

# 3D metal–organic frameworks incorporating water-soluble tetra-*p*-sulfonatocalix[4]arene†

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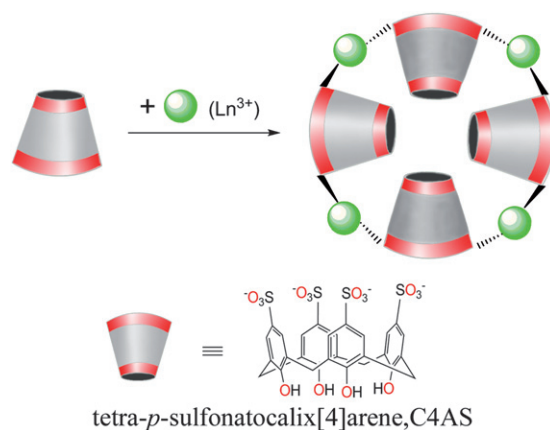
**Water-soluble tetra-*p*-sulfonatocalix[4]arene, acting as a four-connected node, bridges the rare earth cations into a 3D porous MOF in which 1D smaller circular hydrophilic channels and larger quadratic ones are lined up along the *c* axis and interconnected to each other by the calixarene cavities and other interstices.**

Metal–organic frameworks (MOFs) have been receiving growing attention in recent years owing to their potential applications in several technological areas such as gas storage, separation, heterogeneous catalysis and nonlinear optics.<sup>1–2</sup> However, many of the perceived applications for MOFs require large accessible pores, and how to control the network topology and stability of the MOFs is still a great challenge. Calixarenes are a versatile class of macrocyclic compounds which act as host materials and platforms for the synthesis of designed specific receptors.<sup>3</sup> Among them, the smallest water-soluble molecule, tetra-*p*-sulfonatocalix[4]arene (C4AS, shown in Fig. 1), has been considered a versatile supramolecular tecton. Various inclusion and/or coordination complexes of C4AS have been reported with main group, transition metal and lanthanide species, together with additional organic supramolecular building components.<sup>4,5</sup> Nonetheless, nearly all reports are concerned with the compounds assembled through aromatic  $\pi$ -interactions and hydrogen bonding except a unique example of 3D-coordination Ln/C4AS network (Ln = Pr, Nd, Sm).<sup>6</sup> With our ongoing project, we are attempting to prepare some 3D porous MOFs with calixarenes especially C4AS as the bridges.

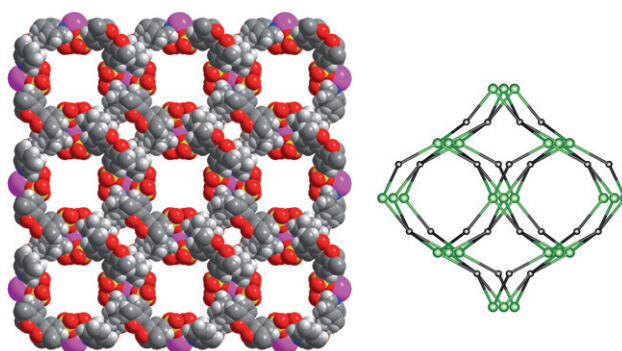
Here we present two 3D microporous MOFs‡ of calixarene and rare earths (isomorphous compounds **1** and **2**,  $M_xLn(\text{phen})_2(\text{C4AS}) \cdot y\text{H}_2\text{O}$  where Ln = Nd or Eu,  $M = (\text{CH}_3)_4\text{N}^+$  or  $(\text{C}_2\text{H}_5)_4\text{N}^+$ , phen = 1,10-phenanthroline,  $x = 1$ ), in which the rigid C4AS molecule bridges rare earth cations into a 3D framework as a tetragonal tetradentate ligand. To the best of our knowledge, it is the first time to yield metal–calixarene covalent networks with 3D porosity (Fig. 2). Notably, the C4AS molecules are arranged in an “up–up” fashion which is quite different from the common “up–down” antiparallel bilayer arrays. Each C4AS is rotated by 90° with

respect to two adjacents (Fig. 1), which is also different from other “up–up” arrangements in the nanospherical or tubular assemblies.<sup>7</sup>

