Supplementary Material (ESI) for Chemical Communications

Closed-surface, metal-organic nanocapsules derived from cavitand ligands

Supporting Information

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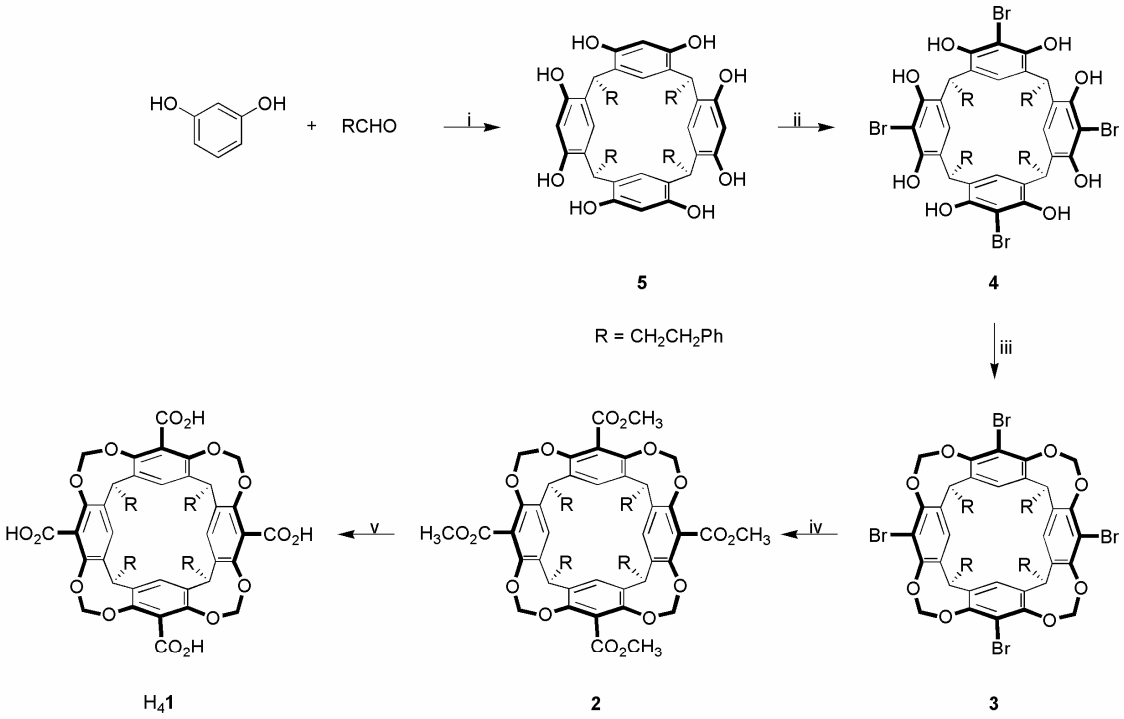
General Information:
All reagents were obtained from Acros (Pittsburgh, PA) or Aldrich (Milwaukee, WI) and used without further purification unless otherwise stated. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl before use. Flash chromatography was carried out on silica gel (32-64μm). ^{1}H (300MHz) and ^{13}C (75.5MHz) NMR were recorded on Varian Mercury 300 NMR. Elemental analysis data were collected using a Perkin Elmer 2400 CHN analyzer. Single crystal X-ray diffraction data was obtained on a Siemens 1000 SMART diffractometer at 100 K. Powder x-ray diffraction was obtained on a Rigaku R-axis 2163A101 diffractometer.

