

Supporting Information

Constructing channel structures based on the assembly of *p*-sulfonatocalix[4]arene nanocapsules and $[M(\text{bpdo})_3]^{2+}$ (M=Cu, Zn)

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Experimental Section:

All reagents were commercial products of high purity and were not further purified except Na_4 [*p*-sulfonato-calix[4]arene], which was prepared via the sulfuric acid reaction with tetra(tert-butyl)calix[4]arene.¹

Mixture of CuCl_2 , Na_4 [*p*-sulfonato-calix[4]arene] and bpdo (3:2:9) (pH=5) was dissolved in hot water. Deep green crystals of the title compound 1 were obtained after volatilizing at room temperature (yield: 68%); Compound 2 was prepared by a

procedure analogous to that used to synthesize compound 1 (yield: 64%). Microanalysis (CHN) was not feasible due to the highly hydrated nature of the complex. Some kind of disorder of water inside the channels are responsible for the relatively high value of agreement factor R1.

Measurement

All single-crystal X-ray data were collected on a Bruker SMART 1000 CCD diffractometer with Mo_{Kα} radiation ($\lambda = 0.071073$ nm) using the ω -scan mode. Data were corrected for absorption using the SADABS program, and solution and refinement of the structure were performed using the SHELX-97 software package. The free water molecules were removed before the cited solvent accessible volume was calculated by Platon. The powder X-ray diffraction (XRD) of the compound 1 and 2 were examined on a Rigaku-Dmax 2500 diffractometer using Cu K α radiation ($\lambda = 0.15405$ nm).

The vapor-phase adsorption measurements of organic molecules on the products were performed at 25°C on a VTI MB-300G Gravimetric Sorption Analyzer. Prior to the adsorption, the sample was evacuated at 150 °C for 5 h. Fourier transform infrared (FTIR) spectra were measured within the 4000-400cm wavenumber range using a Perkin-Elmer model 580B IR spectrophotometer with the KBr pellet technique. Thermogravimetric analysis (TGA) was performed on a SDT2960 analyzer (Shimadzu, Japan) up to 700 °C at a heating rate of 10 °C /min under N₂.

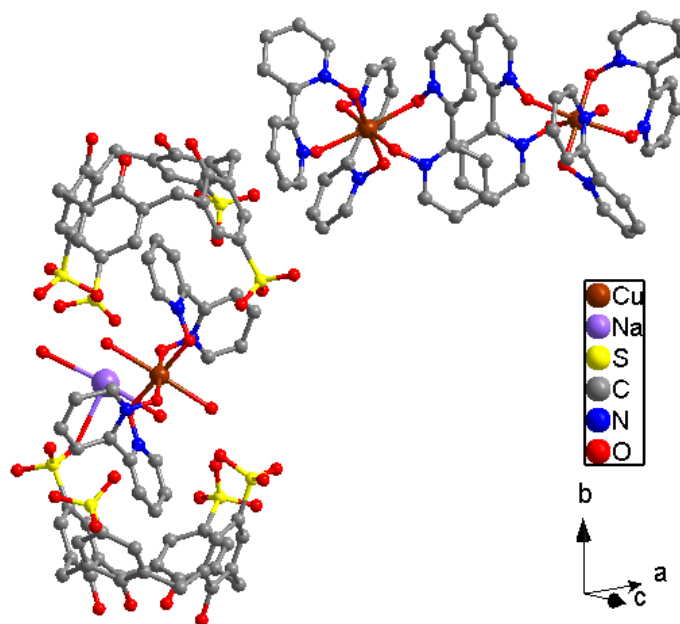


Fig S1 The asymmetric unit of compound 1, water molecules have been removed for clarity.

