

Synthesis, Crystal Structure and Gas Adsorption Properties of Metal-organic Supercontainer Based 2,6-Naphthalenedicarboxylate Linker^①

SHENG Tian-Pu^{a, b} DAI Feng-Rong^{a②}
ZHENG Guo-Zong^{a②} CHEN Zhong-Ning^a

^a (State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China)

^b (University of Chinese Academy of Sciences, Beijing 100049, China)

ABSTRACT A new sulfonylcalixarene-based coordination container **1** was designed and synthesized from the self-assembly reaction of *p*-*tert*-butylsulfonylcalix[4]arene (TBSC), Co(II) ion, and 2,6-naphthalenedicarboxylic acid (NDC). It crystallizes in tetragonal system, space group *I4/m* with $a = b = 30.9119(19) \text{ \AA}$, $c = 43.565(3) \text{ \AA}$, $V = 41628(6) \text{ \AA}^3$, $D_c = 0.731 \text{ g/cm}^3$, $M_r = 9162.36$, $C_{384}H_{348}Co_{24}O_{126}S_{24}$, $Z = 2$, $F(000) = 9384$, $\mu = 0.566 \text{ mm}^{-1}$, the final $GOOF = 1.027$, $R = 0.0987$ and $wR = 0.2474$ for 7240 observed reflections with $I > 2\sigma(I)$. Structural analyses indicate that **1** adopts an edge-directed octahedral geometry and consists of six TBSC-supported Co_4 tetranuclear units locating on the vertices and twelve NDC bridging ligands occupying the edges. The new compound exhibits outstanding performance for the C_2 hydrocarbons separation over CH_4 .

Keywords: coordination container, sulfonylcalix[4]arene, gas separation, self-assembly;

DOI: 10.14102/j.cnki.0254-5861.2011-2855

1 INTRODUCTION

Discrete coordination containers featuring well-defined hollow structures have attracted significant attention in view of their well-organized polyhedral architectures, convenient coordination-driven self-assembly process, as well as promising applications such as gas storage and separation, supramolecular catalysis, molecule recognition, and so on^[1-10]. We devote oneself to the development of a new class of coordination containers named metal-organic supercontainers (MOSCs)^[10-18], which were built from sulfonylcalix[4]arenes, divalent metal ions, and suitable carboxylate linkers. They feature unique multi-pore architecture containing an *endo* cavity defined by metal ions-connected carboxylate linkers and sulfonylcalix[4]arenes, and multiple *exo* cavities from the upper rim of sulfonylcalix[4]arenes. The *exo* cavity is tunable by chemical modification on the

para substituent group of the sulfonylcalix[4]arenes, giving rise to unique selective gas adsorption properties through modulation on the solid-state porosity^[10, 19]. On the other hand, by judicious selection of carboxylate linkers, various molecular topologies of MOSCs have been readily achieved. For example, typical MOSCs with the geometries of face-directed octahedron (type I MOSCs)^[11], edge-directed octahedron (type II MOSCs)^[10], barrel-shaped box (type III MOSCs)^[12], and cylindrical structure (type IV MOSCs)^[13] were readily achieved using trigonal, linear, angular-planar, and angular-nonplanar carboxylate ligand as linkers, respectively. It has been well studied that elongating the tricarboxylate linkers successfully resulted in remarkable extension of the *endo* cavity in the face-directed octahedral type I MOSCs^[11, 20-22]. In contrast, investigations on elongated edge-directed octahedral type II MOSCs are limited^[23].

Received 17 April 2020; accepted 2 June 2020 (CCDC 2004483)

① This work was supported by the National Natural Science Foundation of China (21673239 and 21501179)

② Corresponding authors. E-mails: dfr@fjirsm.ac.cn (F.-R. Dai) and Zhengguozong@fjirsm.ac.cn (G.-Z. Zheng)

