Supporting Information

$M_{18}L_6$ Metal-Organic Nanocapsule with Open Windows Using Mixed Macrocycles

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METHODS

Materials and Characterization. All chemicals were purchased from commercial sources and used without further purification. The single crystal X-ray diffraction (XRD) data was collected on a Brucker Apex II diffractometer at a temperature of 100 (2) K using CuKα (1.5406Å) radiation Inco-tech Microfocus II. The structure was solved and refined using SHELX[1] and Xseed[2]. The NMR samples were prepared by dissolving 2 mg of sample in d^6-DMSO in a 3mm-diameter NMR tube. The ^1H and DOSY spectra were obtained on a Bruker AVIII HD 600 MHz spectrometer equipped with a 5 mm HCN triple resonance cryogenic probe and a Z gradient coil. The operating frequency for ^1H was 599.66 MHz and the sample temperature was at 25 ℃. For DOSY measurement the Bruker supplied pulse sequence named “ledbpgp2s” was used with Z gradient strength stepping from 5 to 95% (totally 16 data points). The probe’s maximum Z gradient strength was 53.5 G/cm. The diffusion delay (d20) was set to 90 ms and the gradient pulse (p30) was set to 2 ms. Diffusion coefficient was obtained by fitting peak intensity as a function of gradient strength using Bruker supplied DOSY2D program. MALDI samples (in $CHCl_3$) were combined with Dithranol matrix solution (10 mg/mL in methylene chloride) and applied to a polished stainless steel target. Positive ion spectra were acquired by MALDI TOF MS on an Applied Biosystems (AB Sciex) Voyager DE™ Pro mass spectrometer equipped with a 20-Hz 337-nm nitrogen laser. Spectra were acquired with delayed extraction in the Reflector mode.

Synthesis of *C*-butylpyrogallol[3]resorcin[1]arene ($P_3R_1C_4$). Pentaldehyde (8.5 mL, 0.08 mol), resorcinol (0.04 mol, 4.4 g) and pyrogallol (0.04 mol, 5.0 g) were mixed in 15 mL of ethanol and 15 mL of water and then 3.5 mL of concentrated HCl was added as a catalyst. The mixture was refluxed at 110 ℃ for 24 hours. The resulting precipitate was filtered, washed with cold ethanol/water (1:1) and dried in vacuum, yielding 5.5 g of pink solid as the final product. The resulting product is a mixture of PgC_4, RsC_4 and $P_xR_{(4-x)}C_4$ (x = 1, 2, or 3), which is directly used for the synthesis of **I**.

Preparation of I, [$Zn_{18}(P_3R_1C_4)_6(DMF)_{12}(H_2O)_{12}$]. *C*-Butylpyrogallol[3]resorcin[1]arene ($P_3R_1C_4$, 100 mg) and $Zn(NO_3)\,6H_2O$ (0.4 mmol, 119.0 mg) were dissolved in 0.5 mL of *N*,*N*-dimethylformamide (DMF) and 1.5 mL of acetonitrile (MeCN) in a 4 ml glass vial. The mixture was sonicated for 5 min to yield a brown solution, and then heated at 100 ℃ overnight. Green block-like crystals were then formed and collected for single crystal X-ray analysis. Yield is 35 mg, 23% based on zinc nitrate.

Supplementary Data

Table S1: Single crystal structure data of **I**.

	I
Crystal system	momoclinic
Space group	C2/m
Temperature (K)	100(2)
a(Å)	27.2432(17)
b(Å)	36.6460(18)
c(Å)	21.3526(11)
α(°)	90
β(°)	117.492(2)
γ(°)	90
V(Å^3)	18910.2(18)
Z	2
Θ range of data collection(°)	2.33-65.19
Total unique reflections	9755
Goodness of fit	2.258
R1 after merging	0.1612
R(int)	0.0413
wR2	0.4756