The synthesis of **1** and **2** was sensitive to the acidity of the feed solution and the target compounds were obtained from a solution with a pH value being of  $\sim 5$ . Otherwise there will be some other products. For instance, a europium compound isostructural with the reported hexanuclear bicapsule compounds of Gd and Tb<sup>8</sup> will form at a pH of  $\sim 4$ . The metal also affects the formation of the title compounds. If the lanthanides are substituted by the early transition metals (Mn–Zn), no similar structures form. So, the bigger radii and higher coordination number of the lanthanides should be helpful in



**Fig. 1** Tetra-*p*-sulfonatocalix[4]arene and the up–up packing of trapezoidal faces in **1** and **2** (Ln<sup>3+</sup> = Nd<sup>3+</sup> and Eu<sup>3+</sup>).



**Fig. 2** A space-filling model of **1** and **2** viewed along the [001] direction (left, the guest cations and solvent molecules have been omitted for clarity) and a schematic presentation of the extended structures with Ln(phen)<sub>2</sub><sup>3+</sup> as green nodes and the C4AS molecules as gray nodes (right).

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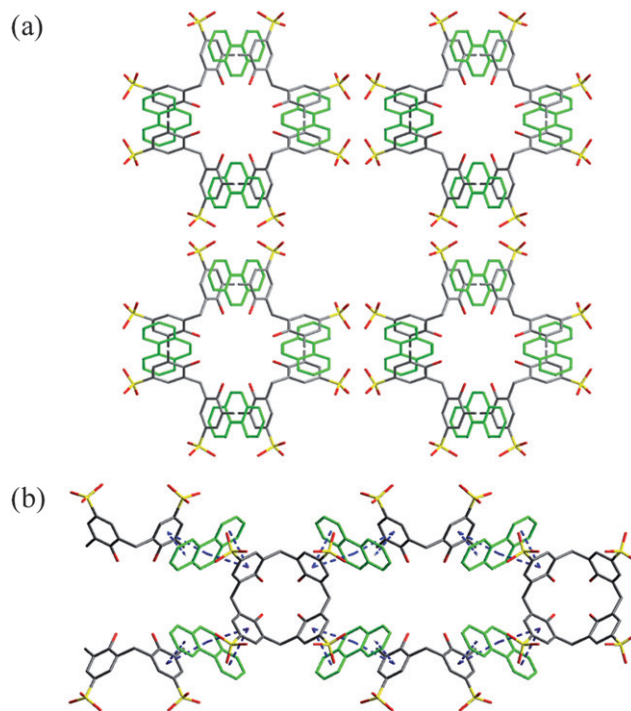
constructing the title 3D porous structures. However, the monovalent guest cations affect little on the title structures, that is, the organic ammonium cations can be replaced by the alkali metals such as Li, Na, K and Cs and the frameworks will keep unchanged.

Both compounds crystallize in a tetragonal system with space group  $P4_2/mcm$ . The refinement of the structures reveals a tetrameric circular subunit in which each C4AS trapezoidal face is arranged in a parallel “up-up” fashion and the B- and D-C4AS bowls are located in a different layer other than that for the A- and C-bowls (Fig. 1 and 3c). The Ln atoms bridge all the C4AS molecules in some circles and further connect the circular subunits which are stacked along the  $c$  axis to form some 1D tubular units. Such four 1D tubular units are then put at the corners of a square to form a bigger square tube. Thus, viewed along the  $c$  axis of the extended structures, there are two kinds of hydrophilic structural channels, a smaller circular one with a diameter of about 5.0 Å and a larger quadratic one of  $10.4 \times 10.4$  Å (for **1**, as an example, see Fig. 3c). These two kinds of 1D channels are interconnected by the calix[4]arene molecular cavities and the interstices between the C4AS molecules. Notably, there is a large percentage (44.5%, calculated with PLATON program) of voids inside the unit cell volume to take up the solvent molecules and the guest ammonium cations.

