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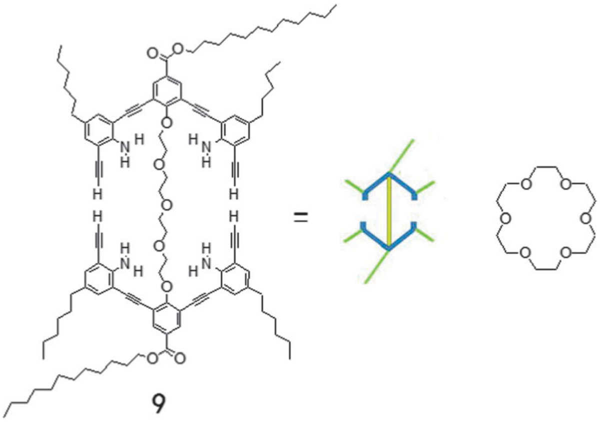
Two-dimensional supramolecular spring: coordination driven reversible extension and contraction of bridged half rings†

Dapeng Luo,‡[a] Xuemei Zhang,‡[b] Yongtao Shen,[b] Jing Xu,[b] Lijin Shu,*[a] Qingdao Zeng*[b] and Chen Wang*[b]

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 generally adopted the fully extended state but changed to the contracted state when triggered by K_2CO_3, and recovered the original fully extended conformation after subsequent addition of 18-crown-6. Such a coordination-controlled reversible assembly reveals supramolecular springs in response to chemical stimuli, which is of great interest in bionics and materials science.

During the past few years, reversible molecular self-assembly technologies have attracted significant attention in the creation of functional nanomaterials.[1–6] The building blocks in these systems are generally able to undergo reversible molecular motions under the effect of external physical or chemical stimuli.[7–10] 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.[11,12] One of the most interesting structures are biological springs which can store the energy of conformation in certain chemical bonds and act as latches.[13] Recently, the dynamic motion of supramolecular springs in solution has been achieved,[14,15] but the direct observation of contraction-to-extension transformation at surfaces or interfaces 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, polyethylene glycols (PEGs) are amphiphilic polymers with a high solubility in water and in many organic solvents including toluene, dichloromethane, alcohols and acetone.[16] Especially, being acyclic analogs of crown ethers, PEGs behave as 'crown-like' agents with complexation ability towards alkali-metal salts to generate flexible helical conformations 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.[17] The tetraethylene glycol bridged derivative **9** with five ether units in our present work also exhibits coordination ability towards alkali-metal ions.



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

As shown in Fig. 1a and b, transmission electron microscopy (TEM) revealed that compound **9** revealed a layered regular texture in which individual multilamellar layers were aggregated to a width of around 0.2 μm, 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$_2$CO$_3$**, a wrinkled topology was observed, suggesting the occurrence of a structural change (diffraction halo rings were observed, suggesting an amorphous structure). To gain more information of the morphology, XRD measurement of both samples **9** and **9+K$_2$CO$_3$** were performed (Fig. 1c and d). For **9**, a sharp intense diffraction peak in the small-angle region ($2\theta = 3.96°$) was detected, corresponding to the fully extended interdigitated

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[a] *Key laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 310012, China. E-mail: shulj@hznu.edu.cn*

[b] *CAS Key Laboratory of Standardization and Measurement for Nanotechnology, National Centre for Nanoscience and Technology, No. 11 Zhongguancun Beiyitiao, Beijing 100190, China. E-mail: zengqd@nanoctr.cn, wangch@nanoctr.cn*

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‡ These authors contributed equally to this work.

