

# $C_{3i}$ -Symmetric Octanuclear Cadmium Cages: Double-Anion-Templated Synthesis, Formation Mechanism, and Properties

Jie Sun,<sup>[a, b]</sup> Di Sun,<sup>[a]</sup> Shuai Yuan,<sup>[a]</sup> Dongxu Tian,<sup>[c]</sup> Liangliang Zhang,<sup>[a]</sup>  
Xingpo Wang,<sup>[a]</sup> and Daofeng Sun\*<sup>[a]</sup>

**Abstract:** A series of  $C_{3i}$ -symmetric bi-capped trigonal antiprismatic  $Cd_8$  cages  $[2X@Cd_8L_6(H_2O)_6] \cdot n Y$ -solvents ( $X = Cl^-$ ,  $Y = NO_3^-$ ,  $n = 2$ : **MOCC-4**;  $X = Br^-$ ,  $Y = NO_3^-$ ,  $n = 2$ : **MOCC-5**;  $X = NO_3^-$ ,  $Y = NO_3^-$ ,  $n = 2$ : **MOCC-6**;  $X = NO_3^-$ ,  $Y = BF_4^-$ ,  $n = 2$ : **MOCC-7**;  $X = NO_3^-$ ,  $Y = ClO_4^-$ ,  $n = 2$ : **MOCC-8**;  $X = CO_3^{2-}$ ,  $n = 0$ : **MOCC-9**), doubly anion templated by different anions, were solvothermally synthesized by means of a

flexible ligand. Interestingly, the  $CO_3^{2-}$  template for **MOCC-9** was generated in situ by two-step decomposition of DMF solvent. For other MOCCs, spherical or trigonal monovalent anions could also play the role of tem-

plate in their formation. The template abilities of these anions in the formation of the cages were experimentally studied and are discussed for the first time. Anion exchange of **MOCC-8** was carried out and showed anion-size selectivity. All of the cage-like compounds emit strong luminescence at room temperature.

**Keywords:** cadmium • cage compounds • ion exchange • luminescence • template synthesis

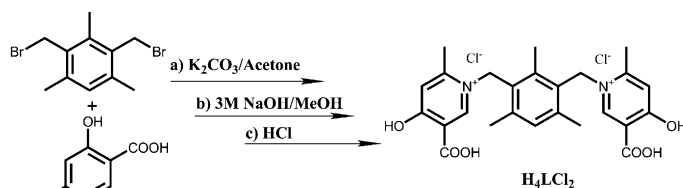
## Introduction

Well-defined metal–organic coordination cages (MOCCs) have attracted enduring attention because of their structural aesthetics and fascinating properties.<sup>[1,2]</sup> Assembly of polynuclear MOCCs usually involves the synergistic action of multiple components; therefore, it is a huge challenge to anticipate and control the assembly outcome. One effective synthetic methodology for MOCCs involves small molecules or ions as templates bearing significant instructions for the assembly process.<sup>[3]</sup> Although single anionic species have been extensively used as templates in the synthesis of interesting coordination compounds,<sup>[4]</sup> double- or multiple-template synthesis of MOCCs remains less explored.<sup>[5]</sup> Recently, Wang and co-workers pioneered the synthesis of giant silver alkynyl cages templated by double anions such as small

$CrO_4^{2-}$  or large  $Mo_6O_{22}^{8-}$ .<sup>[6]</sup> Compared to a single anion template,<sup>[7]</sup> double-anion templation not only effectively increases the nuclearity of the MOCCs but also contributes much more novelty to the final structures. Here we report double-anion-templated synthesis, characterization, and properties of octanuclear cadmium cages. The templates can be univalent or divalent anions, and both can template formation of octanuclear cages with unchanged conformation.

In contrast to the well-established group 11 metal cages or clusters,<sup>[8]</sup>  $Cd^{II}$  cages with comparable nuclearity required formidable synthetic efforts and were difficult to obtain due to the lack of metallophilic interactions and intrinsic electrostatic repulsive nature between neighboring metal centers.<sup>[9]</sup> However, it was envisioned that by synthesizing elaborately tailored flexible polydentate ligands, subsequent coordination to metal centers would result in the formation of polynuclear metal cages.<sup>[10]</sup>

Inspired by the points mentioned above and our previous work,<sup>[10b]</sup> we initially designed and synthesized novel multi-dentate ligand 1,1'-(2,4,6-trimethyl-1,3-phenylene)bis(methylene)bis(5-carboxy-4-hydroxy-2-methylpyridinium chloride) ( $H_4LCl_2$ , Scheme 1), which can be readily synthesized by reaction of 2,4-bis(bromomethyl)-1,3,5-trimethylbenzene and 4-hydroxy-6-methylnicotinic acid in the presence of potassi-



Scheme 1. Preparation of ligand  $H_4LCl_2$ .

