Electronic Supplementary Material (ESI) for Dalton Transactions

$[CdCl4]^{2-}$ Anion-induced coordination of alkaline earth metal ions to cucurbit[7]uril, corresponding supramolecular self-assemblies and potential application

Yi Zhao, Li-Li Liang, Kai Chen, Ning-Ning Ji, Xiao-Jie Cheng, Xin Xiao, Yun-Qian Zhang, Sai-Feng Xue, Qian-Jiang Zhu, Nan Dong* and Zhu Tao*

General materials: The cucurbit[7]uril was prepared by the procedures reported previously. Other chemicals, such as $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $SrCl_2 \cdot 6H_2O$, $CdCl_2 \cdot 2.5H_2O$ and HCl were of reagent grade and used without further purification. All chemicals are of analytic grade and were used without further purification. Elemental analysis was carried out using a EURO EA-3000 element analyzer.

Preparation of $\{Mg(H_2O)_3(Q[7])\}2[CdCl_4]$ $2(H_3O)17H_2O$ **(1).** Q[7] (20 mg, 0.015 mmol), $CdCl_2 \cdot 2.5H_2O$ (20.42 mg, 0.089 mmol), $MgCl_2 \cdot 6H_2O$ (24.24 mg, 0.119 mmol) were dissolved in 2 mL 3.0 $mol \cdot L^{-1}$ HCl. The solution was allowed to stand to allow slow evaporation in air at room temperature. Colorless crystals were obtained from the solution within 2 days. Anal. Calcd for $C_{42}H_{88}N_{28}O_{36}MgCd_2Cl_8$ (%): C 24.09, H 4.21, N 18.74; found: C 24.27, H 4.07, N 18.94.

Preparation of $\{Ca_2(H_2O)_4(Q[7])\}$ $2[CdCl_4]$ $14H_2O$ **(2).** Q[7] (20 mg, 0.015 mmol), $CdCl_2 \cdot 2.5H_2O$ (20.42 mg, 0.089 mmol), $CaCl_2$ (13.23 mg, 0.119 mmol) were dissolved in 2 mL 3.0 $mol \cdot L^{-1}$ HCl. The solution was allowed to stand to allow slow evaporation in air at room temperature. Colorless crystals were obtained from the solution within one day. Anal. Calcd for $C_{42}H_{94}N_{28}O_{40}Ca_2Cd_2Cl_8$ (%): C 22.72, H 4.24, N 17.67; found: C 22.96, H 4.03, N 17.74.

Preparation of $\{Sr_2(H_2O)_9(Q[7])\}2[CdCl_4]19H_2O$ **(3).** Q[7] (20 mg, 0.015 mmol), $CdCl_2 \cdot 2.5H_2O$ (20.42 mg, 0.089 mmol), $SrCl_2 \cdot 6H_2O$ (31.79 mg, 0.119 mmol) were dissolved in 2 mL 3.0 $mol \cdot L^{-1}$ HCl. The solution was allowed to stand to allow slow evaporation in air at room temperature. Colorless crystals were obtained from the solution within one day. Anal. Calcd for $C_{42}H_{98}N_{28}O_{42}Sr_2Cd_2Cl_8$ (%): C 21.46, H 4.17, N 16.69; found: C 21.59, H 4.08, N 16.81.

X-ray Crystallography: The data of the three Q[7]-based supramolecular assemblies compounds **1**~**3** were collected on a Bruker Smart Apex2 CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) in ω and φ scan mode. Lorentz polarization and absorption corrections were applied. Structural solution and full matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program package[1] respectively. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically. Water molecules in the unit cell have been taken into account to SQUEEZE option of the PLATON program. The squeezed water molecules are 19, 22 and 19 for the compounds **1**~**3** respectively. Details of the crystal parameters, data collection, and refinements for compounds **1**~**3** are summarized in Table S1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as deposition Nos. CCDC 951055 (1), CCDC 951056 (2), CCDC 951057 (3). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223/336 033; deposit@ccdc.cam.ac.uk).

