10 Ion Pair Templation Strategies for Synthesis of Interlocked Molecules

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10.1 MECHANICALLY INTERLOCKED MOLECULES

The most common classes of interlocked molecules are catenanes and rotaxanes¹ derived from the Latin *catena*, *rota*, and *axis* (meaning *chain*, *wheel*, and *axle*, respectively. As depicted in Figure 10.1, a catenane is composed of interlocking rings (a). A rotaxane contains a macrocyclic component looped around an axle, held in place by two bulky stoppers (b). A related supramolecular structure is the pseudoro-taxane (c)—an inclusion complex in which an axle without stoppers resides inside a macrocycle. This interpenetrated, but not interlocked, assembly is often a precursor to catenanes and rotaxanes.

It should be noted that in addition to interlocked structures consisting of two components, higher order [n]-catenanes and [n]-rotaxanes and even polymeric interlocked structures may be constructed. However, this chapter will focus on the synergistic concepts behind the preparation and behavior of [2]-catenanes and [2]-rotaxanes that may be applied to larger systems.

The possibility of constructing mechanically interlocked systems has been recognized since the 1950s. Initial research was driven by academic curiosity and the technical challenges of making these exotic molecules.



FIGURE 10.1 (a) Catenane. (b) Rotaxane. (c) Pseudorotaxane.

The first successful preparation of an interlocked molecule was reported by Wasserman in 1960,² and was based on a statistically unlikely process, that is, a macrocyclization reaction occurring while the precursor chain was threaded through a preformed ring (Scheme 10.1). As expected for such a low probability event, caterane **1** was formed in a yield far below 1%. The inherent low yields of this statistical method could not be overcome, and although some alternative strategies were investigated, the area of interlocked molecules lay largely dormant for two decades.

10.1.1 TEMPLATED SYNTHESIS

The break-through that re-ignited interest in interlocked molecules was the development of new templated reactions led by the pioneering work of Sauvage in the 1980s. A chemical template, as defined by Busch,⁴ "organises an assembly of atoms, with respect to one or more geometric [positions] in order to achieve a particular linking of atoms." By replacing *atoms* with *molecular components*, we can see how this definition may apply to interlocked structures.

Accordingly, Sauvage utilized the orthogonal arrangement of bidentate phenanthroline ligands around a copper(I) center to template the synthesis of catenane **2** (Scheme 10.2).⁵ With a hydroxy-functionalized phenanthroline ligand threaded through a similar macrocycle using copper(I) templation, a cyclization reaction afforded the interlocked product in a yield of 42%—far greater than results from any statistical approach.

The advantages of metal templation are the strength of metal–ligand bonds and the well-defined geometries of the resulting complexes. As a result, many metals and geometries have been employed in the templated synthesis of a plethora of distinct interlocked structures.⁶ More recently, the wide ranging catalytic abilities of transition metals have been exploited in a synthetic process called active metal templation, in which the metal mediates both the association of the components and catalyzes the reaction to form the interlocked product.⁷



SCHEME 10.1 Synthesis of first reported catenane **1** that relied on a statistical approach.³

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SCHEME 10.2 Synthesis of Sauvage's copper(I) templated catenane **2**.

Beyond metal templation, the favorable non-covalent interactions of organic cations have also been exploited to template the formations of interlocked structures. The group of Stoddart and co-workers provided major contributions. For example, the attractive charge transfer donor–acceptor interactions between an electron-accepting positively charged bis(4,4'-bipyridinium) macrocycle and an electron-donating dioxynaphthalene thread were used to form a strongly complexed pseudorotaxane (Scheme 10.3).⁸ A copper-catalyzed alkyne-azide cycloaddition (CuAAC) reaction was subsequently employed to form the stoppered dioxynaphthalene axle and yield the target rotaxane **3**.



SCHEME 10.3 Synthesis of Stoddart's rotaxane **3** templated using charge transfer donor–acceptor interactions and stoppered dioxynaphthalene using copper-catalyzed alkyne-azide cycloaddition (CuAAC).

The topic of templated reactions has now expanded to include successful methods for templating the interlocked syntheses of uncharged components using hydrogen bonding, neutral donor–acceptor interactions, and the hydrophobic effect.^{9–11} This chapter, however, focuses on the construction of mechanically interlocked molecules in which a definite ion pair interaction plays a key role in templated synthesis. Ion pairing is both a generalizable strategy to drive component association and a versatile method of producing interlocked structures with functional properties.