[a] Dr. J. Sun,<sup>+</sup> Dr. D. Sun,<sup>+</sup> S. Yuan, L. Zhang, Prof. X. Wang, Prof. Dr. D. Sun  
Key Lab for Colloid and Interface Chemistry, Ministry of Education  
School of Chemistry and Chemical Engineering  
Shandong University, Jinan 250100 (P. R. China)  
Fax: (+86)531-883-64218  
E-mail: dfsun@sdu.edu.cn

[b] Dr. J. Sun<sup>+</sup>  
School of Life Science  
Ludong University  
Yantai, 264025, Shandong (P. R. China)

[c] Dr. D. Tian  
State Key Laboratory of Fine Chemicals  
School of Chemistry, Dalian University of Technology  
Dalian 116012 (P. R. China)

[<sup>+</sup>] These authors contributed equally to this work.

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um carbonate. This versatile ligand has four potential binding sites including two OH and two COOH groups as well as variable conformations. Solvothermal treatment of  $H_4LCl_2$  with cadmium salts gave novel  $C_{3i}$ -symmetric bicapped trigonal-antiprismatic  $Cd_8$  cages  $[2X@Cd_8L_6(H_2O)_6]_nY$ -solvents ( $X=Cl^-$ ,  $Y=NO_3^-$ ,  $n=2$ : **MOCC-4**;  $X=Br^-$ ,  $Y=NO_3^-$ ,  $n=2$ : **MOCC-5**;  $X=NO_3^-$ ,  $Y=NO_3^-$ ,  $n=2$ : **MOCC-6**;  $X=NO_3^-$ ,  $Y=BF_4^-$ ,  $n=2$ : **MOCC-7**;  $X=NO_3^-$ ,  $Y=ClO_4^-$ ,  $n=2$ : **MOCC-8**;  $X=CO_3^{2-}$ ,  $n=0$ : **MOCC-9**) containing a pair of anions, whereby univalent anions  $Cl^-$ ,  $Br^-$ , and  $NO_3^-$  originated from the reaction solution, but divalent  $CO_3^{2-}$  anions were generated in situ from DMF under solvothermal conditions. The anions play the role of templates for formation of the cages, and their templating ability is discussed here for the first time.

## Results and Discussion

**Structure analysis of MOCC-4-9:** Single-crystal X-ray diffraction analysis (Table S1 in Supporting Information) revealed that **MOCC-4-9** crystallize in the trigonal space group  $R\bar{3}m$  and have a new type of  $C_{3i}$ -symmetric octanuclear  $Cd^{II}$  cage encapsulating two anions as templates. Since **MOCC-4-9** have similar structures apart from the templates, the following discussion on structural aspects mainly focuses on **MOCC-9**.

The nanoscale cage has approximate dimensions of  $1.9 \times 1.9$  nm. The asymmetric unit contains two crystallographically independent  $Cd^{II}$  ions, one completely deprotonated L ligand with *syn* conformation, one coordinated water molecule, and  $1/3$   $CO_3^{2-}$  (Figure 1 a). The existence of the  $CO_3^{2-}$  ions was also confirmed by the IR spectrum, which shows two strong bands at  $1486$  and  $1440$   $cm^{-1}$ , similar to C–O antisymmetric stretching frequencies observed for  $\mu_3$ -carbonato bridges, and two weaker bands at  $864$  and  $628$   $cm^{-1}$ , corresponding to the nonplanar bending mode ( $\nu_2$ ) and angular bending mode ( $\nu_4$ ), respectively.<sup>[11]</sup> Analysis of the local symmetry of the metal atoms shows that Cd1 resides on a normal position but Cd2 resides on a special position (site occupancy factor (SOF)= $1/3$ ) containing a threefold axis, which also simultaneously passes through two inversion-related C26 atoms of a pair of  $CO_3^{2-}$  ions. **MOCC-9** is comprised of eight  $Cd^{II}$  ions, six L ligands, two  $CO_3^{2-}$  ions, and six coordinated aqua ligands (Figure 1 b and c). Both Cd1 and Cd2 are located in a slightly distorted octahedral environment. In contrast, Cd1 is triply chelated by deprotonated salicylic acid moieties of L, and Cd2 is coordinated by only one deprotonated salicylic acid moiety, two O atoms from two carboxyl groups, one O atom of a  $CO_3^{2-}$  ion, and one aqua ligand. The Cd–O bond lengths, which vary from  $2.251(3)$  to  $2.346(3)$  Å, lie in the normal range for reported compounds.<sup>[9]</sup> In the  $Cd_8$  cage, two Cd1 cap the top and bottom trigonal faces of a trigonal antiprism built by six Cd2 atoms to form a bicapped trigonal-antiprismatic cage with Cd...Cd distances of  $5.2645(5)$ ,  $5.4760(6)$ , and  $5.8280(7)$  Å (Figure 1 d). Six staple-shaped L ligands with  $\mu_3$

