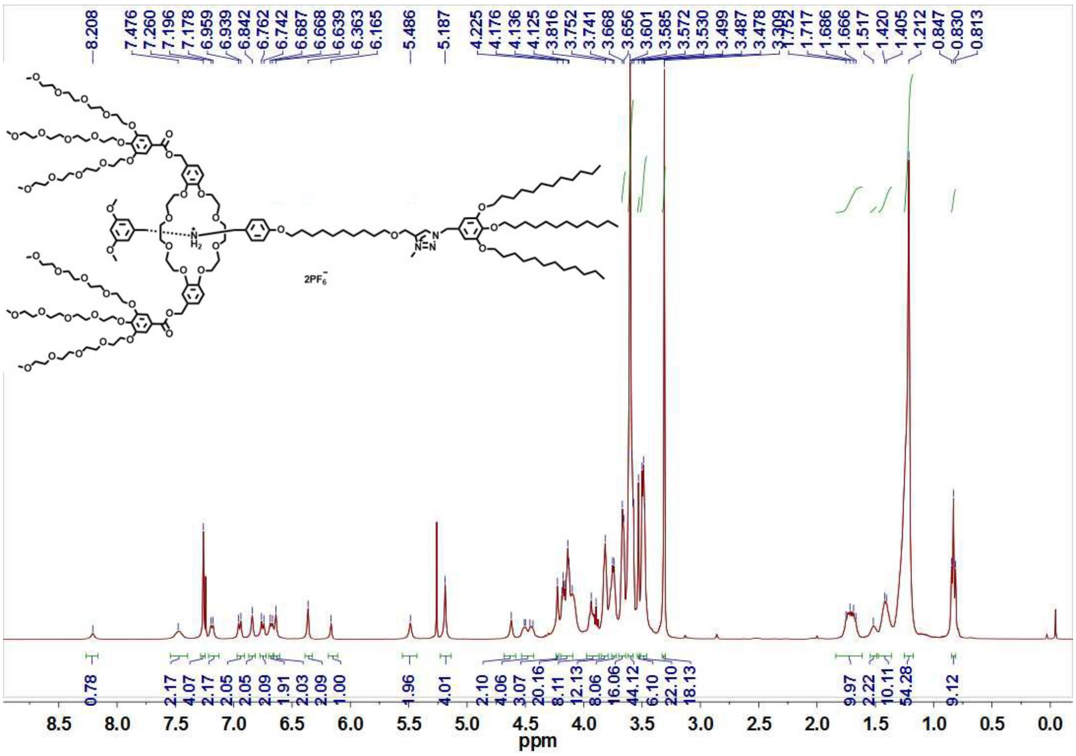
Compound 1-H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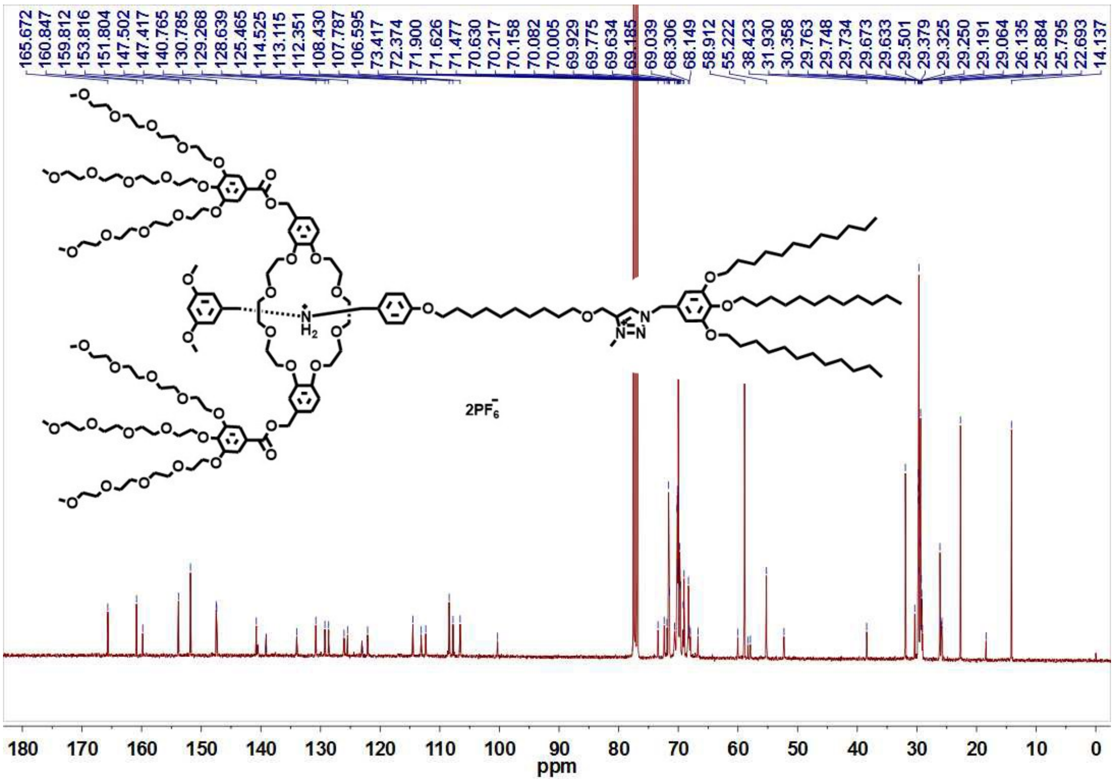