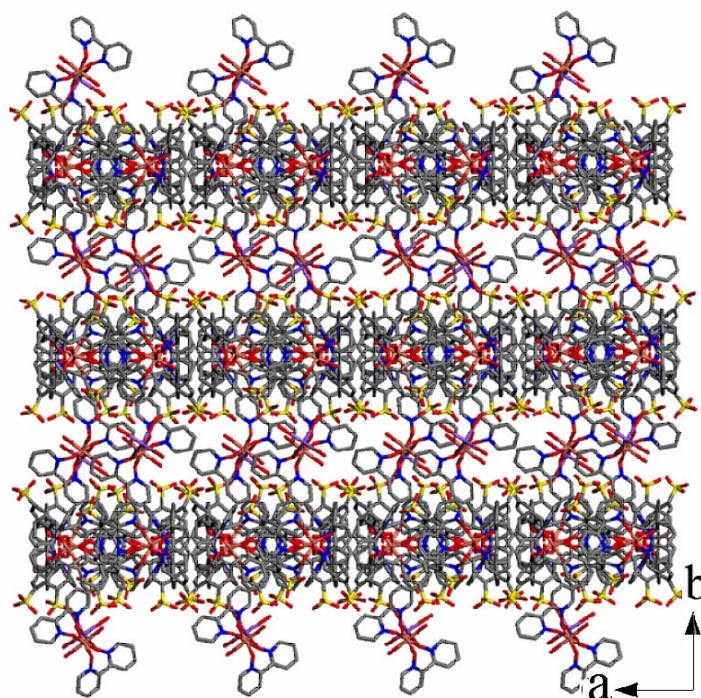


Fig S2 the layers are separated by the $[\text{Cu}(\text{bpdo})_2 \cdot 2\text{H}_2\text{O}]^{2+}$ (viewed down the c direction), water molecules have been removed from the channels for clarity.

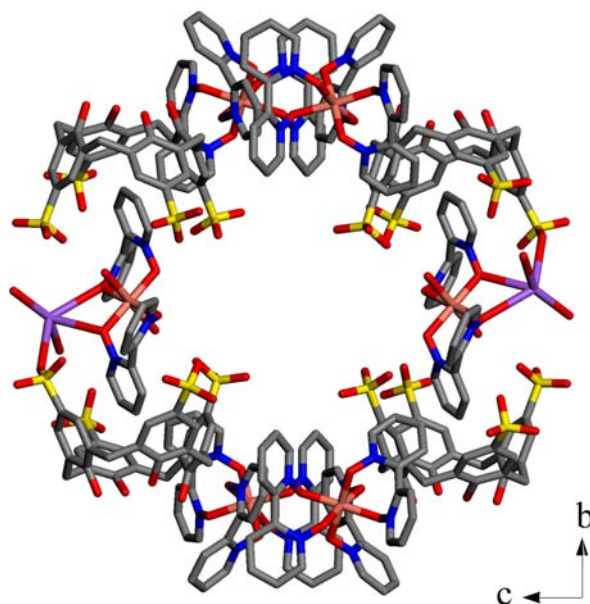


Fig S3 The alignments *p*-Sulfonatocalix[4]arenes nanocapsules and $[\text{Cu}(\text{bpdo})_3]^{2+}$ into void space, water molecules have been removed from the channels for clarity.

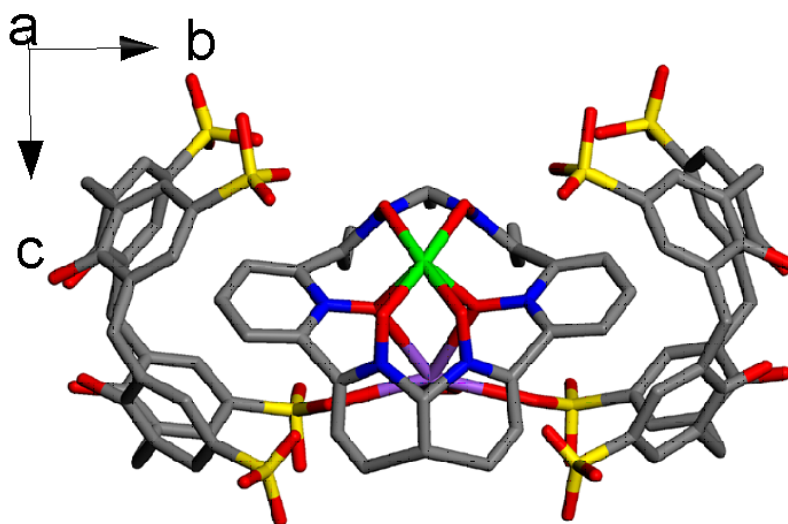


Fig S4 Structure of the supramolecular nanocapsules based on the *p*-sulfonatocalix[4]arenes and $[\text{Zn}(\text{bpdo})_2\text{2H}_2\text{O}]^{2+}$, water molecules have been removed from the channels for clarity.

