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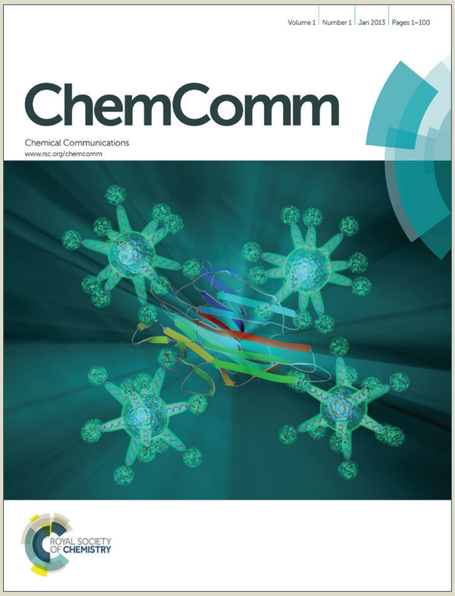

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The first case of actinide polyrotaxane incorporating cucurbituril: A unique 'dragon-like' twist induced by a specific coordination pattern of uranium

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***In situ* assembly of cucurbituril-based pseudorotaxane and uranyl nitrate precursor under hydrothermal conditions affords the first actinide polyrotaxane with a unique 'dragon-like' twist, which is induced by specific coordination pattern of uranium and stabilized by hydrogen bonding between η^1-mode carboxylate group and adjacent methylene moieties of CB[6].**

Metal-organic materials with dynamic components[1], such as mechanically-interlocked molecules (MIMs)[2], integrate the attractive feature of flexibility into rigid frameworks as well as broad functionalities, thus leading to potential applications in molecular docking[3] and electronic devices[4]. As one type of typical MIMs, pseudorotaxane/rotaxane has been employed in lots of cases for establishing supramolecular metal-organic architectures[5], i.e. metal-directed polyrotaxanes[6]. Smilar to coordination polymer[7], metal-directed polyrotaxanes are infinite metal-organic backbones and can be engineerred through reasonable design and ligand screening as well as metal ion selection for achieving specific morphologies and functionalities[8]. Different types of axle-wheel supramolecular motifs, such as rotaxane with cucurbituril[9], dibenzo[24]crown-8 wheels[10] or cyclodextrin[11], have been employed as linkers to make varieties of polyrotaxane-based materials. Metal ion connectors also play important roles in constructing the polyrotaxane architectures. Among plenty of rotaxane-based coordination polymers, transition metal ions[2a, 2b, 9a, 12] and lanthanide ions[5b, 8c, 9b, 10b] have been intensively studied due to their rich coordination patterns and availabilities. However, polyrotaxanes containing actinide cations, such as uranyl or Th(IV) cations, have been never reported. Hence, we are currently pursuing the preparation of actinide polyrotaxanes from uranyl cation and pseudorotaxanes ligands containing cucurbit[6]uril (CB[6]). This effort has finally succeeded to produce the first case of actinide polyrotaxane.

Actinide-bearing materials have gained many research endeavors due to the relevance to nuclear fuel cycles as well as novel topologies[13] and intriguing electronic properties[14]. For example, uranium, one of the most extensively studied actinide elements, exhibits rich coordination chemistry and structural diversity, which is related to the electronic configurations of 5*f* elements and a tendency of uranyl cation to hydrolyze. Constructing actinide (pseudo)rotaxane/polyrotaxane with macromolecular molecules (such as CB[6]) will be a new interesting arena for metal organic materials to explore structures with novel topologies and potential functions. CB[6] is a highly symmetric pumpkin-like macrocycle and has been used as organic building blocks for design of coordination compounds[15]. This precursor of (pseudo)rotaxane has been firstly introduced into uranyl complexes by Thuery et al[16]. Although the attempts to get uranyl-bearing polyrotaxane using dicarboxylic acids have been made by the same group, only uranyl complexes with isolated 'wheel' and 'axle'[17] and a compound containing two independent dinuclear complexes of CB6 and sebacate[16b] could be obtained, where CB[6] just acted as a special type of ligand or a structure-directing agent. New synthesis strategies are still needed in preparing uranyl-bearing polyrotaxane. Therefore, we turn to the fabrication of polyrotaxane with transition metals, for which the same principle might work, and propose a two-step procedure using pseudorotaxane as the intermediate ligand. Herein, we report the *in situ* assembly of the novel polyrotaxane incorporating cucurbituril directed by uranyl cations.

