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COMMUNICATION

## Two-Dimensional Supramolecular Spring: Coordination Driven Reversible Extension and Contraction of Bridged Half Rings

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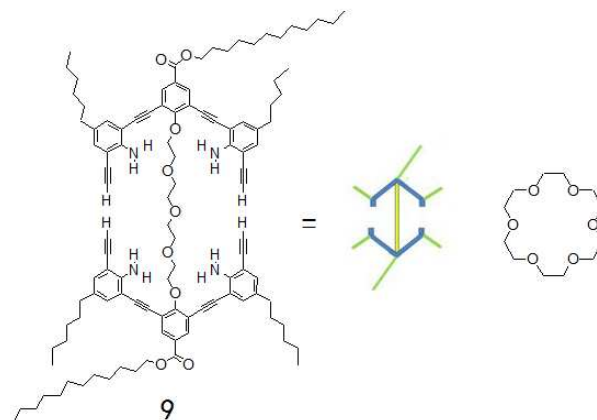
A tetraethylene glycol ether bridged derivative **9** has been designed and synthesized, and its two-dimensional (2D) self-assembled behavior has been investigated at the single-molecule level. Our results revealed that **9** kept the fully extended state in nature but the contracted state when successively triggered by  $K_2CO_3$ , and recovered the original fully extended conformation after the subsequent addition of 18-crown-6. Such coordination controlling reversible assembly may act as supramolecular springs in response to chemical stimuli, which is of great interest in bionics and materials science.

During the past few years, the reversible molecular self-assembly technologies have attracted significant attention in the creation of functional nanomaterials.<sup>1-6</sup> The building blocks in these systems are generally able to undergo reversible molecular motions under the effect of external physical or chemical stimuli.<sup>7-10</sup> As it is easily processed, the ion triggered reversible assembly has flourished in preparing novel nanostructures with increasing structural complexity, ranging from one-dimensional (1D) polymers, over two-dimensional (2D) frames, and to three-dimensional (3D) folded architecture.<sup>11,12</sup> And one of the most interesting structures is biological springs which can store the energy of conformation in certain chemical bonds and act as latches.<sup>13</sup> Recently, the dynamic motion of supramolecular spring in solution has already been achieved,<sup>14,15</sup> but the direct observation of its contraction-to-extension transformation at surface or interface is still challenging.

In this communication, the surface-confined extension and contraction of a tetraethylene glycol ether derivative (**9**, Scheme 1) has been probed. In general, the polyethylene glycols (PEGs) are amphiphatic polymers with a high solubility in water and in many organic solvents including toluene, dichloromethane, alcohol, and acetone.<sup>16</sup> Especially, being acyclic analogs of crown ethers, the PEGs behave as 'crown-like' agents with the complexation ability of metal alkali salts to generate flexible helical conformation or cavities with variable sizes, which

depends on both the nature of the cation and of the anion as well as on the PEG molecular weight.<sup>17</sup> In fact, the tetraethylene glycol ether bridged derivative **9** with five ether units in our present work can also possess the coordination ability.

As shown in Fig. 1a and b, the transmission electron microscope (TEM) experiment revealed that compound **9** fabricated a layered regular texture in which individual multilamellar layer aggregated to a width of around 0.2  $\mu\text{m}$ , indicating the possible crystal structure at the solid state (a sharp diffraction pattern typical for the single crystal structure was recorded, see ESI). However, for sample **9**+ $K_2CO_3$ , a wrinkled topology was observed, suggesting the occurrence of the structural change (a diffraction halo rings was observed, suggesting an amorphous structure). To gain more information of the morphology, the XRD measurement of both samples **9** and **9**+ $K_2CO_3$  were performed (Fig. 1c and d). For **9**, a sharp intense diffraction peak in the small-angle region ( $2\theta = 3.96$  degrees) was detected, corresponding to the fully extended interdigitated intercolumn distance of  $d = 22.3$   $\text{\AA}$ . Besides the fundamental peak,

Scheme 1. Chemical structures of specimen **9** and 18-crown-6.

