DOI: 10.1002/ejic.200701264

Self-Assembly of *p*-Sulfonatocalix[4]arene and a Ag–hmt Coordination Polymer into a Porous Structure

Guo-li Zheng,[a,b] Hong-Jie Zhang,*[a] Shu-Yan Song,[a,b] Yin-Yan Li,[a,b] and Hua-Dong Guo[a,b]

Keywords: Supramolecular chemistry / *p*-Sulfonatocalix[4]arene / Silver / Coordination polymers / Porous structures

A novel porous material constructed from *p*-sulfonatocalix[4]arene molecules and a Ag^I coordination polymer has been structurally characterized. The porous supramolecular complex features a bilayer arrangement of *p*-sulfonatocalix[4]arene molecules linked by a Ag^I–hmt (hmt: hexamethylenetetramine) coordination polymer through metal–ligand bonding, hydrogen bonding and host–guest interactions.

Introduction

Much research has been dedicated to the assembly of coordination complexes into porous materials, which are held together either by strong metal–ligand bonding or by weaker bonding forces such as hydrogen-bonding and π–π interactions.[1,2] Meanwhile, calixarenes, as an interesting family of macrocyclic molecules, have been attracting attention due to their potential application in material science and biological science.[3] New functional porous materials can be created with the use of calixarenes as building blocks. Indeed, calixarenes as building blocks have been widely used in the field of coordination chemistry and supramolecular chemistry.[4,5] However, self-assembly of metals and calixarenes into porous materials have been rarely reported, probably because of their convergent functional groups that would mainly be suitable for host–guest complexation and have limitations in forming metal-coordinated polymers or huge cyclic arrays.[6–8]

In the present communication, *p*-sulfonatocalix[4]arenes were used as building units to construct a new porous material. *p*-Sulfonatocalixarenes have been the most widely studied members of the calixarene family because of their versatile architecture and interesting biological behaviour.[3c,4b,4c,9,10] Nevertheless, research on porous materials based on sulfonatocalixarenes has been very limited.[5c,11,12] Synthesis of new porous materials based on *p*-sulfonatocalixarenes continues to be an attractive area of research.

The title complex we report here is a porous structure based on *p*-sulfonatocalix[4]arene and a Ag^I–hmt coordination polymer. Actually, there are only a few examples in which calixarenes of any sort participate in self-assembly with Ag^I-coordinated polymers.[13] In this work, we choose a labile coordination centre, silver, and the weakly alkaline ligand hmt. The hmt group successfully acts as a secondary ligand forming a new layered coordination polymer with Ag^I atoms instead of being protonated by the hydroxy groups of the *p*-sulfonatocalix[4]arene. The resulting porous complex comprises a bilayer arrangement of *p*-sulfonatocalix[4]arene molecules linked by the Ag^I–hmt coordination polymer with guest molecules inside the pores.

Results and Discussion

Complex **1** belongs to the monoclinic crystal system, crystallizing in the space group $P2_1/c$. Figure 1 shows the basic unit of **1**, which indicates the coordination about each Ag centre. The packing structure along the *a* axis (Figure S1) indicates that the whole structure is made up of *p*-sulfonatocalix[4]arene bilayers alternating with Ag^I-based coordination polymer layers. The basic building block of the title complex (Figure 2) displays the bonding of the Ag1 atom of the coordination polymer layer to the O8 atom of *p*-sulfonatocalix[4]arene (the bond length is 2.576 Å). At the same time, host–guest interactions exist between coordinated acetonitrile (N19) and *p*-sulfonatocalix[4]arene: these are CH···π interactions in which the smallest CH···aryl centroid distance is 2.584 Å. One water molecule (O17) that is coordinated to the Ag5 atom extends toward the four hydroxy groups of the *p*-sulfonatocalix[4]arene molecule in the opposite layer, which results in the formation of hydrogen bonds between the coordinated water (O17) and the hydroxy group (O2) of the *p*-sulfonatocalix[4]arene mole-

