Dalton Transactions

An international journal of inorganic chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: H. Lu, W. Han, X. Yan, Y. Xu, H. Zhang, T. Li, Y. Gong, Q. Hu and Z. Gu, *Dalton Trans.*, 2020, DOI: 10.1039/D0DT00353K.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the <u>Information for Authors</u>.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/dalton

View Article Online

View Journal

View Article Online DOI: 10.1039/D0DT00353K

Graphic abstract

Supramolecular assemblies based on Fe_8L_{12} cubic metal-organic cages:

synergistic adsorption and spin-crossover properties

Hui-Shu Lu,[‡]^a Wang-Kang Han,[‡]^a Xiaodong Yan,^a Ya-Xin Xu,^a Hai-Xia Zhang,^a Tao Li,^a Yu Gong,^a Qing-Tao Hu,^a and Zhi-Guo Gu^{*a,b}



Synopsis

Synergistic adsorption of I_2 and TTF, and solid state spin-crossover behaviors were observed in supramolecular assemblies through Fe_8L_{12} cubic metal-organic cages.

Journal Name



Page 2 of 6

Supramolecular assemblies based on Fe₈L₁₂ cubic metal-organic

edge-capped

(a) self-assembly (b) face-capped Scheme. 1 (a) Self-assembling of cubic MOCs to form porous supramolecular assemblies with three different pores (A, B, C). (b) Two construction strategies of cubic cages, face-capped and

MOCs have been constructed using edge-capped strategy, and their sizes can be finely tuned by controlling the length of diimidazole linkers.¹⁰ Interestingly, a novel flexible supramolecular assemblies featuring aluminosilicate Linde type A zeolite topology was assembled from Fe₄ cages.^{10c} These results inspired us to further construct novel supramolecular assemblies using MOCs as building blocks. It's worth noting cubic MOCs are suitable to form 3D porous packing structures due to their regular molecular geometrical morphology. Under a suitable crystal packing, cubic MOCs will form porous supramolecular assemblies with three different cavities A, B and C, which are accessible and contribute to the overall porosity of the material (Scheme 1a). There are two main construction strategies of cubic MOCs, face-capped assembly and edge-capped assembly (Scheme. 1b).¹¹ Most reported cubic MOCs were face-capped M₈L₆ cages with rigid conjugated plane ligands as the faces of cube.12 It is particularly appealing to construct cubic M₈L₁₂ based porous supramolecular assemblies, and even cubic M₈L₁₂ MOCs through edge-capped assembly.

cages: synergistic adsorption and spin-crossover properties Hui-Shu Lu, ta Wang-Kang Han, ta Xiaodong Yan, Ya-Xin Xu, Hai-Xia Zhang, Tao Li, Yu Gong,

edge-capped.

DOI: 10.1039/x0xx00000x

Received 00th January 20xx,

Accepted 00th January 20xx

www.rsc.org/

Published on 12 March 2020. Downloaded by Uppsala University on 3/12/2020 5:32:05 AM.

Two Fe^{II}₈L₁₂ cubic metal-organic cages were constructed with semi-rigid ligands, which further self-assembled to supramolecular assemblies with three different porous cavities. The supramolecular assemblies showed synergistic adsorption of I2 and TTF, and their solid state spin-crossover behaviors were influenced by the adsorbed guest molecules.

Qing-Tao Hu,^a and Zhi-Guo Gu^{*a,b}

Metal-organic frameworks (MOFs) have attracted considerable attention owing to their structural diversity and potentially wide applications in gas storage, separation, catalysis, drug delivery, and chemical sensing, etc.¹⁻³ In general, the porous units of MOFs are based on cage structures, such as tetrahedron, octahedron, and cube.4-6 These polyhedron cages in MOFs are similar to the discrete metal-organic cages (MOCs), which are formed by the coordination of metal ions and bridging chelate ligands.⁷ It is particularly appealing to construct porous supramolecular assemblies by employing MOCs as building units. Compared with traditional construction strategy of MOFs, MOCs based supramolecular assemblies have several advantages such as fast and facile construction, inherent self-correcting and defect-free assembly, and structurally and functional designability of the MOCs building blocks.⁸⁻⁹ However, organizing MOCs into supramolecular assemblies through selfassembly to achieve new advanced functions are still challenging.

