Construction of Multifunctional Cubeoctahedra via Coordination-Driven Self-Assembly

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**General Procedure for the Preparation of Cubeoctahedra 4 and 5:**

To a 0.5 mL acetone-d_6 solution triflate (for **1**, 5.0 mg, 0.0037 mmol; for **2**, 3.95mg, 0.0037 mmol) was added a 0.5 mL CD_2Cl_2 solution of the tritopic donor precursor **3** drop by drop with continuous stirring (10 min). The reaction mixture was stirred for 12 hrs at room temperature. The solution was evaporated to dryness, and the product was collected.

4. Yield: 6.54 mg (orange solid), 95%. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 8.81 (d, 48H, H_α-Py), 8.08 (s, 24H, Ar-H), 7.96 (s, 48H, Ar*H*), 7.12-6.99 (m, 36H, Ar*H*), 4.96 (s, 24H, H_{Fc}), 4.62 (s, 24H, H_{Fc}), 4.36 (s, 60H, H_{Fc}), 1.96 (m, 288H, PC*H*$_2$CH$_3$), 1.25 (m, 432H, PCH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ = 16.9 (s, $^1J_{Pt\text{-}P}$ = 2311.5 Hz). Anal. Calcd for $C_{780}H_{984}F_{72}Fe_{12}N_{24}O_{96}P_{48}Pt_{24}S_{24}$: C, 44.17; H, 4.68; N, 1.59. Found: C, 44.20; H, 4.87; N, 1.57.

5. Yield: 5.71 mg (white solid), 98%. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 8.66 (brs, 48H, H_α-Py), 8.08 (s, 24H, Ar*H*), 7.86 (brs, 48H, H_β-Py), 7.68 (s, 12H, Ar*H*), 7.1-6.89 (m, 60H, Ar*H*), 4.23-4.08 (m, 96H, α-CH$_2$), 3.91-3.85 (m, 96H, β-CH$_2$), 3.75 (m, 96H, γ-CH$_2$), 1.8 (m, 288H, PC*H*$_2$), 1.23 (m, 432H , PCH$_2$C*H*$_3$). ^{31}P {^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ=18.1 (s, $^1J_{Pt\text{-}P}$ = 2729.31 Hz). Anal. Calcd for $C_{948}H_{1248}F_{72}N_{24}O_{192}P_{48}Pt_{24}S_{24}$: C, 46.75; H, 5.16; N, 1.38. Found: C, 46.87; H, 5.20; N, 1.41.

Figure S1. A) ^1H and B) ^{31}P NMR Spectra of cubeoctahedra **4** in CD_2Cl_2
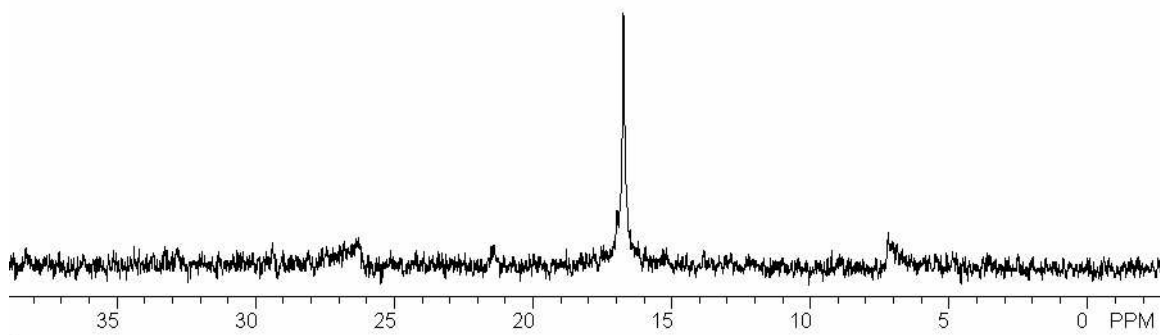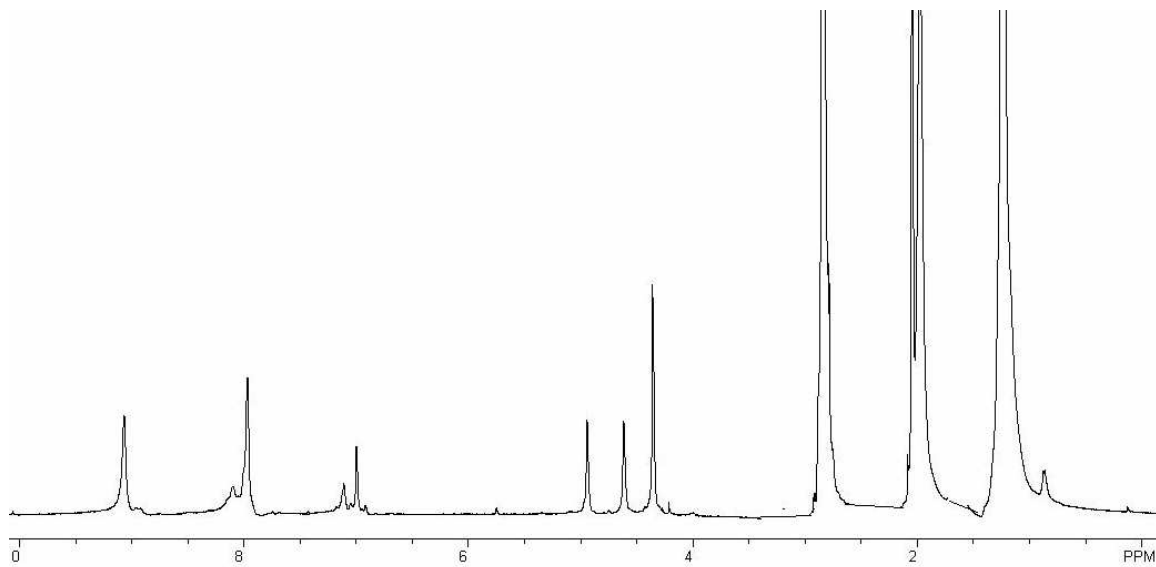
A.
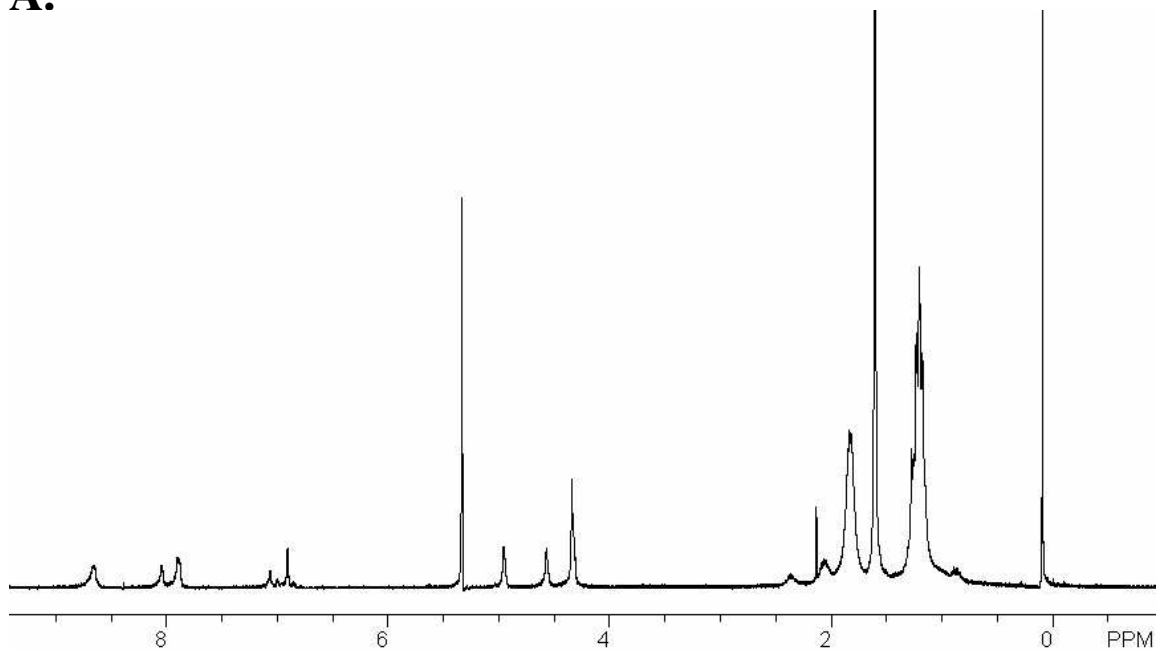
B

