Self-assembly of amphiphilic calix[6]crowns: from vesicles to nanotubes†

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Upon an increase of the medium polarity, the morphology of the aggregates of calix[6]crowns TAC evolves from vesicles to the coexistence of vesicles and nanotubes, and finally to nanotubes only. Meanwhile, nanohybrids were constructed by the incorporation of calcium ions into the TAC nanotubes.

Tailoring proper molecules to construct well-defined and discrete nanostuctures (micelles, vesicles, rods, tubules etc.) is one of the great concerns to fabricate advanced materials and to mimic nature.1 Calixarenes, a family of versatile macrocyclic compounds, have been extensively studied due to their convenient synthesis and broadly potential applications.2 Recently, self-assembly of amphiphilic calixarenes leading to distinct nanoscale aggregates has attracted more and more attention.3 Nevertheless, the resultant assemblies are usually in spherical forms such as vesicles and micelles rather than one-dimensional aggregates such as fibers or nanotubes, and the latter are often used in display, sensors and biological materials. A few reports4 describe the formation of nanofibers formed by calixarenes. For example, Reinhoudt et al. reported that a β-cyclodextrin-calixarene conjugate could form nanofibres and then change into vesicles upon guest addition.4d

In the family of calixarenes, calixcrowns, which combine a calixarene framework and one or two crown ether loops, have drawn special attentions as they may serve as hosts for both cations and organic molecules.5 Due to the incorporation of the crown ether chains, the inversion of the aromatic rings is limited leading to the framework being more rigid.6 In our opinion, such a relatively rigid structure favours the formation of solid assemblies from the calixcrowns. However, they have barely been noticed as building blocks so far, probably because of the weak hydrophilicity, although they possess hydrophilic crown ether loops. In this work we designed and synthesized a new calix[6]crown derivative (TAC in Chart 1.) having both crown ether loops and hydrophilic aminopropanoyl tails. The former and the latter provide the framework rigidity and suitable amphiphility, respectively. TAC shows unique self-assembly behaviour as it forms both nanospheres and ultra-long nanotubes in solutions depending on medium polarity. Stable nanotubes have not been previously reported for all types of calixarenes including calixcrowns.7 Amphiphilic compound 5 (Chart 1), which has the same framework and the tails as TAC but without crown loops, was studied as a reference. TAC was obtained by aminolysis of the precursor of syn-bis(ethoxyxycarbonyl)methylated p-tert-butylcalix[6]biscrown-4 with 1, 3-diaminopropane (compound 3, see ESI†). Compound 3 was produced by the one-pot synthesis with a simplicity and good efficiency we previously developed.8 The 1H NMR spectra of TAC show that it maintains 1,4-alternate conformation as compound 3 does.9 The details of synthesis and characterization of TAC can be found in the ESI†.

TAC is soluble in ethanol but not in water. We tried to perform self-assembly of TAC in the mixed solvents of ethanol and water. It was found that a tinge of blue opalescence appeared when water was added into TAC solutions in ethanol (1 mg mL−1), which indicated the formation of some kind of aggregates. For the case of the volume ratio of water–ethanol 1 : 3, transmission electron microscopy (TEM) revealed that TAC formed spherical aggregates (Fig. 1a). Atomic force microscopy (AFM) (Fig. 1c) shows that the aggregates are spherical in shape and the horizontal distance (248 nm) of the spheres is similar to the diameter of aggregates (289 nm) measured by dynamic light scattering (DLS) (Fig. S3, ESI†), which means that the spheres did not spread in the AFM sample preparation. The size found by AFM is smaller than that in DLS due to the loss of the solvent within the spheres in AFM samples. However, the vertical distance is found to be 40 nm, only one sixth of its diameter. Such remarkable size difference between the vertical and horizontal directions of nanoparticles was often reported by AFM observations and attributed to hollow structures.9 The hollow structure of the aggregates of TAC is also supported by scanning electron microscopy (SEM, Fig. 1b), in which the central part of the aggregate is darker in contrast to its periphery as the shell partially sank. Therefore, we proposed that TAC self-assembled into vesicles in solutions, which collapsed when the sample dried in the air. Interestingly, it should be noticed that in both Fig. 1a and 1b, a tendency of fusion of some spheres is observed, which is probably a precursory procedure for the formation of nanotubes.10

With an increase of the volume ratio of water–ethanol to 2 : 3, the SEM observations show that TAC aggregates evolved from