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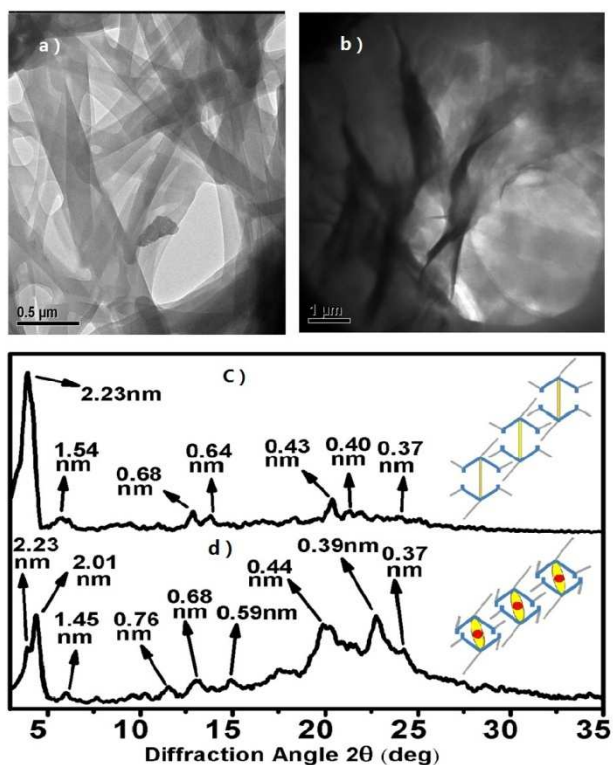
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a peak centered at  $2\theta = 5.72$  degrees ( $d = 15.4 \text{ \AA}$ ) was also observed, corresponding to the distance of the opposite phenylactylene moieties. In comparison, for  $9 + \text{K}_2\text{CO}_3$ , a peak at angle region ( $2\theta = 4.398$  degrees) and one at  $2\theta = 6.0$  degrees were recorded, corresponding to the distance of  $d = 20.1 \text{ \AA}$  (the intercolumn distance of  $9 + \text{K}_2\text{CO}_3$ ) and  $d = 14.5 \text{ \AA}$  (the molecular width of opposite phenylactylene moieties for  $9 + \text{K}_2\text{CO}_3$ ). In addition, the remained distance of  $d = 22.3 \text{ \AA}$  can be attributed to the incompletely complexed  $9$  in the sample of ( $9 + \text{K}_2\text{CO}_3$ ). These results suggest that the bridged  $9$  contracted with the incorporation of  $\text{K}_2\text{CO}_3$ . The distances of  $0.40 \text{ nm}$  and  $0.43 \text{ nm}$  (Fig. 1c) as well as  $0.39$  and  $0.44 \text{ nm}$  (Fig. 1d) can be assigned to the distances of adjacent alkyl chains. Based on these TEM and XRD measurements above, it can be concluded that the introduction of potassium carbonate in  $9$  brought about the change in morphology.

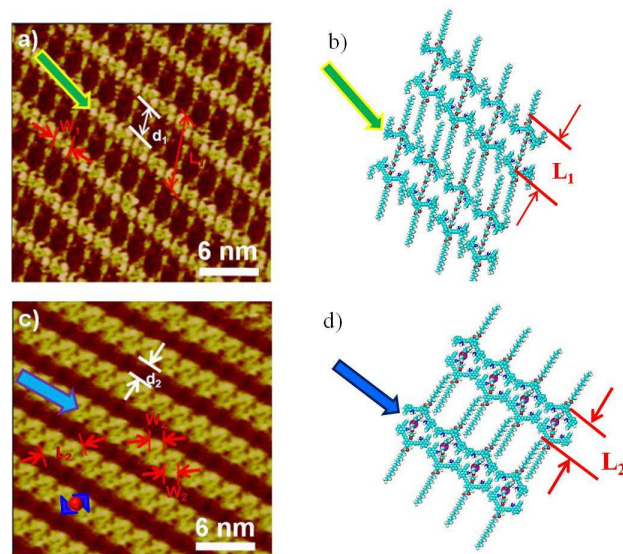


**Fig. 1** (a, b) Transmission electron microscope (TEM) of thin area of specimen  $9$  and  $9 + \text{K}^+$ , respectively; (c, d) XRD plots of specimen  $9$  and  $9 + \text{K}^+$ , respectively.

To have a further insight of the interaction of  $\text{K}_2\text{CO}_3$  with bridged  $9$ , potassium salts of trifluoromethanesulfonate, tetraphenylborate and carbonate were employed in  $^1\text{H}$  NMR analysis. As shown in Fig. S22, S23 and S24, notable chemical shifts were observed in the bridged tetraethylene parts after the addition of the potassium salts for all the three salts, revealing the formation of coordination complexes of  $\text{K}_2\text{CO}_3$  and  $9$ .

More structural details have been probed by scanning tunneling microscopy (STM). As shown in Fig. 2a, the compound  $9$  assembled into an abacus-shaped architecture on the highly oriented pyrolytic graphite (HOPG) surface. With a width ( $W_1$ ) of  $(1.1 \pm 0.1) \text{ nm}$ , the V-shaped bright spot, belonging to different molecules, was parallel to each other along the green arrow and

composed of beads in abacus. And the rows of beads were bridged by the bright pillar whose length ( $d_1$ ) was measured to be  $1.8 \pm 0.1 \text{ nm}$ . The length of each bright pillar was similar to that of the tetraethylene glycol ether and also equal to the substituted dodecyl chains,<sup>18-20</sup> demonstrating that the bright pillar may be contributed to the bridged tetraethylene glycol ether and dodecyl chains. Therefore, compound  $9$  should be composed of two bright beads and three bright pillars. And for one molecule, the distance between two half rings was measured to be  $L_1 = 3.3 \pm 0.1 \text{ nm}$ . At this condition, as displayed in Fig. 2b, the substituted dodecyl chains of adjacent molecules are interdigitated assembled<sup>21</sup> and the tetraethylene glycol ether was fully extended. Here, we named the two half rings combined with the bridged tetraethylene glycol ether as the core part of molecule  $9$  and also defined the core part in nature state (without any treatment) as the extended conformation.