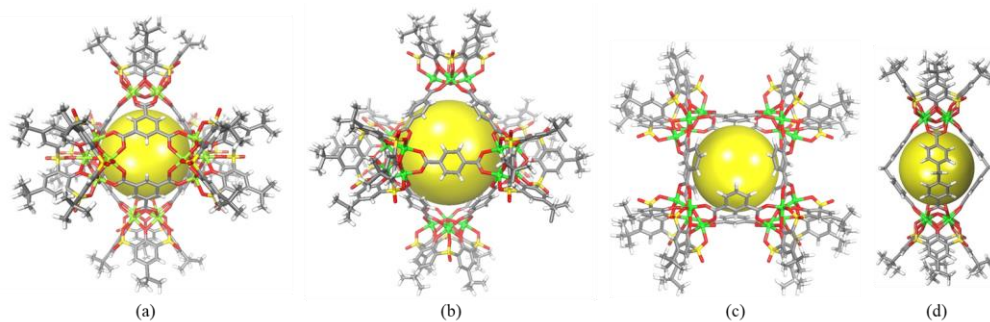


Fig. 1. Structural representations of (a) type I, (b) type II, (c) type III, and (d) type IV MOSCs^[10-13]. The yellow sphere serves to guide the eyes

Type II MOSCs with the 1,4-benzenedicarboxylate (BDC) ligand as linker exhibited remarkable O_2/N_2 adsorption selectivity depending on different degree of porosity collapse, which is closely related to different molecular sizes of MOSCs manipulating by *para* substituent modification on the sulfonylcalix[4]arene precursor^[10]. Herein, we present the assembly of a new MOSC using 2,6-naphthalenedicarboxylate (NDC) ligand as linear ditopic linkers. Replacing the BDC ligand with elongated NDC linker significantly enlarges the molecular size of resulted MOSC, and hence effectively modulates the solid-state porosity and gas adsorption properties.

2 EXPERIMENTAL

2.1 General methods

Unless otherwise noted, starting materials and solvents were purchased from commercial suppliers and used without further purification. *p*-*tert*-Butylsulfonylcalix[4]arene (H_4TBSC)^[24] was prepared according to the reported procedures. Powder X-ray diffraction results were measured on Rigaku Miniflex with $CuK\alpha$ radiation of $\lambda = 1.5405 \text{ \AA}$ operated at 30 kV at the scan rate of 2 degree/min. Thermogravimetric analysis (TGA) was obtained from a Netzsch thermal analyzer (model-STA449C) at a heating rate of 5 °C/min under a constant nitrogen flow. Gas adsorption isotherms were measured using a Micromeritics ASAP3020 instrument based on a volumetric method. Samples were typically washed with methanol and pre-dried on a Schlenk line at 120 °C for 8 h before being transferred to pre-weighed analysis tubes which were then capped with seal frits. The samples were degassed under dynamic vacuum ($< 6 \text{ \mu mHg}$) at 120 °C for about 24~48 h until the outgas rates were lower than 5 \mu mHg/min . The analysis tubes containing the evacuated samples were weighed again to determine the

sample weights before being transferred back to the analysis port of the instrument. The N_2 isotherms were measured at 77 K in a liquid N_2 bath using ultra high pure (UHP) grade gas (99.99%), the CH_4 , C_2H_2 , C_2H_4 and C_2H_6 isotherms were measured at 298 K in a dry water bath using ultra high pure (UHP) grade gases (99.99%).

2.2 Synthesis of container 1

$Co(NO_3)_2 \cdot 6H_2O$ (119.2 mg, 0.4 mmol), 2,6-naphthalenedicarboxylic acid (43.24 mg, 0.2 mmol) and H_4TBSC (84.9 mg, 0.1 mmol) were dissolved in a mixture solvent of dimethylacetamide (DMA) (5 mL) and methanol (1 mL) in a scintillation vial (20 mL capacity). The vial was placed in a sand bath, which was transferred to a programmable oven and heated at a rate of 0.5 °C/min from 30 to 100 °C. The temperature was held at 100 °C for 24 h before the oven was cooled at a rate of 0.2 °C/min to the final temperature of 30 °C. Pink crystals of **1** were formed after one week and isolated by filtration. The crystals were then vacuum dried at 120 °C to give rise to 24.67 mg of the activated material (yield: 10%).