To develop MOCs based porous supramolecular assemblies, it is important to design MOCs with special polyhedron structures. In our previous research, a series of tetrahedral

^{a.} The Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, P.R. China. E-mail: zhiguogu@jiangnan.edu.cn.

^{b.} International Joint Research Center for Photo responsive Molecules and Materials, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, P.R. China

⁺Electronic Supplementary Information (ESI) available: Experimental details, general characterizations, additional plot and discussion. CCDC: 1953146-1953147. For ESI and crystallographic data in CIF or other electronic format. See DOI: 10.1039/x0xx00000x

[‡] These authors contributed equally.

COMMUNICATION

$(X = H \text{ or } CH_3)$

Fig. 1 Synthesis of cubic metal-organic cages through multicomponent self-assembly approach.

Herein, we reported the design, synthesis and crystal structures of two Fe^{II}₈L₁₂ cubic MOCs. Interestingly, supramolecular assemblies 1 and 2 with particular cavities were further formed through crystal packing of these cubic MOCs. The host-guest adsorption of I₂ and tetrathiafulvalene (TTF) molecules of 1 and 2, and the solid state spin-crossover behaviors were investigated.

The semi-rigid di(imidazole aldehyde) components with resorcinol were designed and synthesized (see the ESI⁺). The alkyl chains on both sides of the aromatic rings were expected to enhance the flexibility of the ligands, and the benzene rings provided the rigid cores. The self-assembly reactions of di(imidazole aldehyde) components, R-1-(4methoxyphenyl)ethan-1-amine and iron(II) trifluoromethanesulfonate in acetonitrile solution resulted in the formation of $Fe^{II}_{8}L_{12}$ cubic cages (Fig. 1). 1 and 2 were precipitated as dark purple crystals through slow diffusion of diethyl ether. 1 and 2 are soluble in acetonitrile and DMF, while insoluble in ether and cyclohexane. The crystals of 1 and 2 containing iron(II) centers were air stable, and showed good thermal stability until ca. 300 °C (Fig. S9, ESI⁺). The PXRD results confirmed that 1 and 2 maintained their crystallinity, and the loss of solvent molecules left pores in the desolvated crystals (Fig. S20-S21).

In the FT-IR spectrum of 1 (Fig. S10, ESI⁺), two C=N stretching vibration peaks at 1605 and 1585 cm⁻¹ are observed, which indicate the coexistence of low-spin state and high-spin state Fe(II) centers. By contrast, only one peak at 1597 cm⁻¹ for C=N bond is observed for 2, manifesting that Fe(II) centers in 2 are inclined to low-spin state at room temperature.

X-ray single crystal diffraction analysis revaled that both 1 and 2 crystallized in tetragonal space group /422, and they have similar structures and crystal packing modes. The crystal structure of 1 is discussed in detail as an example (Fig. 2), while the structure of 2 is shown in the ESI⁺ (Fig. S13-S14). In 1, each iron(II) centre coordinated with six nitrogen atoms from three imidazoleimine Schiff-base type ligands, forming an octahedral FeN₆ coordination geometry (Fig. 2a). The average Fe-N bond length was 1.924 Å, which was consistent with the typical lowspin iron(II) centres at 173 K.13 Eight Fe(II) occupy the vertices of the cube, and twelve imidazole-imine Schiff-base ligands act as twelve edges, forming a type Fe_8L_{12} MOC structure (Fig. 2b). The Fe-Fe distance is in the range of 11.709-11.722 Å for 1. It should be note that the well-designed ligands combine with rigid π-electron groups and flexible linkers play an important role in the forming cubic cage structure. The two flexible ethyl



Fig. 2 (a) C₃-symmetric iron coordinate vertex (Green broken lines represent π - π interactions), (b) the cubic cage structure, (c) X-ray crystal structures, (d) the space-filling view of cage 1. All H atoms, counter anions, solvents molecules and disorder have been omitted for clarity (C, grey; N, blue; O, red; Fe, purple). (e) The Xray crystal structures of crystal packing diagram about 1. (f) The space-filling model of 1.

units on the ligands adopt the gauche-gauche conformation with the shortest N···N distances of 9.029 Å and 9.057 Å between the two donor atoms, and the dihedral angles of the two imidazoles of 17.9° and 15.3° for 1 and 2, respectively. To the best of our knowledge, 1 and 2 are the rare examples of cubic cages with semi-rigid ligands based on edge-capped assemblies.

