

# Macroscopic single-crystal tubes assembled with porous supramolecular architecture of water-soluble calixarene and phenanthroline†

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Single-crystal tubular products on the millimetre scale have been synthesized from water-soluble calixarene and phenanthroline in the presence of lanthanides by a hydrothermal method, in which the extended structures contain some 1D infinite channels.

Since the discovery of carbon nanotubes in 1991 by Iijima,<sup>1</sup> considerable attention has been drawn to hollow tubular architectures because of their novel properties and wide range of potential applications in chemistry, biochemistry and material sciences.<sup>2</sup> In fact, significant progress has been made in the preparation and characterization of inorganic or organic complexes.<sup>3</sup> However, most of the reports focused on the crystalline nanotubes or microtubes. The preparation of single-crystal tubes on the millimetre-scale (or macroscopic) has gained little success.<sup>4</sup> Here we present some novel macroscopic single crystal tubes whose extended structure with 1D channels is assembled by the supramolecular stacking of lanthanide-stabilized cone sulfonylcalix[4]arenetetra-sulfonate and 1,10-phenanthroline. Although there are some reports of tubular assemblies or organic nanotubes from calixarenes,<sup>5</sup> to the best of our knowledge, there is no example with the pores discernible to the naked eye found for calixarenes. The present work will give some exceptions with hollow structures of calixarene on the millimetre scale.

The samples were synthesized by a hydrothermal method from water-soluble sulfonylcalix[4]arenetetrasulfonate,<sup>6</sup> LnCl<sub>3</sub>·6H<sub>2</sub>O (Ln = Gd, Sm and Tb) and 1,10-phenanthroline. Light-yellow tubular single crystals were obtained after heating the mixture in water at 130 °C for 3 days. The tubular shape can be observed with the naked eye (Fig. 1). Under an optical microscope, the quadrilateral prisms are found to be with one opened terminus and one closed terminus, that is, they have quadrilateral and subuliform cavities. Most crystal tubes were grown with a length of several millimetres,

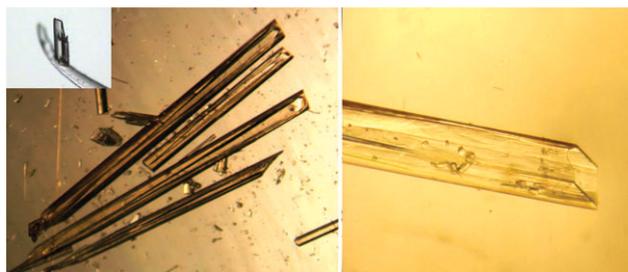


Fig. 1 Optical image of tubular crystals of **1** with a length of several millimetres (insert showing a single crystal for data collection) (left); and a quadrilateral prism with the opened end (right).

width of hundreds of micrometres, and thickness of tens of micrometres.

Single-crystal X-ray diffraction† reveals that the isomorphic compounds (whose formation might be attributed to the similar ionic radii of these three lanthanides) crystallize in a triclinic system. All the calixarene molecules are arranged in an antiparallel bilayer model, which are interconnected into a 3D network by  $\pi \cdots \pi$  stacking interactions and H-bonding interactions between the calixarenes and phenanthroline molecules or among phenanthroline molecules. The feature characteristic of these structures is the infinite 1D quadrilateral channels along the *a* axis (which is  $7.4 \times 14.1$  Å in **1a** as an example, measured between opposite atoms with van der Waals radii of the atoms considered), which are occupied by the solvent water molecules (Fig. 2). Without guest molecules, the effective free volume of **1a** is calculated by PLATON analysis to be 26.0% of the crystal volume ( $1186.8$  Å<sup>3</sup> of the unit cell volume of  $4564.9$  Å<sup>3</sup>).

