### ChemComm

COMMUNICATION



View Article Online

## () Check for updates

Cite this: Chem. Commun., 2020, 56, 2491

Received 8th January 2020, Accepted 21st January 2020

DOI: 10.1039/d0cc00157k

rsc.li/chemcomm

# A calix[4]resorcinarene-based giant coordination cage: controlled assembly and iodine uptake<sup>†</sup>

Wen-Yuan Pei,<sup>a</sup> Jin Yang, 🗅 \*<sup>a</sup> Hui Wu, 🕩 <sup>b</sup> Wei Zhou, 🕩 \*<sup>b</sup> Ying-Wei Yang 🕩 \*<sup>c</sup> and Jian-Fang Ma 🕩 \*<sup>a</sup>

Construction of large multi-component coordination cages becomes much more challenging as the number of building blocks increases. A giant hexameric calix[4]resorcinarene-based coordination cage (cage-1) was successfully designed through the precise tuning of ancillary rigid tetracarboxylic acid. Significantly, cage-1 exhibited reversible uptake of volatile iodine, suggesting that it could serve as a porous material for efficient capture and separation of radioactive iodine.

Coordination cages with large inner voids have attracted considerable attention owing to their aesthetic structures and potential applications in catalysis, adsorption, and guest molecule inclusion.<sup>1</sup> A large number of coordination cages with various shapes and sizes have been successfully synthesized using directional bridging organic ligands and geometrically prefixed metals.<sup>2</sup> In this regard, the large internal cavities and controllable cavity environments would enable the coordination cages to act as advanced functional materials.<sup>3</sup> Nevertheless, rationally controlled assembly of giant coordination cages with large inner voids and potential functions is still substantially challenging in supramolecular chemistry and materials science.<sup>4</sup>

Calix[4]arenes, such as thiacalix[4]arenes, pyrogallol[4]arenes, and calix[4]resorcinarenes (C4Rs), are a class of versatile building blocks for the construction of coordination cages.<sup>5</sup> C4Rs, as a special family of calix[4]arenes, feature well-defined bowl-shaped cavities, and their coordination cages, typically assembled from two metal-bridged C4Rs directly (Scheme 1a and b),<sup>5b,6</sup> usually

- <sup>a</sup> Key Lab for Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, China. E-mail: yangj808@nenu.edu.cn, majf247@nenu.edu.cn
- <sup>b</sup> NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102, USA. E-mail: wzhou@nist.gov
- <sup>c</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, International Joint Research Laboratory of Nano-Micro Architecture Chemistry (NMAC), College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China. E-mail: ywyang@jlu.edu.cn
- † Electronic supplementary information (ESI) available: Experiments, figures, tables, and crystallographic data. CCDC 1843556 for **cage-1**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0cc00157k

bear large internal spaces.<sup>7</sup> Interestingly, by introducing suitable ancillary ligands, two metal-coordinated C4Rs have also been assembled into coordination cages by us (Scheme 1c).<sup>8</sup> However, giant coordination cages assembled from multiple C4R units have been rarely obtained, mainly due to the large steric hindrance arising from the increased number of C4Rs in the assembly process.<sup>5b,7</sup> Particularly, to the best of our knowledge, hexameric



**Scheme 1** Schematic representations:<sup>8</sup> (a) C4R-based ligand, (b) coordination cage assembled from two metal-bridged CRs and (c) dimeric C4R-based coordination cages tuned by the ancillary linkers. The red rectangular block represents the ancillary linker. (d) Synthetic route to the hexameric C4R-based coordination cage (**cage-1**).

View Article Online

C4R-based coordination cages tuned by ancillary polycarboxylic acids still remain unexplored, which is not surprising because the self-assembly of giant coordination cages becomes difficult as the component number increases.<sup>4</sup>