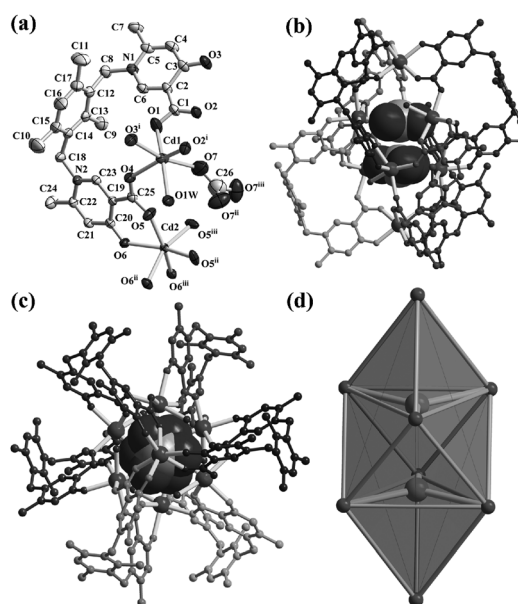


Figure 1. a) Coordination environment of  $Cd^{II}$  ions in **MOCC-9** with thermal ellipsoids at 50% probability. Hydrogen atoms omitted for clarity. Symmetry codes: i)  $y+1/3$ ,  $-x+y+2/3$ ,  $-z+5/3$ ; ii)  $-x+y+1$ ,  $-x+1$ ,  $z$ ; iii)  $-y+1$ ,  $x-y$ ,  $z$ . b, c) Molecular structure of **MOCC-9** incorporating  $CO_3^{2-}$  ions, highlighted in space-filling mode, viewed along different directions. d) Bicapped trigonal-antiprismatic  $Cd_8$  cage encapsulating double anions (green ball:  $\mu_3$ -bridging  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ , and  $CO_3^{2-}$  anions).

mode are attached to the twelve faces of the bicapped trigonal antiprism to complete the whole molecule. The cage of **MOCC-9** is neutral, but uncoordinated counterions such as  $NO_3^-$ ,  $BF_4^-$ , and  $ClO_4^-$  are located in the cavities of the 3D packing of **MOCC-4-8** (Figure 2).

The most fascinating structural feature of **MOCC-9** is that two adventitious  $CO_3^{2-}$  ions were simultaneously captured in the core of the cage. Around the  $\mu_3$ - $\eta^1$ : $\eta^1$ : $\eta^1$ -tridentate bridging  $CO_3^{2-}$  ion, two sets of three equatorial  $Cd^{II}$  ions are trigonally arranged with a Cd–O carbonate distance of  $2.301(5)$  Å, which is comparable to the values of  $2.329(4)$  and  $2.546(4)$  Å found in other  $CO_3^{2-}$ -containing complexes.<sup>[12]</sup> Notably, two concurrent  $CO_3^{2-}$  ions are parallel to each other, and the distance between them is  $3.53(2)$  Å. According to a Cambridge Structural Database (CSD) survey with the help of ConQuest version 1.3,<sup>[13]</sup> only three  $CO_3^{2-}$ -containing Cd compounds have been reported until now.<sup>[12,14]</sup> For all of them the  $CO_3^{2-}$  ions were not added deliberately in the synthetic procedure, but were due to fixation of atmospheric  $CO_2$ . However, the  $CO_3^{2-}$  anions in **MOCC-9** came from decomposition of DMF under acidic condition (see below). The rarity of  $CO_3^{2-}$ -containing Cd compounds may be due to the propensity of  $CO_3^{2-}$  to readily precipitate  $Cd^{II}$  ions from solution. Hence, **MOCC-9** is the first example of a cage that involves double templation of  $CO_3^{2-}$  ions from decomposition of DMF.