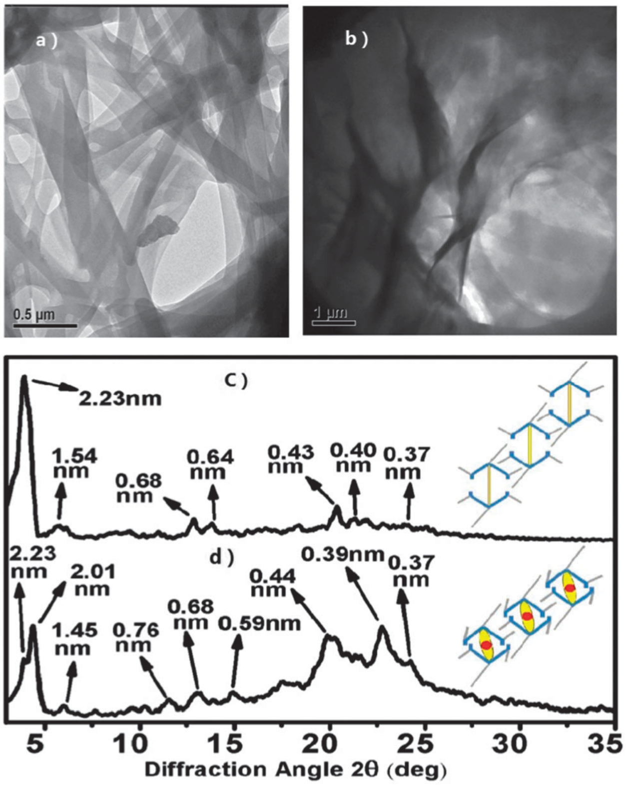

Fig. 1 (a, b) Transmission electron microscope (TEM) images of thin areas of specimen **9** and **9+K$_2$CO$_3$**, respectively; (c, d) XRD plots of specimen **9** and **9+K$_2$CO$_3$**, respectively.

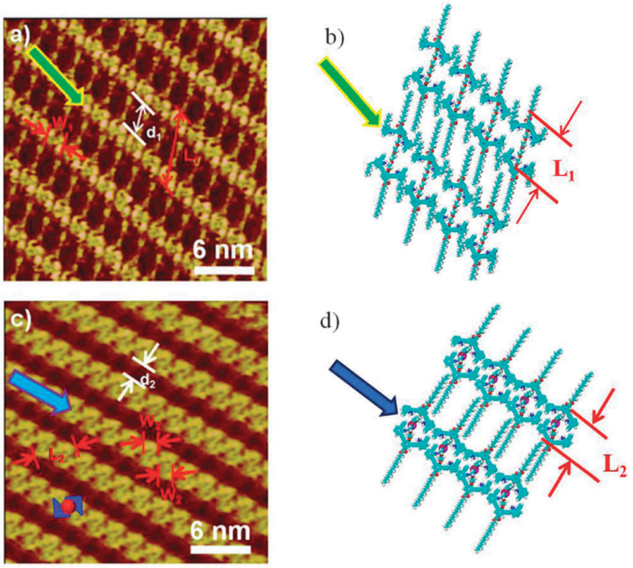

Fig. 2 (a) High-resolution STM image of the self-assembled structure of compound **9** on HOPG; I_{set} = 320.2 PA, V_{bias} = 710.5 mV. (b) A suggested molecular model corresponding the structure in (a). (c) High-resolution STM image of the self-assembled structure of **9+K$_2$CO$_3$** on HOPG, after addition of potassium carbonate; I_{set} = 290.1 PA, V_{bias} = 740.7 mV. (d) A suggested molecular model corresponding to the structure in (c).

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

To have a further insight of the interaction of K$_2$CO$_3$ with bridged **9**, potassium salts of trifluoromethanesulfonate, tetraphenylborate and carbonate were employed in ^{1}H NMR analysis. As shown in Fig. S22–S24 (ESI†), 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 **K$_2$CO$_3$** and **9**.