Inspired by our recent success in the assembly of dimeric C4R-based coordination cages fine-tuned by ancillary ligands,<sup>8</sup> we set out to realize the controlled assembly of giant C4R-based coordination cages by the judicious choice of ancillary ligands containing certain structural features capable of mediating cage formation. Herein, a bowl-shaped C4R cavitand (Pen-TPC4R), bearing four chelating groups of 2-(4H-pyrazol-3-yl)pyridine (PPD) at the upper rim, was chosen as the main building block (Scheme S1, ESI<sup>+</sup>). A rigid aromatic tetracarboxylic acid *i.e.*, 3,3',5,5'-azobenzene tetracarboxylic acid (H<sub>4</sub>TAZB), was selected as the ancillary ligand for the controlled assembly of coordination cages (Scheme 1d). Encouragingly, a giant coordination cage with a large internal void, formulated as [Zn<sub>24</sub>(Pen-TPC4R)<sub>6</sub>(TAZB)<sub>12</sub>]. 54DMF·40MeOH·30H<sub>2</sub>O (cage-1), was successfully achieved through precisely tuning the ancillary rigid tetracarboxylic acid. Cage-1 has a well-defined rhombicuboctahedral cage structure, with a remarkably large outer diameter of ca. 5.1 nm. The cage molecule further self-assembled resulting in a highly ordered, noncovalent, crystalline porous solid material.

The giant cages could have great potential in many applications, because of their large, accessible inner voids.<sup>1,2</sup> Among them, one particularly interesting application will be iodine capture. Currently, nuclear waste products generated from nuclear fission of uranium are receiving considerable attention with the rapid growing and developing demands of nuclear energy.9 Volatile radionuclides such as <sup>129</sup>I, <sup>131</sup>I, <sup>3</sup>H, and <sup>85</sup>Kr as fission products can be released during nuclear waste disposal processes.<sup>10</sup> In this facet, radioactive iodine (<sup>129</sup>I and/or <sup>131</sup>I) attracts particular attention due to its long-lived radioactive half-life (1.57  $\times$  10<sup>7</sup> years) and serious threat to human health.<sup>10</sup> Thus, effective means to capture and store radioactive iodine are highly desired and in urgent need. Several types of new adsorbents, including inorganic materials,<sup>11</sup> porous organic frameworks (POFs),<sup>12</sup> porous organic polymers (POPs)<sup>13</sup> and crystalline metal-organic frameworks (MOFs),<sup>14</sup> are being actively investigated for the removal of volatile iodine. In sharp contrast, coordination cages as emerging host-guest hybrid solid materials received exceedingly less attention in terms of their potential application in the capture of volatile iodine.<sup>13,14</sup> In this work, we show that cage-1 material has high affinity for volatile iodine and exhibits iodine uptakes comparable to those of top-performing MOF materials.

Self-assembly of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O with Pen-TPC4R and H<sub>4</sub>TAZB afforded block-shaped crystals of **cage-1** in a high yield. Single-crystal X-ray diffraction (SC-XRD) measurement revealed that **cage-1** crystallizes in trigonal space group  $R\bar{3}$ . Each individual cage features a giant 24-nucleus polyhedral structure, composed of 24 Zn(II) cations, 12 TAZB<sup>4-</sup> linkers and 6 Pen-TPC4R building blocks. Each Zn(II) center is octahedrally coordinated by two chelating nitrogen atoms from one Pen-TPC4R and four carboxylate oxygen atoms from two different TAZB<sup>4-</sup> linkers (Fig. 1 and Fig. S1, ESI†). Six Pen-TPC4R building blocks and twelve TAZB<sup>4-</sup> linkers bridge twenty-four octahedral Zn(II) cations to generate a giant coordination cage,



Fig. 1 Structures of the giant coordination cage of **cage-1** with the overall dimensions of *ca.*  $5.1 \times 5.1 \times 5.1 \text{ nm}^3$ ; H atoms and pentyl groups are omitted for clarity.

mimicking the shape of a rhombicuboctahedron (Fig. S2, ESI<sup>†</sup>). Note that cage-1 bears an unusually large number of components. Significantly, twenty-four chelating PPD moieties involve coordination with 24 Zn(II) cations, featuring the largest number of PPD components among all the related cages.<sup>3a</sup> More remarkably, cage-1 has an unusually large outer diameter of ca. 5.1 nm and an inner diameter of ca. 3.4 nm. Clearly, the overall sizes of cage-1 are much larger than those of most of the known C4R-based coordination cages.<sup>5b,e,7</sup> The cage-1 molecules further self-assemble during the synthetic process, forming a noncovalent, 3D porous supramolecular architecture. The highly crystalline, trigonal structure can be regarded as a "layered" structure with "ABC" stacking order. Within each layer, the cage molecules have a loose hexagonal packing (Fig. S3a, ESI<sup>+</sup>). Each cage molecule has six nearest neighbors, three from the layer above and three from the layer below (Fig. S3b, ESI<sup>†</sup>). The nearest-neighboring cages form a tilted octahedral geometry (Fig. S3c, ESI<sup>+</sup>). Each cage molecule engages in  $\pi$ - $\pi$  interactions with six nearest counterparts (the centroid-toplane and centroid-to-centroid distances are 3.40 and 3.62 Å, respectively) (Fig. S3d, ESI<sup>+</sup>). Interestingly, there are clear van der Waals interactions between the pentyl groups in one cage and the PPD groups in its neighboring cages. The total potential solvent-accessible void volume is 69085.4 Å<sup>3</sup> in one unit cell, as calculated using the PLATON program,<sup>15</sup> which corresponds to 62.1% of the total crystal cell volume. The cavity is presumably filled with highly disordered solvent molecules.

