LETTER

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A complex 3D 'wavy brick wall' coordination polymer based on *p*-sulfonatocalix[8]arene

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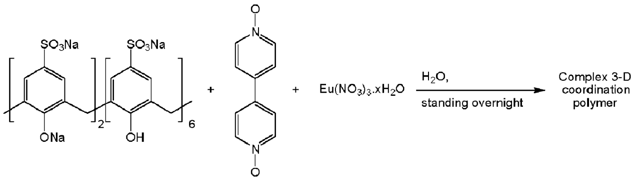
The first structural authentication of *p*-sulfonatocalix[8]arene shows the large host to adopt a 'pleated loop' conformation in the solid state. Each resulting 'groove' in the macrocycle is occupied by a 4,4′-dipyridine-*N*,*N*′-dioxide molecule in an extended multicomponent lanthanide(III) 3D coordination polymer.

The construction of coordination polymers based on bridging ligands to form new topological materials with a range of applications is an area of current interest. Rigid building blocks such as 4,4-bipyridine, amongst others, are particularly good at forming extended polymeric networks and show interesting coordination modes with a range of different metal salts.[1] Recent work by Champness and co-workers focused on the coordination behaviour between 4,4′-dipyridine-*N*,*N*′-dioxide (DiPyNO) and lanthanide metal ions with the structural elucidation of several unusual and highly connected materials.[2] Other work with this ligand (and permutations thereof) generated other coordination polymers with interesting topologies, albeit with lower degrees of connectivity.[3]

p-Sulfonatocalix[*n*]arenes (SO_3[*n*], where $n = 4, 5, 6$) are remarkably versatile in their ability to form solid state complexes in the presence (or absence) of various guest molecules in the solid state.[4,5] The smallest of these interesting macrocycles, SO_3[4], typically adopts a truncated cone conformation, packs in bi-layer arrangements in the solid state, and in our studies has shown an affinity for forming coordination polymers with the early lanthanide metals.[5] These coordination polymers show versatility in the calixarene cone angle and this phenomenon can be used to encapsulate or host appropriately charged molecules of varying size.[5] Other complexes take on the form of 'Russian dolls', 2D hydrogen bonded polymers and amino acid complexes amongst others.[4] One of our primary research goals is to achieve a level of control over the conformational and packing behaviour of the larger and more flexible *p*-sulfonatocalix[*n*]arenes for $n > 5$, with a view to constructing novel supramolecular structures and/or coordination polymers. For SO_3[4] this goal has been achieved to a certain extent and 'breaking the bi-layer' has, in some cases, resulted in the formation of remarkable nanometre scale spheroids that assemble with varied geometries depending on the lanthanide metal and guest molecule employed.[6] Nanotubules have also been characterised, the formation of which is also dependent on the aforementioned variables.[6]

Some recent advances in the supramolecular chemistry of SO_3[6] have demonstrated conformational control over the molecule through the formation of lanthanide crown ether or tetraphenylphosphonium complexes.[7] This allows the formation of bis-molecular capsule or Ferris wheel arrangements with the calixarene in the 'up–up' double cone conformation. Despite these and other recent advances however, the solid state supramolecular chemistry associated with SO_3[6] remains in its infancy.[7,8] More notably, there have been no reported structural authentications of SO_3[8] to date, a fact that may be attributable to the much greater conformational flexibility associated with the larger macrocycle. Herein we report the first structural elucidation of SO_3[8] as a linking unit in a complex 3D 'wavy brick wall' coordination polymer, **1**.

Crystals of complex **1** grew from an aqueous solution containing sodium *p*-sulfonatocalix[8]arene, DiPyNO and europium(III) nitrate (eqn. (1)). Compound **1** crystallises in a triclinic system and the structural solution was performed in the space group $P\bar{1}$.† The asymmetric unit of **1** is large and comprises one deca-anionic *p*-sulfonatocalix[8]arene, a total of six DiPyNO molecules, three and a third poly-aquo europium centres and a total of eight water molecules of crystallisation that are disordered over 24 positions. Given that the asymmetric unit is complex, the structure will be described in parts before going on to describe the structural features of the extended 3D coordination polymer.



