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Hybrid Inorganic–Organic Polyrotaxane, Pseudorotaxane, and Sandwich

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Supporting Information

ABSTRACT: Inorganic copper(I)/silver(I) halide/pseudohalide components are used to thread classical organic tetracationic macrocycles, cyclobis(paraquat-*p*-phenylene) and cyclobis(paraquat-4,4′-biphenylene), to construct crystalline inorganic–organic adducts, featuring an unprecedented hybrid polyrotaxane and several unusual hybrid pseudorotaxanes and sandwiches.

Entangled (e.g., mechanically interlocked molecules[1]) and adducted (e.g., sandwich compounds[2]) structures have long been the targets of chemists, but they usually required sophisticated organic synthesis. Recently, advances have been made in a new range of extended rotaxane coordination polymers (also known as metal–organic rotaxane frameworks)[3] that are promising candidates of crystalline molecular machines.[3e]

The outcomes of introducing metal ions into the self-assembly are entangled hybrid materials,[4] which integrate organic ingredients that warrant designed structure/function and inorganic elements that impart diverse bonding patterns and electronic properties. These extended arrays with the prototypes of polyrotaxane or polypseudorotaxane are constructed either by the reaction of predesigned rotaxane-containing linkers with metals[3] or by the metal- or anion-directed self-assembly of tetracationic organic macrocycles,[5] both of which feature coordination arrays threading organic rings, not a genuine case of hybrid rotaxane.

Remarkably, there are only sporadic examples[6] of mechanical linking of pure inorganic and organic components, representing genuine hybrid rotaxanes, at the molecular level. For instance, the Leigh[6a,b] and Aida[6c] groups demonstrated that inorganic nanocluster "wheels" are penetrable by finite or infinite organic "axles", and more recently a tetrasilver cluster was shown to reside in a polypyridine macrocycle, forming a hybrid inorganic–organic pseudorotaxane.[6d]

Our group has been investigating the coordination chemistry of copper(I) halides[7] and pseudohalides[8] and developed a synthetic protocol[9] by using these pure inorganic segments to encapsulate cationic organic guanidinium,[9b] metal–terpyridine complexes,[9c] and metal–pyrazolate cluster helicates.[9d] The CuSCN aggregates can endow variable coordination configurations (linear, triangular, or tetrahedral) and charge carriers (neutral, cationic, or anionic) to cope with diverse molecular entities via self-adaptation.[9] In an attempt to prepare hybrid rotaxanes, two renowned tetracationic cyclophanes[10] in rotaxane chemistry, namely, cyclobis(paraquat-*p*-phenylene)[11] ($\mathbf{1}^{4+}$, known as "blue box") and cyclobis(paraquat-4,4′-biphenylene)[12] ($\mathbf{2}^{4+}$), are selected in this work (Figure 1). The cationic molecular squares may direct the coordination configurations of anionic inorganic components through weak interactions and steric effects to assemble diverse supramolecular adducts, especially interlocked structures.

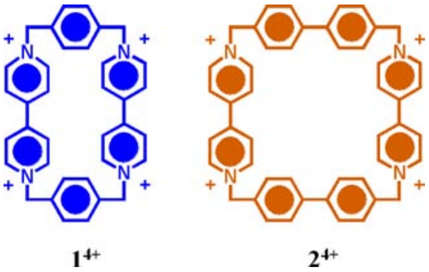
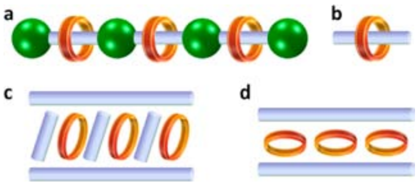


Figure 1. Structures of $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$.