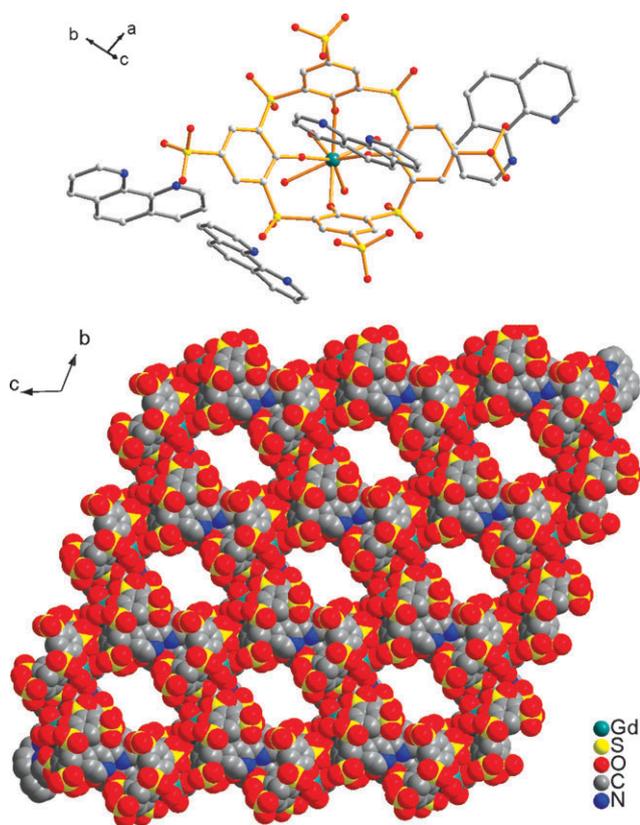
On close examination of the extended structure, one can find one asymmetric calixarene molecule and four independent phenanthroline molecules in a unit cell. The calixarene molecule adopts a cone conformation stabilized by the gadolinium cation. Different from those in the cone conformation stabilized by the sodium cations which bond to calixarene at both the upper rim and the lower rim,<sup>6</sup> the calixarene molecules are associated with the gadolinium cation by their four phenolic oxygen atoms to stabilize their cone conformation. This connection is also different from *p*-butyl-sulfonylcalix[4]arene<sup>7</sup> which bonds to the metals by not only the phenolic oxygen atoms but also the sulfonyl groups. The calixarene cone structure is pinched to give *C*<sub>2v</sub> symmetry with sulfur distances of 9.70 and 13.80 Å (**1**), 9.66 and 13.74 Å (**2**), 9.69 and 13.79 Å (**3**) for oppositely oriented sulfonate groups, which is attributed to the horizontal inclusion of phenanthroline molecules in the

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† Electronic supplementary information (ESI) available: Experimental procedures for preparation of compounds **1–3**, figures showing structural details, optical images of the products, TG/DTA curves of **1** and photoluminescence of **3**. CCDC reference numbers 665652 (**1**), 665653 (**2**), 685585 (**3**) and 715073–715075 (**1a–3a**, SQUEEZED structures). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b821065a

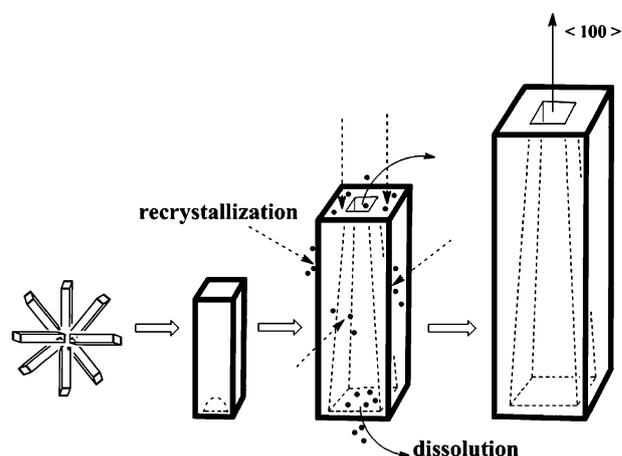


**Fig. 2** Molecular structures of isostructural compounds 1–3 (upper) and a view of the extended assemblies showing some 1D channels (bottom). The hydrogen atoms and solvent molecules are omitted for clarity.

