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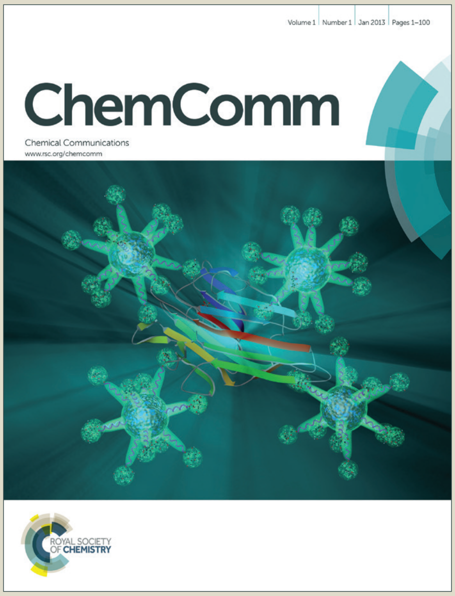

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COMMUNICATION

Well-defined nano-sunflowers formed by self-assembly of a rod-coil amphiphile in water and their morphology transformation based on a water-soluble pillar[5]arene

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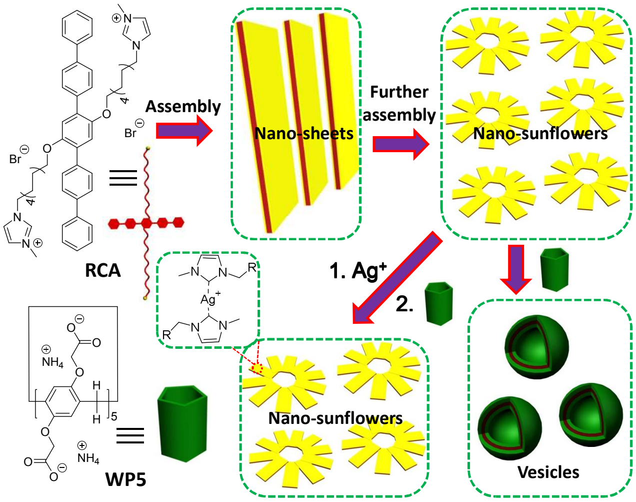
Well-defined nano-sunflowers were constructed by self-assembling a rod-coil amphiphile in water, and their morphologies transformed by addition of a water soluble pillar[5]arene and Ag_2O were also investigated.

Self-assembly of amphiphiles in water has received considerable attention because it can create dynamic materials in terms of their possible applications in the fields of environmental sciences, biomedical sciences, and nanodevices.[1] Among a variety of molecular building blocks for self-assembly, such as block copolymers, peptide derivatives, and lipid molecules, rod amphiphiles, consisting of rigid rod and flexible coil segments, are excellent candidates for creating well-defined supramolecular structures in selective solvents for flexible side chains.[2] For the aqueous self-assembly of rigid-flexible block molecules, the amphiphilic combination of hydrophilic coil and hydrophobic rod segments leads to the formation of a well-defined nanostructure with rigid hydrophobic core surrounded by flexible hydrophilic chains.[3] In contrast to traditional amphiphilic systems, the rod-coils can form well-ordered structures even at very low molecular weights of each block because a stiff rod-like conformation of the rod segments imparts orientational organization.[1c] The packing arrangements of these small anisotropic rod segments are able to rapidly transform into their equilibrium states when faced with very small environmental changes, which is an essential prerequisite for construction of responsive nanostructures.[1c]

On the other side, as a new class of supramolecular hosts after crown ethers,[4] cyclodextrins,[5] calixarenes,[6] and cucurbiturils,[7] pillar[*n*]arenes,[8,9] especially pillar[5]arenes,[8] are useful and interesting macrocyclic compounds due to their various host–guest interactions with different guest molecules and broad applications. In view of this, we present here the formation of well-defined nano-sunflowers from the aqueous self-assembly of rod-coil amphiphile (**RCA**) which contains a rod segment and two flexible imidazolium groups (Scheme 1). The rod-coil amphiphile could self-assemble into nano-sheets in water. Interestingly, these nano-sheets further assembled into well-defined nano-sunflower structures without external stimuli. Due to the host–guest interactions between imidazolium group and water soluble pillar[5]arene **WP5**, upon addition of **WP5**, nano-sunflower structures would transform into fluorescent vesicles. However, silver ions can complex with two imidazolium groups to suppress these nano-sunflowers disassembled by addition of **WP5**.