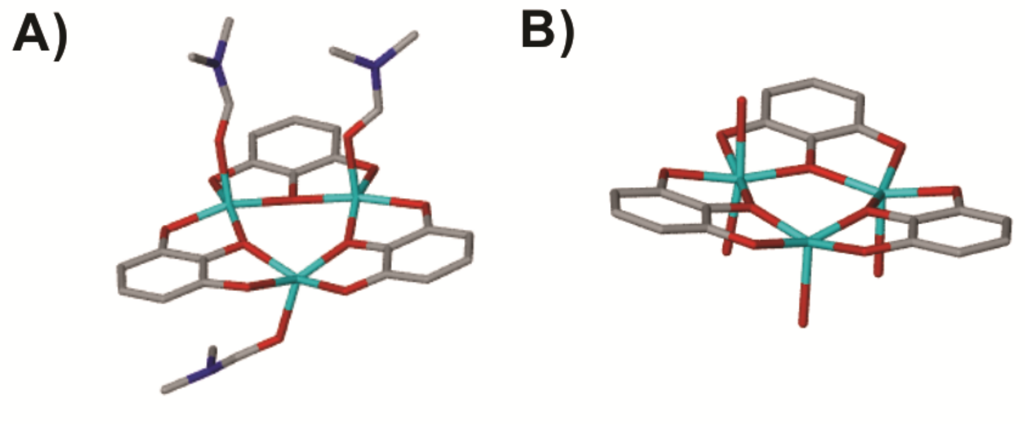

Figure S1. Stick representation of [Zn_3O_3] arrays in **I** with DMF (A) or water (B) molecules at the axial positions of Zn^{2+}. Hydrogen atoms, alkyl chains, and axial ligands have been omitted for clarity. Color codes: grey (carbon), red (oxygen), and light blue (zinc).

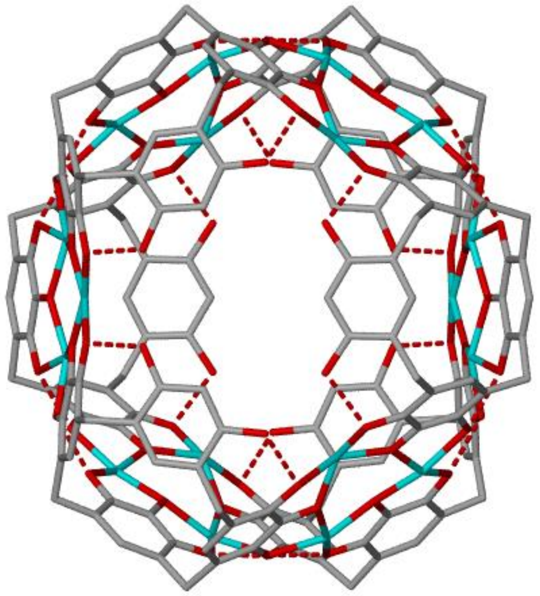

Figure S2. Stick representation of **I** along [101] direction showing the intramolecular hydrogen bonds. Hydrogen atoms, alkyl chains, and axial ligands have been omitted for clarity. Hydrogen bonds are represented by red dashed lines. Color codes: grey (carbon), red (oxygen), and light blue (zinc).

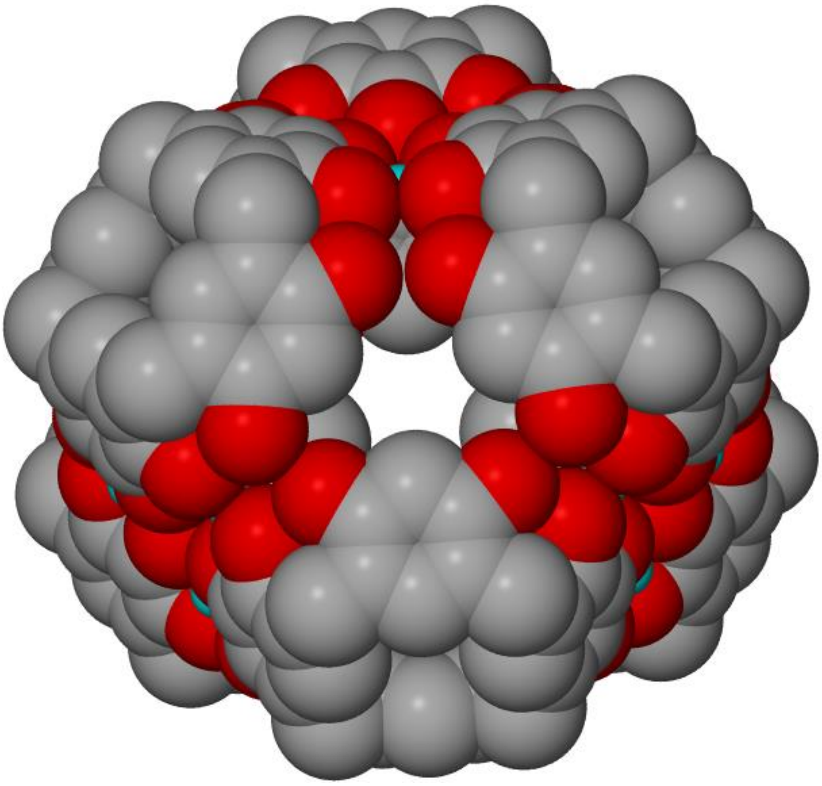

Figure S3. Space filling representation of **I** (top view) showing open windows. Hydrogen atoms, alkyl chains, and axial ligands have been omitted for clarity. Color codes: grey (carbon), red (oxygen), and light blue (zinc).