(1)

The most striking feature in the asymmetric unit of **1** is that the *p*-sulfonatocalix[8]arene adopts a 'pleated loop' conformation (indicated by the two views in Fig. 1a and 1b) that is similar to that found for *p*-^{t}Bu, and *p*-H-calix[8]arene.[9] When in this conformation, the *p*-sulfonatocalix[8]arene has near meridional geometry overall and presents four 'grooves' on either side of the macrocycle that are generated by the kinking of the methylene bridging groups (Fig. 1). Local symmetry expansion around the crystallographically unique SO_3[8] molecule reveals each 'groove' to be bearing host to a DiPyNO molecule (Fig. 1c and 1d). The DiPyNO molecules, some being

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† CCDC reference number 233057. See http://www.rsc.org/suppdata/nj/b4/b418352p/ for crystallographic data in CIF or other electronic format.

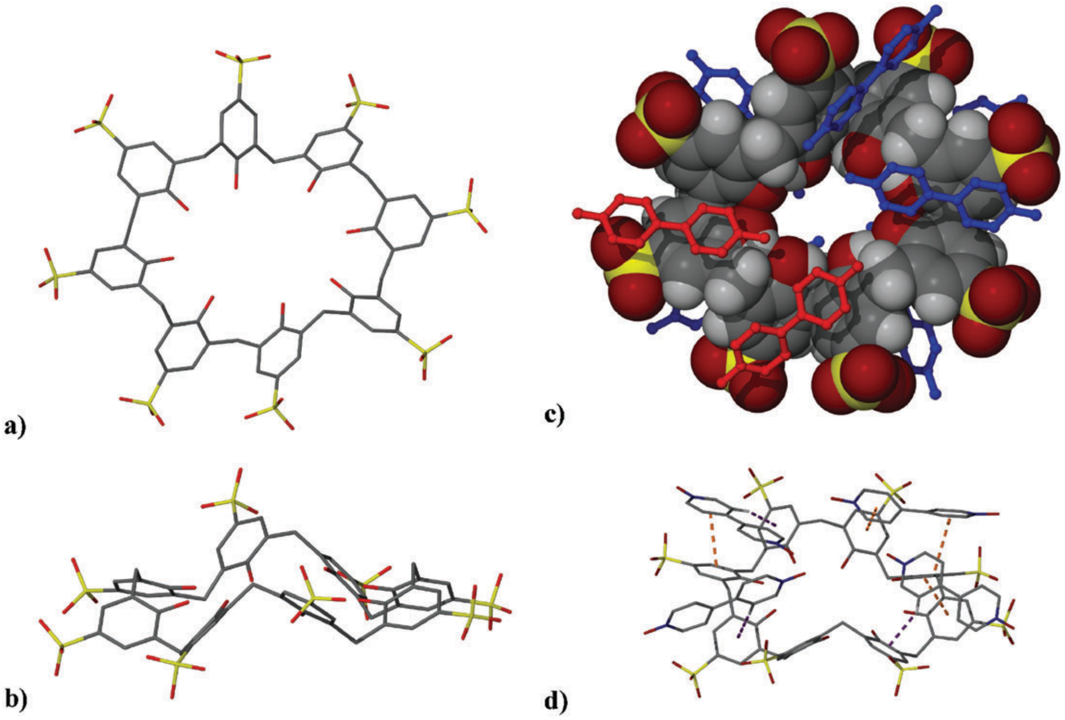

Fig. 1 Projections of the $SO_3[8]$ found in complex **1**: (a) and (b) The 'pleated loop' conformation, similar to that observed for p-^{t}Bu-calix[8]arene (hydrogen atoms omitted for clarity).[9] (c) A partial space filling representation showing DiPyNO molecules in the grooves of the calixarene and complexation with aquated europium(III) ions, and non-coordinating DiPyNO molecules shown in blue and red, respectively (atoms in some disordered positions, europium centres, europium aquo ligands, DiPyNO hydrogen atoms and water molecules of crystallisation have been omitted for clarity). (d) Some of the crystallographically unique π-stacking and CH···π interactions found on one side of the calixarene (shown as dashed orange and purple lines, respectively; several atoms omitted for clarity as in (c).

europium bound and some non-coordinating, interact with the calixarene through a series of crystallographically unique interactions (*i.e.* inter-molecular interactions between components of the asymmetric unit). In **1**, there are a total of eight crystallographically unique π-stacking interactions, the aromatic centroid···centroid distances of which all lie in the range 3.762–4.041 Å (some of which are shown in Fig. 1d). In addition there are a total of seven crystallographically unique CH···π interactions, the distances of which lie in the range 2.716–3.045 Å (also shown in Fig. 1d).