Recent advances highlight the vastly unexplored potential of interlocked structures for a broad range of nanotechnological applications—from selective sensing devices to molecular-scale switches. Crucial to these applications is the concept of synergy, that is, the functional performance of an interlocked molecule is greater than the sum of the individual free components. The central hypothesis of this chapter is that ion pair templation is an effective strategy for producing molecules that exhibit synergistic behaviors.

By definition, ion pairs are low energy assemblies, and removal of one of the ion pair partners after templated synthesis places an interlocked structure in a high energy state. Restoration of the ion pair interaction is highly favorable and produces a spring-like driving force that can be exploited for dynamic molecular functions.

The goal of this chapter is not to present an exhaustive collection of all of the research on this topic, but to provide a clear tutorial-style overview of the fundamental concepts aided by illustrative examples and informative schematics. Three types of ion pair templation strategies are described, namely the use of integrated ionic components, the use of discrete ion templates, and traceless ion pair templation. These approaches can produce systems capable of two different functional behaviors by virtue of their synergistic properties.

First, the removal of a discrete ion pair partner places a structure in a high energy state, and the resulting assembly can retain strong affinity for that ion, most often due to a highly selective binding cavity. Consequently, such structures are well suited for small molecule recognition technologies. Secondly, as the ion pair interaction dictates the relative positions of the components within the interlocked structure, the removal and subsequent restoration of this interaction can result in controlled dynamic molecular motion.

10.1.2 CLASSIFICATION OF INTERLOCKED TEMPLATION MODES AND SYNTHETIC STRATEGIES

Templates are widely used in supramolecular chemistry and classified several ways. In general, they can be classed by whether a reaction is under thermodynamic or kinetic control¹² or by the precise topology of the templation.¹³ For interlocked structures specifically, it is possible for a template to be integrated within the components and thus be incorporated inside the resulting interlocked framework (Figure 10.2a).

Conversely, the template responsible for molecular association can be discrete, separate from the interlocked structure, and thus removable (Figure 10.2b). The templating charge-transfer donor-acceptor in rotaxane **3** (Scheme 10.3) is an example of integrated templation. The copper(I) metal in catenane **2** (Scheme 10.2) is strictly



FIGURE 10.2 Different modes of interlocked templation. (a) Integrated within resulting framework. (b) Discrete and removable.

a discrete template as it can be removed from the molecule, leaving only the interlocked phenanthroline macrocycles.¹⁴

Synthetically, there are a number of ways of approaching the task of interlocked structure formation, with the most widely employed strategies illustrated in Figure 10.3. Catenanes are commonly synthesized using (a) *cyclization* (for example, 1 in Scheme 1 and 2 in Scheme 2); (b) *double cyclization* in which one or both macrocycles are formed in the fabrication of the interlocked product. Rotaxane formation is usually achieved by either (a) *clipping*, the cyclization of a macrocycle around an axle; (b) *stoppering* (for example, **3** in Scheme 10.3), the addition of suitably large stopper groups to a pseudorotaxane; or (c), *snapping* the covalent joining of two half axles within a macrocycle.

Applying these general strategies to the preparation of interlocked molecules requires the incorporation of appropriate functional groups to enable covalent



FIGURE 10.3 Common methods of interlocked structure formation. Cyclization (a) and double cyclization (b) of catenanes. Clipping (c), stoppering (d), and snapping approaches for rotaxane synthesis.

capture of the target structure. Versatile, quantitative, and efficient couplings are ideal for this application, with CuAAC and Grubbs-catalyzed ring-closing metathesis (RCM) the two most common reactions exploited in this manner.^{15,16}

10.2 ION PAIR TEMPLATION OF INTERLOCKED MOLECULES

10.2.1 INTEGRATED ION PAIR TEMPLATION USING IONIC COMPONENTS

The most conceptually simple example of an ion pair templated synthesis involves an electrostatic association of oppositely charged components (Figure 10.4). After they are associated in the correct alignment, a suitable reaction can then be used to convert the ion pair assembly into a permanently interlocked product.