Figure S2. A) ^{1}H and B) ^{31}P NMR Spectra of Cubeoctahedra **4** in Acetone-d_6
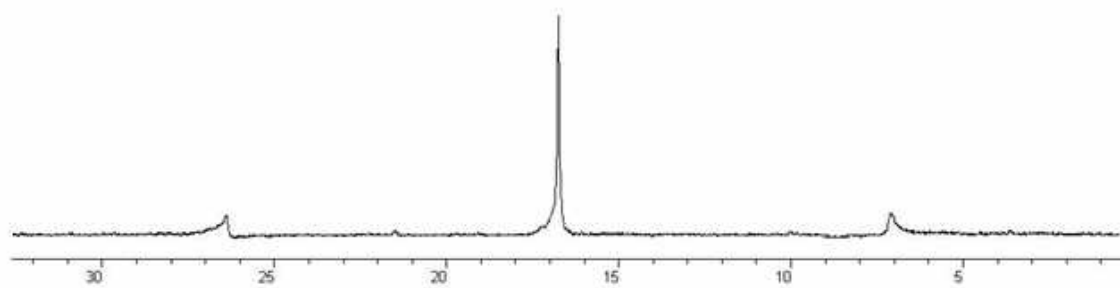
A.

B.

Figure S3. A) ^{1}H and B) ^{31}P NMR Spectra of Cubeoctahedra **4** in CD_3NO_2

A.

B.

Figure S4. A) ^{1}H and B) ^{31}P NMR Spectra of Cubeoctahedra **5** in CD_2Cl_2

A.

B.