Syntheses



i Ethanol, HCl, H_2O; ii NBS, 2-Butanone; iii K_2CO_3, DMA, CH_2BrCl; iv *n*-BuLi, THF, $ClCO_2Me$; v NaOH, H_2O, Ethanol, HCl

Scheme S1. Syntheses of Cavitand tetra acid H_4**1**

***C*-phenethylcalix[4]resorcinarene, 5**[1]

Resorcinol (55 g, 0.5 mol) was dissolved in 400 ml of 95% ethanol and 100 ml of 37% hydrochloric acid. To this mixture stirred at 0ºC was added in a drop wise manner 67 g of dihydrocinnamaldehyde. The clear reaction mixture was warmed to room temperature. After 24 hours at room temperature, it was slowly heated to reflux and held there for 3 days. 150 ml of water was then added to the mixture and the solution was then cooled to room temperature and filtered and the solid washed with cold 50% ethanol-water mixture. This gave 94 g (83%) of product. ^{1}H NMR ($(CD_3)_2CO$) δ 2.35-2.60 (m, 28 H, CH_2CH_2Ar), 4.2-4.32 (t, 4 H methine H, J = 5.0 Hz), 6.2 (s, 4 H, ArH ortho to OH), 7.05-7.28 (m, 20 H, C_6H_5), 7.41 (s, 4 H, meta to OH), 9.04 (s, OH). ^{13}CNMR δ 125.26, 129.17, 129.41, 143.46, 152.87.

4[2]

To a stirred mixture of 27.5g (30.5mmol) **5** in 150ml of 2-butanone was added over 5 minutes 26g (146mmol) of *N*-bromosuccinimide. After the mixture was stirred for 12 hours a thick precipitate developed which was then filtered , washed with methanol and recrystallized from 6:1 CH_3CN-$(CH_3)_2NCHO$ (v/v) to give 39.4g(52.8%) of **4**. ^{1}H NMR ($(CD_3)_2SO$) δ 2.58-2.79 (m, 16 H, CH_2CH_2), 4.52 (t, 4 H methine, J = 5 Hz), 7.11-7.18 (m, 20 H, C_6H_5), 7.75 (s, 4 H ArH meta to OH), 8.36 (s, OH). ^{13}CNMR ($CDCl_3$) δ 101.92, 126.31, 129.22, 142.50, 149.46.

3[2]

To a stirred mixture of 300ml of *N*-*N*-dimethyl acetamide, 15g of K_2CO_3, and 6ml CH_2BrCl (93 mmol) was added over 2 days as a solid 11.0g (8.5 mmol) of **4**. An additional 5ml of CH_2BrCl was added, and the reaction mixture was warmed to 65 ˚C for 3 days. The reaction mixture was cooled down, and the solvent was removed under reduced vacuum. The residue was extracted with $CHCl_3$. The $CHCl_3$ solution was concentrated under vacuum and chromatographed on a gravity column and eluted with CH_2Cl_2 as the mobile phase. The isolated product was recrystallized from $CHCl_3$- CH_3OH to give 5g of **3** (42.5%). ^{1}H NMR (CD_3Cl) δ 2.52 (m, 8H, CH_2CH_2), 2.68 (m, 8H, CH_2CH_2), 4.42 (d, 4H, inner of CH_2, J = 6.0 Hz), 4.96 (t, 4H methine, J = 5.6 Hz), 5.98 (d, 4H, outer of CH_2, J = 6.0 Hz) 7.05-7.23 (m, 24H, ArH, C_6H_5). ^{13}CNMR δ 114.03, 119.00, 126.42, 128.83, 139.24, 141.27, 152.42.

2[2]
To 4.5g (3.5 mmol) of **3** dissolved in 300 of dry THF and cooled to -78˚C was added 20ml of *n*-BuLi (2.5M in hexanes) via syringe. This mixture was left to stir for 1hour after which 15ml of $ClCO_2CH_3$ was added. This mixture was stirred at -78˚C for another 30minutes and then allowed to warm to room temperature. The solvent was removed *in vacuo*, and the residue extracted with chloroform and water mixture with the aqueous phase extracted three times with chloroform. The combined organic portions were then dried over magnesium sulfate, concentrated, chromatographed on a gravity column and eluted with a 2:1 ethyl acetate hexane solution yielding 3.0g of tetraester **2** (70%); ^{1}H NMR (CD_3Cl) δ 2.43-2.73 (m, 16H, CH_2CH_2), 4.27 (d, 4 H, inner of CH_2, J = 5.7 Hz), 4.89 (t, 4H, methine, J = 5.1 Hz), 5.7 (d, 4H, outer of CH_2, J = 6.0 Hz) 7.07-7.34 (m, 24 H, ArH, C_6H_5). ^{13}CNMR ($CDCl_3$) δ 123.97, 126.36, 128.48, 138.25, 141.3, 151.73, 165.8

