

The Marriage of Inorganic and Organic Building Blocks for the Assembly of Rotaxanes

Euan K. Brechin* and Leroy Cronin*

functional devices · organic–inorganic hybrid composites · rotaxanes · self-assembly

The synthesis of functional organic–inorganic hybrid architectures has been exploding in recent years in an effort to produce molecules and materials that combine the physical and chemical properties of both “hard” inorganic and “soft” organic building blocks.^[1] This goal is attractive, as success would allow the engineering of systems that could have physical properties associated with “hard” inorganics,^[2] for example, high conductivity and magnetic properties, with those of “soft” organics, for example, easy processing, self-assembly, and molecular recognition. This type of approach has yielded exciting new structures and polymeric materials such as metal–organic frameworks (MOFs),^[3] new types of molecular magnets,^[4] and new approaches to catalyst design employing supramolecular principles.^[5] In the area of molecular metal oxides (polyoxometalates), grafting organic^[6] linkers have been used to “program” the self-assembly of the hard architecture and to produce new types of amphiphilic molecules that can self-assemble into large superstructures. Further, the use of charged systems creates countless opportunities, as combinations of organic and inorganic charged species can allow the assembly of crystalline materials^[7] or the construction of layer-by-layer^[8] hybrids. However, although the architectural principles are fascinating, the engineering of new physical properties exploiting all the subunits remains a challenge. An even greater challenge lies in the engineering of hybrid organic–inorganic systems that could form the basis of prototype molecular devices or machines.^[9] In recent years, the development of advanced molecular devices based on mechanically interlocked architectures has been of great interest.^[10] Pioneering work in this area has produced bistable molecules with switchable states that have been used to form a variety of devices, including surface arrays of switches.^[11]

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The assembly of mechanically interlocked molecular systems relies heavily on templating strategies that preassociate the components before locking the units to produce the overall architecture. This approach not only enables high yields to be obtained, but also exploits molecular recognition and the mutual compatibility of the components. The assembly of a hybrid organic–inorganic system would therefore require the selection of subunits in which the organic part could be used to template formation of the inorganic part. By combining the activities of their two groups, Winpenny and Leigh^[12] have successfully assembled a beautiful family of inorganic–organic rotaxanes and molecular shuttles comprising inorganic rings assembled around organic axes or threads that contain a templating alkylammonium group (Figure 1).

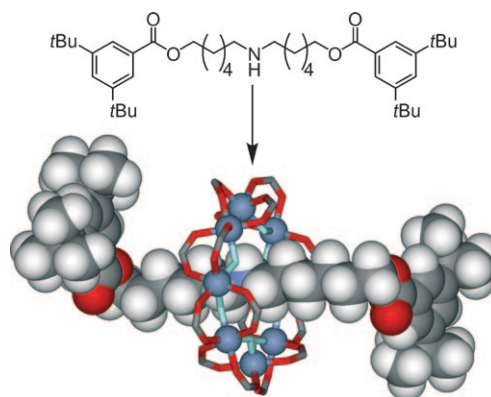


Figure 1. Synthesis of the rotaxane from a thread with a templating central alkylammonium group. Conditions: $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ (7 equiv), $[\text{Co}_2(\text{H}_2\text{O})(\text{tBuCO}_2)_4(\text{tBuCO}_2\text{H})_4]$ (1 equiv), tBuCO_2H (solvent), 140°C , 12h. The thread acts as the template for $[\text{Cr}^{\text{III}}_7\text{Co}^{\text{II}}\text{F}_8(\text{O}_2\text{CtBu})_{16}]^-$, leading to the overall [2]rotaxane comprising one thread and one $\{\text{Cr}_7\text{Co}\}$ wheel cluster, the crystal structure of which is shown. C gray; H white; O red; Cr, Co blue-gray; N blue; F light blue; tBu groups on the bridging carboxylate ligands are omitted.

The catalyst that sparked the idea was provided by the observation that the even- and odd-numbered heterometallic wheels $\{\text{Cr}^{\text{III}}_7\text{M}^{\text{II}}_n\}$ ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}, \text{Cu}$) made in the Winpenny group^[13] require the presence of similar templating organic cations to the rotaxanes made in the Leigh group. Dumbbell-shaped secondary amine threads of various

lengths, employed as sole templating agents, were added to reaction mixtures used to form the heterometallic wheels. Steric considerations mean that no products are formed with short threads, but a [2]rotaxane is formed when the spacer between the single central ammonium center and the peripheral stoppers is six carbon atoms long (Figure 1). Furthermore, $^1\text{H NMR}$ spectroscopy studies reveal that the structure remains intact in solution, with the $[\text{Cr}^{\text{III}}_7\text{Co}^{\text{II}}\text{F}_8(\text{O}_2\text{CtBu})_{16}]^-$ wheel rapidly spinning around its axis.