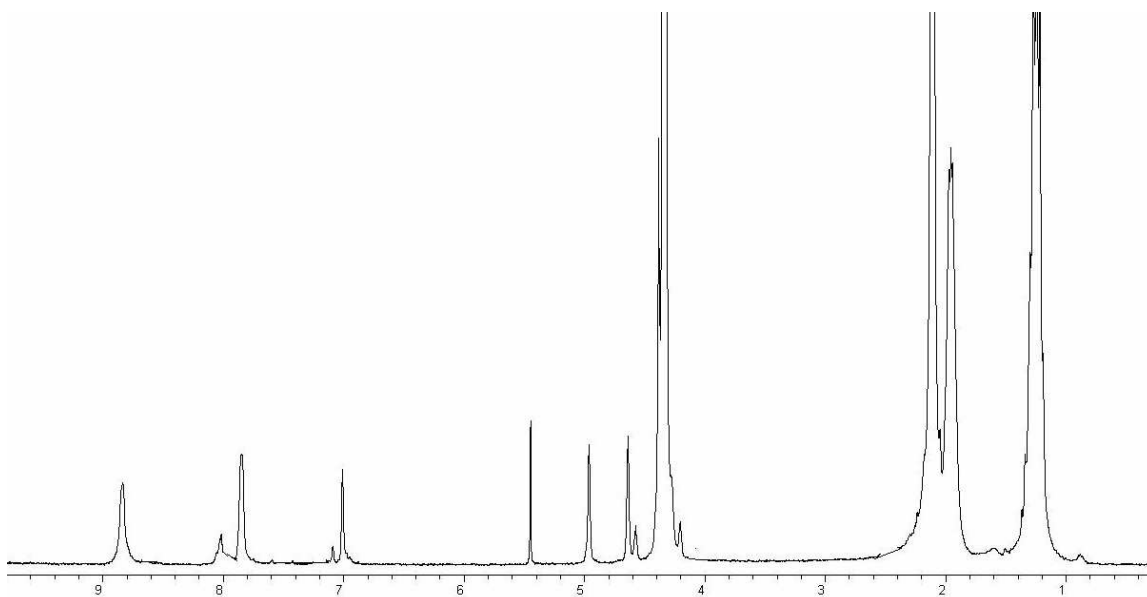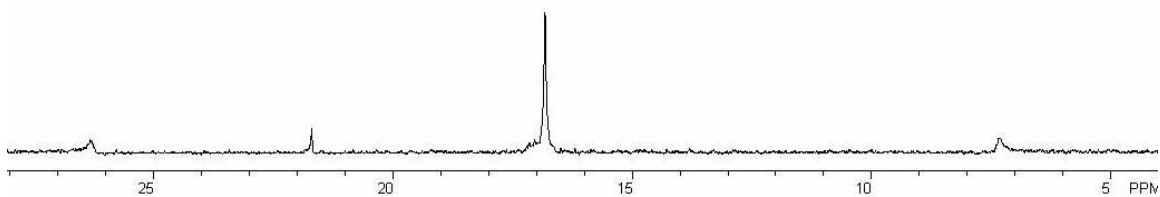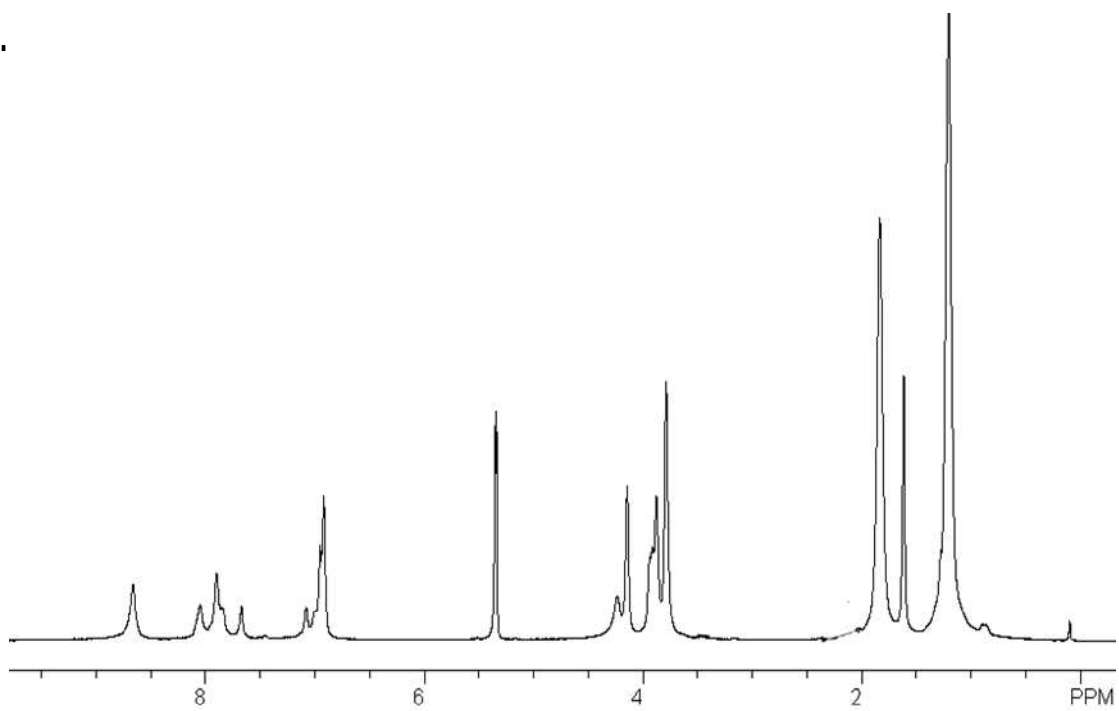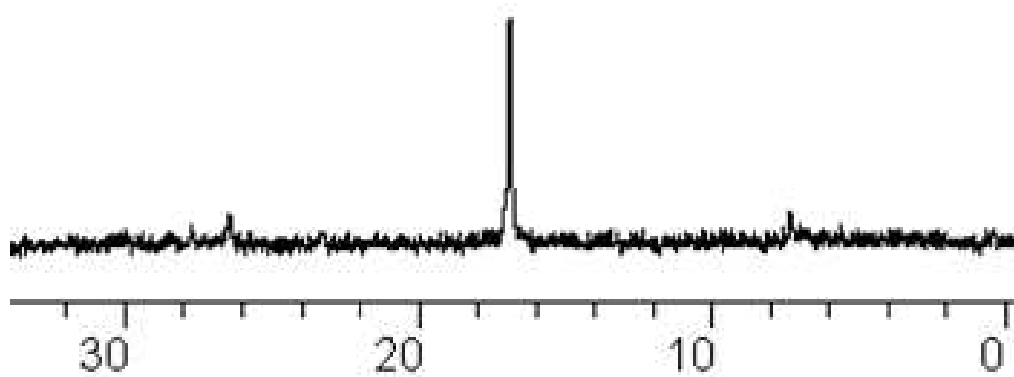**Figure S5**. A) ^{1}H and