As separated by the long semi-rigid ligands, the cavity volume of **1** is about 950 $Å^3$ with the diameter of 8.3 Å (Fig. 2c). The cavity volume of **2** (659 $Å^3$) is smaller than **1**, which can be attributed to the steric hindrance of methyl groups on the benzene rings. The imidazole rings and benzene rings are decorated outside of the cage. In each [Fe₈L₁₂]¹⁶⁺ cation, twenty four intramolecular face-to-face $\pi-\pi$ stacking interactions existed between each benzene rings and imidazole rings of the adjacent ligands, further stabilizing the supramolecular structure (Fig. 2d).

Interestingly, cages can form porous supramolecular assemblies with three different pores during crystal packing. As shown in Fig. 2e and 2f, cubic cages pack closely with the mode of "window-window", and form 1D cavity hole A with the size of 8.3 x 8.3 Å by connecting with each other through their inherent cavity structure. At the same time, every four cube cages are packed around each other to form hole B with a size of about 9.8 x 9.8 Å. What's more, with the mode of "window-window", the ligands around the cages wrap around

Journal Name



Fig. 3 The UV/vis spectra of I_2 /cyclohexane solution (2.0 × 10⁻³ mol·L⁻¹, 3 mL) was adsorbed by (a) **1** and (b) **2**. The UV/vis spectra of TTF/cyclohexane solution (2.0 × 10⁻³ mol·L⁻¹, 3 mL) was adsorbed by (c) **1** and (d) **2**. The UV/vis spectra of I_2 and TTF were collaborative adsorbed by (e) **1** and (f) **2**. (g) Schematic representation of the charge transfer upon oxidation/reduction of I_2 and TTF.

to form pore C ($5.3 \times 5.3 \text{ Å}$). In this way, the supramolecular assemblies are finally constructed in the form of a simple cubic arrangement of the MOCs connected by hole C, and producing larger hole B. The porous crystalline supramolecular assemblies with special channels in **1** and **2** provide a unique platform for studying of solid state host-guest chemistry with guest molecules adsorption.

Thus, we investigated I_2 and TTF to explore the guest binding ability of **1** and **2**. UV-vis measurements were used to monitor the absorption (see the ESI⁺). As shown in Fig.3 (a) and (b), the characteristic absorption peaks of I_2 at 525 nm decreased with time, and disappeared completely after 24 h, indicating all the I_2 in the solution is absorbed by the cages. At the same time, the solution gradually turns from dark purple to colorless. And the absorption quantity of I_2 is about 530 mg/mmol for **1**, and 480 mg/mmol for **2**. The adsorption of TTF for **1** and **2** was also investigated. The characteristic absorption peaks of TTF appear at 380 and 450 nm have no obvious change under the testing conditions, and the color is still yellow, which indicated that the TTF was hardly adsorbed by **1** and **2** (Fig. 3c and 3d).

However, it was found that the adsorption of TTF can be greatly enhanced when I_2 molecules were adsorbed by **1** and **2** in advance. As shown in Fig. 3e and 3f, the absorption peaks at 380 and 450 nm decreased obviously with time, suggesting that the TTF guest was captured by the porous host. When the adsorption time reaches 12 h, the characteristic absorption



Fig. 4 Variable-temperature magnetic susceptibility measurements for (a) **1** and $[I_2/TTF \subset \mathbf{1}]$, (b) **2** and $[I_2/TTF \subset \mathbf{2}]$.