---

[a] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences,
Changchun 130022, P. R. China
Fax: +86-431-85698041
E-mail: hongjie@ciac.jl.cn
[b] Graduate School of the Chinese Academy of Sciences, Beijing, P. R. China

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

cule opposite it, as shown in Figure 2. The distance between O17 and O2 is 2.717 Å, and the angle O17–H···O2 is 166.9°, which indicates the presence of a strong hydrogen bond here. In addition, the coordinated water molecule (O17) also forms a hydrogen bond with the oxygen atom (O13) on the sulfonate group of its neighbouring *p*-sulfonatocalix[4]arene (bond length O17–O13 2.788 Å and bond angle O17–H···O14 110.6°). The coordinated water molecule (O17) therefore links the neighbouring and opposite *p*-sulfonatocalix[4]arene molecules together to create a porous structure surrounded by a bilayer of *p*-sulfonatocalix[4]arene and the Ag-based polymer layer. Typically, neighbouring bilayers of *p*-sulfonatocalix[4]arenes are in so close proximity that π–π-stacking interactions have been proved to be ubiquitous in bilayered arrays of calixarenes.[14] In the present example, however, the neighbouring and opposite *p*-sulfonatocalix[4]arene molecules, which are bridged up together by a coordinated water molecule (O17) through hydrogen bonds (Figure 2), have no obvious interactions, with the nearest aromatic centroid–centroid separation of 5.032 Å. The Ag-based polymer layers control the arrangement of *p*-sulfonatocalix[4]arenas, keeping the neighbouring and opposite calixarenes oriented away from each other and forming a void space to construct the porous material (Figure 2 and S2). In addition, hydrogen bonds are also formed between the other coordinated water O18 and sulfonate group (O14) of the calixarene (bond length O18–O14 2.853 Å and bond angle O18–H···O14 149.8°). Although hydrogen atoms of dissociative O19 and O20 were not located, hydrogen bonds with the neighbouring sulfonate groups of *p*-sulfonatocalix[4]arene are implied by short O···O contacts.

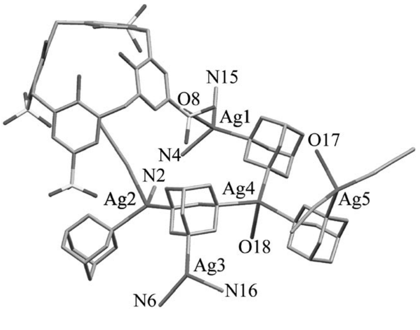

Figure 1. The coordination mode of the Ag centres.

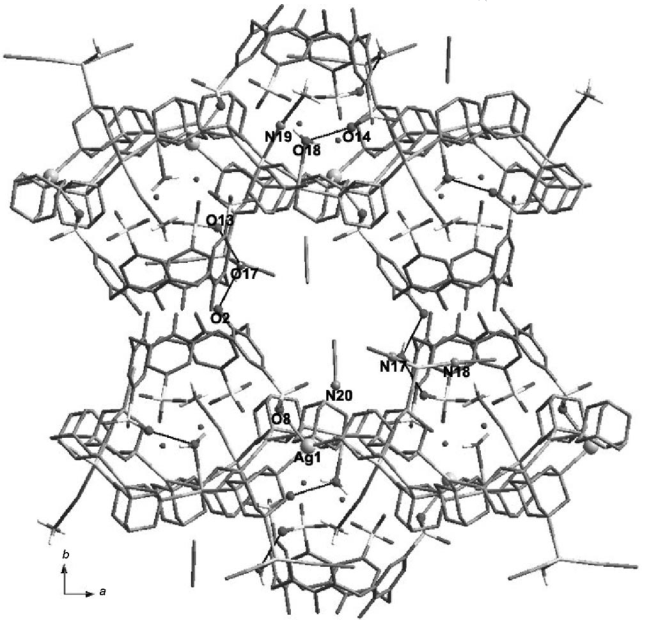

Figure 2. Stick diagram down the *c* axis showing the hydrogen bonding and hexagonal porous structure.