B) ^{31}P NMR Spectra of Cubeoctahedra **5** in Acetone-d_6
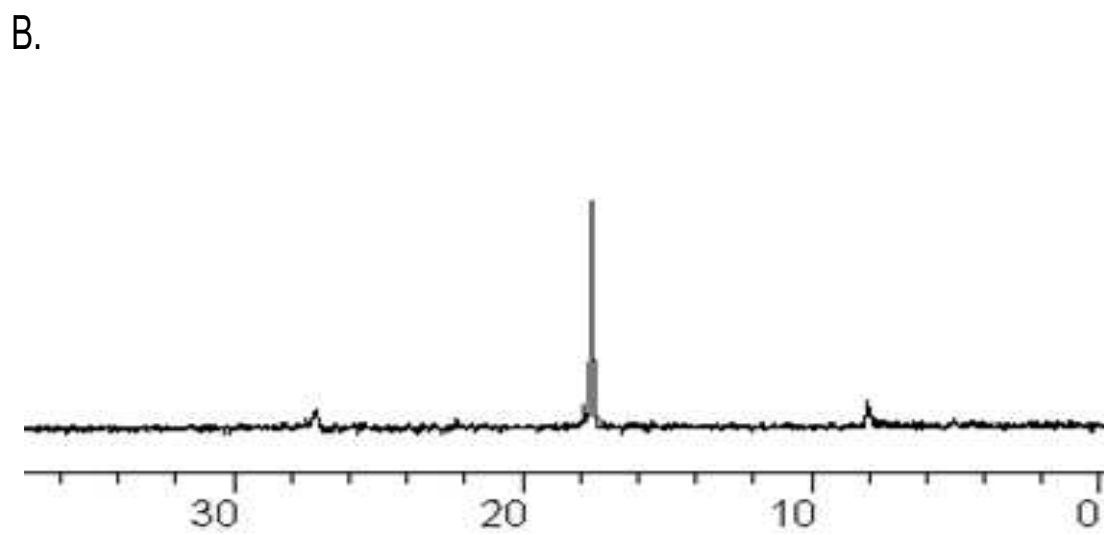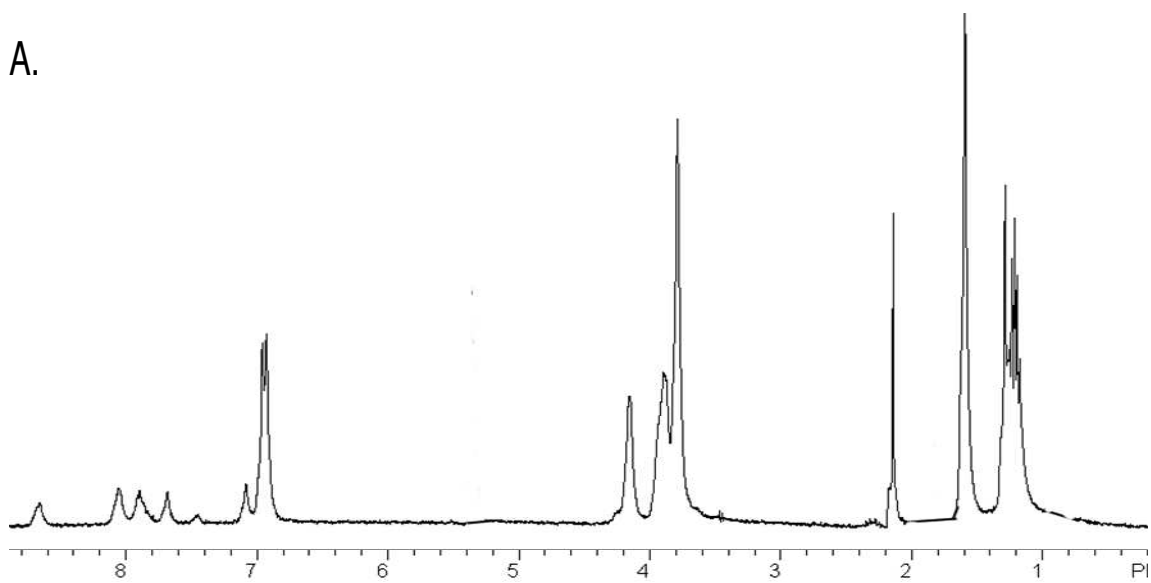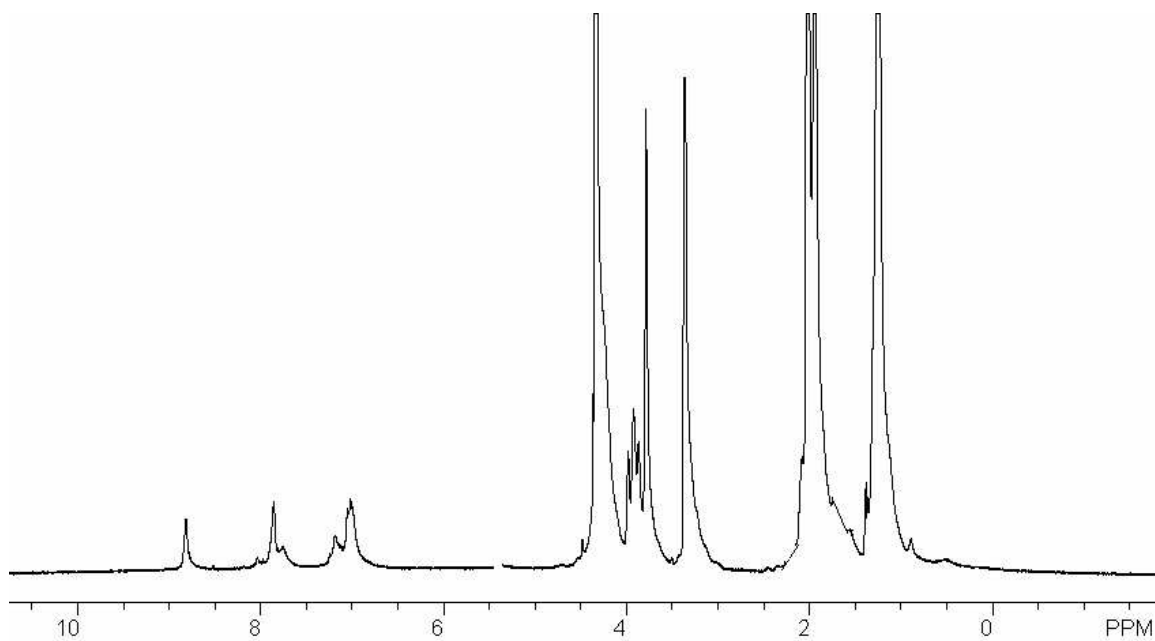
A.