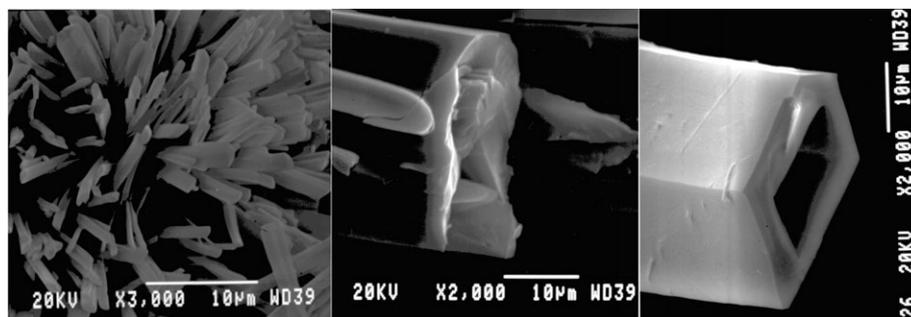
calixarene cavity as in the thiacalix[4]arene–phenanthroline complex.<sup>8</sup> Viewed along the *a* axis, the pinched calixarenes are arranged in an antiparallel way to form some bilayers which are further stacked into the porous extended structure with some columns stacked by some phenanthroline molecules through  $\pi \cdots \pi$  stacking interactions along the *a* axis (Fig. S1†). The interstices are filled by the solvent molecules. Viewed along a direction perpendicular to the *a* axis, the bilayers exhibit some antiparallel assembly of calixarene separated by the phenanthroline molecules (Fig. S2†). On the other hand, the extended structure can be considered as the grid arrangement of some calixarene capsules (Fig. S3†). The parallel capsules are located on the quadrilateral corners and the phenanthroline molecules, except those encapsulated by the

calixarenes, are inserted between the capsules. All the solvent molecules are located inside the grids.

To further elucidate the mechanism of formation of the tubular structures with quadrilateral cross section, the temporal evolution of morphology was studied by optical microscope and SEM. The products obtained by heating the feed at 130 °C for 12 h contained almost exclusively white sea-urchin-like aggregates (Fig. S4†). When heating becomes longer, the sea urchins disappear gradually and more and more transparent tubes appear. If the feed was heated for more than 36 h, almost no sea-urchin aggregates can be observed and the tubes become longer and thicker. The length of some tubes even reaches one centimetre. Close observation with SEM on the sea-urchin-like aggregates revealed that they are assembled from some thin sticks with the diameter of several to tens of micrometres. Some big sticks with a diameter of tens of micrometres are found to have the starting formation of a tube or with the quadrilateral hollow end (Fig. 3). On the basis of SEM and optical observations, the following tube growth steps with Ostwald ripening mechanism,<sup>9</sup> which is commonly applied in nanoscience, may be speculated as depicted in Scheme 1. Firstly, some little crystalline products formed and grew into small sticks which adhered at one end to form the sea-urchin-like aggregates.



**Scheme 1** Possible tube shape evolution steps: (a) initial crystallization of rodlike crystals in sea-urchin-like aggregates; (b) Ostwald ripening process; (c) dissolution and recrystallization of rodlike crystals; (d) recrystallization at rim of rod crystal on (100) face leading to the formation of tube.



**Fig. 3** SEM images of the sea-urchin-like aggregate showing shape evolution of tubular crystals: crystalline sticks (left), partly growing hollow rod (middle) and a well-developed tube (right).

This is expected because the extended structures with 1D channels are stacked along the *a* axis and the (100) face is the fast growing direction. Then some sticks on the sea-urchins kept growing while the others disappeared to provide feed for the growing ones. At the same time, one end of the bigger sticks began to dissolve to form a hollow body while they are growing in their length and diameter. The dissolved feed from the inner part then recrystallized on the outer shell of the sticks. When the dissolution and recrystallization continue, the big hollow structures formed.

In order to probe the factors which may affect the formation of the tubular crystals, we varied the acidity of the feed and the metals. It is found that the crystals became fewer when the acidity of the mixtures was reduced, that is, single crystal tubes (along with a little plate crystalline by-product) in a limpid solution were obtained at a pH value of about 2, while some white floccules appeared and the crystal sticks became fewer with increasing pH values. When the pH value of the mother solution reached 4.5, only white floccules were found. This might be due to the fact that the higher acidities are helpful in the protonation of phenanthroline to stabilize the crystal stacking and prevent the hydrolysis of the lanthanide cations. As mentioned above, the calixarenes adopt a cone conformation. In order to examine the effect of the metals on the formation of the tubular structures, the synthesis was also processed with the smaller transition metals. It was found that the smaller metals are helpful for the calixarene to adopt non-cone conformations such as partial cone and 1,2-alternate conformation<sup>10</sup> and there is no similar tubular product. That is, the proper metals that can stabilize the cone conformation of calixarene are crucial to the formation of the tubular crystals.