Examination of the lanthanide coordination spheres in **1** reveals that one europium centre is disordered over two positions with partial occupancies of 0.75 and 0.25. In the former of the two positions, the metal centre participates in coordination polymer formation with $SO_3[8]$ and DiPyNO molecules. In the latter of the two positions, the metal is bound only to a calixarene sulfonate group and does not interact with any DiPyNO molecules. Similarly, the europium centre that is at a third occupancy is also only bound to a calixarene sulfonate group and does not participate in coordination polymer formation with DiPyNO molecules. If, at this stage, we consider only the coordinated DiPyNO molecules and related coordinating europium centres, the metal centres are either two- or three-connecting. Symmetry expansion around each metal centre reveals an unusual 2D 'wavy brick wall' coordination polymer that is partly composed of chains of three-connecting europium centres linked by DiPyNO molecules (Fig. 2a). These chains are linked by perpendicular 'zig-zag' sections formed between DiPyNO molecules and two-connecting europium centres (Fig. 2a). If a topology diagram is constructed by connecting only three-connected europium centres, each brick has large dimensions of ~25 × 50 Å. To our knowledge this is the first example of a network of this kind for DiPyNO–Ln systems although several other interesting coordination polymer frameworks have been reported for various related systems.[2,3]

If the extended host–guest structure relating to the p-sulfonatocalix[8]arene is examined, each $SO_3[8]$ is found to link to six others (three on either side of the pleated host) in a distorted trigonal prismatic fashion through a series of intermolecular interactions with DiPyNO molecules. These $SO_3[8]$–DiPyNO links are either in the form of two neighbouring $SO_3[8]$ molecules sandwiching a DiPyNO or as a dimeric arrangement where neighbouring DiPyNO molecules display intermolecular π-stacking or CH···π interactions (an example of which is shown in Fig. 3a). When p-sulfonatocalix[8]arene is considered in the context of the extended coordination polymer, a very complex structure is revealed. The calixarenes are found to make the 3D link between adjacent 2D Eu–DiPyNO coordination polymer layers through europium/sulfonate coordination (indicated by the different coloured europium centres in Fig. 3b and the different coloured coordination polymer layers in Fig. 3c).

The charge of the p-sulfonatocalix[8]arene is suggested to be 10− (*i.e.* two calixarene base hydroxyl groups deprotonated) by the presence of a europium metal centre that is at a third occupancy, thus providing a 10+ counter cationic charge when considering all the Eu^{3+} centres in **1**. We have previously shown that at low pH, the conformation of p-sulfonatocalix[6]arene can be controlled to assemble in a double cone conformation.[7,8] This is likely to be due to maintaining the calixarene base hexa-hydrogen bonding regime that is optimised in this conformation. From the structure of $SO_3[8]$ in **1**, the destruction of a possible conformationally controlled hydrogen bonded regime (by use of the calixarene sodium salt) results in 'pleated loop' conformation. At lower pH (*i.e.* < 1), p-sulfonatocalix[8]arene may rearrange into a large double cone conformation akin to that of $SO_3[6]$.