To our knowledge, **cage-1** represents the first example of the giant hexameric C4R-based coordination cages precisely tuned by the ancillary rigid tetracarboxylic acid ligand.<sup>5–8</sup> Noticeably, the flexibility of the ancillary ligand plays a crucial role in the coordination cage structure. For example, the flexible tetracarboxylic acids  $(H_4L^4, H_4L^5 \text{ and } H_4L^6)$  support the formation of

the dimeric coordination cages (Fig. S4, ESI<sup> $\dagger$ </sup>).<sup>8</sup> In contrast, the structurally different hexameric C4R coordination **cage-1** was achieved when the rigid tetracarboxylic acid H<sub>4</sub>TAZB was used in the assembly.

Efficient capture of radioactive iodine is of particular importance, relevant to the environment and human health.<sup>13</sup> Considering the large, accessible inner-cage cavity of giant cage-1 and the specific structural flexibility of the cage-cage packing in the crystal structure, we further investigated its potential applications for iodine capture. The efficient volatile iodine enrichment based on cage-1 was performed by exposing the activated sample to iodine vapor, mimicking typical nuclear fuel reprocessing conditions (ambient pressure and 75 °C). Upon sorption of iodine vapor, the color of the sample changed gradually from yellow to dark brown for the iodine loaded sample (Fig. 2). Overall, the iodine uptake reached up to saturation after  $\sim$  36 h. The maximum I<sub>2</sub> sorption was calculated from the difference of the sample weights before and after being exposed to iodine vapor by the gravimetric method. One gram of activated cage-1 can adsorb ca. 1.42 g of iodine. The very large aromatic internal voids produced high affinity for iodine, thus enhancing the iodine adsorption amount.<sup>12</sup> The I<sub>2</sub> uptake in activated cage-1 is comparable to those of the well-known MOFs reported in the literature, such as ZIF-8 (1.25 g  $g^{-1}$ ),<sup>14b</sup> MFM-300(Sc) (1.54 g  $g^{-1}$ )<sup>14a</sup> and HKUST-1 (1.75 g  $g^{-1}$ ) (Table S1, ESI†).<sup>14c</sup>

Moreover, to remove the adsorbed iodine molecules on the surfaces of the cages, the sample of I<sub>2</sub>-loaded **cage-1** was washed with enough *n*-hexane until the effluent became colorless. The gravimetric method demonstrates that the iodine adsorption amount entrapped within the cavity of **cage-1** is *ca.* 1.17 g g<sup>-1</sup>.

It is noteworthy that the iodine sorption by activated **cage-1** is reversible. The adsorbed  $I_2$  could be easily released by soaking the  $I_2$ -adsorbed sample in methanol at room temperature. After immersing the  $I_2$ -loaded sample in methanol, the colorless solvent gradually became dark brown and the dark brown sample turned back to yellow, demonstrating the successful release of the iodine molecules (Fig. 2). Therefore, **cage-1** is a highly promising porous material for efficient capture and separation of radioactive iodine.<sup>9–13</sup> Importantly, the PXRD pattern of the  $I_2$  released sample obtained by simply soaking the  $I_2$ -loaded sample in DMF solvent well corresponds to the simulated one, demonstrating that the structures of





**Fig. 2** (a) lodine vapor uptakes (mg g<sup>-1</sup>) over time by activated **cage-1** at ambient pressure and 75 °C (the inset shows the colour change of the sample from yellow to dark brown upon iodine adsorption). (b) Release of iodine from the I<sub>2</sub>-loaded sample of **cage-1**, with color changes of the solvents from colorless to dark brown and the sample from dark brown to yellow.