As mentioned above, the noteworthy aspect of the title complex is that when the bilayer structure is viewed along the *c* axis, the whole framework forms pores constructed by layers of *p*-sulfonatocalix[4]arene and Ag^I-based coordination polymer, which is clearly shown in Figure 3. The coordination polymers in this structure show wavelike layers and the *p*-sulfonatocalix[4]arene molecules fit in the concave parts of the layers. In contrast to the common bilayered calix[4]arene framework, in which placement of the next layer fills up the voids of one layer, which should be the optimum place for the next layer, in the present structure, neighbouring layers line up face to face to each other through their hydrophilic layers and enclose a larger void space. In doing so, a hexagonal pore structure was formed when viewed along the *c* axis (Figure 2). Four *p*-sulfonatocalix[4]arene molecules set up four sides of the hexagon pore, while the Ag^I-based coordination layers occupy the other two sides. The solvent acetonitrile molecules are distributed in the pores of the materials.

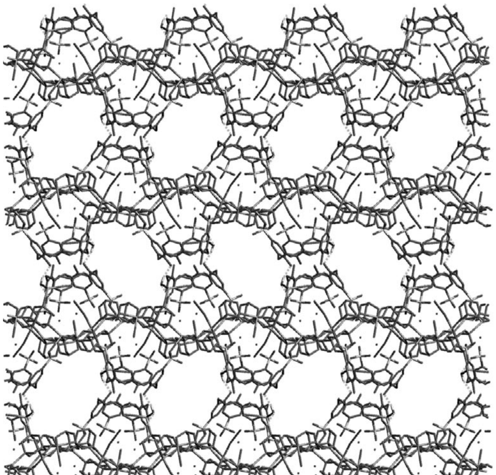

Figure 3. The packing diagram down the *c* axis showing the porous structure; the acetonitrile molecules are omitted for clarity.

It is interesting to contrast the structure of **1** with the previously reported porous structure resulting from iminodicarboxylate resorcinarenes and metal ions.[8a] The common structural characteristic in both cases is that the lower rims (the four hydroxy groups in complex **1** and the four methyl groups in iminodicarboxylate resorcinarene) of their calixarene framework have a head-to-head layout, which leads to porous materials. In the title structure, the opposite layers are interconnected indirectly through one water oxygen atom (O17) (provided by the Ag-based layer), which simultaneously contacts two opposite *p*-sulfonatocalix[4]arene molecules with hydrogen bonds. In the previous case,[8a] the arrangement of the iminodicarboxylate resorcinarene is controlled by metal cations, while in the present case the structure of the *p*-sulfonatocalix[4]arene arrays is determined by the coordination polymer.

In the Ag^I-based coordination polymer layer, there are five crystallographically independent Ag atoms and four crystallographically independent hmt molecules. The different Ag atoms and hmt molecules link up one another to build an unprecedented netlike coordination polymer (Figure 1). The assembly of porous metal compounds relies on the coordination ability of metal ions and the proper choice of organic ligand. The Ag^I ions in this structure display trigonal and tetrahedral configurations. The flexible coordination geometry of the Ag^I ions enables their coordination with both the second ligand (hmt) molecules and solvent molecules (water and acetonitrile) to form a layered structure that offers enough opportunity (including various bond interactions) for *p*-sulfonatocalix[4]arene molecules to form an array in one direction and line up face to face with their lower rims. A novel porous material is finally formed on the basis of *p*-sulfonatocalix[4]arene.