B.

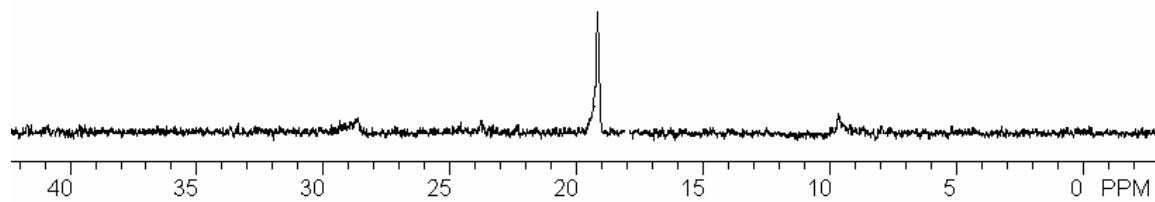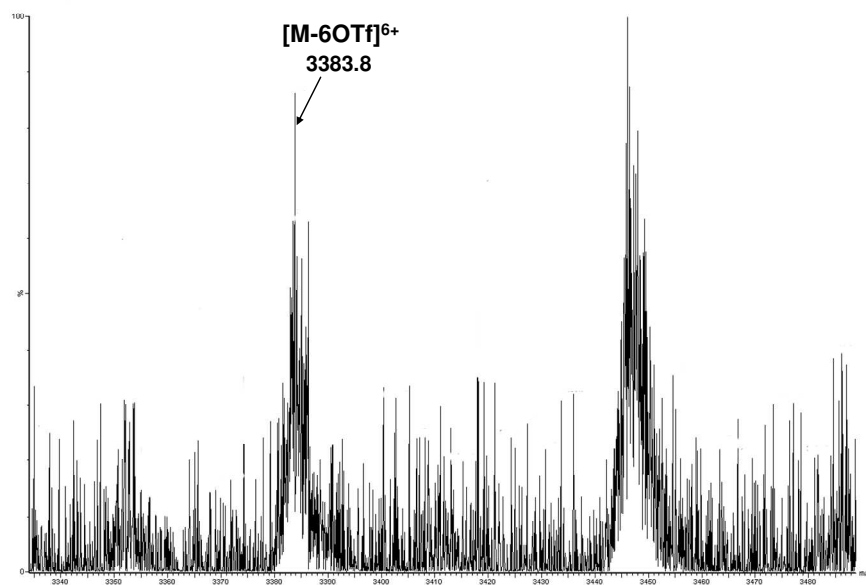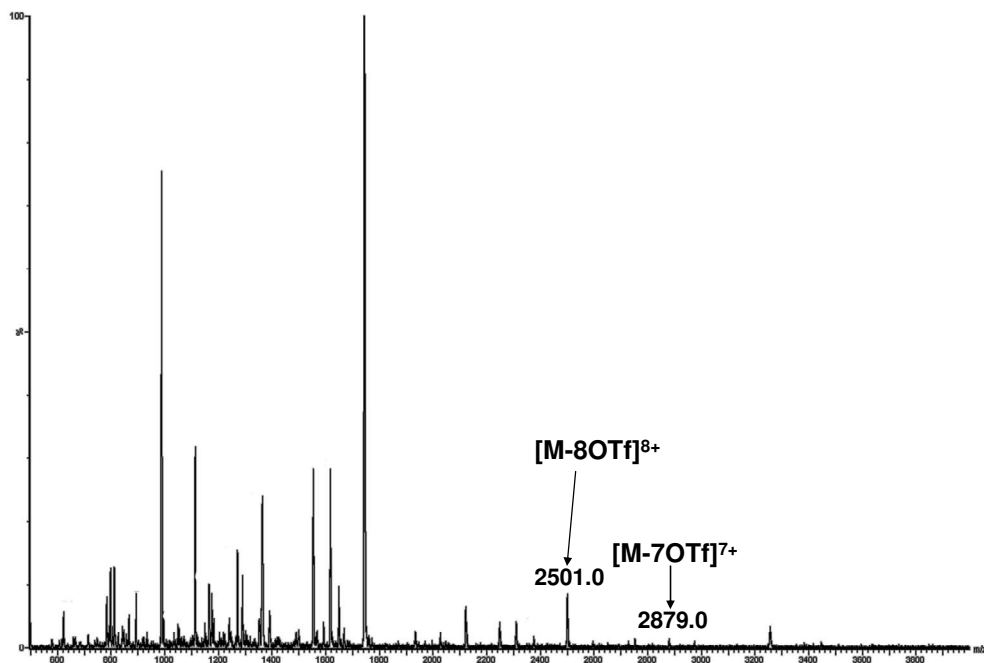**Figure S6**. A) ^{1}H and B) ^{31}P NMR Spectra of Cubeoctahedra **5** in CD$_3$NO2

A.

B.

Figure S7: ESI Mass Spectrometry of 4:

[M-8OTf]$^{8+}$
2501.0

[M-7OTf]$^{7+}$
2879.0

[M-6OTf]$^{6+}$
3383.8

PGSE Measurement:

Pulsed gradient spin-echo (PGSE) NMR diffusion measurements were done by pulse-sequence developed by Stejskal and Tanner [1].

$$\ln(I/I_0) = -\gamma_X^2 \delta^2 G^2 (\Delta - \delta/3) D \qquad (1)$$

$\gamma_X =$ gyromagnetic ratio of the X nucleus;
$\delta =$ length of the gradient pulse; $G =$ gradient strength;
$\Delta =$ delay between the midpoints of the gradients;
$D =$ diffusion coefficient

Temp: 298K

Instrument: Inova 500 MHz

Stokes-Einstein Equation: The molecular size is obtained from the diffusion coefficient via the Stokes-Einstein equation where k_B is the Boltzmann constant, T is the absolute temperature and r_H is the hydrodynamic radius of the species under investigation.

$$D = \frac{k_B T}{6\pi \eta r}$$

Gradient Calibration: The gradient strengths need to be carefully calibrated to obtain accurate D values to fit equation 1. Gradient strengths were calibrated using the width (in Hz) of a sample of known length along the NMR-tube (Z) axis, back-calculation of the coil constant from a diffusion experiment on D_2O using $D = 1.9 \times 10^{-5}$ cm^2/s for D_2O at 298K[2] was used to calculate the gradient strengths of both the probes.