**Fig. 3** (a) Temporal evolution of UV-Vis absorption spectra of the iodine *n*-hexane solution. (b) Changes in the maximum adsorption intensity with time (the inset shows color changes of the iodine *n*-hexane solutions from purple to light pink with iodine removal by **cage-1**).

individual cage molecules are well maintained upon adsorption and release of  $I_2$  (Fig. S5a, ESI<sup>†</sup>).

To probe the valence of the loaded  $I_2$  in activated **cage-1**, X-ray photoelectron spectroscopy (XPS) measurement was conducted (Fig. S5b and S6, ESI†). As shown in Fig. S5b (ESI†), the single characteristic peak appeared at 618.7 eV, demonstrating that one type of loaded  $I_2$  molecule exists in activated **cage-1** and all  $I_2$  species are neutral.

Furthermore, iodine sorption from the liquid phase was studied as well. Typically, the sample of **cage-1** (30 mg) was dispersed in an iodine *n*-hexane solution (5 mL, 4 mM) in a glass vial at room temperature. The content of  $I_2$  in solution was monitored by UV-Vis absorption spectroscopy. As shown in Fig. 3, the concentration of  $I_2$  solution drastically decreased with increasing sorption time, and *ca.* 86% of  $I_2$  was adsorbed by the crystalline sample of **cage-1** after 6 h. Accordingly, the colour of *n*-hexane solutions varied from purple to light pink. By calculation, *ca.* 12  $I_2$  molecules in the *n*-hexane solution were included in the cavity of each cage molecule (Fig. S7, ESI<sup>+</sup>).

For **cage-1**, the uptake values of iodine in the iodine vapor and solution are 1420 mg g<sup>-1</sup> and 146 mg g<sup>-1</sup>, respectively. The adsorption rate in the iodine vapor is much faster than that in the solution (Fig. 2a and Fig. S8, ESI†). After 6 h, *ca.*1090 mg iodine was captured by one gram of **cage-1** in the iodine vapor, while only *ca.*126 mg iodine was absorbed by one gram of **cage-1** in the solution.

In summary, we described the design and synthesis of an unusually large hexameric C4R-based coordination cage through precisely tuning the ancillary rigid tetracarboxylic acid. The result demonstrated the versatile applicability of an ancillary ligandcontrolled design approach for the assembly of giant C4R-based coordination cages, thus opening up a new route for constructing large multi-component coordination cages. The giant cage molecule possesses large and accessible internal cavities. Importantly, **cage-1** exhibited the reversible uptake of volatile iodine and has potential applications in uptake and separation of radioactive iodine.

This work was supported by the National Natural Science Foundation of China (21771034 and 21471029).

### Conflicts of interest

There are no conflicts to declare.

#### Notes and references

1 (a) M. L. Saha, X. Yan and P. J. Stang, Acc. Chem. Res., 2016, **49**, 2527; (b) F. J. Rizzuto and J. R. Nitschke, Nat. Chem., 2017, **9**, 903; (c) D. Fiedler, D. H. Leung, R. G. Bergman and K. N. Raymond, Acc. Chem. Res., 2005, 38, 349.