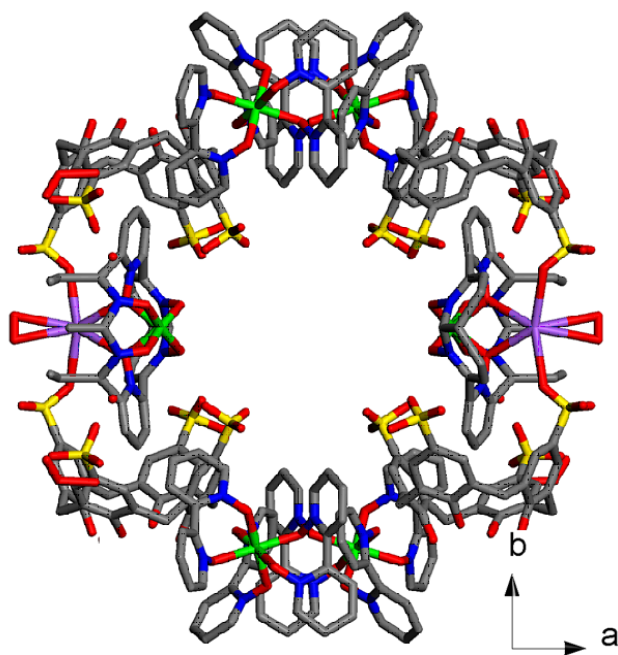


Fig S5 The alignments *p*-Sulfonatocalix[4]arenes nanocapsules and $[\text{Zn}(\text{bpdo})_3]^{2+}$ into void space (viewed down the *a* direction), water molecules have been removed from the channels for clarity.

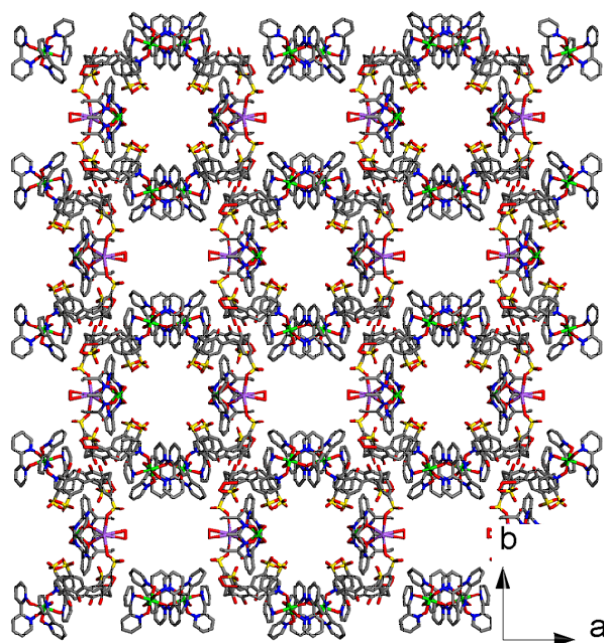


Fig S6 The Packing diagram down the *c* axis showing the porous structure of compound 2, the dissociative water molecules are omitted for clarity.

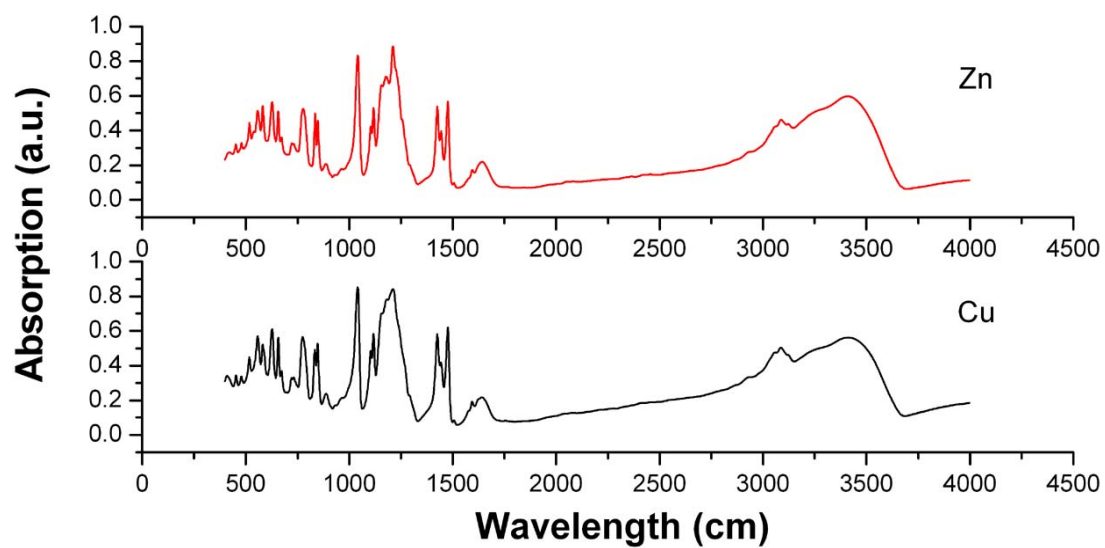


Fig S7 The infrared spectra of compound 1 (black) and 2 (red) before activation.