Issue of Viscosity: The effect of variable viscosity in different batch of same solvents was examined using the D values observed for the residual protons of the solvent resonance.

Pulse sequence: Stejskal-Tanner Pulse sequence

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                    4.8u                        9.6u

                                                                      1.9s

Tx       1.0s            400.0u   2.5m   19.0m       400.0u   2.5m   19.0m
         d1        p1    d0       g1     d2     pw   d3       g2     d4-alfa


Dec


z

         A                            B                    C
                    /vnmr/seqlib/pge
```
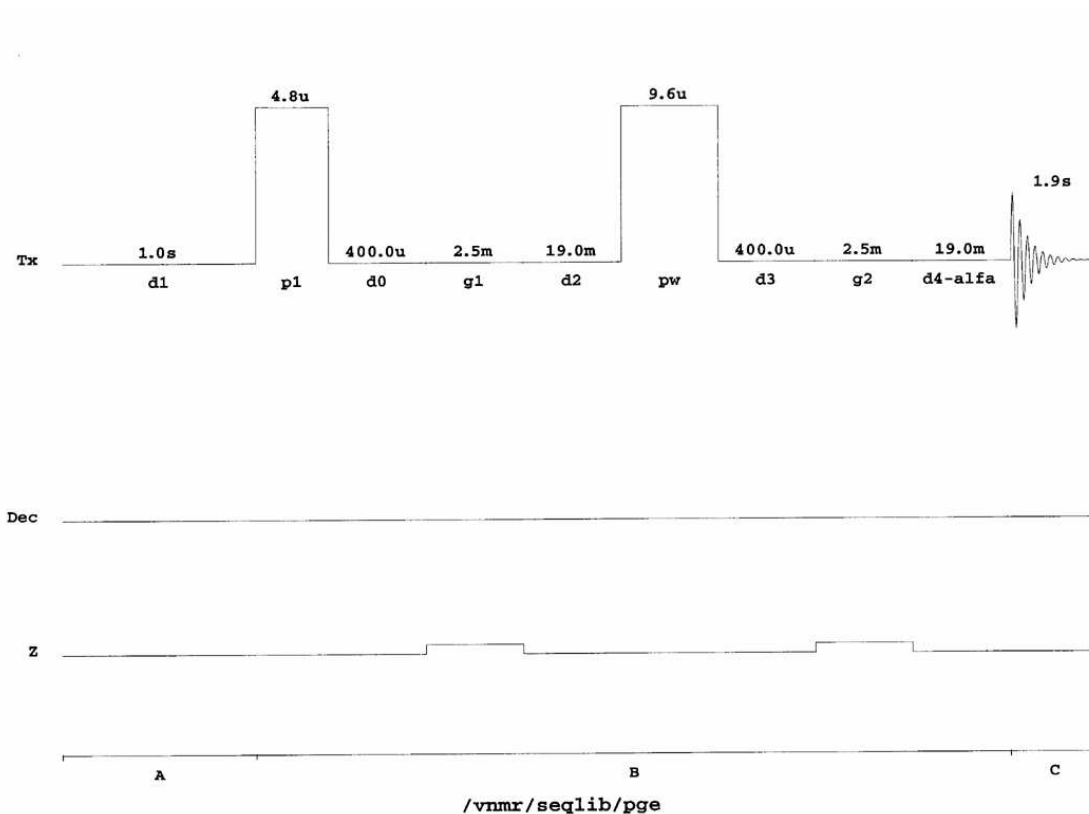
Diffusion Coefficients in different solvents:

	$D_{acetone}$ $(10^{-6}cm^2/s)$	$D_{dichloromethane}$ $(10^{-6}cm^2/s)$	$D_{nitromethane}$ $(10^{-6}cm^2/s)$
4	2.12 ± 0.1	1.59 ± 0.2	1.1 ± 0.1
5	1.82 ± 0.1	1.45 ± 0.1	0.92 ± 0.1

Cyclic Voltammetry.

Cyclic voltammetry (CV) was performed in a Faraday cage using a 3-electrode cell and a potentiostat (Pine Instrument Co., RDE4). The working electrode was a platinum disk embedded in glass with surface area of about 1 mm^2. A Ag/AgCl (3.0M KCl) electrode was used as reference electrode and a Pt wire as the counter. Voltammetric data were recorded using in-house virtual instrumentation written in LabVIEW 8.0 (National Instrument).

The CV measurements were carried out in a acetone solution containing 0.1 M tetra-n-butylammonium hexafluorophosphate (n-Bu$_4$NPF$_6$). The concentration of redox molecule in solution was: (4) cubeoctahedra, 2.0×10^{-6} M, Scan rates are indicated in the figures.

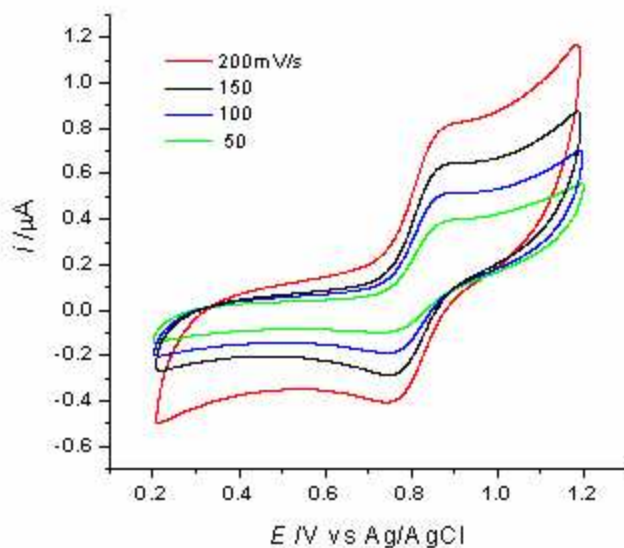**Figure S8.** Cyclic voltammetric response of 2.0×10^{-6} M cubeoctahedra **4** in acetone containing 0.1M n-Bu$_4$NPF$_6$.

Steady-State Measurements using Pt microdisk electrodes.