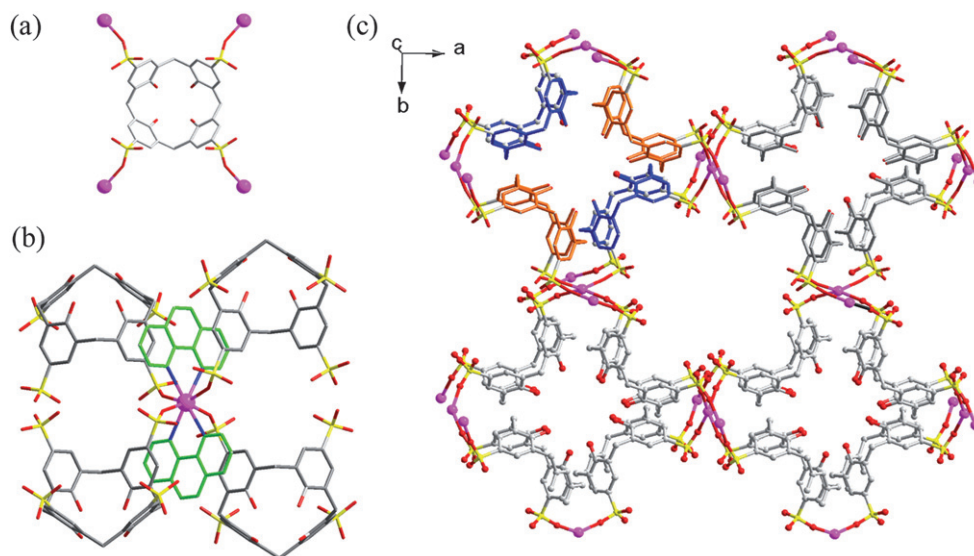
In the structures, the rare earth atoms are in a 8-fold coordination with four N atoms from two phen molecules and four sulfonato oxygen atoms from four different C4AS molecules (Fig. 3b), each of which acts as a tetradentate bridge to connect four different metal atoms. Considering the metal atom and two coordinated phen molecules as a subunit, one finds that these subunits are coordinated by four different sulfonato oxygen atoms in a tetrahedral model. These tetrahedral units are extended into a 3D framework (Fig. 2, right) with micropores.

Upon closer inspection of the structure, one can find additional  $\pi \cdots \pi$  stacking interactions between the phen molecules and the calixarene aromatic ring. One phen forms two  $\pi \cdots \pi$  stacking

interactions with one calixarene by (a) the middle of the aromatic ring  $\cdots$  calixarene aromatic ring (3.54 Å) and (b) one heterocyclic ring  $\cdots$  calixarene ring (3.58 Å). These two  $\pi \cdots \pi$  stacking interactions



**Fig. 4** (a) Extended structure without the rare earth atoms (the guest atoms and solvent molecules have been omitted for clarity) viewed along [001] showing separated nanotubular assemblies of C4AS and phen molecules; (b) A nanotubular assembly viewed along the [110] direction showing the  $\pi \cdots \pi$  stacking interactions between the phen and C4AS molecules.



**Fig. 3** (a) One C4AS molecule bonded by four rare earth metals (in purple); (b) Coordination environment of a rare earth center showing two phen molecules and four different C4AS molecules bonding one rare earth atom (phen molecules in green); (c) Tetrameric circular subunit shown in different colors (the brown and blue ones located in two different layers, phen molecules omitted) and their arrangement into an extended structure with a larger quadratic pore.

bond one phen and two calixarene molecules into a C-shape subunit. Neglecting the metal–sulfonato oxygen bonding, one also finds that the phen molecules bridge the C4AS molecules into tetrameric circle subunits which are further interconnected into a 1D tubular assembly by the  $\pi\cdots\pi$  stacking interactions (Fig. 4). Different tubular assemblies, however, are not bridged by the phen molecules, while they are interconnected by the Ln–phen nitrogen bonding and Ln–sulfonato oxygen bonding. In other words, the phen molecules rearrange the packing of C4AS molecules such as to maximize the  $\pi\cdots\pi$  stacking interactions in the C-shaped subunit, which further facilitates the Ln(phen)<sub>2</sub><sup>3+</sup> to be coordinated by four C4AS molecules in a tetrahedral model. Eventually, these tetrahedral units extend to a 3D network. The key factor for forming the target structures is the Ln(phen)<sub>2</sub><sup>3+</sup> cations being coordinated by four C4AS in a tetrahedral model. There was another evidence that four C4AS molecules are located in a plane without the existence of phen in the solution to yield just a 2D layer structure.<sup>9</sup>