Incorporation of additional ammonium binding sites on longer organic threads allows for the isolation of multiring [3]- and [4]rotaxanes and dynamic molecular shuttles in which the inorganic wheels can be observed shuttling between ammonium binding sites. C_{12} spacers between two central ammonium groups afford a [3]rotaxane with $[\text{Cr}^{\text{III}}_7\text{Co}^{\text{II}}\text{F}_8(\text{O}_2\text{CtBu})_{16}]^-$. By modifying the $\text{M}^{\text{III}}/\text{M}^{\text{II}}$ ratio and changing the M^{II} ion from Co to Cu, a spectacular doubly encircled and doubly stranded rotaxane (Figure 2) is isolated, in which the inorganic wheel now contains ten octahedral Cr^{III} ions and two square-planar Cu^{II} ions.

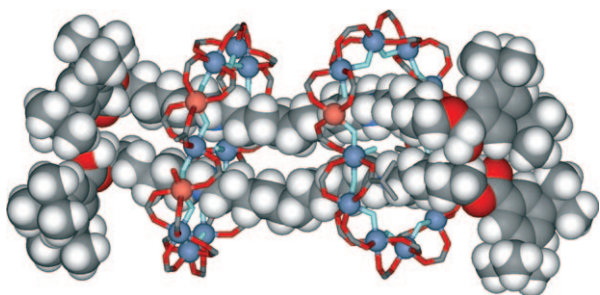


Figure 2. Crystal structure of the [4]rotaxane comprising two threads and two wheel clusters $\{\text{Cr}_{10}\text{Cu}_2\}$. C gray, H white, O red, Cu orange, Cr blue-gray, N blue, F light blue; *t*Bu groups on the bridging carboxylate ligands are omitted.

Shortening to a C_6 spacer allows room for one only wheel to reside on a thread containing two ammonium sites, and the result is a hydrogen-bonded molecular shuttle in which the thread is encircled by a $[\text{Cr}^{\text{III}}_7\text{Co}^{\text{II}}\text{F}_8(\text{O}_2\text{CtBu})_{16}]^-$ wheel. For such systems the transit of the encircling macrocycle (the inorganic wheel) between ammonium binding sites is much slower on the timescale of NMR spectroscopy than the rotation of the wheel around the thread. The activation energy of the former ($19.3 \pm 0.2 \text{ kcal mol}^{-1}$) is at least double that of the latter, as the spinning of the wheel involves only the transfer of a series of “short” $\text{NH}\cdots\text{F}$ hydrogen bonds around the symmetric wheel, while the shuttling requires complete breaking of all the intercomponent H-bonds before translocation can occur.

The self-assembly, yields, and purities of these inorganic–organic molecular hybrids from reaction systems containing up to 98 separate components is really rather remarkable and promises routes and access to molecules with fascinating composite properties, for example, by combining the magnetic properties of inorganic clusters with the dynamic properties of organic “machine” systems. The amalgamation of two previously unconnected areas of chemistry is a timely illustration that, with some imagination, chemists can create extraordinary functional molecules with a great deal of potential. For example, the architecture of the rotaxanes ensures that the electronic, magnetic, and paramagnetic characteristics of the inorganic rings—properties that could make them suitable as qubits for quantum computers, or as magnetic switchable units—can influence, and potentially be affected by, the organic portion of the molecule.^[12] This principle could be extended to see if the shuttling of units with a high magnetic moment could be influenced by an applied magnetic field, thereby allowing the engineering of a magnetic molecular solenoid.

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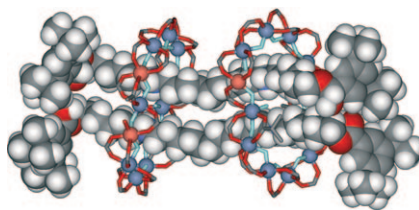
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Highlights

Rotaxanes

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Take this ring ... Hybrid organic–inorganic rotaxanes can be prepared using a thread incorporating an alkyl ammonium functionality to template the self-assembly of an inorganic wheel cluster. This approach was used to assemble a range of examples, including a system combining two rings and two threads (see picture; C gray, H white, O red, Cu orange, Cr blue-gray, N blue, F light blue).