Pseudorotaxane precusor was prepared from threading of *N,N*'-Bis(3-cyanobenzyl)-1,4-diammoniobutane dinitrate (C4CN3) with CB[6] (Scheme S1, ESI†). The doubly charged ionic peak of 658.21 in mass spectrometry and characteristic signals in ^{1}H-NMR (Fig. S2, ESI†) is consistent with the encapsulated structure of pseudorotaxane. The corresponding X-ray quality crystal **1** (C4CN3-CB6) (Fig. S3, ESI†) was obtained from an aqueous solution of pseudorotaxane with slow evaporation. The crystallographic analysis gives the further evidence of pseudorotaxane. Pseudorotaxane obtained above was then reacted with uranyl-nitrate hexahydrate under hydrothermal conditions to produce the yellow platelet crystal **2** (UO_2-C4CA3-CB6) in a few micron scale (Fig. S4, ESI†). **2** crystallizes in the monoclinic space group $P2_1/c$ to form a uranyl-directed polyrotaxane (Fig. S5, ESI†), which displays a different PXRD pattern from the pseudorotaxane **1** and matches well with the calculated pattern (Fig. S6, ESI†). Crystallographic analysis demonstrates that each asymmetric unit contains one uranyl ion, half a pseudorataxane with mono-coordinated (η^1) carbonate group and half of another one with bidentate (η^2) chelating mode (Fig. S7, ESI†). A total weight loss in thermogravimetric analysis is close to the theoretical value corresponding to the transformation of **2** to U_3O_8 at this temperature range (Fig. S8, ESI†). IR spectra show the expected [U=O] stretching band in the region of 930 cm^{-1} together with disappearance of bands around 2232 cm^{-1} corresponding to cyano group, which hydrolyzes *in situ* to carboxylate group during the preparation (Fig. S9, ESI†). Raman spectroscopy demonstrates a typical fluorescence emission mode and a slight red shift can be found compared to a benchmark compound $UO_2(NO_3)_2{\cdot}6H_2O$. This phenomenon is also found in the fluorescence spectrum (Fig. S10, ESI†). All the facts above afford the proof of composition in **2**.

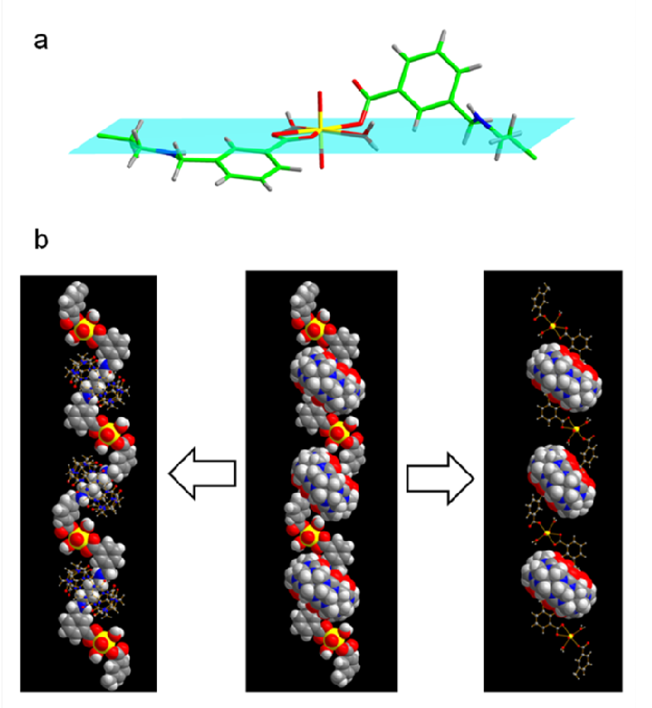

Fig. 1. Uranyl coordination sphere (a) and view of uranyl polyrotaxane with a 'dragon-like' twist in **2** (b). Left (b): coordination polymer chain in space-filling representation and CB[6] in capped-stick representation. Right (b): coordination polymer chain in capped-stick representation and CB[6] in space-filling representation.