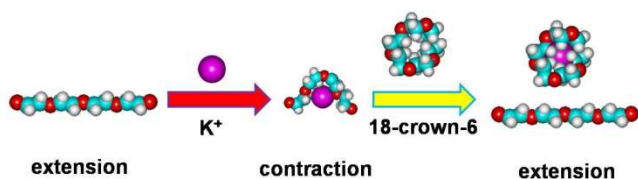


**Fig. 2** (a) High resolution STM image of the self-assembled structure of specimen  $9$  on HOPG.  $I_{\text{set}} = 320.2 \text{ PA}$ ,  $V_{\text{bias}} = 710.5 \text{ mV}$ . (b) A suggested molecular model corresponding the structure in (a). (c) High resolution STM image of the self-assembled structure of ( $9 + \text{K}^+$ ) on HOPG, after addition of potassium carbonate.  $I_{\text{set}} = 290.1 \text{ PA}$ ,  $V_{\text{bias}} = 740.7 \text{ mV}$ . (d) A suggested molecular model corresponds to the structure in (c).

Upon addition of  $\text{K}_2\text{CO}_3$  solution, the structural changes of the compound  $9$  can be identified by STM observations. As shown in Fig. 2c, there appears a zigzag architecture along the blue arrow. Carefully inspecting this novel structure, we found that the zigzag part was assembled by the periodic unit consisted of two V-shaped half rings and one bright dot. The width of each half ring ( $W_2$ ) was determined to be  $1.1 \pm 0.1 \text{ nm}$ , the whole length ( $L_2$ ) of the periodic unit was  $2.7 \pm 0.1 \text{ nm}$ , and the distance ( $d_2$ ) between the two adjacent zigzag lamellae was  $1.6 \pm 0.1 \text{ nm}$ . On the basis of these phenomena, we think that the zigzag architecture may be highly possible to the coordinated  $9 + \text{K}_2\text{CO}_3$  complex, and the periodic unit in zigzag lamella should belong to the coordinated parts as well as the whole V-shaped conjugated parts (Fig. 2d). Upon the incorporation  $\text{K}_2\text{CO}_3$ , the bridged tetraethylene glycol moieties distorted, followed by the closer two V-shaped half rings, and more importantly, the length of core part in  $9$  becomes shorter (from  $(3.3 \pm 0.1) \text{ nm}$  to  $(2.7 \pm 0.1) \text{ nm}$ ).

In other words, the target molecule **9** was in its contracted conformation when treated by potassium carbonate.

Interestingly, the extended assembly of compound **9** can be obtained again if some solution containing 18-crown-6 was added onto the **9**- $\text{K}_2\text{CO}_3$  sample (Fig. S25). It was reported that the cyclic crown ether was able to combine with alkali metal through the strong metal-coordination interaction,<sup>22</sup> which can extract the alkali metal ions from the other ligands. In our present system, as displayed in Fig. 3, the added  $\text{K}_2\text{CO}_3$  was firstly combined with the tetraethylene glycol bridged compound **9** to form a (**9**+ $\text{K}_2\text{CO}_3$ ) complex, and then to form a new complex (**18-crown-6**+ $\text{K}_2\text{CO}_3$ ) in the presence of solution of 18-crown-6. Induced by the adsorption and disadsorption of  $\text{K}_2\text{CO}_3$  on two-dimensional structure, the compound **9** underwent the extension-contraction-extension structural transformation, which acted a supramolecular spring effect. Based on these investigation, we think that the bridging tetraethylene glycol unit in compound **9** plays an essential role in the complexation with  $\text{K}_2\text{CO}_3$  (see ESI). However, it is still difficult to describe the detailed coordination pattern of the ions by the currently provided STM and NMR results.



**Fig. 3** An illustration model for the transformation of specimen **9** from extension to contraction and come back to extension (The purple ball represents the  $\text{K}^+$ ).

In summary, a bridged compound **9** has been designed as a novel supramolecular spring. The two-dimensional (2D) self-assembled behavior of specimen **9** has been studied at the solid/gas interface, with the help of TEM, XRD, and STM. Our results revealed that the target molecule assembled into an abacus-shaped architecture which then transformed into the zigzag architecture triggered by  $\text{K}_2\text{CO}_3$ . Interestingly, the whole coordination-driven supramolecular self-assembly was reversible, because of the different metal-coordination interactions. We think compound **9** kept the extended state in nature but the contracted one when successively triggered by  $\text{K}_2\text{CO}_3$ , and recovered the original extended conformation after the subsequent addition of 18-crown-6. Such coordination-driven reversible assembly may act as supramolecular springs in response to chemical stimuli, which is of great interest in bionics and materials science.

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## Footnotes

- †Electronic Supplementary Information (ESI) available: Experimental details, characterization data and additional STM images. See DOI: 10.1039/b000000x/