The crystal structure contains both dissociative and coordinated water and acetonitrile molecules. The observed mass loss (10%) (as shown in Figure S4 in the Supporting Information) while heating up to 180 °C is attributed to the loss of dissociative or coordinated water and acetonitrile molecules, which is consistent with the ratio found by crystallography: 11.37%. Then, the TGA curve reaches a plateau in which the weight remains constant up to 212 °C, demonstrating that the backbone of the framework keeps intact. Upon further heating, the whole framework is destroyed and fast weight loss is observed.

Conclusions

In summary, a novel porous material was constructed from *p*-sulfonatocalix[4]arene bilayers alternating with layers of a new Ag^I-based coordination polymer. The structure provides new opportunities for *p*-sulfonatocalix[4]arene to be applied in the field of porous materials, for example, for chemical separation and storing molecules. More novel materials can be expected to be formed from the flexible and functional ligand *p*-sulfonatocalix[4]arene. Further investigations on synthesis of novel porous materials based on calixarene are underway in our laboratory.

Experimental Section

Synthesis: A mixture of $AgNO_3$, Na_4 *p*-sulfonatocalix[4]arene and hmt (5:1:4) was dissolved in a 1:3 (v/v) mixture of acetonitrile and water. Colourless crystals of the title complex were obtained after concentration at room temperature in the dark (yield 26%). Microanalysis (CHN) was not feasible because of the highly hydrated nature of the complex.

X-ray Crystallography: Complex **1** crystallized in the monoclinic space group $P2_1/n$. $C_{60}H_{86}Ag_5N_{20}O_{19.5}S_4$, $M = 2067.08$, $a = 15.5462(10)$ Å, $b = 33.135(2)$ Å, $c = 16.4944(10)$ Å, $V = 8460.1(9)$ Å^3, $Z = 4$, $T = 193$ K, $\lambda = 0.71073$ Å, $R_{int} = 0.0553$. A total of 48857 reflections were collected in the range $1.38 < \theta < 26.06$, of which 16693 were unique. The structure was solved and refined by full-matrix least-squares on F^2 with the SHELXL-97 program.[15] Non-hydrogen atoms were refined anisotropically. The final $R1$ value is 0.0885 (0.0587 after SQUEEZE) for 11359 independent reflections [$I > 2\sigma(I)$]. The contribution from the disordered solvent was subtracted from the observed data by the "SQUEEZE" method as implemented in PLATON.[16]

CCDC-664488 contains 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.

Supporting Information (see footnote on the first page of this article): Supplementary pictures, XRD patterns and TGA diagram.

Acknowledgments

The authors are grateful for the financial aid from the National Natural Science Foundation of China (Grant Nos. 20490210, 206301040, 20602035 and 20771099) and the MOST of China (Grant Nos. 2006CB601103, 2006DFA42610).

---

[1] a) B. Kesanli, W. B. Lin, *Coord. Chem. Rev.* **2003**, *246*, 305–326; b) O. M. Yaghi, H. Li, C. Cavis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474–484.

[2] a) M. D. Ward, *Chem. Commun.* **2005**, 5838–5842; b) K. S. Suslick, P. Bhyrappa, J. H. Chou, M. E. Kosal, S. Nakagaki, D. W. Smithenry, S. R. Wilson, *Acc. Chem. Res.* **2005**, *38*, 283–291; c) S. Kitagawa, K. Uemura, *Chem. Soc. Rev.* **2005**, *34*, 109–119.

[3] a) S. J. Dalgarno, P. K. Thallapally, L. J. Barbour, J. L. Atwood, *Chem. Soc. Rev.* **2007**, *36*, 236–245; b) F. Perret, A. N. Lazar, A. W. Coleman, *Chem. Commun.* **2006**, 2425–2438; c) S. Richeter, J. Rebek, *J. Am. Chem. Soc.* **2004**, *126*, 16280–16281.