peak of TTF disappears, which means that the TTF molecules are close to completely removed from the solution. Meanwhile, the solution also changes from yellow to colourless, and the absorption quantity of TTF is about 480 mg/mmol for 1, and 430 mg/mmol for 2. Moreover, the length of I₂ and TTF molecules is about 2.9 Å and 7.9 Å, respectively. The holes A and B are larger than the two size of guest molecules. Therefore, we think that holes A and B could absorb I₂ and TTF, while hole C could only absorb I₂. In solid state UV-vis-NIR absorption spectra and UV-vis spectra, the appearance of characteristic peaks for guest molecules in $I_2/TTF \subset 1$ and $I_2/TTF \subset 2$ proved the synergistic adsorption (Fig. S15-S19). The PXRD results confirmed that the structures were maintained and that the channels were still present in the crystals during the uptake experiments (Fig. S22-S23). EDX analyses have measured the iodine and TTF adsorption for 1 and 2 (Fig. S24 and S25). After adding 1 and 2 crystals to TTF cation solution, no obvious change in solution colour and intensity of absorption peaks was observed, indicating that TTF cation can hardly be adsorbed by 1 and 2 (Fig. S26-S27). The collaborative adsorption may be attribute to the charge transfer behavior between I_2 and TTF. I_2 was reported as a modest oxidant for conversion of TTF into its radical state TTF⁺⁺ (Fig. 3g).¹⁴ As a result, I₂ in the cavity of **1** and **2** will induce TTF gradually to enter the cages and conduct chargetransfer action with it. This synergistic adsorption in 1 and 2 is rare in the area of porous materials.

As **1** and **2** contain FeN₆ coordination environment, we further studied their spin-crossover (SCO) properties. SCO phenomenon have drawn great attention due to the bistable nature of spin states, named high-spin (HS) and low-spin (LS), which can be triggered by external stimuli such as light irradiation and variation in temperature or pressure.¹⁵ As shown in Fig. 4a, the $\chi_M T$ value of **1** was maintained at 5.96 cm³ mol⁻¹ K from 2 to 150 K, indicating that 24% of the ferrous ions in **1** were in a high-spin state within this temperature range. As the temperature increases, the $\chi_M T$ value increases gradually. At room temperature of 298 K, $\chi_M T$ value is approximately 16.05 cm³ mol⁻¹ K, suggesting that 67% of the ferrous ions in **1** is at high spin state. The $\chi_M T$ reached a maximum value of 22.08 cm³ K mol⁻¹ at 400 K when all metal centres were high spin state. The magnetic investigation

COMMUNICATION

COMMUNICATION

results show that cage **1** has a gradual spin crossover behavior, and its transition temperature $T_{1/2}$ is around 256 K, slightly lower than room temperature. The multiple down-up magnetic cycles measurement confirms that the SCO is reversible and stable. Despite many attempts, the determination of the crystal structures with different spin states failed due to the very rapid decay of these crystals.

Compared with **1**, complex **2** is more inclined to low-spin state (Fig. 4b). As the temperature increased from 30 to 298 K, the $\chi_M T$ value increased slowly from 3.47 to 5.29 cm³ mol⁻¹ K, indicating that 22% of the ferrous ions in **2** were in high-spin state within the temperature range. The $\chi_M T$ showed an abrupt rise up to a maximum value of 17.38 cm³ K mol⁻¹ at 400 K. This value is much lower than the theoretical value of eight high-spin ferrous ions ($\chi_M T = 24$ cm³ mol⁻¹ K, g = 2.0). The results show that about 72% of the ferrous metals are in high-spin state at 400 K. Therefore, **2** exhibited incomplete spin crossover behaviour in the range of test temperature.

Compared with 1, the inclusion of I_2 and TTF resulted in stabilization of the high-spin state of iron(II) centers in the host-guest material $[I_2/TTF \subset 1]$ (Fig. 4a). For $[I_2/TTF \subset 2]$, the guest changed its spin-crossover behaviors slightly (Fig. 4b). 2 is less affected by the TTF/I₂ mixtures due to the TTF radical cation. The difference of the magnetic behaviour between $I_2/TTF \subset 1$ and $I_2/TTF \subset 2$ was explained by the different degrees of interaction between the guest molecules and host assemblies. 1 adsorbed more guest molecules than 2, and $I_2/TTF \subset 2$. This is in consistent with other reported porous SCO compounds, in which the guest molecules caused assemblies to move high-spin state.¹⁶

In conclusion, two porous supramolecular assemblies were constructed based on Fe^{II}₈L₁₂ cubic metal-organic cages, both of which synergistically adsorbing I₂ and TTF, and showing solid state spin-crossover behaviors. To the best of our knowledge, these are the rare supramolecular assemblies based on cubic SCO cages with 3D connected porous. We believe that these results will initiate the search for other supramolecular assemblies with polyhedral metal organic cages as building blocks.