2.3 Structure determination

X-ray single-crystal diffraction data were collected on a Bruker D8 Venture diffractometer using $I\mu S$ 3.0 microfocus source Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and PHOTON II CPAD detector. Frames were integrated with the Bruker SAINT software package (V8.38A) using a SAINT algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS)^[25]. The structure was solved and refined using the Bruker SHELXTL Software Package (SHELXT 2014/5), a computer program for automatic solution of crystal structures, and refined by the full-matrix least-squares method with ShelXle Version 4.8.6, a Qt graphical user interface for the SHELXL-2016/6^[26, 27]. Hydrogen atoms are obtained by theoretical calculations, and all non-hydrogen atoms were generated by Fourier synthesis

and correction by difference electron density function. The electron count due to disordered solvent molecules in the void space of the crystals was calculated using the program SQUEEZE in PLATON software package and refined further using the data generated^[28]. SQUEEZE gives 5142 electrons/unit cell for the voids, which are occupied by the solvents (DMA, 48 e⁻ and/or CH₃OH, 18 e⁻). Taking into account of the TGA data, container **1** can be formulated as [Co₄(μ₄-H₂O)(TBSC)]₆(NDC)₁₂(DMA)₂₅(CH₃OH)₇₆.

A total of 59011 reflections were collected in the range of $2.28 \leq \theta \leq 25.00^\circ$, of which 18433 were unique ($R_{\text{int}} = 0.1203$). The empirical formula of container **1** is C₃₈₄H₃₄₈Co₂₄O₁₂₆S₂₄, tetragonal system, space group *I4/m*, with $a = b = 30.9119(19)$ Å, $c = 43.565(3)$ Å, $V = 41628(6)$ Å³, $D_c = 0.731$ g/cm³, $M_r = 9162.36$, $Z = 2$, $F(000) = 9384$, $\mu = 0.566$ mm⁻¹, the final $GOOF = 1.027$, $R = 0.0987$ and $wR = 0.2474$ for 7240 observed reflections with $I > 2\sigma(I)$.

3 RESULTS AND DISCUSSION

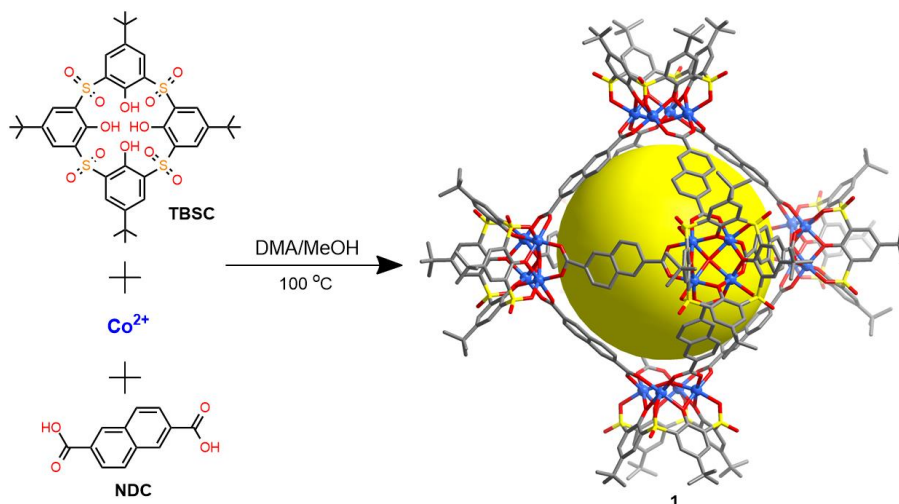


Fig. 2. Synthetic scheme of container **1**. The yellow sphere serves to guide the eyes