Scheme 1 Chemical structures and cartoon representations of rod-coil amphiphile (**RCA**) and water soluble pillar[5]arene (**WP5**) and the schematic representations of their self-assembly in water.

RCA was synthesized by our previous report.[8w] From the report, it is known that when **RCA** was dissolved in water, it could self-assemble into nano-sheets immediately. To our surprised, these nano-sheets can further self-assemble into well-defined nano-sunflower structures after one night. The self-assembly behavior of **RCA** was firstly studied in aqueous solution by using dynamic light scattering (DLS). As shown in Fig. 1a, the fresh assemblies of **RCA** have a diameter of ~500 nm and a broad size distribution, however, after one night, the diameter of the resultant assemblies was changed to ~1000 nm and a narrow size distribution, indicating the formation of new nano-structures. Transmission electron microscopy (TEM) experiments assisted in the visualization of the resultant nanostructures self-assembled from **RCA** in water. Fig. 1b shows a micrograph obtained from a 2.00 × 10^{-5} M aqueous of **RCA** which prepared more than 12 hours. Well-defined nano-sunflower structures with the diameter of ~1000 nm were observed. Furthermore, small-angle X-ray scattering (SAXS) measurements were performed for the determination of the thickness of the nano-sunflowers. The profile taken from a 2.00 × 10^{-5} M aqueous solution of **RCA** shows a strong scattering at 2.90° (Fig. 1c), so the thickness of the nano-sunflowers was calculated to be 3.00 nm, which is close to the fresh nano-sheets and the estimated length of a fully extended molecule of **RCA**.[8w]

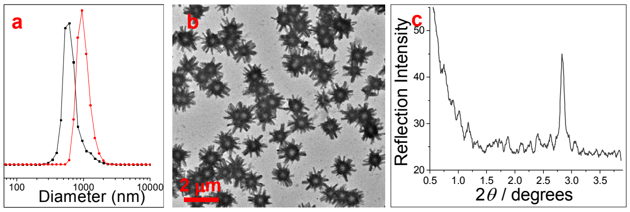


Fig. 1 (a) DLS studies of the self-assembly of **RCA** in water: I. fresh prepared; II. Prepared after one night. (b) TEM image of nano-sunflowers self-assembled from **RCA**. (c) Small-angle X-ray scattering study of the nano-flowers.

Further investigation provided us with deeper insight into the nature of the self-assembly. It was interesting that nano-sheets appeared to transform into nano-sunflowers with increasing incubation time (Fig. 2), suggesting a possible mechanism for the formation of the nano-sunflowers. This observation was very important since it highlighted the significance of nano-sheets in the self-assembly process to form nano-sunflowers. Fig. 2a shows a TEM image of the fresh aggregates **RCA** in water, in which a large number of nano-sheets lying irregularly can be seen. Then the nano-sheets attach to each other when the aggregates self-assembled for 2 hours (Fig. 2b). Furthermore, when the incubation time was increased to 4 hours, nano-sheets further attach to each other and peanut-likes structures were observed (Fig. 2c). Remarkably, almost all of the nano-sheets were converted to nano-sunflowers after 12 hours (Fig. 2e). An enlarged TEM image of one nano-sunflower showed that the sun-flowers formed by nano-sheets packing to each other (Fig. 2f).

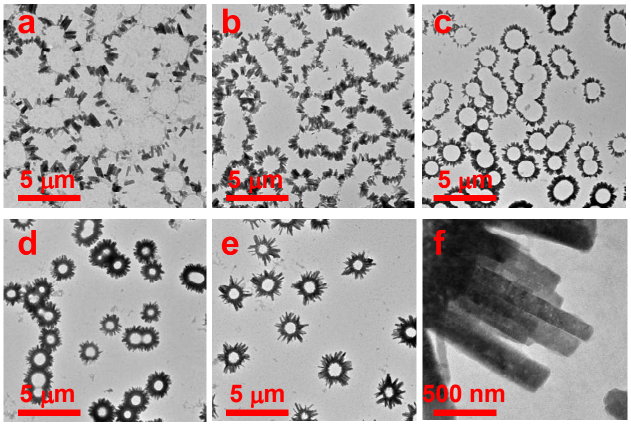


Fig. 2 TEM images of the self-assembly of **RCA** in water with different time: (a) fresh prepared; (b) 2 hours; (c) 4 hours; (d) 8 hours; (e) 12 hours; (f) enlarged TEM image of e.