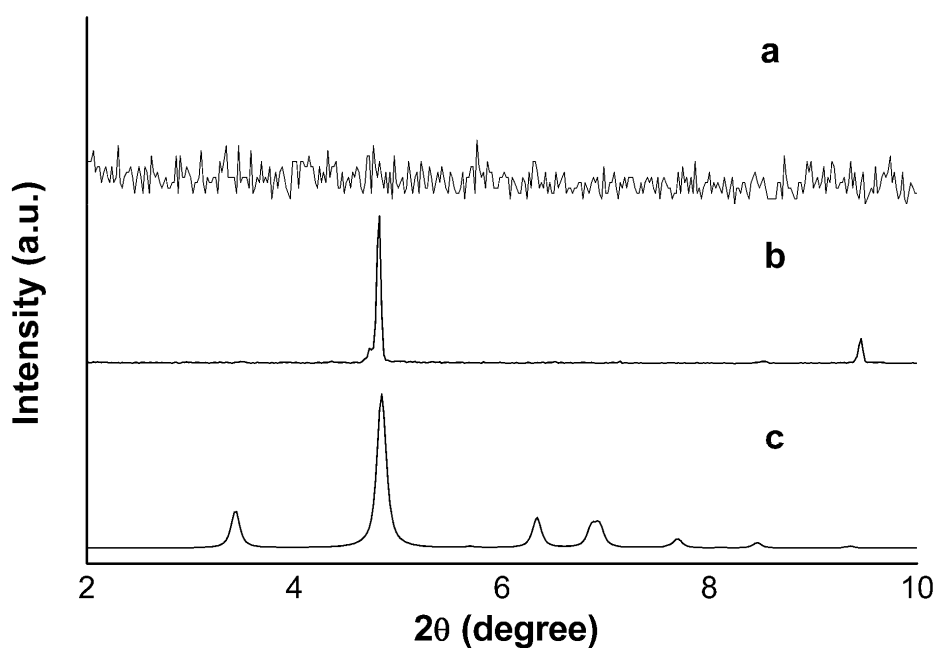


Fig S8 (a) Powder XRD patterns of compound 1 after evacuated at 150 °C for 5 h; (b) Powder XRD patterns of compound 1; (c) simulated from single crystal data.

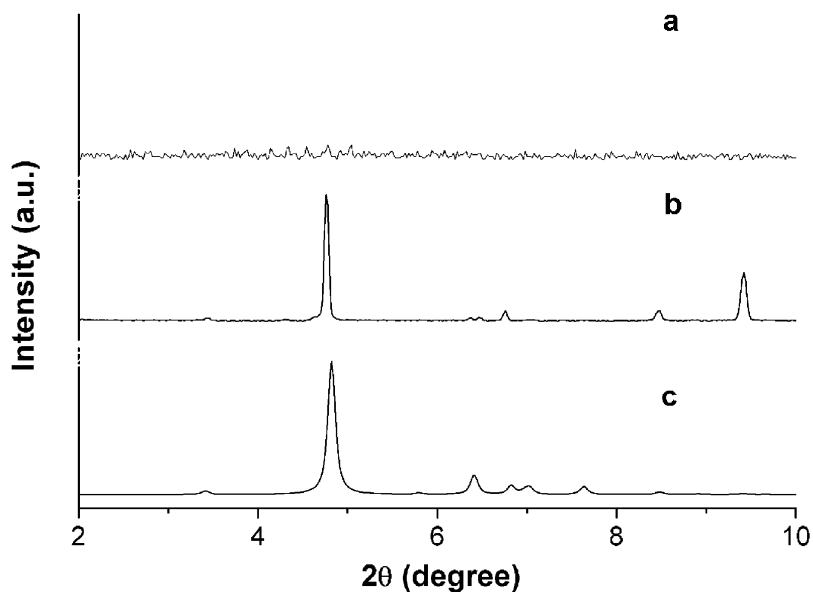


Fig S9 (a) Powder XRD patterns of compound 2 after evacuated at 150 °C for 5 h; (b) Powder XRD patterns of compound 2; (c) simulated from single crystal data.