More structural details have been probed by scanning tunneling microscopy (STM). As shown in Fig. 2a, compound **9** assembled into an abacus-shaped architecture on the highly oriented pyrolitic graphite (HOPG) surface. With a width (W_1) of 1.1 ± 0.1 nm, the V-shaped bright spots, belonging to different molecules, were parallel to each other along the green arrow, corresponding to the ''beads'' in the abacus. The rows of beads were bridged by bright pillars whose length (d_1) was measured to be 1.8 ± 0.1 nm. The length of each bright pillar was similar to that of the tetraethylene glycol ether and also equal to the substituted dodecyl chains,[18–20] demonstrating that the bright pillar may correspond to the bridged tetraethylene glycol ether and dodecyl chains. Therefore, compound **9** should be composed of two bright beads and three bright pillars. For each molecule, the distance between two half rings was measured to be L_1 = 3.3 ± 0.1 nm. At this condition, as displayed in Fig. 2b, the substituted dodecyl chains of adjacent molecules are assembled *via* interdigitation[21] and the tetraethylene glycol ether was fully extended. Here, we refer to the two half rings combined with the bridged tetraethylene glycol ether as the core part of molecule **9** and also define the core part in the uncomplexed state (without any treatment) as the extended conformation.

Upon addition of K$_2$CO$_3$ aqueous 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 ± 0.1 nm, the whole length (L_2) of the periodic unit was 2.7 ± 0.1 nm, and the distance (d_2) between the two adjacent zigzag lamellae was 1.6 ± 0.1 nm. On the basis of these phenomena, we attribute the zigzag architecture to the coordinated **9+K$_2$CO$_3$** complex, and the periodic unit in zigzag lamella should belong to the coordinated parts as well as the whole V-shaped conjugated

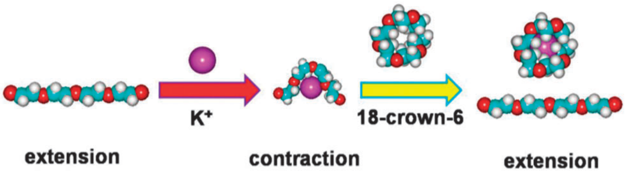

Fig. 3 An illustration model for the transformation of specimen **9** from extension to contraction and back to extension (the purple ball represents K^+).

parts (Fig. 2d). Upon the incorporation of K_2CO_3, the bridged tetraethylene glycol moieties become distorted, followed by the closer movement of the two V-shaped half rings, and more importantly, the length of core part in **9** becomes shorter (from 3.3 ± 0.1 to 2.7 ± 0.1 nm). In other words, the target molecule **9** adopted a contracted conformation when treated with potassium carbonate.

Interestingly, the extended assembly of compound **9** can be obtained again if a solution containing 18-crown-6 was added to the **9-K**$_2$CO$_3$ sample (Fig. S25, ESI†). It is well known that the cyclic crown ether is able to combine with alkali metals through strong metal-coordination interaction,[22] which can extract the alkali-metal ions from the other ligands. In our present system, as shown in Fig. 3, the added K_2CO_3 was first combined with the tetraethylene glycol bridged compound **9** (to form the **9+K**$_2$CO$_3$ complex), and then reformed **9** (and K(18-crown-6)) in the presence of 18-crown-6. Induced by the adsorption and de-adsorption of K_2CO_3 on the two-dimensional structure, compound **9** underwent an extension–contraction–extension structural transformation, which can be regarded as a supramolecular spring effect. Based on these investigations, we propose that the bridging tetraethylene glycol unit in compound **9** plays an essential role in the complexation with K_2CO_3 (see ESI†). However, the detailed coordination mode of the ions is not fully clear according to the present STM and NMR results.

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 a zigzag architecture triggered by K_2CO_3. Interestingly, the whole coordination-driven supramolecular self-assembly was reversible, because of the different metal-coordination interactions. Compound **9** adopts the extended state when free but the contracted state is triggered by K_2CO_3, and the original extended state recovered after the subsequent addition of 18-crown-6. Such coordination-driven reversible assembly can be viewed as supramolecular springs in response to chemical stimuli, which is of great interest in bionics and material science.

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