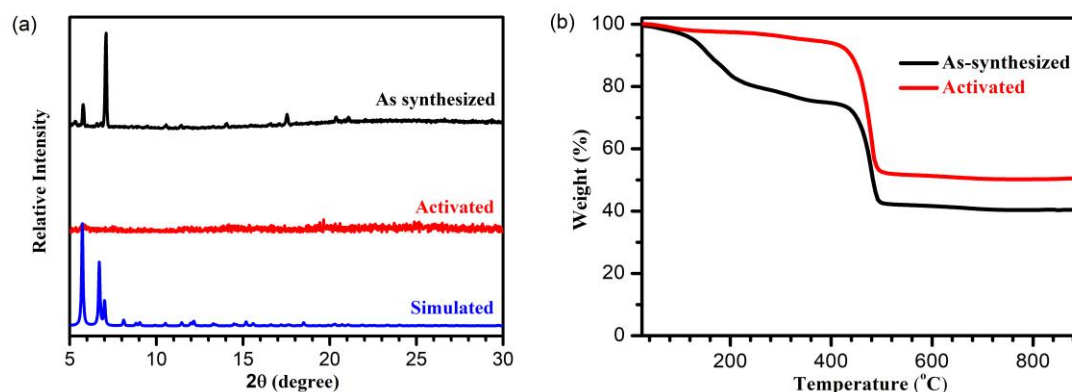


Fig. 3. (a) Experimental measured PXRD patterns of the as-synthesized (black) and activated (red) sample of **1** in comparison with the simulated patterns (blue) from single-crystal structures; (b) TGA of as-synthesized (black) and activated (red) sample of **1**

3.1 Synthesis and characterizations

The new coordination container **1** was prepared from the reaction of *p*-*tert*-butylsulfonycalix[4]arene (TBSC), 2,6-naphthalenedicarboxylic acid (NDC), and Co(NO₃)₂·6H₂O in the mixture solvent of DMA and MeOH at 100 °C for 24 h (Fig. 2), wherein red block crystals suitable for single-crystal X-ray diffraction (SCXRD) analysis were obtained after one week. As shown in Fig. 3a, the powder X-ray diffraction (PXRD) studies indicated the phase purity and crystallinity of the as-synthesized material of **1**, however, it lost its crystallinity after removal of solvent molecules, plausibly attributing to partial structural collapse of the activated sample^[10]. The thermogravimetric analysis (TGA) (Fig. 3b) revealed the excellent thermal stability of compound **1** with the decomposition temperature higher than 420 °C. The ca. 25% weight loss observed from the starting point to 300 °C was ascribed to the escape of solvent molecules (DMA and/or MeOH).

3.2 Crystal structure

The SCXRD study revealed that container **1** crystallized in the tetragonal crystal system and $I4/m$ space group as same as the BDC analogue of MOSC-II-tBu-Co^[10]. The molecular structure of container **1** adopted an edge-directed octahedral architecture with C_{4h} symmetry, consisting of six TBSC-capped tetranuclear cluster subunits occupying the vertices and twelve NDC bridging ligands locating in edges (Fig. 2 and 4a). In the TBSC-capped tetranuclear unit, the TBSC serves as a tetrakis tridentate ligand to coordinate with the square Co₄ cluster through four phenoxo and four sulfonyl O atoms. Each Co(II) ion is octahedrally coordinated with eight oxygen atoms from TBSC (two μ -phenoxo and one sulfonyl O atoms), carboxylate ligand (two oxygen atoms from two

carboxylate units), and μ_4 -H₂O. Noticeably, two TBSC-capped tetranuclear units of compound **1** located in the axial position (Fig. 4b) slightly rotated along the C_4 axis as compared to the corresponding BDC-based MOSC-II-tBu-Co (Fig. 4c) due to the obvious dislocation of two carboxylate groups in NDC ligand. Additionally, four NDC linkers occupied in the equatorial position are disordered over two positions. With the elongated NDC dicarboxylate linker, the inner and outer dimension of compound **1** (ca. 2.0 and 3.6 nm, respectively) are slightly longer than those of the BDC-based analogue (ca. 1.7 and 3.3 nm, respectively)^[10]. The hydrophobic interactions between *tert*-butyl groups from six adjacent container molecules (Fig. 5) resulted in a *pseudo* body-centered cubic (bcc) crystal packing in 3D dimension.