Herein we report success in constructing crystalline hybrid inorganic–organic adducts via solvothermal synthesis, which represents an underdeveloped route that could complement other better studied threading strategies. All reported complexes consist of two independent but not separate components: anionic inorganic copper(I)/silver(I) halide/pseudohalide aggregates and cationic organic macrocycles. Their crystal structures fall into three categories (Scheme 1): polyrotaxane $[\mathbf{1}\supset Cu_4(SCN)_8]_n$ (**3**), sandwiches $[\mathbf{1}(Cu_2I_5)I_3]$ (**4**) and $[\mathbf{1}(Ag_6I_{10})]$ (**5**), and pseudorotaxanes $[(\mathbf{2}\supset Cu_2I_4)I_2]$ (**6**) and $[(\mathbf{2}\supset Ag_2I_4)I_2]$ (**7**). To the best of our knowledge, **3** represents the first example of a genuine hybrid polyrotaxane composed of mechanically interlocked infinite inorganic "axles" and finite organic "wheels".

Scheme 1. Topological Alignments between Organic Macrocycles and Inorganic Aggregates: (a) Polyrotaxane, (b) Pseudorotaxane, and (c and d) Sandwiches



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Complex **3** was synthesized by a one-pot reaction of CuSCN and $\mathbf{1}\cdot 4\mathrm{PF}_6$ in acetonitrile at 100 °C in high yield [see the Supporting Information (SI) for details]. Single-crystal X-ray diffraction reveals that **3** crystallizes in triclinic space group $P\bar{1}$ and features a one-dimensional polyrotaxane structure. The asymmetric unit of **3** contains two independent $\mathrm{Cu^I}$ atoms, four $\mathrm{SCN^-}$ anions, and half-macrocycle $\mathbf{1}^{4+}$ (Figure 2a). The Cu1 atom adopts a triangular coordination geometry and is coordinated by three N-donor atoms from $\mathrm{SCN^-}$. The Cu2 atom is four-coordinated by three S-donor atoms and one N-donor atom from $\mathrm{SCN^-}$ and adopts a distorted tetrahedral coordination geometry. Three $\mathrm{SCN^-}$ anions adopt a μ_2 bridging mode, and one terminal $\mathrm{SCN^-}$ binds to Cu1 through N3. The $\mathrm{Cu^I}$ ions are bridged by $\mathrm{SCN^-}$ anions and form a novel anionic polymeric $[\mathrm{Cu_2(SCN)_4}^{2-}]_n$ chain (Figure 2b), which is composed of 8-membered $(\mathrm{CuSCN})_2$ rings and 16-membered $(\mathrm{CuSCN})_4$ rings. These two types of CuSCN rings share the tetrahedral $\mathrm{Cu^I}$ sites.

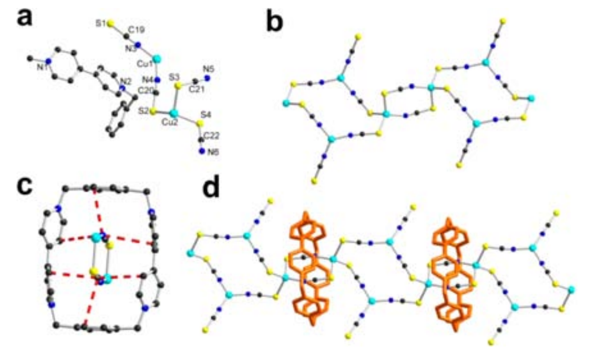

Figure 2. Crystal structure of **3**: (a) asymmetric unit; (b) polymeric anionic CuSCN chain containing 8- and 16-membered rings; (c) location of the 8-membered CuSCN ring in the macrocycle $^{4+}\mathbf{1}$; (d) hybrid polyrotaxane structure of **3**.