Table S1. Crystal Data and Structure Refinement Details for Q[7]-based porous materials **1-3**

Compound	1	2	3
empirical formula	$C_{42}H_{88}N_{28}O_{36}MgCd_2Cl_8$	$C_{42}H_{94}N_{28}O_{40}Ca_2Cd_2Cl_8$	$C_{42}H_{98}N_{28}O_{42}Sr_2Cd_2Cl_8$
formula weight	2094.11	2220.01	2351.12
crystal system	monoclinic	orthorhombic	monoclinic
space group	P 21/n	P 21 21 21	P 21/n
a(Å)	16.7744(15)	17.070(3)	16.8058(19)
b(Å)	17.5872(16)	17.240(3)	17.638(2)
c (Å)	28.665(3)	28.560(5)	29.047(4)
α(°)	90.00	90.00	90.00

β(°)	94.248(3)	90.00	94.556(4)
γ (°)	90.00	90.00	90.00
V(Å^3)	8433.3(13)	8405(2)	8582.8(17)
	4	4	4
Å)	0.71073	0.71073	0.71073
Dcalcd(g·cm^{-3})	1.649	1.754	1.820
F(0,0,0)	4272	4536	4760
μ(MoKα)(mm^{-1})	0.864	0.988	2.081
T(K)	223	223	223
unique reflns	16328	14725	16627
obsd reflns	73997	38726	76874
params	883	911	946
Rint	0.0679	0.0886	0.0898
R [I > 2σ(I)][a]	0.0487	0.0593	0.0785
wR[I>2σ(I)][b]	0.1326	0.1403	0.2268
R [all data][a]	0.0693	0.1056	0.1240
wR[all data][b]	0.1415	0.1583	0.2525
Goodness of fit (GOF)	0.948	0.891	1.031

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = (F_o^2 + 2F_c^2)/3$.

References

1 (a) G. M. Sheldrick, *Acta Crystallogr. Sect. A*, **2008**, 64, 112-122; (b) G. M. Sheldrick, SHELXL-97, *Program for the Solution and Refinement of Crystal structures*, University of Göttingen, Germany, 1997.

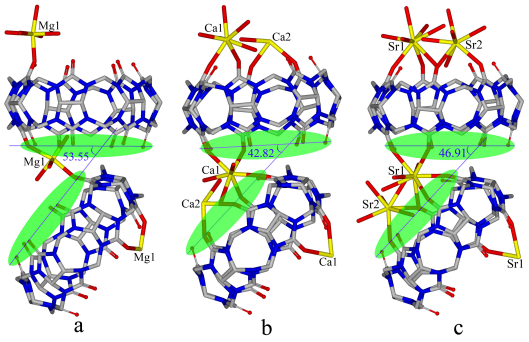

Figure S1 The angle of two portal planes of two adjacent Q[7] molecules in three compounds.

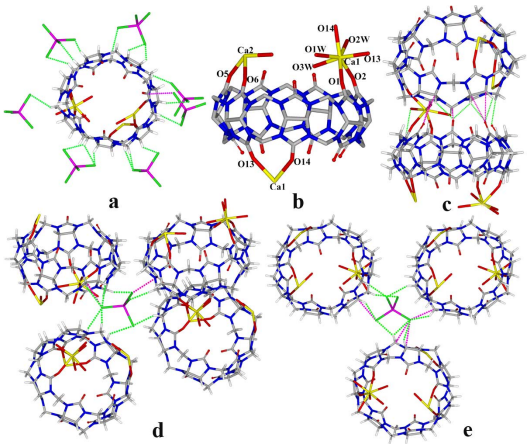

Figure S2 Detailed interactions in compound **2**: (a) a Q[7] molecule with eight $[CdCl_4]^{2-}$ anions; (b) a Q[7] molecule with two Ca^{2+} cations; (c) two neighboring Q[7] molecules; (d and e) a $[CdCl_4]^{2-}$ anion with four Q[7] molecules.

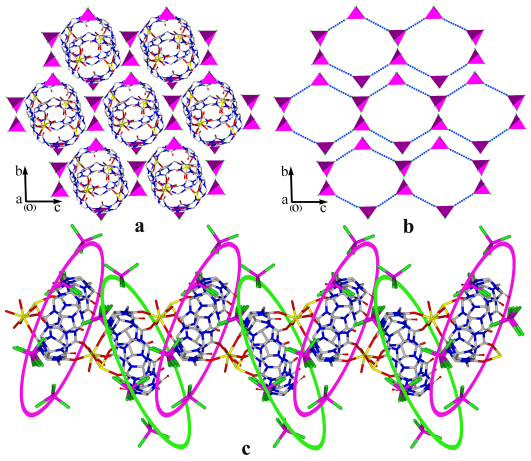

Figure S3 X-ray crystal structures of **2**: a) an overall view of the coordination feature and the supramolecular assembly in the compound **2**; b) the $[CdCl_4]^{2-}$ anions honeycomb-like framework; c) a zigzag coordination polymer of Ca^{2+} cations to Q[7] molecules surrounded by the $[CdCl_4]^{2-}$ anions.