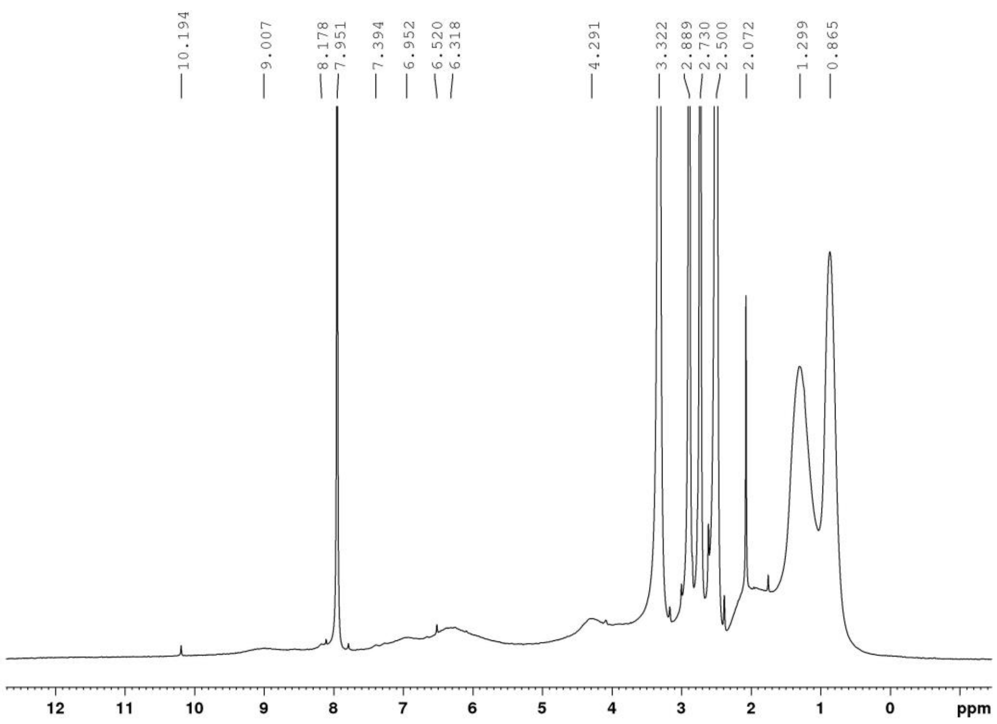

Figure S4. NMR spectrum of compound **I**.