The most interesting structural feature of **3** is that all organic macrocycles $\mathbf{1}^{4+}$ are penetrated by the inorganic CuSCN chain, which leads to a unique inorganic−organic polyrotaxane structure (Figure 2d and Scheme 1a). The small 8-membered ring acts as the thread and locates at the center of the cavity of $\mathbf{1}^{4+}$ (Figure 2c). The distances between the N/C atoms of $\mathrm{SCN^-}$ and the C atoms of $\mathbf{1}^{4+}$ are similar and range from 3.367 to 3.838 Å. The 16-membered ring with the dangled $\mathrm{SCN^-}$ acts as the bulky stopper. The distance between the two S atoms of two dangled $\mathrm{SCN^-}$ anions is 14.894 Å, which is longer than the length of $\mathbf{1}^{4+}$ (about 10.0 Å). Therefore, the $\mathbf{1}^{4+}$ wheels cannot escape from or move along the CuSCN axles without breaking the bonds in CuSCN. In comparison to this inorganic−organic polyrotaxane, pure organic macromolecular polyrotaxanes are extensively reported,[13a] but usually there are only two stoppers at the end of the thread.[13b,c] The formation of pure organic polyrotaxanes like **3** featuring an elaborate arrangement of host $\mathbf{1}^{4+}$ with multiple stoppers may be difficult.

Attempts are also made to synthesize polyrotaxanes by the use of macrocycle **1** and CuI or AgI because both of the latter can form anionic aggregates with rich structures.[7a] Compounds **4** and **5** were yielded by the solvothermal reaction of CuI (or AgI), KI, and $\mathbf{1}\cdot 4\mathrm{PF}_6$ in a mixture solvents of acetonitrile and water at 80 °C (see the SI for details). Single-crystal X-ray analyses found that **4** and **5** crystallize in monoclinic space groups $P2_1/c$ and $P\bar{1}$, respectively, and feature sandwich-like structures (Figure 3 and Scheme 1c,d). In compound **4**, all $\mathrm{Cu^I}$ atoms adopt a tetrahedral coordination geometry and are bridged by $\mathrm{I^-}$ anions (Figure S4 in the SI), giving an extended anionic $[\mathrm{Cu_2I_5}^{3-}]_n$ chain. Except for the anionic CuI chain, there are additional $\mathrm{I_3}^-$ anions in the lattice to balance the positive charge of the tetracationic rings. As shown in Figure 3a, the cationic macrocycle $\mathbf{1}^{4+}$ is surrounded by the $[\mathrm{Cu_2I_5}^{3-}]_n$ chain and $\mathrm{I_3}^-$ anions, forming a special sandwich structure (Scheme 1c). In complex **5**, the $\mathrm{Ag^I}$ ions adopt both triangular and tetrahedral geometry, coordinated by $\mathrm{I^-}$. A complex anionic $[\mathrm{Ag_6I_{10}}^{4-}]_n$ chain is formed by connecting $\mathrm{Ag_3I_3}$ and $\mathrm{Ag_2I_6}^{4-}$ segments (Figure 3b). Similar to **4**, the sandwich structure is presented in **5**, but the orientation of the macrocycle $\mathbf{1}^{4+}$ is different (Scheme 1d). The polyrotaxane structure in **3** is not formed in **4** and **5**, indicating that the threading ability of the CuI or AgI anionic chain is less flexible than that of CuSCN.

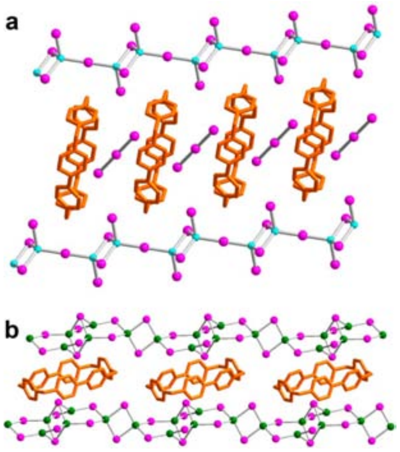

Figure 3. Hybrid sandwich structures of **4** (a) and **5** (b). Color code: I, purple; Cu, cyan; Ag, green; C and N, orange. H atoms are omitted.

