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Anion-driven self-assembly: from discrete cages to infinite polycatenanes step by step†

Qihui Chen, Feilong Jiang, Daqiang Yuan, Lian Chen, Guangxun Lyu and Maochun Hong*
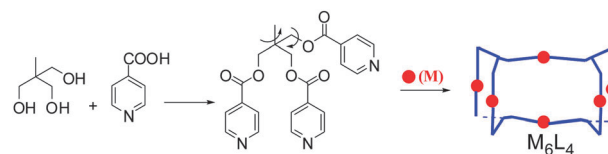
Induced by different anions, two different polycatenanes constructed from Ag$_6$L$_4$ units with different conformations have been prepared. Intermediates Ag$_6$L$_4$ and Ag$_5$L$_4$ are observed to participate in interlocking, and the related possible self-assembly routes are also presented.

Nature has the ability to assemble simple molecule into extremely complex biomolecules by using a variety of weak interactions such as hydrogen bonding and charge–charge interactions.[1] Inspired by this deliberate approach, many elegant assemblies driven by coordination have been prepared.[2–4] Catenanes and rotaxanes have attracted considerable attention not only for their interesting topological structures, but also for their astonishing applications such as in molecular machines and motors.[5] In 1999, the Fujita group firstly synthesized a [2]catenane based on discrete three-dimensional (3D) interlocking metallacages.[6] Since then, there have been several examples of [2]catenanes constructed from discrete 3D metallacages;[6–9] however, an infinite polycatenane assembled from discrete metallacages seems more intriguing and challenging. The first infinite polycatenane assembled from discrete cages was reported by the Lu group in 2010.[10] Recently, another type of polycatenane was prepared by Dehnen and coworkers.[11] To the best of our knowledge, only two infinite polycatenanes constructed from discrete metallacages have been reported, and the assembly process seems still obscure.[10,11] Thus, construction of such highly organized architectures from discrete metallacages and an understanding of these processes have therefore remained a challenge for chemists. Herein, we report an interesting self-assembly system: a new polycatenane is constructed from Ag$_6$L$_4$ cages through introducing ClO$_4^-$ anions. If larger PF$_6^-$ anions are introduced, a different polycatenane with larger Ag$_{12}$L$_8$ cages composed of two Ag$_6$L$_4$ units is produced. The key intermediate which participates in interlocking directly is observed firstly, and the related possible self-assembly routes are also presented.

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In order to achieve a metallacage with a suitable window for interlocking, a novel tripodal ligand **L** (**L** = tris(isonicotinoxymethyl)ethane) was designed and synthesized. The ligand **L** is so flexible that it can adopt various conformations to satisfy the construction of a metallacage. For example, a M$_6$L$_4$ cage can be constructed from four molecular **L** and six molecular 2-coordinated metal ions. (Scheme 1)

Layering a CHCl$_3$ solution of ligand **L** with a MeOH solution of AgClO$_4$ provided colorless rectangular crystals of compound **1**. Single crystal X-ray diffraction analysis indicated that compound **1**, [Ag$_6$L$_4$(ClO$_4$)$_6$·CHCl$_3$]$_n$, has a polycatenated chain consisting of interlocking discrete metallacages. As shown in Fig. 1, the cage has a similar hypothetical structure to that illustrated in Scheme 1, which is comprised of six Ag(I) ions and four **L** ligands. The angles between the three coordinated pyridines in **L** are about 30, 81 and 102°, respectively. The Ag$_6$L$_4$ cage has a (20 × 16 × 4 Å) cavity with the ClO$_4^-$ ions near the 2-coordinated Ag(I) to stabilize it.

As shown in Fig. 2, the polycatenane in **1** is constructed by the interlocking of neighboring Ag$_6$L$_4$ cages. The neighboring pyridine groups of **L** ligands twist in the same direction with the distance of *ca.* 4 Å between them, which indicates that the

Scheme 1 Ligand **L** and a possible cage constructed from *anti* conformations of **L** with M (M = 2-coordinated metal ions, such as Ag).
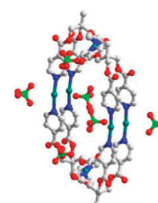

Fig. 1 The Ag$_6$L$_4$ cage in compound **1** (H atoms are omitted for clarity, grey: C; red: O; blue: N; green: Cl; teal: Ag).
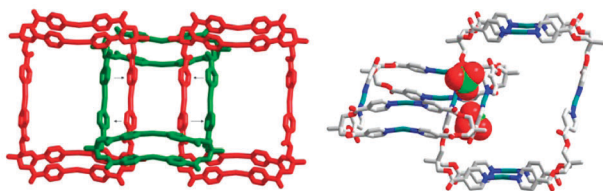
Fig. 2 Left, structural fragment containing three interlaced metallacages; right, the interlocking knot is further stabilized by strong charge–charge interactions.