As would be expected with a structure of this size and composition, a large number of potential hydrogen bonding interactions are identifiable. However, given that there is disorder associated with several molecular components, water

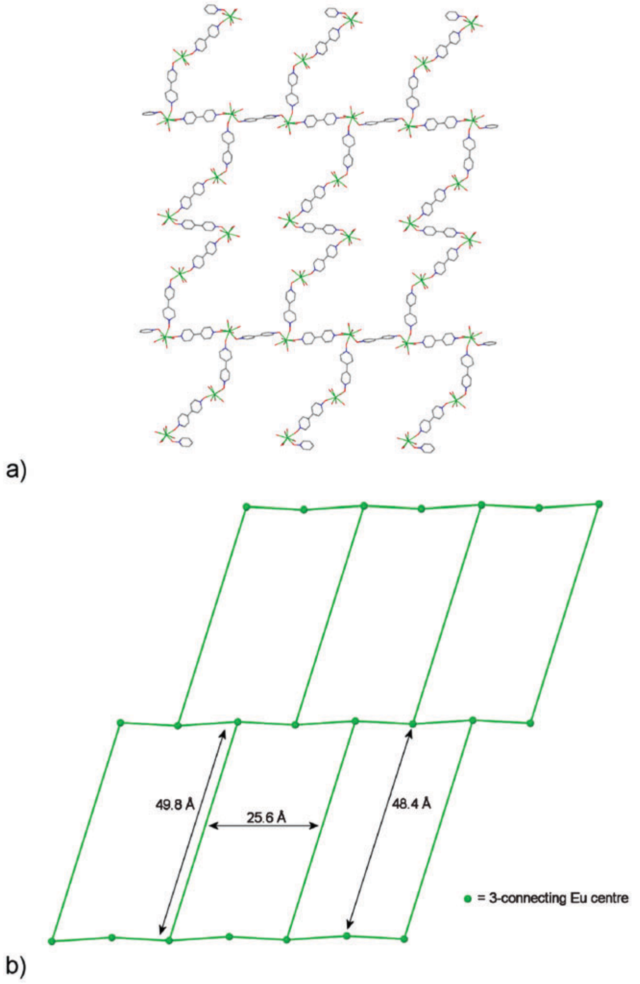

Fig. 2 The coordination polymer formed between some of the DiPyNO molecules and europium(III) centres in **1**. (a) The 'wavy brick wall' motif is formed by two- and three-connecting europium centres. (b) Dimensions of the bricks formed between three-connecting europium centres and DiPyNO molecules.

molecules of crystallisation and calixarene sulfonate groups, these shall not be discussed in this article.

To conclude, we have reported the first structure of *p*-sulfonatocalix[8]arene as part of a supramolecular 3D coordination polymer. The calixarene adopts a 'pleated loop' conformation and bears host to 4,4′-bipyridine-*N*,*N*′-dioxide molecules in all of the resultant 'grooves'. The calixarene acts as a linking unit between 2D 'wavy brick wall' coordination polymer layers that display large intra-polymer dimensions. Clearly DiPyNO is an excellent choice of guest for *p*-sulfonatocalix[8]arene as it fits well with the host when it is in this particular conformation. Other guests of similar atomic composition and shape are currently under investigation with a view to either constructing other large, unusual and interesting coordination polymers or gaining a degree of control over the $SO_3[8]$ conformation in a bid to form nano-scale spherical structures similar to those found for $SO_3[4]$.[6]

Experimental

p-Sulfonatocalix[8]arene[9] was synthesised by literature methods whilst 4,4′-dipyridine-*N*,*N*′-dioxide and europium(III) nitrate were purchased from Aldrich and used as supplied. X-Ray data for complex **1** were collected at the SRS Station 9.8 facility on a Bruker SMART-1K diffractometer using synchrotron radiation at wavelength of 0.69030 Å. Integration was undertaken using SAINT and beam decay and absorption corrections were undertaken using SADABS. The structure of **1** was solved by direct methods using SHELXS-97 and refined by 'blocked matrix' least squares on F^2 using SHELXL-97.†