[4] a) S. M. Biros, J. Rebek, *Chem. Soc. Rev.* **2007**, *36*, 93–104; b) S. J. Dalgarno, J. L. Atwood, C. L. Raston, *Chem. Commun.* **2006**, 4567–4574; c) J. L. Atwood, L. J. Barbour, M. J. Hardie, C. L. Raston, *Coord. Chem. Rev.* **2001**, *222*, 3–32; d) C. Wieser, C. B. Dieleman, D. Matt, *Coord. Chem. Rev.* **1997**, *165*, 93–161; e) C. Redshaw, *Coord. Chem. Rev.* **2003**, *244*, 45–70.

[5] a) J. L. Atwood, J. W. Steed, *Encyclopaedia of Supramolecular Chemistry: Self-Assembling Capsules*, Marcel Dekker Inc., New York, **2004**, pp. 1231–1239; b) E. Botana, E. D. Silva, J. Benet-Buchholz, P. Ballester, J. D. Mendoza, *Angew. Chem. Int. Ed.* **2007**, *46*, 198–201; c) G. W. Orr, L. J. Barbour, J. L. Atwood, *Science* **1999**, *285*, 1049–1052.

[6] C. D. Gutche in *Calixarenes Revisited Monographs in Supramolecular Chemistry* (Ed.: J. F. Stoddart), The Royal Society of Chemistry, Cambridge, **1998** and references cited therein.

[7] a) Y. Kondo, K. Endo, F. Hamada, *Chem. Commun.* **2005**, 711–712; b) K. Endo, Y. Kondo, Y. Aoyamab, F. Hamada, *Tetrahedron Lett.* **2003**, *44*, 1355–1358.

[8] a) R. G. Harrison, N. K. Dalley, A. Y. Nazarenko, *Chem. Commun.* **2000**, 1387–1388; b) R. G. Harrison, O. D. Fox, M. O. Meng, N. K. Dalley, L. J. Barbour, *Inorg. Chem.* **2002**, *41*, 838–843; c) O. D. Fox, N. K. Dalley, R. G. Harrison, *J. Am. Chem. Soc.* **1998**, *120*, 7111–7112.

[9] a) S. J. Dalgarno, C. L. Raston, *Dalton Trans.* **2003**, 287–290; b) S. J. Dalgarno, M. J. Hardie, M. Makha, C. L. Raston, *Chem. Eur. J.* **2003**, *9*, 2834–2839; c) T. Ness, P. J. Nichols, C. L. Raston, *Eur. J. Inorg. Chem.* **2001**, 1993–1997.

[10] a) S. J. Dalgarno, J. Fisher, C. L. Raston, *Chem. Eur. J.* **2006**, *12*, 2772–2777; b) A. Drljaca, M. J. Hardie, T. J. Ness, C. L. Raston, *Eur. J. Inorg. Chem.* **2000**, 2221–2229.

[11] a) C. Gaeta, C. Tedesco, P. Neri in *Calixarenes in the Nano World* (Eds.: J. Vicens, J. Harrowfield), Springer **2007**, ch. 16, pp. 335–355; b) P. J. Nichols, C. L. Raston, J. W. Steed, *Chem. Commun.* **2001**, 1062–1063.

[12] a) M. Makha, A. N. Sobolev, C. L. Raston, *Chem. Commun.* **2006**, 511–513; b) Y. Liu, D. Guo, H. Zhang, F. Ding, K. Chen, H. Song, *Chem. Eur. J.* **2007**, *13*, 466–472.

[13] a) G. Mislin, E. Graf, M. W. Hoddeini, A. D. Cian, N. Kyritsakas, J. Fischer, *Chem. Commun.* **1998**, 2545–2546; b) C. Kleina, E. Graf, M. W. Hoddeini, A. D. Cian, J. Fischer, *Chem. Commun.* **2000**, 239–240.

[14] A. P. Côté, G. K. H. Shimizu, *Coord. Chem. Rev.* **2003**, *245*, 49–64.

[15] G. M. Sheldrick, *SHELXL-97*, *Program for X-ray Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**.

[16] P. van der Sluis, A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, 194.

Received: November 26, 2007