Fig. 4 Left, two interlocked metallacages stabilized by the strong charge–charge interactions from one PF_6^- anion and four Ag^+ ions; right, structural fragment containing three interlaced metallacages.

interlocking of the Ag_6L_4 cages is driven by $\pi\cdots\pi$ interactions. The interlocking knot is further stabilized by the strong charge–charge interactions between two ClO_4^- anions and two Ag^+ ions, in which the distances between Ag and O atoms are 2.797 Å.

The formation of infinite architectures from discrete cages is very difficult and sensitive;[10,11] even if using similar anions such as I^- and Br^- anions to replace Cl^- anions, the results are entirely different.[11] The 2-coordinated Ag(I) in compound **1** is unsaturated, and we wanted to know whether the Ag_6L_4 cage could be extended into a larger unit induced by a larger counter anion.

Employing the PF_6^- anion as the larger counter anion led to a new compound **2**.[12] Single crystal X-ray diffraction analysis indicated that compound **2**, $[Ag_{12}L_8(PF_6)_{12}\cdot xCHCl_3]_n$, is another new polycatenane, however, its basic units here for interlocking are $Ag_{12}L_8$ cages, composed of two Ag_6L_4 units with different conformation from compound **1** (the angles between the three coordinated pyridines are about 34, 101 and 111°, respectively) stabilized by the larger PF_6^- anions. The cavity of the $Ag_{12}L_8$ cage is up to ($22 \times 17 \times 10$ Å) (Fig. 3).

The interlocking knot is stabilized only by the strong charge–charge interactions from one PF_6^- anion and four Ag(I) ions, with a distance of 2.872 Å between the Ag and F atoms. Driven by these interactions, the $Ag_{12}L_8$ cages interlock with each other to generate an elegant polycatenane (Fig. 4).

Induced by different anions, two different polycatenanes constructed from Ag_6L_4 units with different conformations have been prepared. The two novel structures represent the third example of the extension of discrete metallacages into an infinite polycatenane.[10,11]

There are several examples in which discrete cages are extended into complicated topological motifs,[6–11] however, only three examples demonstrate that the discrete cages can assemble into an infinite polycatenane rather than a less complex [2]catenane.[10,11] There is a question as to why some discrete cages can generate infinite frameworks instead of limited [2]catenanes.[6–9] Herein, we give our opinion on what induces discrete cages into infinite polycatenated frameworks.
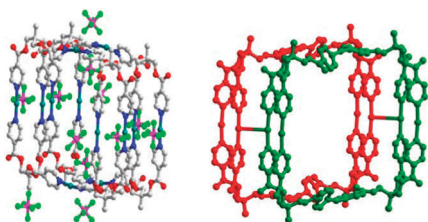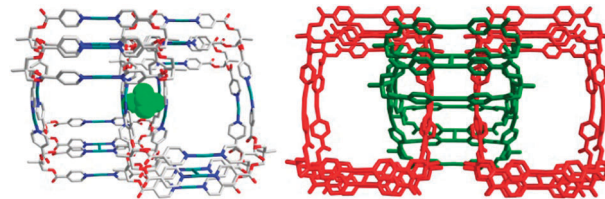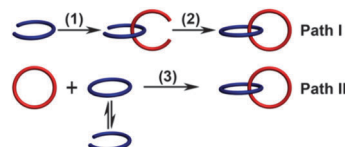
Firstly, a suitable window and large cavity; to the best of our knowledge, all of the discrete cages that can generate complicated motifs possess suitable windows and large cavities.[6–11] Secondly, the interlocking is an entropically unfavourable process and needs suitable interactions to stabilize it. In Fujita, Clever, Kuroda and Hardie's examples,[6–9] the cavities in newly-formed [2]catenanes are not large enough for the next interlock. In our case, the large windows and cavities from the cages sustain interlocking and, even after interlocking twice, the cavities in the polycatenanes still seem large (Fig. 2 and 4). Moreover, strong charge–charge interactions between counter anions and positively charged cages make the interlocking stable. There are also discrete cages with large windows and cavities and suitable interactions in Lu and Dehnen's systems.[10,11]

The reason why discrete cages can further extend into infinite polycatenated architectures rather than limited [2]catenanes seems clear; nevertheless, the concrete process is still inexplicit.[6–11] There may be two possible paths for the formation of [2]catenanes: path I, two open precursors are firstly locked to give an interlocking knot and closing this intermediate finally leads to the [2]catenane;[13] path II, the closed unit is firstly formed, the unit has reversible 'on/off' ability, and the interlocking of two units directly leads to the [2]catenane (Scheme 2).