As a comparison, we also explore the larger macrocycle $\mathbf{2}^{4+}$ as the host. The reaction of $\mathbf{2}\cdot 4\mathrm{PF}_6$ with CuI and AgI under similar conditions gave compounds **6** and **7**, respectively. Single-crystal X-ray diffraction analyses reveal that both complexes **6** and **7** crystallize in monoclinic space group $P2_1/c$, and they are isomorphous and feature the pesudorotaxane structure (Figure 4). Only the structure of **6** will be described here. The asymmetric unit of **6** contains one $\mathrm{Cu^I}$ atom, three $\mathrm{I^-}$ molecules, and a half-molecule of $\mathbf{2}^{4+}$ (Figure S5 in the SI). The $\mathrm{Cu^I}$ ion adopts a triangular geometry and is bound by three $\mathrm{I^-}$ ligands. Two $\mathrm{Cu^I}$ atoms are bridged by μ_2-I to form a common anionic $\mathrm{Cu_2I_4}^{2-}$ cluster[7a] with two terminal $\mathrm{I^-}$ ions. $\mathrm{Cu_2I_4}^{2-}$ acts as an inorganic thread and resides within the window of the cationic macrocycle $\mathbf{2}^{4+}$ in an inclined fashion, giving a pesudorotaxane pattern (Scheme 1b). The dimension of the $\mathrm{Cu_2I_2}$ rhombus is 2.889 × 4.269 Å^2 (Cu···Cu and I···I diagonals), significantly smaller than that of $\mathbf{2}^{4+}$ (ca. 11.5 × 7.5 Å^2), which would warrant the threading of $\mathrm{Cu_2I_4}^{2-}$ stabilized by electrostatic interaction to

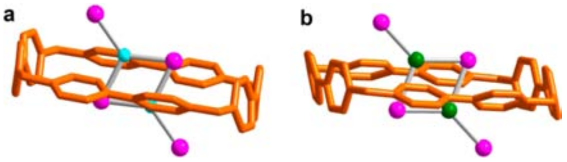

Figure 4. Hybrid pesudorotaoxane structures of **6** (a) and **7** (b). Color code: I, purple; Cu, cyan; Ag, green; C and N, orange. H atoms are omitted.

reside in the cavity of 2^{4+}. There exist two I^- per $[(2\supset Ag_2I_4)I_2]$ unit as a counterbalancing charge. This pesudorotaoxane structure resembles that of an early organic pesudorotaoxane of tetrathiafulvalene threading 1^{4+}.[14] The reaction of CuSCN with $2\cdot 4PF_6$ yielded an interesting structure, featuring hybrid inorganic−organic capsulation (Figure S11 in the SI), which cannot be presented in detail because of poor crystal data.

The thermal stability of **3** was characterized by thermogravimetric analysis (Figure S2 in the SI). The solid sample stayed stable until 250 °C. The temperature-dependent powder X-ray diffraction pattern (Figure S3 in the SI) indicated that a crystal-to-amorphous transition occurred upon increasing temperature. Compounds **4**−**7** showed similar thermal stabilities and crystallization degrees (Figures S6−S8 in the SI). All complexes are poorly soluble in common organic solvents, e.g., *N*,*N*-dimethylfomamide, methanol, and acetonitrile.

In summary, the self-adaptation ability of copper(I)/silver(I) halide/pseudohalide aggregates, particularly that of CuSCN, is taken advantage of to form anionic inorganic chain- or rodlike clusters, threading or nonthreading classical cationic organic cyclophanes. The resulting hybrid inorganic−organic adducts, featuring a polyrotaxane, pseudorotaxanes, and sandwiches, indicate that this synthetic methodology may be generalized for obtaining wider ranges of crystalline hybrid materials. Further considerations that seem plausible include the replacement of the "axles" with higher-coordination metal pseudohalides such as $Fe(CN)_6^{3-}$ or $Mo(CN)_8^{4-}$ and the substitution of the "wheels" with other famous supramolecular hosts such as crown ethers, cyclodextrins, cucurbiturils, or macrocyclic amides.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystal data (CCDC 946603−946607), and physical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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