This work was supported by the National Natural Science Foundation of China (21771089), the Fundamental Research Funds for the Central Universities (JUSRP21936, JUSRP51725B),

the project for Jiangsu scientific and technological innovation team, and the MOE & SAFEA for the 111 Project (B13025). We gratefully thank the members of the Central Laboratory, School of Chemical and Material Engineering, Jiangnan University for help with experimental methodologies.

Conflicts of interest

There are no conflicts to declare.

Notes and references

 (a) H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, The chemistry and applications of metal-organic frameworks, *Science*, 2013, **341**, 1230444; (b) Y. Bai, Y. Dou, L.-H. Xie, W. Rutledge, J.-R. Li and H.-C. Zhou, Zr-based metal-organic frameworks: design, synthesis, structure, 100 Sapple address, *Chem. Soc. Rev.*, 2016, **45**, 2327-2367; (c) Z. X. Cai, Z. L. Wang, J. Kim and Y. Yamauchi, Hollow functional materials derived from metal-organic frameworks: synthetic strategies, conversion mechanisms, and electrochemical applications, *Adv. Mater.*, 2019, **31**, 1804903.

- 2 (a) X. Li, Y. Liu, J. Wang, J. Gascon, J. Li and B. Van der Bruggen, Metal-organic frameworks based membranes for liquid separation, *Chem. Soc. Rev.*, 2017, 46, 7124-7144; (b) W. P. Lustig, S. Mukherjee, N. D. Rudd, A. V. Desai, J. Li and S. K. Ghosh, Metal-organic frameworks: functional luminescent and photonic materials for sensing applications, *Chem. Soc. Rev.*, 2017, 46, 3242-3285.
- 3 (a) Q. Yang, Q. Xu and H.-L. Jiang, Metal-organic frameworks meet metal nanoparticles: synergistic effect for enhanced catalysis, *Chem. Soc. Rev.*, 2017, **46**, 4774-4808; (b) A. Dhakshinamoorthy, Z. Li and H. Garcia, Catalysis and photocatalysis by metal organic frameworks, *Chem. Soc. Rev.*, 2018, **47**, 8134-8172; (c) J.-D. Xiao and H.-L. Jiang, Metal-organic frameworks for photocatalysis and photothermal catalysis, *Acc. Chem. Res.*, 2019, **52**, 356-366.
- 4 (a) H. Assi, G. Mouchaham, N. Steunou, T. Devic and C. Serre, Titanium coordination compounds: from discrete metal complexes to metal-organic frameworks, *Chem. Soc. Rev.*, 2017, 46, 3431-3452; (b) E. A. Dolgopolova, A. M. Rice, C. R. Martin and N. B. Shustova, Photochemistry and photophysics of MOFs: steps towards MOF-based sensing enhancements, *Chem. Soc. Rev.*, 2018, 47, 4710-4728.
- 5 (a) I. Stassen, N. Burtch, A. Talin, P. Falcaro, M. Allendorfc and R. Ameloot, An updated roadmap for the integration of metal-organic frameworks with electronic devices and chemical sensors, *Chem. Soc. Rev.*, 2017, 46, 3185-3241; (b) G. Mínguez Espallargas and E. Coronado, Magnetic functionalities in MOFs: from the framework to the pore, *Chem. Soc. Rev.*, 2018, 47, 533-557.
- 6 (a) K. Adil, Y. Belmabkhout, R. S. Pillai, A. Cadiau, P. M. Bhatt, A. H. Assen, G. Maurin and M. Eddaoudi, Gas/vapour separation using ultra-microporous metal-organic frameworks: insights into the structure/separation relationship, *Chem. Soc. Rev.*, 2017, **46**, 3402-3430; (b) M. L. Ding, R. W. Flaig, H. L. Jiang and O. M. Yaghi, Carbon capture and conversion using metal-organic frameworks and MOFbased materials, *Chem. Soc. Rev.*, 2019, **48**, 2783-2828.
- 7 (a) R. W. Hogue, S. Singh and S. Brooker, Spin crossover in discrete polynuclear iron(II) complexes, *Chem. Soc. Rev.*, 2018, **47**, 7303-7338; (b) M. Pan, K. Wu, J.-H. Zhang and C.-Y. Su, Chiral metal-organic cages/containers (MOCs): from structural and stereochemical design to applications, *Coord. Chem. Rev.*, 2019, **378**, 333-349.
- 8 (a) Y.-Y. Zhang, W.-X. Gao, L. Lin and G.-X. Jin, Recent advances in the construction and applications of heterometallic macrocycles and cages, *Coord. Chem. Rev.*, 2017, **344**, 323-344; (b) S. Wang, Q. Wang, X. Feng, B. Wang and L. Yang, Explosives in the cage: metal-organic frameworks for high-energy materials sensing and desensitization, *Adv. Mater.*, 2017, **29**, 1701898; (c) F. Beuerle and B. Gole, Covalent organic frameworks and cage compounds: design and applications of polymeric and discrete organic scaffolds, *Angew. Chem.*, Int. Ed., 2018, **57**, 4850-4878.
- 9 (a) D. Luo, X.-P. Zhou and D. Li, Beyond molecules: mesoporous supramolecular frameworks self-assembled from coordination cages and inorganic anions, *Angew. Chem., Int. Ed.*, 2015, 54, 6190-6195; (b) L. Chen, Q. Chen, M. Wu, F. Jiang and M. Hong, Controllable coordination-driven self-assembly: from discrete metallocages to infinite cagebased frameworks, *Acc. Chem. Res.*, 2015, 48, 201-210; (c) S.