This approach in which both the cation and anion are integrated within opposing components of the target interlocked structure has been applied successfully in several systems and is illustrated by Furusho and Yashima's "salt bridge" catenane **6** from 2010 (Scheme 10.4).¹⁷

A salt bridge is a recognition motif composed of both a strong electrostatic attraction and directional hydrogen bonding; it can be formed between amidine and carboxylic acid groups upon proton transfer. Both starting components **4** and **5** contain crescent-shaped m-terphenyl structural frameworks functionalized with the respective amidine and carboxylic acid motifs and terminal vinyl groups for RCM reactions. Thus, when salt bridge formation mediates the association of **4** and **5**, the vinyl groups are suitably aligned for catenane formation *via* double cyclization.

To promote association, the reaction was undertaken in a toluene non-polar solvent and the interlocked product was isolated in 68% yield. The salt bridge was retained in the rigid catenane framework due to the integrated nature of this templating interaction. Protonation of this motif using trifluoroacetic acid removed the ion pair interaction and unlocked the macrocycles to allow relatively free rotation with respect to each other.

Subsequent deprotonation using N,N-diisopropylethylamine restored the salt bridge, re-locking the macrocycles. As noted previously, the ability to remove the templating ion pair interaction within an interlocked structure can lead to controlled dynamic molecular motion. In this case, the result is acid–base switching between locked and unlocked states.



FIGURE 10.4 Fundamental approach to interlocked structure formation using integrated ionic templation.



SCHEME 10.4 Amidinium–carboxylate salt bridge templated catenane 6.

While the above example unavoidably contains a significant hydrogen bonding contribution to the templation reaction, other systems rely on purely non-directional electrostatic ion pair interactions. A rather impressive demonstration is Leigh and Winpenny's hybrid organic–inorganic rotaxane 7 also from 2010 (Figure 10.5).¹⁸ The axle component of 7 is composed of a dialkylammonium group with bulky 3,5-di*tert*-butyl benzene stopper groups.

The macrocycle is a heterometallic ring containing one cobalt(II) and seven chromium(III) metals, bridged by multiple fluoride and alkyl carboxylate anions. The synthesis of **7** involved the 33-component dynamic assembly of the monoanionic inorganic macrocycle around the cationic axle to afford product in a yield of 23%. Remarkably, this hybrid system exhibited good solubility in non-polar organic solvents. The solubilization of the anionic octametallic core was achieved by both charge balance with the cationic axle and the presence of a highly lipophilic periphery arising from extensive *tert*-butyl functionalization on both interlocked components.

10.2.2 ION PAIR TEMPLATION USING DISCRETE IONS

The use of discrete ion templates facilitates the exchange or removal of one of the templating ion pair partners after interlocked structure formation, placing



FIGURE 10.5 Hybrid organic–inorganic rotaxane **7** containing cationic ammonium axle and anionic heterometallic marcocycle.

the system in a higher energy state primed for spring-like functional behavior. To illustrate this point, consider rotaxane 10 which was synthesized using the chloride salt of a positively charge pyridinium axle (8) and a *bis*-vinyl-appended macrocycle precursor (9) containing an anion binding isophthalamide cleft (Scheme 10.5).¹⁹



SCHEME 10.5 Beer's anion binding rotaxane **10** synthesized using discrete anion templation. *(continued)*



SCHEME 10.5 (*continued*) Beer's anion binding rotaxane **10** synthesized using discrete anion templation.

Association of these two components is mediated by the chloride anion *via* N-H···Cl⁻ and C-H···Cl⁻ hydrogen bonding and further stabilized by donor–acceptor interactions between the electron-rich hydroquinone groups of **9** and electron-deficient pyridinium axle **8**. Conversion of this orthogonal association complex into a permanently interlocked rotaxane was achieved by RCM clipping to afford **10** in 47% yield.

In this form, rotaxane **10** retains the tight pyridinium–chloride ion pair and additional convergent hydrogen bonding interactions. Silver salt precipitation, however, provides a facile method to remove the choride template from the interlocked cavity and replace it with a non-coordinating hexafluorophosphate anion. Although an ion pair interaction is formed between the rotaxane cation and new counter anion, it is not as strong as the previous chloride-containing ion pair, and this larger, more diffuse anion is not able to reside in the constrained anion binding cavity.