Steady-state voltammetric measurements were made using the same solution, but a two electrode compartment using a 26 µm diameter Pt disk with the diameter of as the working and a Ag/AgCl electrode as the counter and reference). A PAR (Princeton Applied Research) model 175 Universal Programmer and Dagan Cornerstone Chem-Clamp Potentiostat were used for potential generation and current measurement, respectively. The size of this micro-Pt disk was determined by steady-state voltammetric measurement using an acetonitrile solution containing 5.0 mM ferrocene and 0.1M $TBAPF_6$.

. The limiting current can be calculated from the equation:

$$i_{lim} = 4n\mathrm{F}Da\mathrm{C}\theta_{sites} \tag{1}$$

where n is the number of electrons transferred per ferrocene (=1), F is the Faraday constant C is the bulk concentration, θ_{sites} is the number of reacting ferrocenyl sites per the redox molecule, and a is the radius of the electrode.

To determine if the oxidation of the compounds correspond to independent serial electron transfer reactions, the current function $\log[(i_{lim}-i)/i]$ from the steady-state voltammograms was plotted vs E. For this compound, the slope (ca 1mV) corresponded closely to the one-electron value, (59 mV for n = 1) supporting the conclusion that oxidation of the ferrocenyl groups occurs independently of one another.
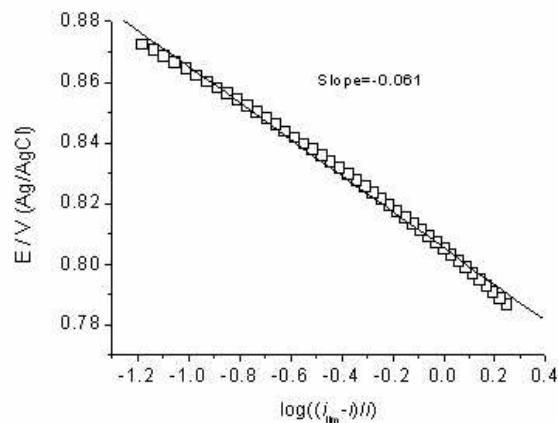
Figure S9. Plot of $\log[(i_{lim}-i)/i]$ vs E from the steady-state measurements using a Pt microelectrode: Dots are the experimental data and black lines represent best fit lines to the data.

Chronoamperometry Measurements

Chronoamperometry was performed by stepping the electrode potential from a value where no electron transfer occurred to a value where the oxidation of the redox molecule was diffusion limited. The normalized time-dependent current with respect to the steady-state limiting current (i_{lim}) of a microdisk can be expressed as:[3]

$$\frac{i(t)}{i_{lim}} = 1 + (2/\pi^{3/2})a(Dt)^{-1/2}$$