H_4**1**[3]
To 1.32g of tetramethyl ester **2** in 250ml of ethanol was 20ml of water and 8g of NaOH. This mixture was refluxed for 16 hours, after which the ethanol was removed *in vacuo*, and the residue was diluted with water and extracted with CH_2Cl_2 to remove any unreacted starting material. The aqueous solution was then acidified with 6M HCl and then extracted with 2-butanone, washed with brine and the solvent was removed under vacuum to give 1g of H_4**1** (80%); ^{1}H NMR ($(CD_3)_2CO$) δ 2.68 (bs, 8 H, CH_2CH_2), 4.549 (d, 4 H, inner of CH_2, J = 5.6 Hz), 4.84 (t, methine, J = 4.8 Hz), 5.75 (d,4 H, outer of CH_2, J = 5.6 Hz) 7.22 (m, 24 H, pendant C_6H_5) 7.78 (ArH). ^{13}CNMR ($(CD_3)_2SO$) δ 123.26, 126.21, 126.75, 129.09, 129.14, 139.09, 142.10, 150.52, 166.03, 209.59.

$[Zn_{16}(1)_6(\mu\text{-}OH)(H_2O)_{14}][NO_3]_7 \cdot x(CH_3COCH_3) \cdot y(H_2O)$, ($x \approx 12$, $y \approx 50$)
A vial was charged with 35mg (0.03mmol) of H_4**1,** 12ml of acetone and 37mg (0.12mmol) of $Zn(NO)_3 \cdot 6H_2O$, white precipitate formed after a few hours. This precipitate was collected after 72 hours to afford 51 mg (21%) of the title compound. Anal Calc. (%) for $[Zn_{16}(\mathbf{1})_6(\mu\text{-}OH)(H_2O)_{14}][NO_3]_7 \cdot 12CH_3COCH_3 \cdot 47H_2O$, $Zn_{16}C_{444}H_{507}O_{191}N_7$, C 53.09, H 5.09, N 0.98; obs. C 49.91, H 5.39, N 1.23.

X-ray Single Crystal Structure

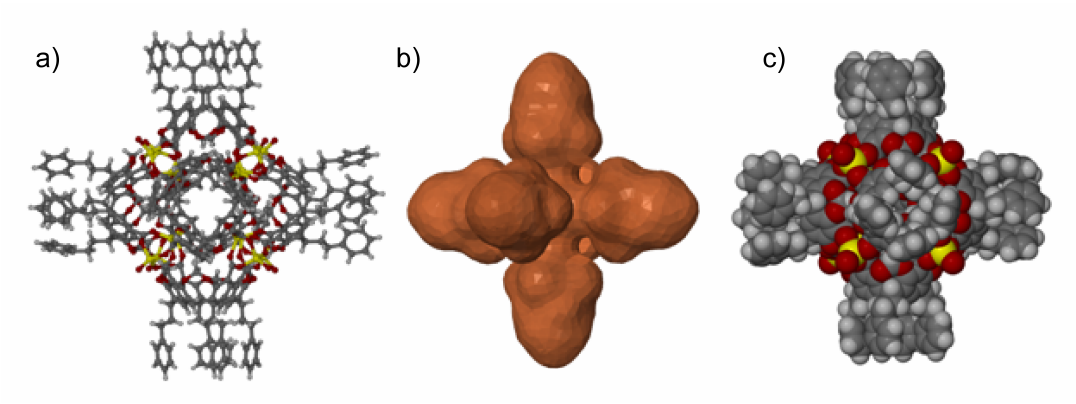


Figure S1. Ball and stick (a) and spacefill (c) renditions of the nanocapsules in $[Zn_{16}(\mathbf{1})_6(\mu\text{-}OH)(H_2O)_{14}][NO_3]_7 \cdot solvent$. For clarity, only one of the two disordered nanocapsule orientations is shown. (b) The 680 $Å^3$ solvent accessible internal cavity volume as calculated form Connolly surface models.