Pullen and G. H. Clever, Mixed-ligand metal-organic frameworks and heteroleptic coordination cages as multifunctional scaffolds-a comparison, *Acc. Chem. Res.*, 2018, **51**, 3052-3064.

- 10 (a) D.-H. Ren, D. Qiu, C.-Y. Pang, Z. Li and Z.-G. Gu, Chiral tetrahedral iron(II) cages: diastereoselective subcomponent self-assembly, structure interconversion and spin-crossover properties, Chem. Commun., 2015, 51, 788-791; (b) S. Xi, L. Bao, J. Lin, Q. Liu, L. Qiu, F. Zhang, Y. Wang, Z. Ding, K. Li and Z. Gu, Enantiomers of tetrahedral metal-organic cages: a new class of highly efficient G-quadruplex ligands with potential anticancer activities, Chem. Commun., 2016, 52, 10261-10264; (c) W.-K. Han, H.-X. Zhang, Y. Wang, W. Liu, X. Yan, T. Li and Z.-G. Gu, Tetrahedral metal-organic cages with cube-like cavities for selective encapsulation of fullerene guests and their spin-crossover properties, Chem. Commun., 2018, 54, 12646-12649; (d) H.-X. Zhang, X.-D. Yan, Y.-X. Chen, S.-H. Zhang, T. Li, W.-K. Han, L.-Y. Bao, R. Shen and Z.-G. Gu, A zeolite supramolecular framework with LTA topology based on a tetrahedral metal-organic cage, Chem. Commun., 2019, 55, 1120-1123.
- (a) C. Browne, S. Brenet, J. K. Clegg and J. R. Nitschke, Solvent-dependent host-guest chemistry of an Fe₈L₁₂ cubic capsule, *Angew. Chem.*, Int. Ed., 2013, **52**, 1944-1948; (b) B.
 S. Pilgrim, D. A. Roberts, T. G. Lohr, T. K. Ronson and J. R. Nitschke, Signal transduction in a covalent post-assembly modification cascade, *Nat. Chem.*, 2017, **9**, 1276-1281; (c) S.
 M. Jansze, G. Cecot, M. D. Wise, K. O. Zhurov, T. K. Ronson, A. M. Castilla, A. Finelli, P. Pattison, E. Solari, R. Scopelliti, G.
 E. Zelinskii, A. V. Volgzhanina, Y. Z. Voloshin, J. R. Nitschke and K. Severin, Ligand aspect ratio as a decisive factor for the self-assembly of coordination cages, *J. Am. Chem. Soc.*, 2016, **138**, 2046-2054.
- 12 (a) M. Otte, P. F. Kuijpers, O. Troeppner, I. Ivanović-Burmazović, J. N. H. Reek and B. de Bruin, Encapsulation of metalloporphyrins in a self-assembled cubic M₈L₆ cage: a new molecular flask for cobalt-porphyrin-catalysed radicaltype reactions, *Chem.-Eur. J.*, 2013, **19**, 10170-10178; (b) L. Yang, X. Jing, C. He, Z. Chang and C. Duan, Redox-active M₈L₆ cubic hosts with tetraphenylethylene faces encapsulate organic dyes for light-driven H₂ production, *Chem.