**Formation mechanism of MOCC-9:** To understand and confirm the formation mechanism of **MOCC-9**, especially the

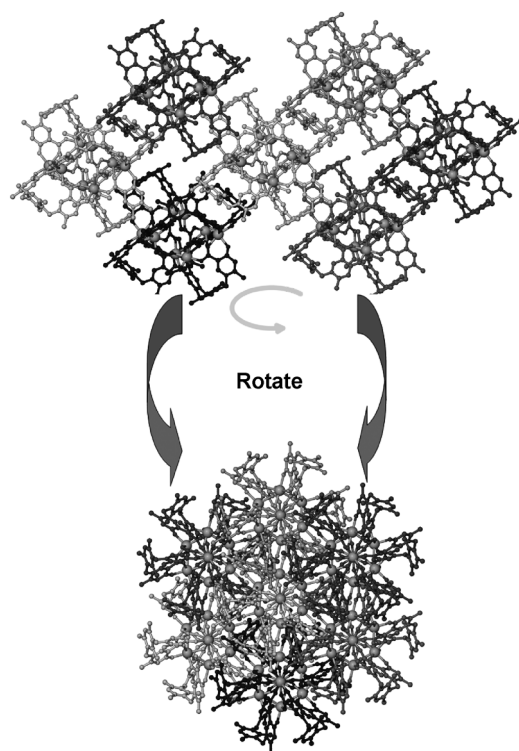
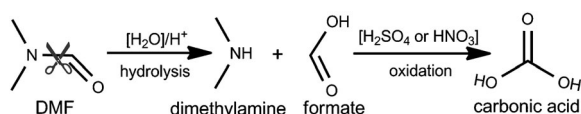


Figure 2. The 3D packing of **MOCC-8** showing the cavities. Different cages are shown in different colors.

origin of  $\text{CO}_3^{2-}$  ions, several comparative experiments were performed. The enclosed carbonate species in **MOCC-9** cannot be generated by fixation of atmospheric  $\text{CO}_2$ , because the synthesis of **MOCC-9** was performed in a sealed Pyrex tube under vacuum. Hence, the  $\text{CO}_3^{2-}$  ions must be derived from the reactants or solvents. Since no  $\text{CO}_3^{2-}$  ions were included in the starting materials, it is presumably derived from the decomposition of DMF under solvothermal conditions.<sup>[15]</sup> The C–N bond cleavage of DMF under solvothermal conditions can readily produce both dimethylamine and formate in the presence of some acidic or basic materials.<sup>[16]</sup> Attempts to prepare the MOCC series in *N,N*-diethylformamide or other common organic solvents were unsuccessful and always yielded white intractable solids, which indicates that use of DMF is very important in the formation of MOCCs.

Given the presence of strongly oxidizing  $\text{H}_2\text{SO}_4$ , we rationally assign the  $\text{CO}_3^{2-}$  ions to the further oxidation of formate by  $\text{H}_2\text{SO}_4$  (Scheme 2). In this system, the introduced  $\text{H}_2\text{SO}_4$  not only promotes the hydrolysis of DMF but also oxidizes one of the hydrolysis products of DMF. Interestingly, a large number of bubbles dramatically sprang out



Scheme 2. Proposed decomposition route of DMF to  $\text{CO}_3^{2-}$ .

once we opened the sealed Perex tube (Supporting Information Figure S14), like opening a bottle of carbonated beverage or beer. This suggested that plenty of gas was produced during the reaction. When the gas was introduced into fresh  $\text{Ca}(\text{OH})_2$  solution, a white precipitate formed immediately, proving that the gas was carbon dioxide. To confirm the role of the oxidizing acid in the formation of **MOCC-9**, other acids were used in the reaction. However, when  $\text{H}_2\text{SO}_4$  is replaced by other, nonoxidizing acids (hydrofluoric or fluoroboric acid) no insoluble crystalline material is produced.

**Comparison of template abilities among halide anions,  $\text{NO}_3^-$ , and  $\text{CO}_3^{2-}$ :** A large number of bubbles also sprang out once we opened sealed Pyrex tubes for **MOCC-4-8**, and the gas was also shown to be carbon dioxide, that is,  $\text{NO}_3^-$  can also oxidize formate to carbon dioxide. However, the fact that the coordinated anions in **MOCC-4-8** were not  $\text{CO}_3^{2-}$  prompted us to study the template ability of the anions in the formation of **MOCC-4-8**. The following observations were made and are detailed in Table 1: 1) When

Table 1. Summary of products isolated with different salts and acids.