From our previous study, it is known that **WP5** can complex with imidazolium groups to induce nanosheets transforming into fluorescent vesicles.[8w] We wonder whether **WP5** can also induce them transform into vesicles when **RCA** further self-assemle into more stable nano-sunflowers. As shown in Fig. 3a, upon addition of **WP5**, a dramatic increase of the fluorescence intensity is clearly observed. Furthermore, transmission electron microscopy (TEM) experiments assisted in the visualization of the new nano-structures after addition of **WP5**. Vesicles with an average diameter of ~200 nm were observed (Fig. 3b), which indicate that even when **RCA** further assemble into nano-sunflowers, **WP5** can still induce them transforming into vesicles (Fig. 3c).

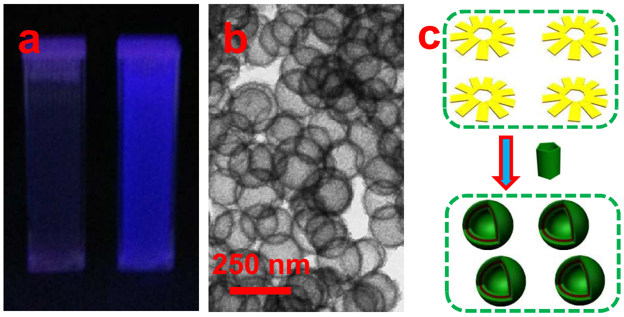


Fig. 3 (a) Fluorescent photographs of nano-sunflowers self-assembled from **RCA** (left) and upon addition of **WP5** (right) in water. (b) TEM image of vesicles self-assembled from **RCA** upon addition of **WP5**. (c) Schematic representation of nano-sunflowers transforming into vesicles.

On the other hand, imidazolium groups on **RCA** can not only complex with **WP5**, but also complex with silver ions (Fig. S1).[10] As shown in Fig. S2, when we added excess Ag_2O to the nano-sunflowers system and stirred for 1 hour, the nano-sunflowers kept their structures. EDX spectrum confirmed that the silver ions exist in the nano-structures (Fig. S3). However, further addition of **WP5** could not induce these nano-sunflowers which contain silver ions disassembly (Fig. S4). A possible mechanism is that one silver ion complex with two imidazolium groups, which is too large to penetrate into the cave of **WP5** (Fig. 4). It provides an efficient method to keep these nano-sunflower structures stable.

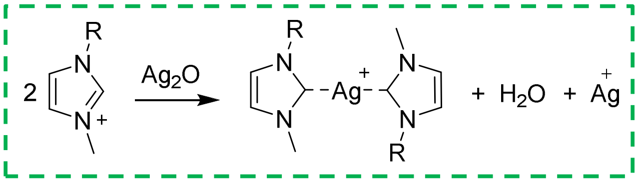


Fig. 4 The possible mechanism of imidazolium group reacting with silver oxide.

In conclusion, **RCA** can self-assemble into nano-sheets immediately when dissolved in water. Interestingly, these nano-sheets can further self-assemble into well-defined nano-sunflower structures after one night without any stimulus. Furthermore, **WP5** can also induce the resultant nano-sunflowers to disassemble into fluorescent vesicles. However, if we added silver ions into the nano-sunflowers first, two imidazolium groups can complex with one silver ion, so these nano-sunflowers could not change their morphologies upon addition of **WP5**. This research supplies a new clue for the fabrication of well-defined nano-structures.

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† Electronic Supplementary Information (ESI) available: Fluorescent picture, TEM images, EDX spectrum, and other materials. See DOI: 10.1039/b000000x/

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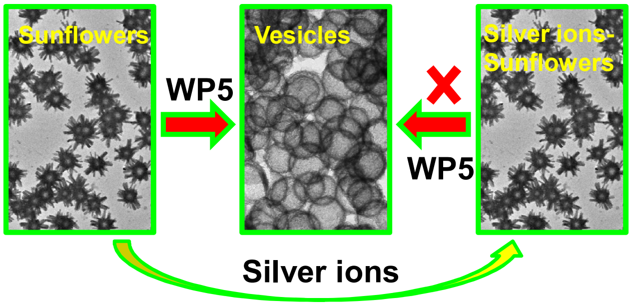

Text:

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