-Eur. J.*, 2016, **22**, 18107-18114; (c) N. Struch, C. Bannwarth, T. K. Ronson, Y. Lorenz, B. Mienert, N. Wagner, M. Engeser, E. Bill, R. Puttreddy, K. Rissanen, J. Beck, S. Grimme, J. R. Nitschke and A. Lützen, An octanuclear metallosupramolecular cage designed to exhibit spin-crossover behavior, *Angew. Chem., Int. Ed.*, 2017, **56**, 4930-4935.
- 13 S. Brooker, Spin crossover with thermal hysteresis: practicalities and lessons learnt, *Chem. Soc. Rev.*, 2015, **44**, 2880-2892.
- 14 J. Su, S. Yuan, H. Y. Wang, L. Huang, J. Y. Ge, E. Joseph, J. Qin, T. Cagin, J. L. Zuo and H. C. Zhou, Redox-switchable breathing behavior in tetrathiafulvalene-based metal-organic frameworks, *Nat. Commun.*, 2017, **8**, 2008-2015.
- (a) M. B. Duriska, S. M. Neville, B. Moubaraki, J. D. Cashion, G. J. Halder, K. W. Chapman, C. Balde, J.-F. Létard, K. S. Murray, C. J. Kepert and S. R. Batten, A nanoscale molecular switch triggered by thermal, light, and guest perturbation, *Angew. Chem.*, Int. Ed., 2009, **48**, 2549-2552; (b) S. Chorazy, R. Podgajny, K. Nakabayashi, J. Stanek, M. Rams, B. Sieklucka and S. Ohkoshi, Fe^{II} spin-crossover phenomenon in the pentadecanuclear {Fe₉[Re(CN)₈]₆} spherical cluster, *Angew. Chem., Int. Ed.*, 2015, **54**, 5093-5097; (c) K. Senthil Kumar and M. Ruben, Emerging trends in spin crossover (SCO) based functional materials and devices, *Coord. Chem. Rev.*, 2017, **346**, 176-205; (d) Y.-S. Meng and T. Liu, Manipulating spin transition to achieve switchable multifunctions, *Acc. Chem. Res.*, 2019, **52**, 1369-1379.

16 (a) R. G. Miller and S. Brooker, Reversible quantitative guest sensing via spin crossover of an iron(H) triagely. Germo Scik 2016, 7, 2501-2505; (b) A. J. McConnell, C. M. Aitchison, A. B. Grommet and J. R. Nitschke, Subcomponent exchange transforms an Fell₄L₄ cage from high- to low-spin, switching guest release in a two-cage system, J. Am. Chem. Soc., 2017, 139, 6294-6297; (c) K. A. Zenere, S. Duyker, E. Trzop, E. Collet, B. Chan, P. W. Doheny, C. J. Kepert and S. M. Neville, Increasing spin crossover cooperativity in 2D Hofmann-type materials with guest molecule removal, Chem. Sci., 2018, 9, 5623-5629.