	HCl	HBr	HF	$\text{HNO}_3$
$\text{Cd}(\text{NO}_3)_2$	<b>MOCC-4</b>	<b>MOCC-5</b>	<b>MOCC-6</b>	<b>MOCC-6</b>
$\text{Cd}(\text{OAc})_2$	–	–	–	<b>MOCC-6</b>
	$\text{HBF}_4$	$\text{HClO}_4$	$\text{H}_2\text{SO}_4$	
$\text{Cd}(\text{NO}_3)_2$	<b>MOCC-7</b>	<b>MOCC-8</b>	<b>MOCC-6</b>	
$\text{Cd}(\text{OAc})_2$	–	–	<b>MOCC-9</b>	

HCl and HBr were added in the reaction, the coordinated anions were  $\text{Cl}^-$  and  $\text{Br}^-$ , but not  $\text{NO}_3^-$  or  $\text{CO}_3^{2-}$ , that is,  $\text{Cl}^-$  and  $\text{Br}^-$  have greater template ability than  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$ . 2) Addition of HF to the reaction resulted in the formation of **MOCC-6**, perhaps because  $\text{F}^-$  is too small to act as template. 3) When  $\text{HNO}_3$ ,  $\text{HBF}_4$ ,  $\text{HClO}_4$ , and  $\text{H}_2\text{SO}_4$  were added to the reaction, the coordinated anions in the cage were  $\text{NO}_3^-$  ions, that is,  $\text{NO}_3^-$  has greater template ability in the formation of the cages than  $\text{CO}_3^{2-}$ . 4) If no  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{NO}_3^-$  ions are present in the reaction mixture,  $\text{CO}_3^{2-}$  templates formation of **MOCC-9**, that is,  $\text{CO}_3^{2-}$  has the lowest template ability compared to  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{NO}_3^-$  ions in the formation of cages. 5) Attempts to synthesize I- or F-templated cages failed, since  $\text{F}^-$  is too small and  $\text{I}^-$  too large to act as template by being fixed in the cavity of the cages. Hence, the template abilities of these anions follow the series  $\text{X} (\text{Br}^-, \text{Cl}^-) > \text{NO}_3^- > \text{CO}_3^{2-}$  (Figure 3).

**Calculations of cage stability:** To compare the stabilization of the clusters and the template abilities of the anions, DFT calculations were performed with the GGA/PW91 exchange-correlation functional (see Supporting Information). The calculations showed that the cluster coordinated by  $\text{Br}^-$  (**MOCC-5**) is most stable in energy. The stabilization order is  $\text{Br}^- > \text{Cl}^- > \text{NO}_3^- > \text{CO}_3^{2-}$ . The stabilization energy of  $\text{Br}^-$  is more favorable than those of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{CO}_3^{2-}$  by

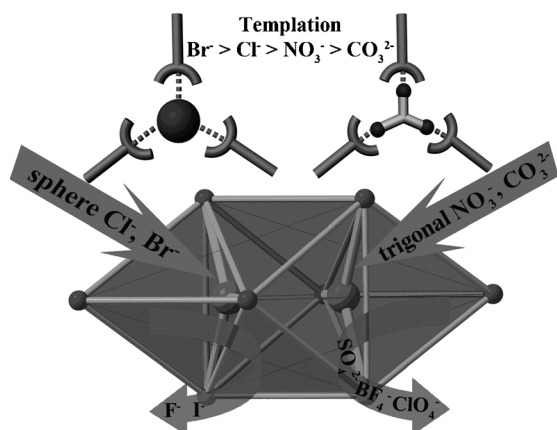


Figure 3. Schematic representation of templated formation of the cages.

24.29, 149.37, and 303.56 kJ mol<sup>-1</sup> (Supporting Information Table S2).