In conclusion, some single-crystal tubular products on the millimetre-scale have been synthesized with calixarene and phenanthroline. The metals with the proper size to stabilize the cone conformation of calixarene are crucial to the formation of the target products. The evolution of the tubular products might be explained by the dissolution of the network and extension of 1D channels in the extended structure following the crystal growth. This work presents an example for constructing macroscopic tubular structures using calixarenes and may be helpful in designing new functional materials with calixarenes.

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## Notes and references

† The *SQUEEZE* command<sup>11</sup> in *PLATON* was used in the structure refinement and the *SQUEEZED* structures (**1a**–**3a**) are presented in the paper whereas the un-*SQUEEZED* data are available in the ESI. Crystal data for **1a**: C<sub>72</sub>H<sub>53</sub>N<sub>8</sub>GdO<sub>28</sub>S<sub>8</sub>, *M* = 1891.95 g mol<sup>-1</sup>, triclinic, *P*1̄, *a* = 14.3385(8) Å, *b* = 18.183(1) Å, *c* = 19.253(1) Å, *α* = 112.598(1)°, *β* = 92.753(1)°, *γ* = 97.722(1)°, *V* = 4564.9(4) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.376 g cm<sup>-3</sup>, *μ* = 0.985 mm<sup>-1</sup>, *T* = 120(2) K, *θ*<sub>max</sub> = 26.00°, *F*(000) = 1914, crystal dimensions 0.35 × 0.12 × 0.07 mm, reflections collected/unique 33 441/17 622 (*R*<sub>int</sub> = 0.037), final *R*<sub>1</sub> = 0.0499, *wR*<sub>2</sub> = 0.1274 [*I* > 2σ(*I*)], GoF = 1.02. Crystal data for **2a**: C<sub>72</sub>H<sub>53</sub>N<sub>8</sub>SmO<sub>28</sub>S<sub>8</sub>, *M* = 1885.05 g mol<sup>-1</sup>, triclinic, *P*1̄, *a* = 14.350(2) Å, *b* = 17.955(2) Å, *c* = 19.182(2) Å, *α* = 112.135(2)°, *β* = 92.414(2)°, *γ* = 97.789(2)°, *V* = 4512(1) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.387 g cm<sup>-3</sup>, *μ* = 0.912 mm<sup>-1</sup>, *T* = 120(2) K, *θ*<sub>max</sub> = 25.00°, *F*(000) = 1910, crystal dimensions 0.45 × 0.10 × 0.09 mm, reflections collected/unique

29 922/15 599 (*R*<sub>int</sub> = 0.085), final *R*<sub>1</sub> = 0.0749, *wR*<sub>2</sub> = 0.1572 [*I* > 2σ(*I*)], GoF = 0.94. Crystal data for **3a**: C<sub>72</sub>H<sub>53</sub>N<sub>8</sub>TbO<sub>28</sub>S<sub>8</sub>, *M* = 1893.62 g mol<sup>-1</sup>, triclinic, *P*1̄, *a* = 14.360(1) Å, *b* = 18.166(1) Å, *c* = 19.290(1) Å, *α* = 112.728(1)°, *β* = 92.590(1)°, *γ* = 97.621(1)°, *V* = 4574.5(5) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.375 g cm<sup>-3</sup>, *μ* = 1.031 mm<sup>-1</sup>, *T* = 150(2) K, *θ*<sub>max</sub> = 25.00°, *F*(000) = 1916, crystal dimensions 0.33 × 0.14 × 0.13 mm, reflections collected/unique 30 983/15 908 (*R*<sub>int</sub> = 0.037), final *R*<sub>1</sub> = 0.0486, *wR*<sub>2</sub> = 0.1245 [*I* > 2σ(*I*)], GoF = 1.01. The X-ray intensity data for compounds **1**–**3** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo Kα radiation (*λ* = 0.71073 Å) operated at 2.0 kW (50 kV, 40 mA). The crystal structure was solved by means of Direct Methods and refined employing full-matrix least squares on *F*<sup>2</sup> (*SHELXL-97*).<sup>12</sup> All the non-hydrogen atoms were refined anisotropically. All the oxygen atoms of the solvent water molecules were refined without hydrogen atoms. The oxygen atoms of two sulfonate groups (O17–O19, O26–O28) were refined with disordered positions and the same displacement parameters for all oxygen atoms on one sulfonate group.

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