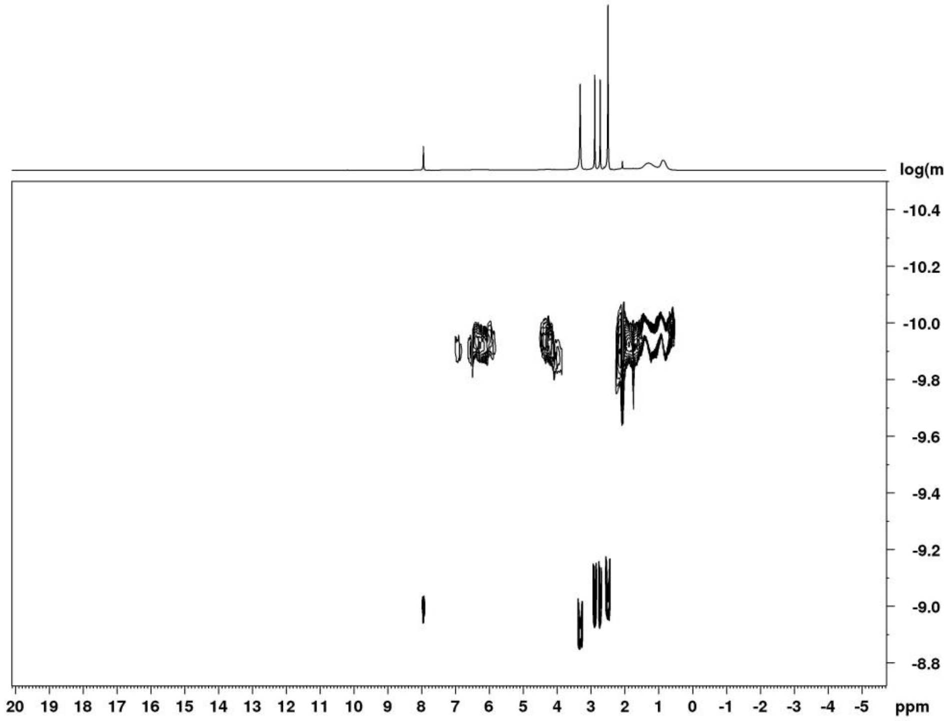

Figure S5. 2-D DOSY spectrum of compound **I**. The peaks at δ 8.0, 2.9, and 2.7 ppm represent DMF molecules. The peak at δ 3.3 ppm is water. The DOSY measurements illustrate that the diffusion coefficient is 1.2e-10 m^2/s for capsule **I** and 1.0e-9 m^2/s for solvent molecules such as water and DMF. This indicates the stability of capsule **I** in solution state.

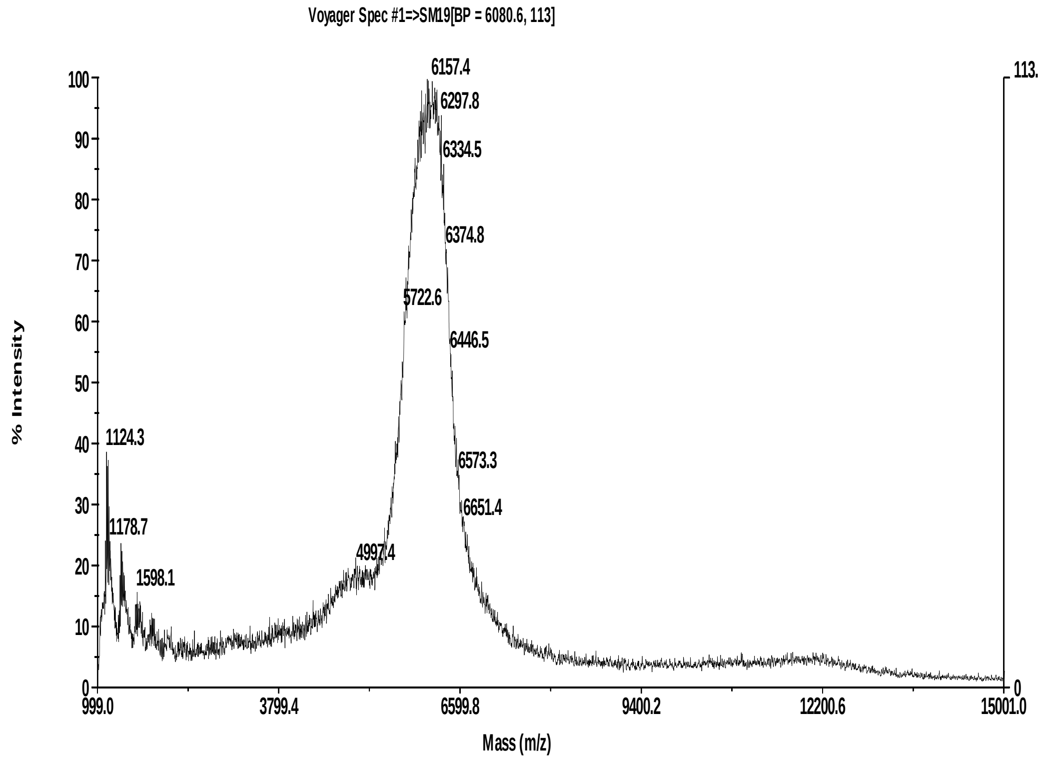

Figure S6. MALDI-TOF mass spectrum of capsule **I**. The peak at 6157.4 Da represents the mass peak for the capsule, one DMF and twenty one water molecules. The solvent molecules (water or DMF) can act as either axial ligands or encapsulated guest molecules.

Reference

[1] M. Sheldrick George, *Acta crystallographica. Section A, Foundations of crystallography* **2008**, *64*, 112-122.

[2] L. J. Barbour, *Journal of Supramolecular Chemistry* **2003**, *1*, 189-191.