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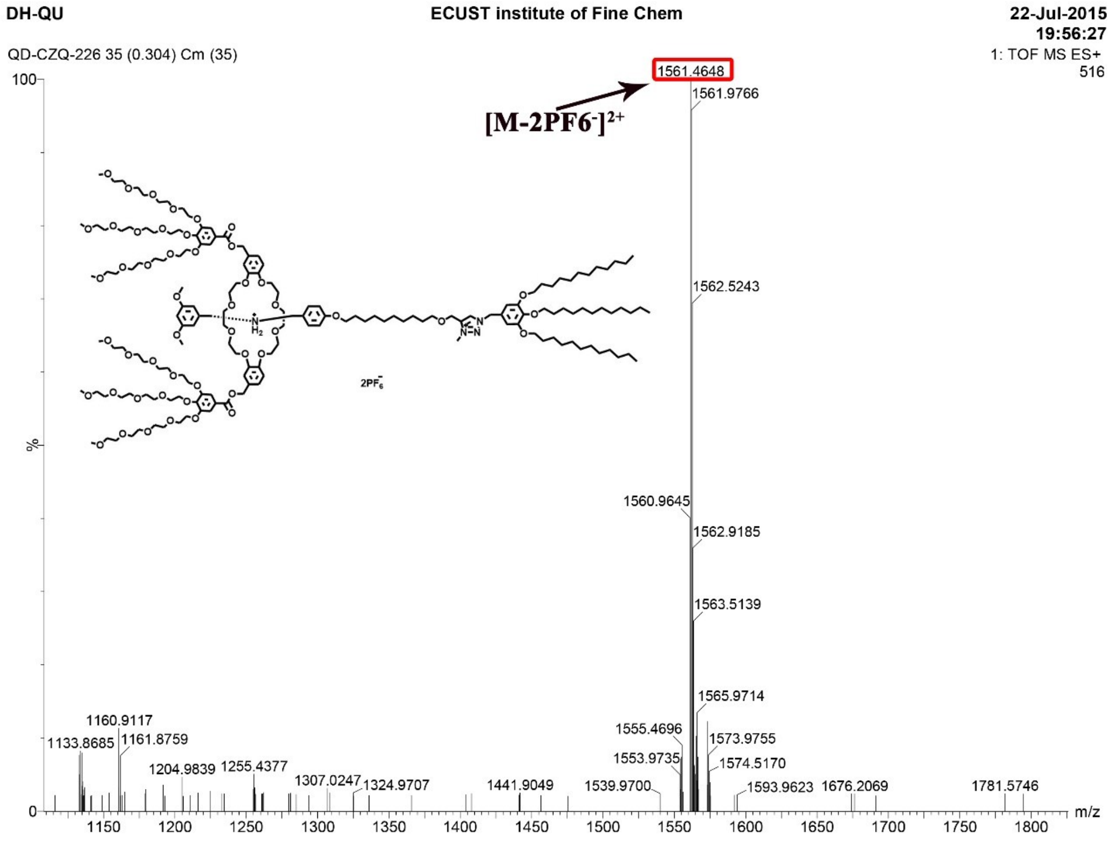
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