After many attempts, we found that the Ag_6L_4 unit could be assembled quickly in MeOH–CHCl$_3$ solution induced by ClO_4^- anions (see ESI†). More importantly, an unexpected spectral peak (2677) corresponding to Ag_5L_4 is firstly observed, which results from the loss of one Ag(I) ion from an Ag_6L_4 unit. The peak intensities of two different units (Ag_6L_4 and Ag_5L_4) are comparable, indicating a fast dynamic equilibrium between the Ag_6L_4 unit and Ag_5L_4 unit[14] (Fig. 5). These observed intermediates demonstrate that the assembly process of compound **1** should follow path II rather than path I.

A possible assembly process of compound **1** is presented in detail (Scheme 3): the ligand **L** and Ag(I) quickly assemble into a Ag_6L_4 cage induced by ClO_4^- ions in CHCl$_3$–MeOH solution (within 5 min); the Ag_6L_4 cage can open and lose a Ag(I) ion to form Ag_5L_4 and the process is reversible and fast; interlocking of one Ag_6L_4 cage with the newly formed Ag_5L_4 unit leads to a [2]catenane; the newly-formed [2]catenane continues to interlock, finally resulting in

Fig. 3 The $Ag_{12}L_8$ cage in **2**; which is comprised of two Ag_6L_4 units linked by Ag⋯Ag interactions (H atoms are omitted for clarity, grey: C; red: O; blue: N; green: F; teal: Ag; pink: P).

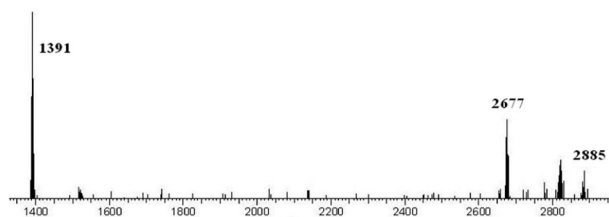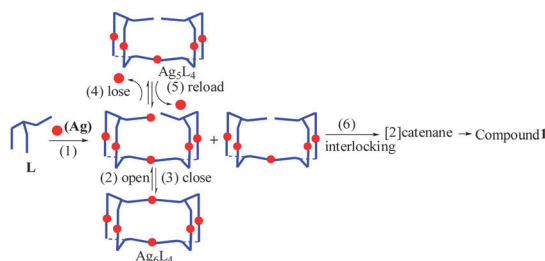**Scheme 2** The two possible paths for the formation of [2]catenanes: (1) locking, (2) closing, (3) interlocking directly.

Fig. 5 ESI-MS spectrum of Ag_6L_4 cage and Ag_5L_4 unit generated *in situ*, in which the 1391 peak corresponds to $Ag_6L_4(ClO_4)_4{}^{2+}$, the 2885 peak to $Ag_6L_4(ClO_4)_5{}^{+}$, and the 2677 peak to $Ag_5L_4(ClO_4)_4{}^{+}$.

Scheme 3 Possible process of formation of compound **1**, in which the reactions (1), (2), (3), (4), (5) are fast, and the reaction (6) is slow.

compound **1**. The interlocking process is slow and can self-correct (only the interlocking knots with lowest energy are stable), even if the basic cage unit can be assembled within 5 min, the infinite interlocking products are obtained after two weeks. Induced by larger $PF_6{}^{-}$ ions, Ag_6L_4 units rather than $Ag_{12}L_8$ are assembled immediately (see ESI†). Thus, the formation of compound **2** is presented as follows: stabilized by the larger counter anions, the *in situ* formed Ag_6L_4 units can spontaneously dimerize into larger $Ag_{12}L_8$ cages, and finally lead to compound **2** after infinite interlocking and self-correcting.

As we know, Ag_5L_4 is a key unit for interlocking in our system, while no such similar intermediates for interlocking have been reported.[10,11] So we believe that suitable metal–donor joints such as Pd–N,[6,8,9] Ag–N,[7b,10] Zn–N,[7a,11] which can quickly associate and disassociate should be another important factor for interlocking. So far, two different polycatenanes based on discrete cages have been synthesized successfully, which may be ascribed to the following factors: firstly, suitable windows and large cavities of the cages can satisfy the interlocking; secondly, suitable metal–donor joints can provide the key intermediates for interlocking; thirdly, the strong charge–charge interactions from anions and positive frameworks make the interlocking knots stable.

In summary, two different polycatenanes constructed from different discrete cages have been prepared based on a rationally designed ligand **L** and Ag(ɪ). Further research indicates that the basic units for interlocking, Ag_6L_4 and Ag_5L_4, can be generated immediately, induced by both $ClO_4{}^{-}$ and $PF_6{}^{-}$ anions. Possible routes of our assembly system and new design principles to prepare novel polycatenated assemblies based on discrete metallacages have been presented. Further research on preparing more complicated assemblies is ongoing.

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