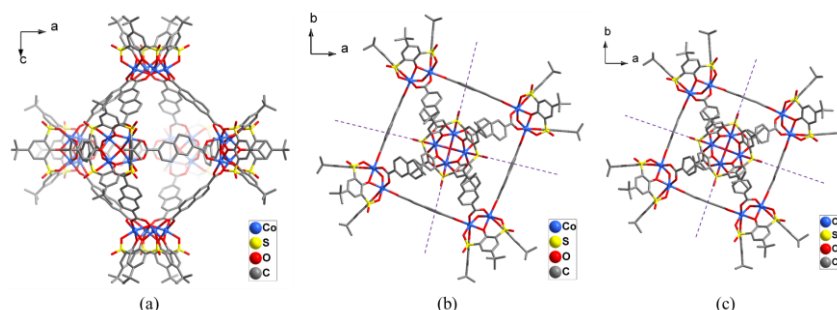


Fig. 4. Crystal structure of **1** along (a) b axis and (b) c axis, and (c) MOSC-II-tBu-Co^[10] along c axis

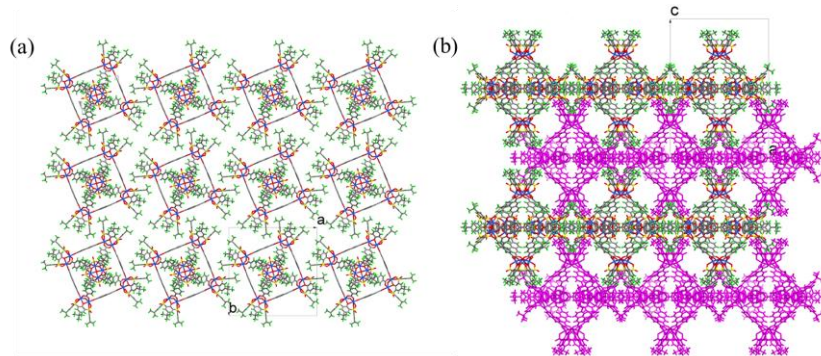


Fig. 5. (a) 2D and (b) 3D packing of **1** through hydrophobic interactions

3.2 Gas adsorption properties

The solid porosity was confirmed by the N₂ adsorption experiment using activated sample of compound **1**. As depicted in Fig. 6a, the adsorption isotherm of N₂ at 77 K displayed a “pseudo” type I model indicating the micro porous structure of **1** similar to the MOSC-II-tBu-Co^[10]. However, the Brunauer-Emmett-Teller (BET) surface area of **1** (205 cm²/g) was calculated to be only half of MOSC-II-tBu-Co (423 cm²/g) due to more severe degree of porosity collapse after enlarging the molecular size^[10]. Gas adsorption experiments of CH₄, C₂H₂, C₂H₄ and C₂H₆ were

further investigated at 298 K (Fig. 6b). The C₂H₂ adsorption capacity for **1** is higher than its C₂H₄ and C₂H₆ uptake capacities and much higher than its CH₄ uptake. At 298 K and 100 kPa, it shows the highest uptake of 22.2 cm³/g for C₂H₂, which is nearly six times its CH₄ adsorption capacity (3.8 cm³/g). Meanwhile, it adsorbs 12.4 cm³/g of C₂H₄ and 11.6 cm³/g of C₂H₆ at 298 K and 100 kPa, which are three times its CH₄ uptake capacity. The results indicated its potentially relevant application in separation and purification of light hydrocarbons.

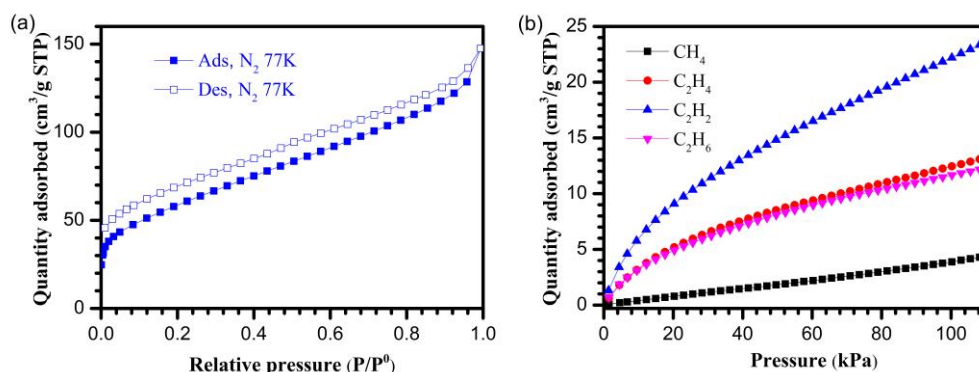


Fig. 6. (a) N₂ isotherm for 1 at 77 K; (b) CH₄, C₂H₂, C₂H₄ and C₂H₆ adsorption isotherms of 1 at 298 K