The crystal structure exhibits extreme so-called "whole molecule" disorder. The extreme disorder gives rise to low diffraction intensities at high resolution and only data below $2\theta = 42.0°$ were used in the refinement. The nanocapsules reside on sites of crystallographically imposed -3 symmetry. Thus, one-sixth of the capule is unique by symmetry. As the crystallography site symmetry is higher than that which can be sustained by the chiral nanocapsules themselves, the refinement model consists of a superposition of two enantiomeric capsules such that the singular cavitand ligand within the asymmetric unit is disordered over two equivalent positions. The refinement model additionally consists of the apical ligands and two acetone molecules per cavitand ligand, one residing wihtin the cavitand bowl and the other residing within the phenthyl feet of the cavitand. Due to the extensive disorder and low resolution, only the Zn atoms and apical water ligands could be modelled with anisotropic displacement parameters. All other atomic positions were refined with isotropic displacement parameters. All other atoms were refined with isotropic displacement paramters. The arene rings of the cavitand ligands were fixed to be regular hexagons. Extensive disorder of other residual solvents and anions precluded accurate modelling. The data were therefore treated with the SQUEEZE subroutine of PLATON[4] to account for the residual electron density associated within these highly disordered regions containing anions and solvent. Per formula unit, SQUEEZE estimates 691 e^- within 2765 $Å^3$ of unmodelled space, corresponding to seven $[NO_3]^-$ anions and the electron density equivalent of 47 assumed molecules of water (calc. 694 e^-).

The estimation of seven molecules of acetone (or nitrate) encapsulated within the nanocapsules is in line with the available volume of 680 $Å^3$. Given a molecular volume of 62 $Å^3$ per molecule of acetone, the percent of the internal volume occupied by acetone measures 64%, in line with packing fractions observed for related capsular species.

Powder X-ray Diffraction (XRD)

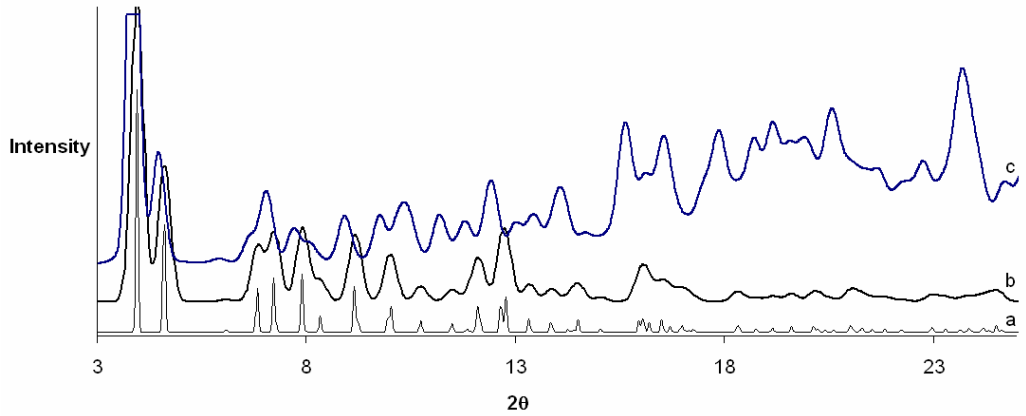


Figure S2. X-ray powder diffraction patterns of $[Zn_{16}(\mathbf{1})_6(\mu\text{-}OH)(H_2O)_{14}][NO_3]_7 \cdot solvent$. (a) calculated from single crystal structure (85K); (b) calculated from single crystal structure (85K), artificially broadened; (c) experimentally observed pattern of fully solvated material soaked with mother liquor (298K).