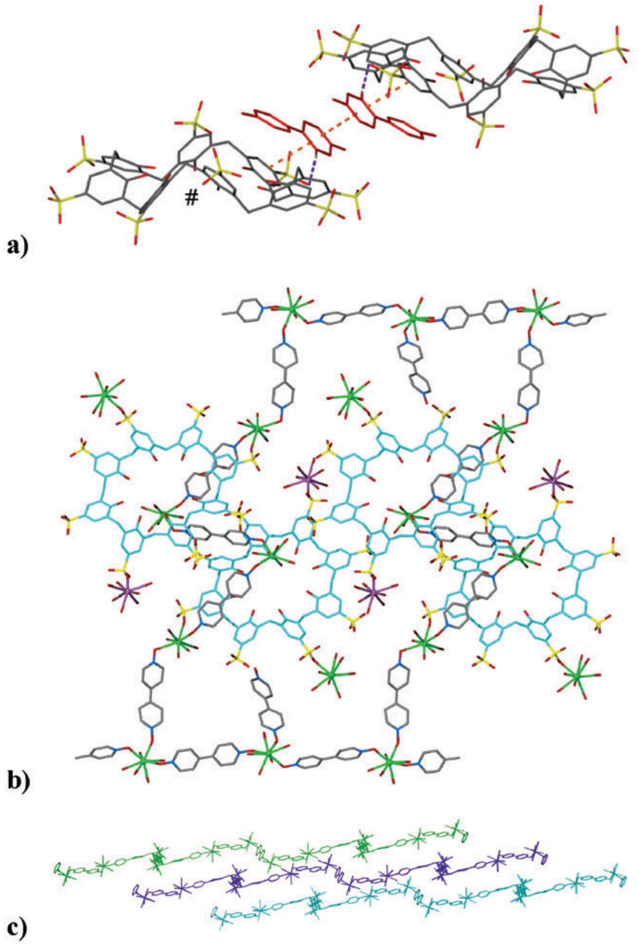

Fig. 3 Extended structure of **1**. Disordered atoms are shown in one position to aid clarity. (a) An example of π-stacking and CH···π interactions linking adjacent $SO_3[8]$ molecules (# denotes crystallographically unique calixarene). (b) Section showing coordination of calixarenes (DiPyNO shown in grey and $SO_3[8]$ in light blue). The europium centres shown in purple bond to the Eu–DiPyNO 2D layer from above or below the plane. (c) The arrangement of 2D Eu–DiPyNO layers that are linked *via* $SO_3[8]$ molecules (omitted for clarity).

Synthesis of the complex 3D coordination polymer $\{[Eu(H_2O)_7]_{0.33}[Eu(H_2O)_4]_2[Eu(H_2O)_6]$(4,4′-dipyridine-*N*,*N*′-dioxide)$_{4.5}$(*p*-sulfonatocalix[8]arene-2H)$\}$ · 1.5(4,4′-dipyridine-*N*,*N*′-dioxide) · $8H_2O$, 1

Sodium *p*-sulfonatocalix[8]arene (51 mg, 0.030 μmol) and 4,4′-dipyridine-*N*,*N*′-dioxide (34 mg, 0.18 mmol) were dissolved in distilled water (2 cm^{-3}). Upon addition of europium(III) nitrate (35 mg, 0.104 mmol), a white precipitate formed which dissolved slowly overnight. Near cubic shaped yellow crystals suitable for X-ray diffraction studies grew from the resulting solution over a two day period. Yield 21 mg, 22%.

Crystal data†

$C_{113.5}H_{134}N_{11.5}O_{68.5}S_8Eu_{3.33}$, $M = 3518.28$, triclinic, $a = 16.9935(8)$, $b = 22.1127(11)$, $c = 23.0089(11)$ Å, $\alpha = 69.117(1)$, $\beta = 69.422(1)$, $\gamma = 71.419(1)°$, $U = 7375.6(6)$ Å^3, $\mu = 1.584$ mm^{-1}, $T = 123$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, synchrotron radiation ($\lambda = 0.690\,30$ Å). Final GOF = 1.029, $R_1 = 0.0699$, 50041 reflections measured, 35981 unique ($R_{int} = 0.0281$) which were used in all calculations. The final $wR(F^2)$ was 0.2147 (all data). The overall charge of the calixarene was determined by calixarene 'base' residual electron density peaks that indicated two de-protonated phenoxy groups. The hydrogen atoms of the *p*-sulfonatocalix[8]arene base hydroxyl groups were calculated at positions suggested by residual electron density from the difference map. Some disordered waters of crystallisation, metal aquo ligands, one DiPyNO molecule (at a partial occupancy of 0.75), some europium aquo ligands and the oxygen atoms of two calixarene sulfonate groups (one of which is disordered) were all refined isotropically. Residual electron density was located around 1 Å from europium metal centres.

Acknowledgements

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