4 CONCLUSION

In conclusion, a new metal-organic supercontainer adopting edge-direct octahedral architecture has been successfully obtained by using *p*-*tert*-butylsulfonylcalix[4]arene as the capping ligand and 2,6-naphthalenedicar-

boxylate as the bridging ligand. Gas adsorption studies indicated that the new supercontainer is porous and show good adsorption selectivity of C₂ hydrocarbons over CH₄, suggesting the potential applications of this material for light hydrocarbons adsorption and separation.

REFERENCES

- (1) Cook, T. R.; Stang, P. J. Recent developments in the preparation and chemistry of metallacycles and metallacages via coordination. *Chem. Rev.* **2015**, 115, 7001–7045.
- (2) Duriska, M. B.; Neville, S. M.; Lu, J. Z.; Iremonger, S. S.; Boas, J. F.; Kepert, C. J.; Batten, S. R. Systematic metal variation and solvent and hydrogen-gas storage in supramolecular nanoballs. *Angew. Chem. Int. Ed.* **2009**, 48, 8919–8922.
- (3) Liu, T. F.; Liu, Y.; Xuan, W. M.; Cui, Y. Chiral nanoscale metal-organic tetrahedral cages: diastereoselective self-assembly and enantioselective separation. *Angew. Chem. Int. Ed.* **2010**, 49, 4121–4124.
- (4) Jiao, J.; Tan, C.; Li, Z.; Liu, Y.; Han, X.; Cui, Y. Design and assembly of chiral coordination cages for asymmetric sequential reactions. *J. Am. Chem. Soc.* **2018**, 140, 2251–2259.
- (5) Takezawa, H.; Kanda, T.; Nanjo, H.; Fujita, M. Site-selective functionalization of linear diterpenoids through u-shaped folding in a confined artificial cavity. *J. Am. Chem. Soc.* **2019**, 141, 5112–5115.
- (6) Zhao, D.; Yuan, D. Q.; Krishna, R.; van Baten, J. M.; Zhou, H. C. Thermosensitive gating effect and selective gas adsorption in a porous coordination nanocage. *Chem. Commun.* **2010**, 46, 7352–7354.
- (7) Sudik, A. C.; Millward, A. R.; Ockwig, N. W.; Côté, A. P.; Kim, J.; Yaghi, O. M. Design, synthesis, structure, and gas (N₂, Ar, CO₂, CH₄, and H₂) sorption properties of porous metal-organic tetrahedral and heterocuboidal polyhedra. *J. Am. Chem. Soc.* **2005**, 127, 7110–7118.
- (8) Jing, X.; He, C.; Yang, Y.; Duan, C. A metal-organic tetrahedron as a redox vehicle to encapsulate organic dyes for photocatalytic proton reduction. *J. Am. Chem. Soc.* **2015**, 137, 3967–3974.
- (9) Yang, L.; Jing, X.; He, C.; Chang, Z.; Duan, C. Redox-active M₈L₆ cubic hosts with tetraphenylethylene faces encapsulate organic dyes for light-driven H₂ production. *Chem. Eur. J.* **2016**, 22, 18107–18114.
- (10) Dai, F. R.; Sambasivam, U.; Hammarstrom, A. J.; Wang, Z. Synthetic supercontainers exhibit distinct solution versus solid state guest-binding behavior. *J. Am. Chem. Soc.* **2014**, 136, 7480–7491.
- (11) Dai, F. R.; Wang, Z. Modular assembly of metal-organic supercontainers incorporating sulfonylcalixarenes. *J. Am. Chem. Soc.* **2012**, 134, 8002–8005.
- (12) Dai, F. R.; Becht, D. C.; Wang, Z. Modulating guest binding in sulfonylcalixarene-based metal-organic supercontainers. *Chem. Commun.* **2014**, 50, 5385–5387.
- (13) Dai, F. R.; Qiao, Y.; Wang, Z. Designing structurally tunable and functionally versatile synthetic supercontainers. *Inorg. Chem. Front.* **2016**, 3, 243–249.
- (14) Bhuvaneswari, N.; Annamalai, K. P.; Dai, F. R.; Chen, Z. N. Pyridinium functionalized coordination containers as highly efficient electrocatalysts for