The above powder XRD data were indexed to an *R*-3 trigonal unit cell. Comparison between the unit cell parameters extracted from the single crystal X-ray determination and the indexed powder X-ray data are given in the table below.

Table S1. Unit cell determinations.

	Single crystal (Å)	Powder XRD (Å)
a,b	44.783(6)	45.918(4)
c	22.093(6)	22.720(4)
V	38373(12)	41489(8)

Thermal Gravimetric Analysis (TGA)

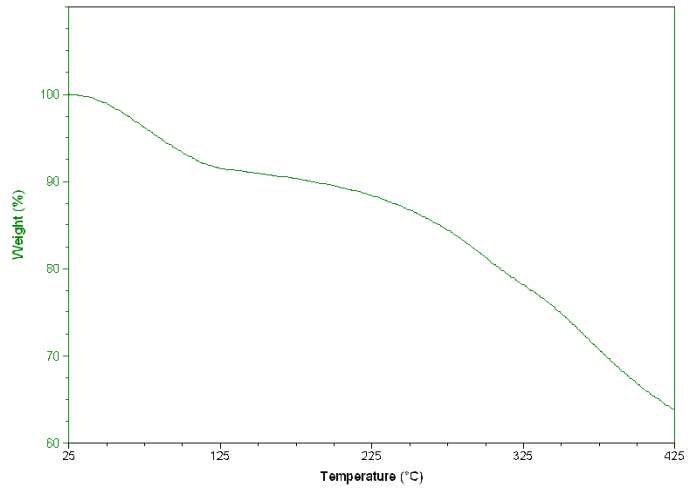


Figure S3. TGA profile of $[Zn_{16}(\mathbf{1})_6(\mu\text{-}OH)(H_2O)_{14}][NO_3]_7 \cdot solvent$.

Infra-Red Spectroscopy

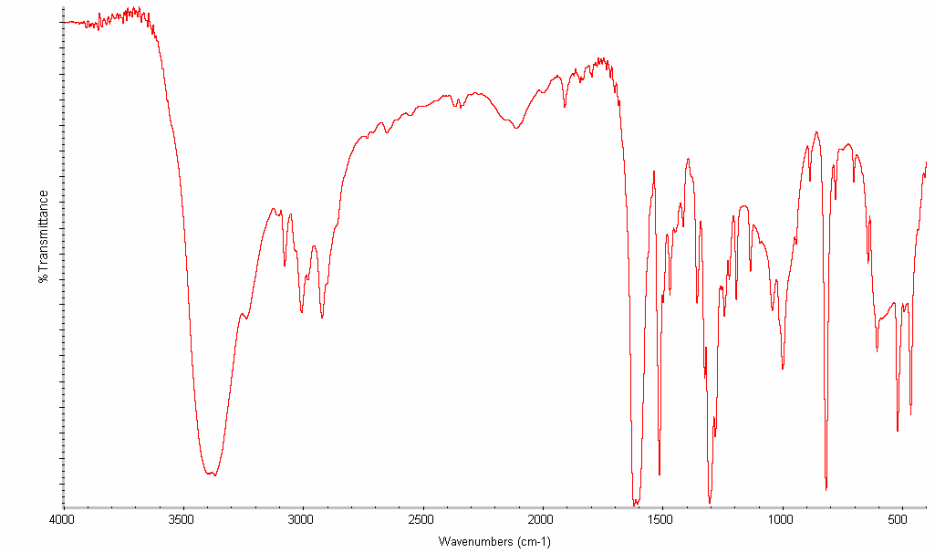


Figure S4. IR spectrum of $[Zn_{16}(\mathbf{1})_6(\mu\text{-}OH)(H_2O)_{14}][NO_3]_7 \cdot solvent$.

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