The uranyl coordination sphere displays an interesting structural feature, where an unique coordination fashion arises. Besides two axial oxo groups, five equatorial oxygen atoms from a η^1-O , two η^2-O and two water O are included to define a pentagonal bipyramid. The axial UO_2 moiety shows an exceptionally short U=O distance of 1.650(13) Å with O=U=O angle of 178.9(7)°. Though partly because of the moderate quality of the structure refinement, we can still assign it to few reports on U=O distance below 1.70 Å[18], considering acceptability for such a small crystal size. The bond lengths of U-$O_{(water)}$ in the pentagonal plane range from 2.326(18) to 2.398(13). Two types of U-$O_{(carboxylate)}$ afford different bond lengths of 2.418(16) and 2.445(17) in η^2-mode and 2.186(15) in η^1-mode. It should be noted that the η^1-mode shows much shorter bond length than that of η^2-mode and this leads to a distortion of the pentagon as indicated by the equatorial O-U-O angles which range from 49.5° to 90.3°. This special coordination geometry also induces a deflection of the corresponding phenyl carboxylate moiety from the equatorial plane with a dihedral angle of 44.43(39)°(Fig. 1a), which results in a 'dragon-like' twist of 1D uranyl polyrotaxane (Fig. 1b). Moreover, a slight difference of orientations of adjacent cucurbit[6]urils threading on the axles with an angle of 12.15(14) is observed due to this twisted shape (Fig. 1b).

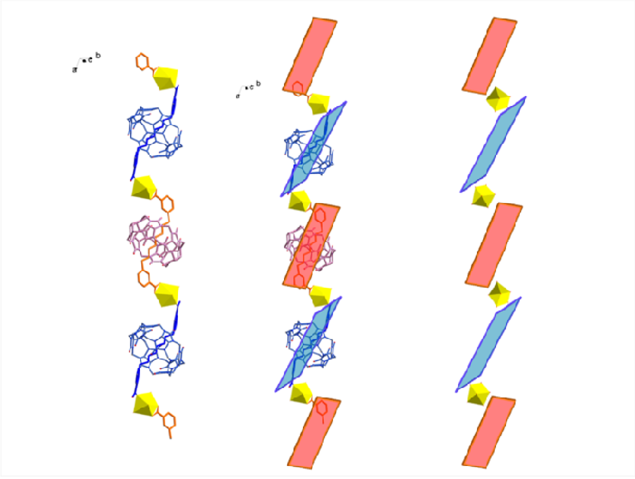

Fig. 2. Schematic diagrams of uranyl polyrotaxane with a 'dragon-like' twist in 2. Left: capped-stick representation; middle: capped-stick representation simplified with plane models; right: simplified plane models.

Fig.2 gives the schematic diagram of uranyl polyrotaxane in **2**. It consists of uranyl nodes linked by two types of pseudorotaxane spacers with different coordination modes and spatial orientations. It is interesting that only one coordination mode (η^1 or η^2) of carboxylate groups in each pseudorotaxane moiety is available, whereas different coordination modes exist in adjacent pseudorotaxane moiety. Though a variety of topologies have been reported (including sawtooth-wave shape) in transitional metal polyrotaxane (mostly based on pyridyl coordinating groups), the fact about the sawtooth-wave shape with an obvious twist in this case has not been observed previously. Comparing with pyridine-coordinated polyrotaxane, this unique topology could be attributed to various coordination modes of carboxylate groups and specific coordination pattern with uranyl ion, as reported in several uranyl carboxylate complexes[19]. Nevertheless, another question about crystallographic stability of this 'dragon-like' twisted structure arises as there is a tension with significant energy in it. So other factors cannot be ignored in stabilizing this unique structure. Further analyses of the structure revealed that crystal packing in three dimentions and hydrogen bonding are important to the formation of this twisted polyrotaxane. As depicted in Fig. 3., each free oxygen atom from η^1-mode carboxylate group could be stabilized by formating of hydrogen bonding with two methylene moieties of CB[6] in adjcent coordination polymer chain (O•••H distances are 2.1605 and 2.1608 Å, respectively). Meanwhile, these hydrogen bondings crosslink adjacent polyrotaxane chains to form a 2D sheet. This unique type of hydrogen bonding based on η^1-mode carboxylate group was also found in Cu-polyrotaxane[2c]. Weaker hydrogen bondings with O•••H distances of 2.4465~2.6991 Å between the uncoordinated carboxylic oxygen and another two neighboring methylidynes can enhance the linking forces to obtain the packing diagrams (Fig. S11 and S12, ESI†).