- sustainable oxygen evolution. *J. Mater. Chem. A* **2017**, 5, 23559–23565.
- (15) Bhuvaneswari, N.; Dai, F. R.; Chen, Z. N. Sensitive and specific guest recognition through pyridinium-modification in spindle-like coordination containers. *Chem. Eur. J.* **2018**, 24, 6580–6585.
- (16) Sun, C. Z.; Sheng, T. P.; Dai, F. R.; Chen, Z. N. Sulfonylcalixarene-based ortho-dicarboxylate-bridged coordination containers for guest encapsulation and separation. *Cryst. Growth Des.* **2019**, 19, 1144–1148.
- (17) Liu, M.; Liao, W. P.; Hu, C. H.; Du, S. C.; Zhang, H. J. Calixarene-based nanoscale coordination cages. *Angew. Chem. Int. Ed.* **2012**, 51, 1585–1588.
- (18) Xiong, K.; Jiang, F.; Gai, Y.; Yuan, D.; Chen, L.; Wu, M.; Su, K.; Hong, M. Truncated octahedral coordination cage incorporating six tetranuclear-metal building blocks and twelve linear edges. *Chem. Sci.* **2012**, 3, 2321–2325.
- (19) Cheng, L. J.; Fan, X. X.; Li, Y. P.; Wei, Q. H.; Dai, F. R.; Chen, Z. N.; Wang, Z. Engineering solid-state porosity of synthetic supercontainers via modification of exo-cavities. *Inorg. Chem. Commun.* **2017**, 78, 61–64.
- (20) Du, S.; Hu, C.; Xiao, J. C.; Tan, H.; Liao, W. A giant coordination cage based on sulfonylcalix[4]arenes. *Chem Commun.* **2012**, 48, 9177–9179.
- (21) Du, S.; Yu, T. Q.; Liao, W.; Hu, C. Structure modeling, synthesis and X-ray diffraction determination of an extra-large calixarene-based coordination cage and its application in drug delivery. *Dalton Trans.* **2015**, 44, 14394–14402.
- (22) Fang, Y.; Lian, X.; Huang, Y.; Fu, G.; Xiao, Z.; Wang, Q.; Nan, B.; Pellois, J. P.; Zhou, H. C. Investigating subcellular compartment targeting effect of porous coordination cages for enhancing cancer nanotherapy. *Small* **2018**, 14, e1802709.
- (23) Tan, C.; Jiao, J.; Li, Z.; Liu, Y.; Han, X.; Cui, Y. Design and assembly of a chiral metallosalen-based octahedral coordination cage for supramolecular asymmetric catalysis. *Angew. Chem. Int. Ed.* **2018**, 57, 2085–2090.
- (24) Iki, N.; Kumagai, H.; Morohashi, N.; Ejima, K.; Hasegawa, M.; Miyanari, S.; Miyano, S. Selective oxidation of thiacalix[4]arenes to the sulfinyl- and sulfonylcalix[4]arenes and their coordination ability to metal ions. *Tetrahedron Lett.* **1998**, 39, 7559–7562.
- (25) Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Crystallogr.* **2015**, 48, 3–10.
- (26) Hubschle, C. B.; Sheldrick, G. M.; Dittrich, B. ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **2011**, 44, 1281–1284.
- (27) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, C71, 3–8.
- (28) Spek, A. L. *Acta Cryst.* **2009**, D65, 148–155.