![Chart 1: Chemical structure of TAC and 5](chart.png)
predominant vesicles to the coexistence of vesicles and fibers (Fig. 1d). TEM clearly shows a string of fused spheres (Fig. 1e) indicating that in this higher polarity medium the vesicles connect to each other forming one-dimensional nanoaggregates. Finally, by further increasing the ratio of water to ethanol to 1:1, we found by TEM plenty of ultra-long fibrous aggregates (Fig. 2a) with no vesicular aggregates left. The length of the fibrils is mostly above 10 μm while the width is only 100–200 nm. Similar motifs of the nanofibrils were observed by SEM (Fig. 2c). A clear contrast between the center and periphery shown by the TEM image at a high magnification suggests the tubular structure and the wall thickness is about 20 nm (Fig. 2b). Moreover, this conclusion is justified by the AFM results shown in Fig. 2d, that the horizontal and vertical distances of the aggregates are 128.3 and 28.1 nm, respectively. Furthermore, on standing of the solutions the tubular aggregates can be easily packed into bundles, which remained stable in the medium for months (Fig. S4 and S5, ESI†).

In short, we observed a remarkable effect of media polarity on the morphologies of TAC self-assembly, i.e. when the solution composition (water–ethanol ratio) changes from 1:3 to 2:3 and then to 1:1, the aggregates vary from vesicles to the coexistence of vesicles and nanotubes and finally to nanotubes exclusively. All of the self-assembly processes are completed in a few seconds and were reproducible. As the UV and IR and NMR spectra of the TAC aggregates in the mixed solutions did not show substantial differences with those of the unassembled TAC, we may suggest that the hydrophobic interactions between the TAC frameworks rather than the π–π or hydrogen-bonding interactions play a major role in driving the self-assembly of TAC.

To gain further insight into the molecular packing within self-assembled tubular structures, a small-angle X-ray diffraction pattern was measured. As shown in Fig. 3, the nanotube TAC displays a sharp peak at 2θ = 6.2° corresponding to a long period of 1.43 nm, which is consistent with the molecular length of TAC (1.5 nm by CPK model). Combining this value with the wall thickness (around 14 nm) of the tubes judged by AFM (Fig 2.), we may propose that TAC are aligned to form layers and the wall has a multilayer structure with the hydrophilic groups facing aqueous phase (Fig. 4).

To evaluate the influence of the framework rigidity of the calixcrown on their self-assembly, we studied the morphologies of the aggregates of compound 5 as a reference, which possesses more flexible conformation due to the absence of the crown loops attached to the framework. TEM showed the formation of vesicular aggregates of 5 in water–ethanol 1:3 (Fig. S6, ESI†). Interestingly, unlike TAC, 5 only gives rise to lose and irregular aggregates as the water content of the solution was further increased. In other words, the stable tubular structure can only be engendered from TAC but not compound 5. It proved that besides proper hydrophilicity, the rigidity of the framework is also an important factor governing the formation of solid regular aggregates of calixarenes.

Fig. 1 TEM, SEM and AFM image showing the aggregates of TAC in solution (water–ethanol = 1:3 for a, b and c; water–ethanol = 2:3 for e and f): a) TEM, scale bar represents 1 μm; b) SEM image, scale bar represents 400 nm; c) AFM, tapping mode; d) SEM, scale bar represents 400 nm; e) TEM, scale bar represents 200 nm.

Fig. 2 TEM, SEM and AFM images showing the aggregates of TAC in solution (ethanol–water = 1:1): a) TEM, scale bar represents 2 μm; b) TEM at a higher amplification, scale bar represents 200 nm; c) SEM, scale bar represents 400 nm; d) AFM, tapping mode.

Fig. 3 X-Ray diffraction pattern of the nanotubes formed from TAC.
Our previous study reported that compound 3 has shown excellent selectivity for caesium ions. This inspired us to investigate whether caesium ions could be incorporated into the aggregates of TAC or not. We injected ethanol solution of TAC into CsCl–water (0.5 mg mL\(^{-1}\)) to prepare the aggregates in water–ethanol (3 : 1) mixture. TEM shows that long fibrils formed just as the case without caesium. The EDX spectra (Fig. 5) within the tubular aggregates and of the blank section near the aggregates show a remarkable contrast of the caesium ion peaks, which clearly indicates that the aggregates are enriched with caesium ions. This result reveals that, as a platform, the amphiphilic calix[6]crown derivatives with varieties of different structures, can be designed to hold specific cations (Ag\(^+\), Cu\(^{2+}\) etc.) and then be utilized to fabricate magnetic or electronic nanomaterials.

In conclusion, to our knowledge, this communication presents the first example of a morphological transition from vesicles to nanotubes in self-assemblies of calixarenes. Unlike the remarkably broad and deep studies on self-assembly of block copolymers which started in the 1970’s, the investigation on self-assembly of the calixarenes is still at the very beginning. Great efforts are needed to exploit the relationship between the resultant morphologies and the structural parameters of the calixarenes, including the conformation of the framework, the structure and length of the attached hydrophilic chains etc., some of which is currently underway in our laboratory.

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Notes and references