Thus, by plotting $i(t)/i_{lim}$ vs $t^{-1/2}$, D can be evaluated from the slope when a is known. Figure S7 shows two examples of $i(t)/i_{lim}$ vs $t^{-1/2}$ plots. The fitted slope value is 0.365 ($s^{0.5}$). D is then calculated from equation (4) as $2.18\times10^{-6}cm^2/s$. By using D value, θ_{sites} can be obtained from Eq. (3).

The plot shows:
- slope=0.365
- $D = 2.18 \times 10^{-6} \, cm^2/s$
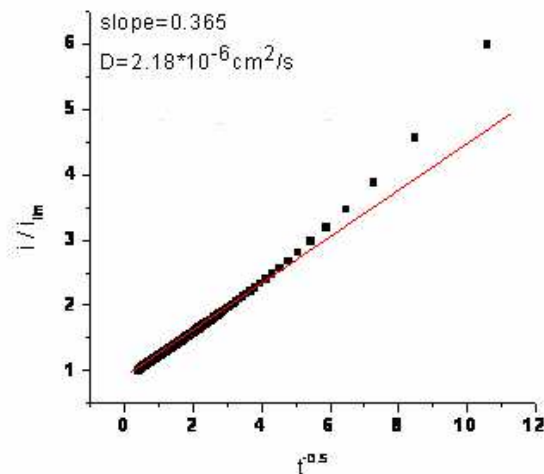- y-axis: i / i_{lim}
- x-axis: $t^{-0.5}$

Figure S10. Plot of the experimental ratio $i(t)/i_{lim}$ vs $t^{-1/2}$ for the oxidation of **4** in acetone containing 0.1M n-Bu$_4$N$^+$PF$_6^-$ using a 13µm microelectrode.

Molecular Modeling Procedures:

The molecular structures of multiferrocene complex **4** and multi-crownether complex **5** were constructed within the input mode of the program Maestro v8.0.110 with the OPLS force-field.[4] and MMFF force field respectively. A 1.0 ns molecular dynamics simulation (0.05 fs timestep) at a simulation temperature of 300 K was used to equilibrate each structure. Following each molecular dynamics simulation a full energy minimization was used to obtain the final optimized structures.
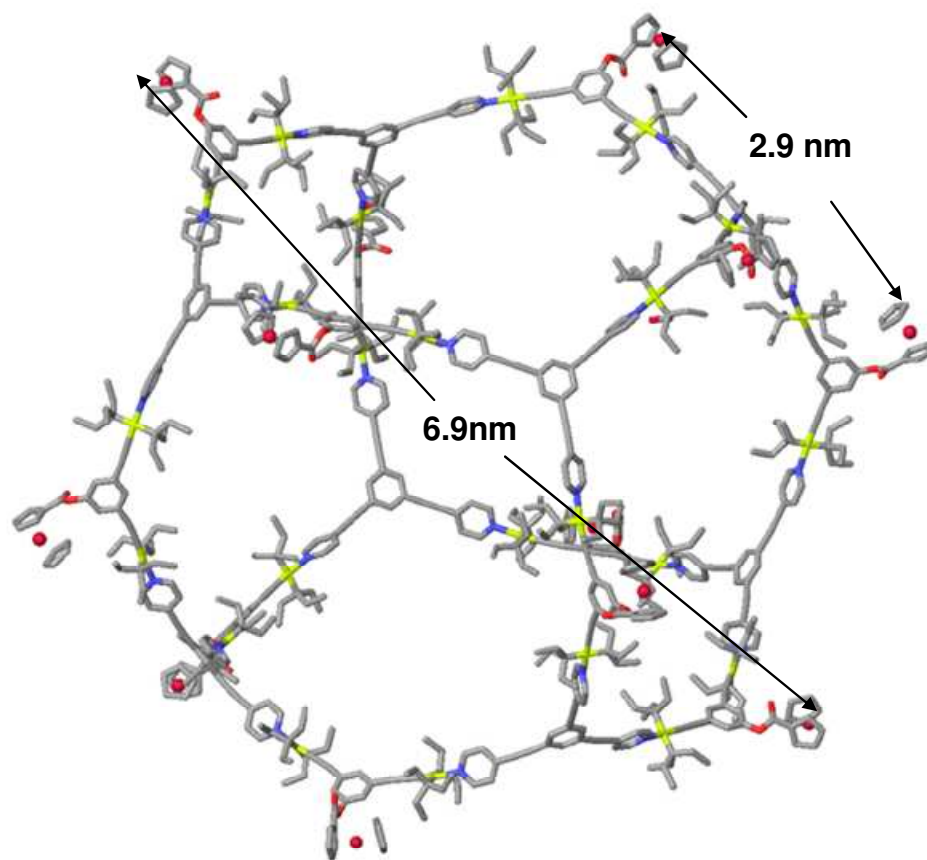
2.9 nm

6.9nm

Figure S11. Simulated molecular model of multiferrocene **4** optimized with the OPLS force-field. All other hydrogen atoms have been removed for clarity.
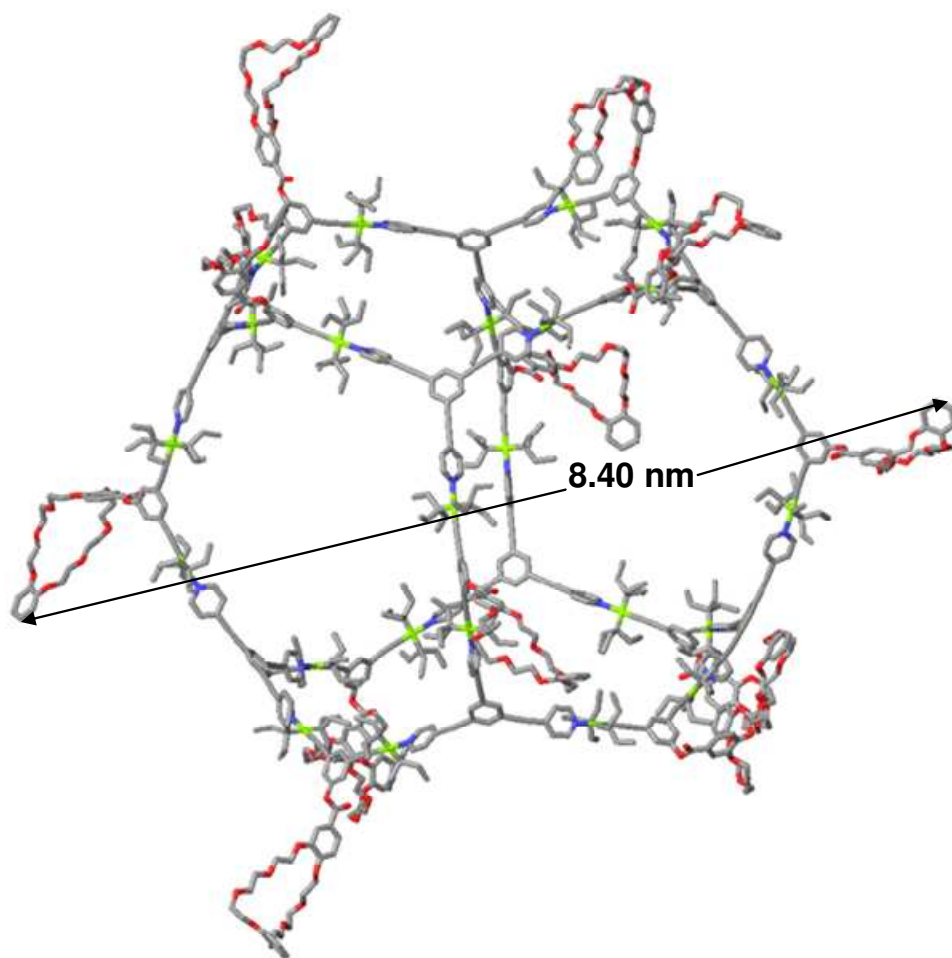
Figure S12. Simulated molecular model of multicrownether **5** optimized with the MMFF force-field. All other hydrogen atoms have been removed for clarity.

References:

1. Stejskal, E. 0.; Tanner, J. E. *J. Chem. Phys.* **1965,** *42,* 288.
2. Longsworth, L. G. *J. Phys. Chem.* **1960**, *64*, 1914.
3. Denault, G.; Mirkin, M. Bard, A. J.; *J. Electroanal. Chem.,* **1991**, *308*, 27

4. Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.;

Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440.

1.