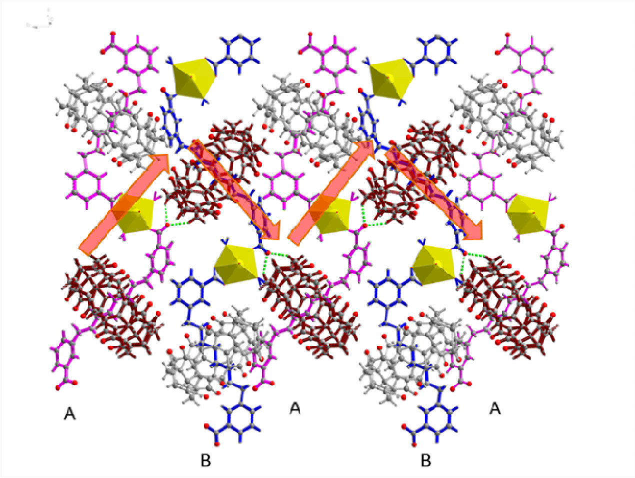

Fig. 3. Representation of hydrogen bonding between free oxygen atom from carboxylate in η1-mode and two methylene moieties of CB[6] in adjcent coordination polymer chain. (O•••H distances: 2.1605 and 2.1608 Å, respectively) and 2D sheet of polyrotaxane through crosslinked by hydrogen bondings.

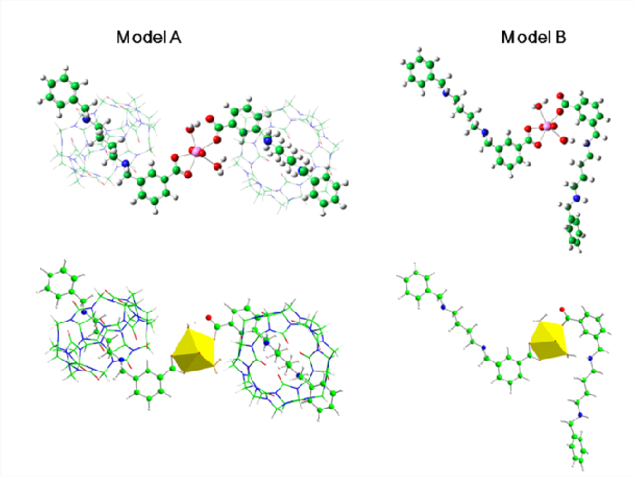

Fig. 4. Geometry optimizations of models A and B. Model A: fragment containing uranyl center coordinated by two rotaxane ligands using combination of the ONIOM method and quantum method; model B: fragment fragment without CB[6] using quantum method.

A quantum chemical calculation (see ESI†) was subsequently conducted to evaluate the effect of CB[6] on the formation of polyrotaxane structure. A fragment containing uranyl center coordinated with two rotaxane ligands is set as molecular model (model A), and another fragment in the absence of CB[6] as the control (model B). Because model A is relatively larger, the optimization was carried out using ONIOM, which is a hybrid method that enables different theory level to be applied in different parts of a system[20]. Geometry optimizations show that both of the models maintain the configuration of pentagonal bipyramids, indicating the inner stability of this penta-coordinating configuration, though the corresponding bond lengths and angles do not match well with the crystallographic data(Table. S1, ESI†). Deflections related to η^1-carboxylate group are also found in both models. As displayed in Fig 4, the molecular geometry of model B has a distortion due to the formation of hydrogen bond between coordinating H_2O and amino group of ‘axle’, whereas the overall molecular geometry of model A is close to that of crystal **2**. This dramatic discrepancy demonstrates the importance of CB[6] to the stabilization of polyrotaxane structure. We have attempted to synthesize crystal from ‘axle’ ligand without CB[6] (diamine compound, **C4CN3**) under hydrothermal conditions but failed. This fact is in consistent with the deduction above and prove the key role of CB[6] in the formation of polymer framework in **2**.

In conclusion, we have presented the first actinide polyrotaxane incorporating cucurbituril in which uranyl ion center was coordinated with two different types of carboxylate ligand to form a novel ‘dragon-like’ twist, and demonstrate the importance of the cucurbituril macromolecule polyrotaxane for the stabilization of structure and stacking in crystals. Preparation of this structurally unique uranyl-bearing material has afforded us a new way to incorporate supramolecular moieties to 5f elements and more understanding of their intriguing coordination features. Moreover, special structure and consequent proproties of this material, especially for mechanically-interlocked moieties and fluorescent emission, will enable it to have potential applications in molecular machine and luminescent sensor. The acquirement of 1D uranyl polyrotaxane impels us to conduct researches on actinide polyrotaxane frameworks with higher dimensions (2D and 3D).

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Notes and references

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† Electronic Supplementary Information (ESI) available: General preparation methods, ^{1}H NMR spectra, crystal structures, SEM images, Powder-XRD, TGA curves, IR, Raman and fluorescence spectrum, Quantum chemistry calculation, crystal structures. CCDC reference numbers 978771 (**1**) and 978772 (**2**). See DOI: 10.1039/c000000x/

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