- Z. Lu, C. B. Knobler, H. Furukawa, B. Wang, G. Liu and O. M. Yaghi, J. Am. Chem. Soc., 2009, 131, 12532; (b) W. Y. Zhang, D. Yang, J. Zhao, L. K. Hou, J. L. Sessler, X. J. Yang and B. Wu, J. Am. Chem. Soc., 2018, 140, 5248; (c) T. T. Guo, D. M. Cheng, J. Yang, X. X. Xu and J. F. Ma, Chem. Commun., 2019, 55, 6277; (d) J. J. Henkelis, C. J. Carruthers, S. E. Chambers, R. Clowes, A. I. Cooper, J. Fisher and M. J. Hardie, J. Am. Chem. Soc., 2014, 136, 14393.
- (a) W. Cullen, M. C. Misuraca, C. A. Hunter, N. H. Williams and M. D. Ward, *Nat. Chem.*, 2016, 8, 231; (b) D. Luo, X. Z. Wang, C. Yang, X. P. Zhou and D. Li, *J. Am. Chem. Soc.*, 2018, 140, 118; (c) K. Wu, K. Li, Y. J. Hou, M. Pan, L. Y. Zhang, L. Chen and C. Y. Su, *Nat. Commun.*, 2016, 7, 10487.
- 4 (a) Q. F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi and M. Fujita, *Science*, 2010, **328**, 1144; (b) D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka and M. Fujita, *Nature*, 2016, **540**, 563.
- 5 (a) S. Pasquale, S. Sattin, E. C. Escudero-Adán, M. Martínez-Belmonte and J. Mendoza, Nat. Commun., 2012, 3, 785; (b) K. Kobayashi and M. Yamanaka, Chem. Soc. Rev., 2015, 44, 449; (c) L. Chen, Q. H. Chen, M. Y. Wu, F. L. Jiang and M. C. Hong, Acc. Chem. Res., 2015, 48, 201; (d) P. Jin, S. J. Dalgarno and J. L. Atwood, Coord. Chem. Rev., 2010, 254, 1760; (e) O. D. Fox, J. Cookson, E. J. Wilkinson, S. M. G. B. Drew, E. J. MacLean, S. J. Teat and P. D. Beer, J. Am. Chem. Soc., 2006, 128, 6990; (f) T. Schroder, R. Brodbeck, M. C. Letzel, A. Mix, B. Schnatwinkel, M. Tonigold, D. Volkmer and J. Mattay, Tetrahedron Lett., 2008, 49, 5939.
- 6 R. Pinalli, V. Cristini, V. Sottili, S. Geremia, M. Campagnolo, A. Caneschi and E. Dalcanale, *J. Am. Chem. Soc.*, 2004, **126**, 6516.
- 7 (a) M. Yamanaka, M. Kawaharada, Y. Nito, H. Takaya and K. Kobayashi, J. Am. Chem. Soc., 2011, 133, 16650; (b) R. Pinalli, E. Dalcanale, F. Ugozzoli and C. Massera, CrystEngComm, 2016, 18, 5788; (c) T. Haino, M. Kobayashi, M. Chikaraishi and Y. Fukazawa, Chem. Commun., 2005, 2321; (d) O. Ugono, J. P. Moran and T. Holman, Chem. Commun., 2008, 1404.
- 8 W. Y. Pei, G. H. Xu, J. Yang, H. Wu, B. L. Chen, W. Zhou and J. F. Ma, J. Am. Chem. Soc., 2017, **139**, 7648.
- 9 R. C. Ewing and F. N. von Hippel, Science, 2009, 325, 151.
- 10 N. Yoshida and J. Kanda, Science, 2012, 336, 1115.
- 11 K. S. Subrahmanyam, C. D. Malliakas, D. Sarma, G. S. Armatas, J. S. Wu and M. G. Kanatzidis, J. Am. Chem. Soc., 2015, 137, 13943.
- 12 (a) Z. J. Yan, Y. Yuan, Y. Y. Tian, D. M. Zhang and G. S. Zhu, Angew. Chem., Int. Ed., 2015, 54, 12733; (b) A. P. Katsoulidis, J. He and M. G. Kanatzidis, Chem. Mater., 2012, 24, 1937; (c) T. Hasell, M. Schmidtmann and A. I. Cooper, J. Am. Chem. Soc., 2011, 133, 14920.
- 13 D. Shetty, J. Raya, D. S. Han, Z. Asfari, J. C. Olsen and A. Trabolsi, *Chem. Mater.*, 2017, **29**, 8968.
- 14 (a) X. R. Zhang, I. D. Sliva, H. G. W. Godfrey, S. K. Callear, S. A. Sapchenko, Y. Q. Cheng, I. Vitórica-Yrezábal, M. D. Frogley, G. Cinque, C. C. Tang, C. Giacobbe, C. Dejoie, S. Rudic, A. J. Ramirez-Cuesta, M. A. Denecke, S. H. Yang and M. Schröder, J. Am. Chem. Soc., 2017, 139, 16289; (b) D. F. Sava, M. A. Rodriguez, K. W. Chapman, P. J. Chupas, J. A. Greathouse, P. S. Crozier and T. M. Nenoff, J. Am. Chem. Soc., 2011, 133, 12398; (c) D. F. Sava, K. W. Chapman, M. A. Rodriguez, J. A. Greathouse, P. S. Crozier, H. Zhao, P. J. Chupas and T. M. Nenoff, Chem. Mater., 2013, 25, 2591.
- 15 A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7.