**Anion exchange of MOCC-8:** Since **MOCC-4-8** contain counterions, anion exchange was carried out for **MOCC-8**. As-synthesized crystals of **MOCC-8** were washed with DMF several times and immersed in a DMF solution of NaPF<sub>6</sub> (2M, 1.5 mL) or NaCF<sub>3</sub>SO<sub>3</sub> (2M, 1.5 mL) for a period of time. Anion exchange was monitored by the enhanced intensity at 1265 cm<sup>-1</sup> of the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> bending band and appearance of PF<sub>6</sub><sup>-</sup> at 834 cm<sup>-1</sup>, as well as the reduced intensity at 622 cm<sup>-1</sup> of ClO<sub>4</sub><sup>-</sup>. The ClO<sub>4</sub><sup>-</sup> ions could be fully exchanged by PF<sub>6</sub><sup>-</sup> after three weeks, as confirmed by IR spectra, in which the peak at 622 cm<sup>-1</sup> for ClO<sub>4</sub><sup>-</sup> disappeared completely and the peak at 834 for PF<sub>6</sub><sup>-</sup> appeared. However, anion exchange of ClO<sub>4</sub><sup>-</sup> with CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> does not occur even after immersing crystals of **MOCC-8** in a DMF solution of NaCF<sub>3</sub>SO<sub>3</sub> for three weeks, as confirmed by IR spectra (Figure 4), which may be due to the confinement of interspace between discrete cages.

**Photoluminescence of MOCC-4-9:** The solid-state luminescence of **MOCC-4-9** and free ligand H<sub>4</sub>LCl<sub>2</sub> were investigated at room temperature (Figure 5). The emission band is observed at 342 nm (λ<sub>ex</sub> = 300 nm) for H<sub>4</sub>LCl<sub>2</sub>, which can be assigned to the ligand-centered electronic transitions (π\* → n or π\* → π electronic transitions). The emissions of **MOCC-4-9** at 388, 395, 410, 398, 415, and 400 nm (λ<sub>ex</sub> = 300 nm), are redshifted by 46, 53, 68, 56, 73, and 58 nm, respectively, compared to the free H<sub>4</sub>LCl<sub>2</sub> ligand; they can be assigned to ligand-to-metal charge transfer (LMCT).<sup>[17]</sup>

## Conclusion

A series of novel Cd<sup>II</sup> cages doubly templated by different anions have been solvothermally synthesized and structurally characterized. The significance of the present work is that the cages can be templated by univalent or divalent anions without changing the cluster backbone. Results and conclu-

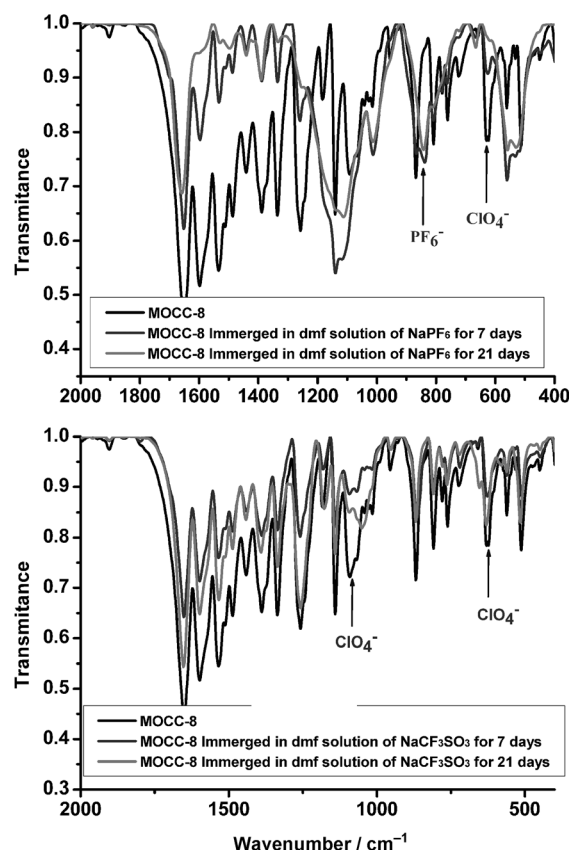


Figure 4. IR spectrum showing anion exchange with PF<sub>6</sub><sup>-</sup> (top) and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> (bottom) for **MOCC-8**.

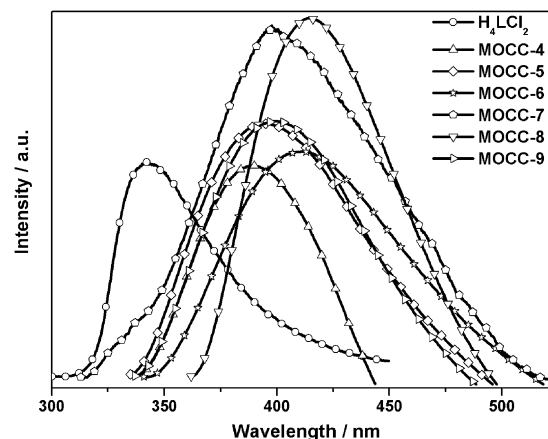


Figure 5. Solid-state emission spectra of free H<sub>4</sub>LCl<sub>2</sub> and **MOCC-4-9**.