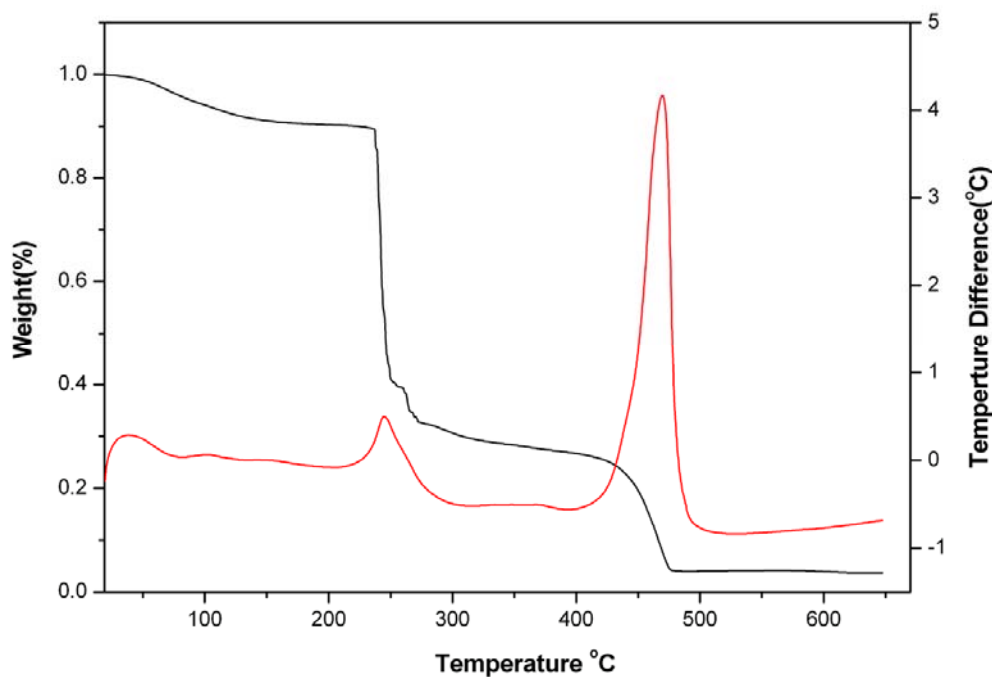


Fig S10 TGA of compound 1.

The crystal structure of compound 1 contains both dissociative and coordinated water molecules. The observed mass loss (9.9%) while heating up to 180 °C is

attributed to the loss of dissociative or coordinated water molecules. Then, the TGA curve reaches a plateau and the weight remains constant until 237 °C.

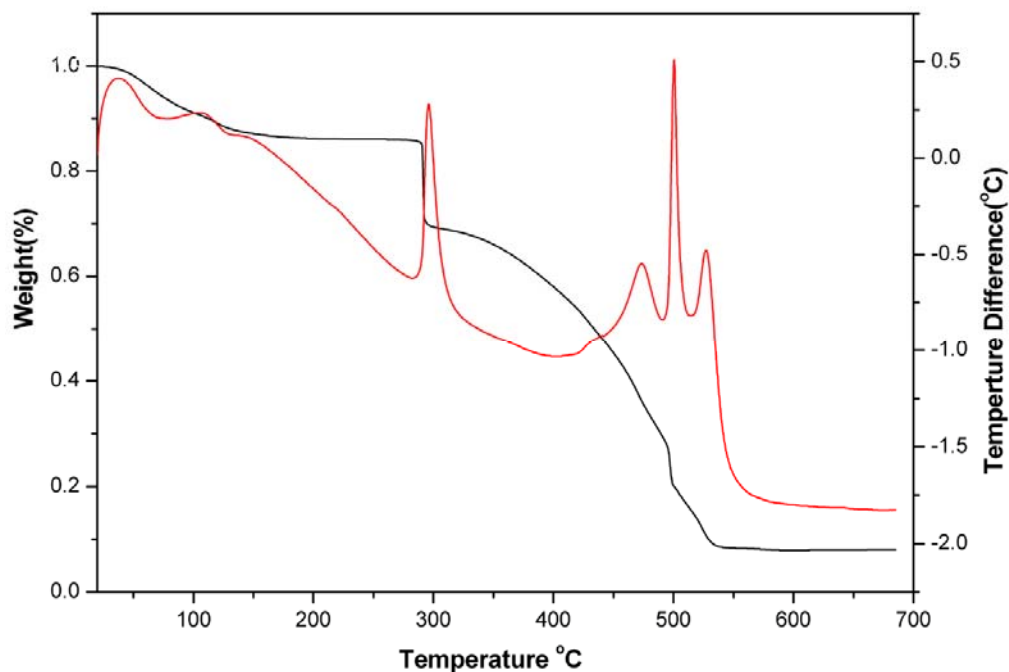


Fig S11 TGA of compound 2.

The crystal structure of compound 2 contains both dissociative and coordinated water molecules. The observed mass loss (13.8%) while heating up to 175 °C is attributed to the loss of dissociative or coordinated water molecules. Then, the TGA curve reaches a plateau and the weight remains constant until 290 °C.

Reference:

M. Makha and C. L. Raston, *Chem. Commun.*, **2001**, 2470.