Supporting Information

Self-assembly of M7L2 Metal-Organic Nanocapsules Using

Mixed Macrocycles

Chen Zhang,^a Kanishka Sikligar,^a Rahul S. Patil,^a Charles L. Banes,^a Simon J. Teat^b and Jerry L. Atwood^a*

^a Department of Chemistry University of Missouri-Columbia
601 S College Ave, Columbia MO 65211 United States E-mail: Atwoodj@missouri.edu

^bAdvanced Light Source Lawrence Berkeley National Laboratory 1 Cyclotron Rd, MS6R2100, CA 94720 United States

METHODS

Materials and Characterization. All solvents and chemicals were purchased and used without further purification. The single crystal X-ray diffraction data was collected on a Brucker Apex II diffractometer at 100 (2) K using CuKa (1.54056Å) radiation with incotec Microfocus tube. The structure was solved and refined using SHELX¹ and Xseed². The NMR samples were prepared by dissolving 2 mg of compound **3** 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 5mm 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 °C. 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. Mass spectroscopy was done using a Thermo-Finnigan LCQ Deca XP plus ion trap mass spectrometer with ESI+ ionization source. Samples were directly injected into the source. MALDI samples 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*-propyl pyrogallol[3]resorcin[1]arene ($P_3R_1C_3$). Butyraldehyde (7.21 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 followed by the addition of 3.5 mL of concentrated HCl. Thereafter, the mixture was refluxed at 110 °C for 24 hours. After cooling down, the precipitate was filtered, washed with cold ethanol/water (1:1) and dried in vacuum. 5.5 g of white solid was prepared as the final product. In the synthesis of $P_3R_1C_4$, butylaldehyde was replaced by pentaldehyde (8.5 mL, 0.08 mol). **Preparation of 2 [Co₇(P_3R_1C_4)_2(py)₇(NO_3)_2]Hpy⁺NO_3⁻**. *C*-Butyl mixed macrocycles ($P_3R_1C_4$, 100.0 mg) and Co(NO_3) 6H₂O (0.4 mmol, 116.4 mg) were dissolved in 2 mL of acetonitrile (MeCN) followed by the addition of 100 µL of pyridine (1.2 mmol) in a 4 mL glass vial. The mixture was then sonicated for 5 min and heated at 100 °C overnight. Large purple block crystals were then formed and collected for single crystal X-ray analysis. Yield is 32 mg, 20% based on cobalt nitrate.

Preparation of 3 [Zn₇(P₃R₁C₃)₂(py)₇(NO₃)₂] py. *C*-Propyl mixed macrocycles (P₃R₁C₃, 100.0 mg) and Zn(NO₃) 6H₂O (0.4 mmol, 119.0 mg) were dissolved in 0.5 mL of *N*,*N*-dimethylformamide (DMF) and 1.5 mL of acetonitrile (MeCN) followed by the addition of 100 μ L of pyridine (1.2 mmol) in a 4 mL glass vial. The mixture was then sonicated for 5 min and heated at 100 °C overnight. Thereafter, the resulted brown solution was placed at room temperature for one day. Large yellow block

crystals were then formed and collected for single crystal X-ray analysis. Yield is 35.5

mg, 24% based on zinc nitrate.

Supplementary Data

Table S1: Single crystal structure data of 2 and 3.

	2	3
Molecular formula	$[Co_7(P_3R_1C_4)_2(py)_7(NO_3)_2][Hpy]^+NO_3^-$	$[Zn_7(P_3R_1C_3)_2(py)_7(NO_3)_2] py$
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
Temperature (K)	100	100
a(Å)	29.060(7)	28.6437(12)
b(Å)	25.535(6)	25.8870(10)
c(Å)	17.029(5)	16.8049(6)
a(°)	90	90
β(°)	93.26(2)	90.588(2)
γ(°)	90	90
V(Å ³)	12616(5)	12460.2(8)
Z	4	4
Calculated desnity	1.433	1.378
Θ range of datacollection()	2.30-66.22	2.30-65.17
Total unique reflections	9987	9907
Goodness of fit	2.047	2.022
R1 after merging	0.2508	0.1566
R(int)	0.1606	0.0565
wR2	0.4451	0.4575



Figure S1. Side view of M_7L_2 cobalt-seamed dimeric nanocapsules, 2. Color codes: cobalt (purple), carbon (grey), oxygen (red) and nitrogen (blue). Hydrogen bonds are represented by green dashed lines. Hydrogen atoms, exterior axial ligands and alkyl tails have been removed for clarity.



Figure S2. Packing arrangements of (A) **1**, (B) **2**, and (C) **3** along [001] direction. Color codes: cobalt (purple), zinc (light blue), carbon (grey), and oxygen (red). Distances between centroids are represented by green dashed lines. Hydrogen atoms, exterior axial ligands and alkyl tails have been removed for clarity.



Figure S3. The products in the synthesis of $P_3R_1C_3$ and $P_3R_1C_4$ is a mixture of *C*-alkyl pyrogallol[x]resorcin[4-x]arene, where x is the number of Pg moieties, x = 0-4). There are two isomers for x =2. The six types of mixed macrocycles are represented by A1 - A6 and B1 - B6 here. ESI-MS spectra of the products show that A1 : A2 : A3&A4 : A5 = 0.75 : 1 : 0.5 : 0.15 and B1 : B2 : B3&B4 : B5 : B6 = 0.6 : 1 :

0.8 : 0.4 : 0.1. m/z: 722.02 (A1), 705.97 (A2), 690.08 (A3 & A4), 673.16 (A5), A6 is not detected, 778.13 (B1), 762.23 (B2), 746.27 (B3 & B4), 730.15 (B5), and 713.25 (B6).



Figure S4. NMR spectrum of compound 3 (Zn_7L_2 capsule). NMR analysis of compound 2 (Co_7L_2 capsule) is not successful due to the paramagnetic effect of cobalt ions.



Figure S5. 2-D DOSY spectrum of compound **3** (Zn₇L₂ capsule). The peaks at δ 8.5, 7.8, and 7.4 ppm represent free pyridines. The DOSY measurements illustrate that the diffusion coefficient is 1.5382e-10 m²/s for Zn₇L₂ capsule and 1.0423e-9 m²/s doe free pyridine molecules. The peak at δ 11.8 ppm is the non-coordinated phenolic group of Zn₇L₂ capsule. Its relatively slower diffusion compared to Zn₇L₂ capsule is probably due to the proton exchange with water molecules. The faster diffusion of pyridine molecules indicates that the periphery pyridine ligands are exchanged with DMSO in the solution phase.



Figure S5. Top: MALDI-TOF mass spectrum of compound 2 (Co_7L_2 capsule). The peak at 2082 Da represents the mass peak for the capsule, one pyridinium, one nitrate and one water molecules. Bottom: MALDI-TOF mass spectrum of compound 3 (Zn_7L_2 capsule). The peak at 2006 Da represents the mass peak for the capsule, one

pyridinium, and four water molecules. In both compounds, pyridine/pyridinium molecule could be encapsulated within the capsule and the water molecules could be either exterior axial ligands or guest molecules inside the capsule. The insets show the calculated isotopic distributions of the two mass peaks.

References:

- 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.