sions of these investigations are summarized as follows: 1) decomposition of DMF to generate CO<sub>3</sub><sup>2-</sup> plays an important role in the formation of **MOCC-9**; 2) the cage backbone of the remains unchanged, no matter what the anion template involved. The templating abilities of the anions in the formation of cages were studied experimentally and follow the order X (Br<sup>-</sup>, Cl<sup>-</sup>) > NO<sub>3</sub><sup>-</sup> > CO<sub>3</sub><sup>2-</sup>; 3) anion exchange of **MOCC-8** showed anion-size selectivity. The pres-

ent study highlights the significance of double-anion templation in synthetic chemistry of cage compounds. Further work on spherical, tetrahedral, and octahedral anion templation in this system is underway.

## Experimental Section

All reagents and solvents were commercially available and used as received without further purification.  $^1\text{H}$  NMR spectra were recorded on a Bruker AVANCE-400 NMR spectrometer. Elemental analysis was carried out on a CE instruments EA 1110 elemental analyzer. The FTIR spectra were recorded from KBr pellets in the range 4000–400  $\text{cm}^{-1}$  with a Nicolet AVATAR FT-IR360 spectrometer. X-ray powder diffraction was performed on a Bruker AXS D8 Advance with  $\text{Cu}_{\text{K}\alpha}$  radiation ( $\lambda = 1.5418 \text{ \AA}$ , 40.0 kV, 30.0 mA). Photoluminescence spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer (slit width: 5 nm; sensitivity: high). TG curves were measured on a SDT Q600 instrument at a heating rate of  $10^\circ\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere ( $100 \text{ mL min}^{-1}$ ).

Single-crystal X-ray diffraction was performed on a Bruker Apex II CCD diffractometer equipped with a fine-focus sealed-tube X-ray source ( $\text{Mo}_{\text{K}\alpha}$  radiation, graphite-monochromated). All absorption corrections were performed with the SADABS program.<sup>[18]</sup> All structures were solved by direct methods by using SHELXS-97<sup>[19]</sup> and refined by full-matrix least-squares techniques with SHELXL-97.<sup>[20]</sup> Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions geometrically (C–H 0.96  $\text{\AA}$ ) with isotropic displacement parameters set to  $1.2U_{\text{eq}}$  of the attached atom. The crystallographic details of **MOCC-4-9** are summarized in Supporting Information Table S1. The guest molecules in **MOCC-9** were treated with the SQUEEZE program of PLATON.<sup>[21]</sup> CCDC 866039 (**MOCC-4**), 866040 (**MOCC-5**) and 866041 (**MOCC-6**), 866042 (**MOCC-7**), 866043 (**MOCC-8**) and 866044 (**MOCC-9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Synthesis of 1,3-Bis(bromomethyl)-2,4,6-trimethylbenzene:** HBr/acetic acid solution (40 mL, 31 wt %) was added rapidly to a mixture of mesitylene (12.0 g, 0.10 mol), paraformaldehyde (6.15 g; 0.20 mol), and glacial acetic acid (50 mL). The mixture was kept for 8 h at  $80^\circ\text{C}$  and then poured into 100 mL of water. The product was filtered off on a G3 glass frit and dried in vacuum. The yield was 29.1 g (95 %) of white powder.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.89$  (s, 1H), 4.57 (s, 4H), 2.44 (s, 3H), 2.38 (s, 6H).

**Synthesis of  $\text{H}_4\text{LCl}_2$ :** A mixture of 4-hydroxy-6-methylnicotinic acid (3.06 g, 20 mmol), 1,3,5-trimethyl-2,4-bromomethylbenzene (2.73 g, 9 mmol), and  $\text{K}_2\text{CO}_3$  (2.76 g, 20 mmol) in acetone (80 mL) was heated to reflux for 12 h. This resulting solution was filtered while hot and then cooled to room temperature, and a white precipitate formed. The white precipitate and aqueous NaOH solution (24 mL, 3M) were mixed with 60 mL of methanol and heated to reflux for 8 h. After cooling to room temperature, the solution was acidified to pH 2 with dilute hydrochloric acid, and a white precipitate formed. Yield: 28%.  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta = 16.46$  (s, 2H, OH) 7.74 (s, 2H), 7.30 (s, 1H), 6.82 (s, 2H), 5.40 (s, 4H), 2.64 (s, 6H,  $\text{CH}_3$ ), 2.30 (s, 6H,  $\text{CH}_3$ ), 2.08 (s, 3H,  $\text{CH}_3$ ).