In summary, two novel 3D microporous MOFs with tetra-*p*-sulfonatocalix[4]arene were obtained by a similar hydrothermal synthesis. In the extended structures, two kinds of hydrophilic 1D channels with different shapes and sizes are interconnected with each other by the calixarene cavities and the interstices between the calixarenes. This work presents an example of calixarenes for the MOFs with different pores and indicates the potential of calixarenes in constructing the porous materials.

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## Notes and references

‡ Crystal data for **1**: C<sub>56</sub>H<sub>55</sub>NdN<sub>5</sub>O<sub>19.50</sub>S<sub>4</sub>, *M<sub>r</sub>* = 1382.53, light-yellow block, 0.23 × 0.21 × 0.15 mm, tetragonal, space group *P4<sub>2</sub>/mcm* (no. 132), *a* = *b* = 18.931(1), *c* = 20.989(2) Å, *V* = 7522(1) Å<sup>3</sup>, *Z* = 4,  $\rho_c$  = 1.221 g cm<sup>-3</sup>,  $\mu$  = 0.864 mm<sup>-1</sup>, Mo *K*α radiation,  $\lambda$  = 0.71073 Å, *T* = 145(2) K,  $\theta_{\max}$  = 25.00°, 56 661 reflections collected, 3580 unique (*R*<sub>int</sub> = 0.0683). Final GooF = 1.135, *R*<sub>1</sub> = 0.1259, *wR*<sub>2</sub> = 0.3533, *R* indices based on 2699 reflections with *I* > 2σ(*I*) (refinement on *F*<sup>2</sup>), 196 parameters, 5 restraints. After the contribution from the disordered solvent molecules were subtracted by the *SQUEEZE* command<sup>10</sup> in *PLATON*, *R*<sub>1</sub> = 0.0691, *wR*<sub>2</sub> = 0.2120 [*I* > 2σ(*I*)], GooF = 1.084. Crystal data for **2**: C<sub>60</sub>H<sub>66</sub>EuN<sub>5</sub>O<sub>21</sub>S<sub>4</sub>, *M<sub>r</sub>* = 1473.38, light-yellow block, 0.24 × 0.22 × 0.15 mm, tetragonal, space group *P4<sub>2</sub>/mcm* (no. 132), *a* = *b* = 19.1147(4), *c* = 21.1495(7) Å, *V* = 7727.4(3) Å<sup>3</sup>, *Z* = 4,  $\rho_c$  = 1.266 g cm<sup>-3</sup>,  $\mu$  = 0.986 mm<sup>-1</sup>, Mo *K*α radiation,  $\lambda$  = 0.71073 Å, *T* = 184(2) K,  $\theta_{\max}$  = 24.99°, 49 026 reflections collected, 3660 unique (*R*<sub>int</sub> = 0.0432). Final GooF = 1.551, *R*<sub>1</sub> = 0.0926, *wR*<sub>2</sub> = 0.3401, *R* indices based on 2648 reflections with *I* > 2σ(*I*) (refinement on *F*<sup>2</sup>), 206 parameters, 4 restraints. After squeezed with *SQUEEZE*, *R*<sub>1</sub> = 0.0629, *wR*<sub>2</sub> = 0.2064 [*I* > 2σ(*I*)], GooF = 1.168. All non-hydrogen atoms except the water oxygen atoms were refined anisotropically. The phenolic oxygen atoms, water atoms

and carbon atoms in the ammonium cations were refined without hydrogen. The large second parameter in WGHT for the non-squeezed data of **1** might be attributed to more weak diffraction patterns in the high-angle region and the disordered solvent molecules.

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