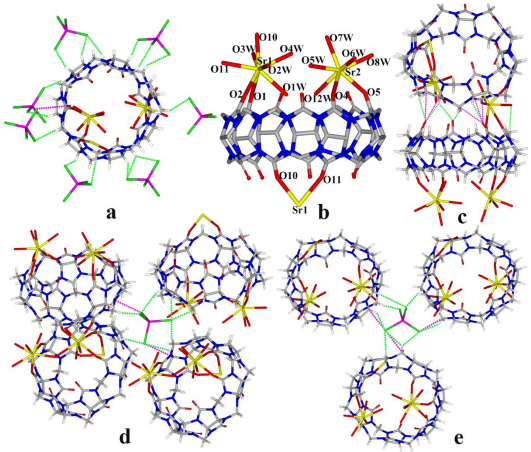

Figure S4 Detailed interactions in compound **3**: (a) a Q[7] molecule with eight $[CdCl_4]^{2-}$ anions; (b) a Q[7] molecule with three Sr^{2+} cations; (c) two neighboring Q[7] molecules; (d and e) a $[CdCl_4]^{2-}$ anion with four Q[7] molecules.

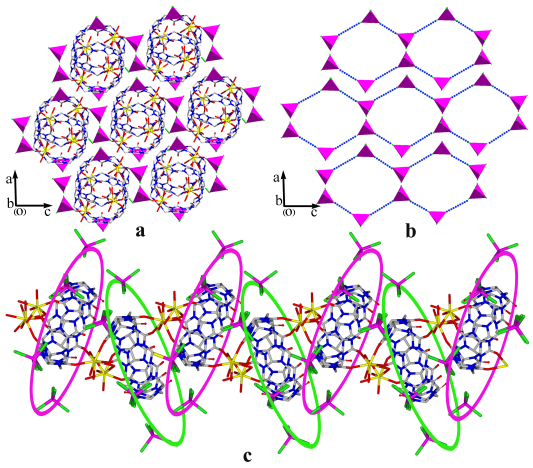

Figure S5 X-ray crystal structures of **3**: a) an overall view of the coordination feature and the supramolecular assembly in the compound **3**; b) the $[CdCl_4]^{2-}$ anions honeycomb-like framework; c) a zigzag coordination polymer of Sr^{2+} cations to Q[7] molecules surrounded by the $[CdCl_4]^{2-}$ anions.

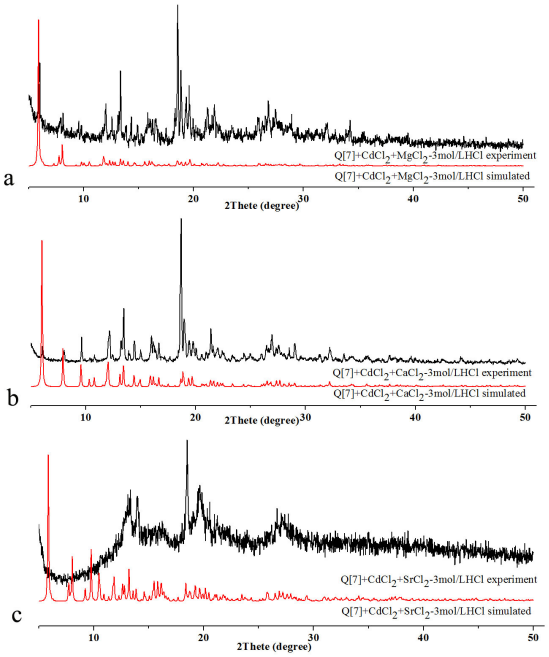

Figure S6 Powder X-ray diffraction (PXRD) of the compounds and the corresponding comparison with simulation.