**Synthesis of MOCC-4:**  $\text{H}_4\text{LCl}_2$  (2.5 mg, 0.005 mmol) and  $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (4.9 mg, 0.018 mmol) were dissolved in DMF/1,4-dioxane/ $\text{H}_2\text{O}$  (1/1/1, v/v/v, 1 mL), and one drop (0.05 mL) of dilute hydrochloric acid (1M) was added. Then the solution was sealed in a glass tube, slowly heated to  $120^\circ\text{C}$  from room temperature in 300 min, kept at  $120^\circ\text{C}$  for 4000 min, and then slowly cooled to  $30^\circ\text{C}$  in 1000 min. The colorless block crystals that formed were collected, washed with DMF, and dried in air. Yield:  $\approx 46\%$  based on  $\text{H}_4\text{LCl}_2$ . Selected IR peaks ( $\text{cm}^{-1}$ ): 3450 (w), 1647 (s), 1571 (s), 1404 (s), 1254 (w), 1140 (w), 860 (s), 628 (w).

**Synthesis of MOCC-5:** **MOCC-5** was prepared by a route similar to that of **MOCC-4** but by using dilute hydrobromic acid (1M) instead. Yield:

$\approx 42\%$  based on  $\text{H}_4\text{LCl}_2$ . Selected IR peaks ( $\text{cm}^{-1}$ ): 3368 (m), 2917 (w), 1651 (s), 1590 (s), 1539 (m), 1443 (m), 1387 (m), 1336 (m), 1249 (m), 864 (s), 629 (m), 636 (m).

**Synthesis of MOCC-6:** **MOCC-6** was prepared by a route similar to that of **MOCC-4** but by using dilute nitrate acid (1M) instead. Yield:  $\approx 39\%$  based on  $\text{H}_4\text{LCl}_2$ . Selected IR peaks ( $\text{cm}^{-1}$ ): 3441 (w), 2919 (w), 1651 (s), 1595 (s), 1529 (s), 1443 (w), 1386 (m), 1335 (m), 1254 (m), 864 (s), 807(m), 622 (m).

**Synthesis of MOCC-7:** **MOCC-7** was prepared by a route similar to that of **MOCC-4** but by using dilute fluoroboric acid (2.5M) instead. Yield:  $\approx 51\%$  based on  $\text{H}_4\text{LCl}_2$ . Selected IR peaks ( $\text{cm}^{-1}$ ): 3441 (w), 2919 (w), 1651 (s), 1595 (s), 1523 (s), 1434 (w), 1386 (s), 1333 (m), 1259 (s), 866 (m), 807(m), 629 (m).

**Synthesis of MOCC-8:** **MOCC-8** was prepared by a route similar to that of **MOCC-4** but using dilute perchloric acid (1M) instead. Yield:  $\approx 55\%$  based on  $\text{H}_4\text{LCl}_2$ . Selected IR peaks ( $\text{cm}^{-1}$ ): 2919 (w), 1651 (s), 1588 (s), 1522 (s), 1484 (w), 1386 (s), 1335 (s), 1257 (s), 866 (m), 807(m), 626 (m).

**Synthesis of MOCC-9:**  $\text{H}_4\text{LCl}_2$  (2.5 mg, 0.005 mmol) and  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (5 mg, 0.018 mmol) were dissolved in DMF/1,4-dioxane/ $\text{H}_2\text{O}$  (1/1/1, v/v/v, 1 mL), and one drop (0.05 mL) of dilute sulfuric acid (1M) was added. The solution was sealed in a glass tube, slowly heated to  $120^\circ\text{C}$  from room temperature in 300 min, kept at  $120^\circ\text{C}$  for 4000 min, and then slowly cooled to  $30^\circ\text{C}$  in 1000 min. The colorless crystalline block that formed was collected, washed with DMF, and dried in air. Yield:  $\approx 53\%$  based on  $\text{H}_4\text{LCl}_2$ . Selected IR peaks ( $\text{cm}^{-1}$ ): 3443 (s), 2920 (m), 1651 (s), 1599 (s), 1534 (m), 1487 (w), 1441 (w), 1385 (m), 1335 (m), 1259 (m), 1140 (m), 866 (m), 809 (m), 628 (w).

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