A return to the previous lower energy state is highly favorable, and thus chloride binding to the rotaxane host is strong. Furthermore, the inability of other discrete anions to fit within the interlocked binding cavity, which would maximize the desirable ion pair and hydrogen bonding interactions, provides selectivity to this



SCHEME 10.6 Bromo-imidazolium homocatenane **11** exhibiting halogen bond-mediated sensing of chloride and bromide anions.

recognition event. Namely, selective chloride binding is observed over the more basic oxonanions, dihydrogen phosphate, and acetate; 1:1 association constants of 1130, 300 and 100 M^{-1} , respectively, were obtained by ¹H NMR titration experiments in 1:1 CDCl₃:CD₃OD.¹⁹ Importantly, this is a complete reversal in the selectivity exhibited by the free pyridinium axle **8**. The enhanced chloride recognition function is achieved by the synergistic binding behaviors of the two interlocked components and control over the ion pair interaction.

This strategy for constructing effective anion receptors has been employed extensively by Beer since 2002,^{20,21} and more recently by a small number of other groups.^{22,23} In addition, the incorporation of an optical or electrochemical reporter group within the interlocked structure enables these systems to be further extended into the area of anion sensing.^{22–24,26} A recent example of this from 2012 is Beer's bromide-templated catenane **11** (Scheme 10.6) in which each macrocyclic component contains a bromo-imidazolium group for anion binding and a naphthalene reporter group for fluorescent sensing.²⁴ Anion binding occurs *via* halogen bonding—the highly directional interaction between covalently bound electron-deficient halogen atoms and Lewis basic anions which is a new and promising addition to the supramolecular chemist's tool kit of solution-phase non-covalent interactions.^{27,28}

In MeCN, host structure **11** exhibited significant emission spectral changes upon chloride and bromide complexation, while a large range of other relevant anions did not induce such responses. This impressive discrimination demonstrates the potential of ion pair templated interlocked hosts for application in molecular sensing devices.

Ion pair templation of interlocked molecules using discrete ions can also produce systems capable of controlled dynamic intercomponent motion. One such example is another ion pair templated rotaxane from Leigh and co-workers²⁹ that exhibited reversible shuttling behavior induced by a removable chloride template. The templating ion pair is created by displacing the neutral MeCN ligand of palladium(II)-based macrocycle **13** with the chloride counter anion of pyridinium thread **12** (Scheme 10.7). This reaction generates a negative charge associated with the macrocycle component, inducing electrostatically driven threading onto the cationic thread. The resulting pseudorotaxane is subjected to a CuAAC reaction with a suitable azide stopper to capture the target interlocked rotaxane **14** in 64% yield.

While this system could be classified alternatively as integrated templation because the negative charge exists within the macrocycle component, the ion pair interaction is entirely dependent on the chloride ligand. The shuttling behavior of **14** arises from the ability to strip this anion from the palladium(II) metal by silver



SCHEME 10.7 Threading-followed-by-stoppering synthesis of Leigh's palladium(II)-based ion pair rotaxane 14. *(continued)*



SCHEME 10.7 (*continued*) Threading-followed-by-stoppering synthesis of Leigh's palladium(II)based ion pair rotaxane 14.

salt precipitation (Scheme 10.8). This removes the negative charge of the macrocycle component and, as a consequence, the favorable ion pair templating interaction.

The axle, however, contains an alternative "station" for the macrocycle. Specifically, the triazole group formed in the stoppering reaction is able to chelate to the newly vacant coordination site on the metal upon macrocycle translocation. Despite this stabilization, this secondary rotaxane co-conformation is still higher in energy than its original ion paired state, and hence the molecular motion is completely reversed upon chloride addition.

In addition to systems constructed by utilizing halide counter anions as discrete templates, other anions can play similarly vital roles in controlling the formation of interlocked structures. For example, the formation of Sekiya and Kuroda's quadruply interlocked assembly **16** from palladium(II)-based coordination cage **15** is highly

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SCHEME 10.8 Reversible shuttling behavior of rotaxane 14.

dependent on the exact nature of the anion template (Scheme 10.9).³⁰ In the presence of nitrate, the interlocked dimer is formed quantitatively upon heat-induced dynamic metal-ligand behavior. The new counter anions can be encapsulated completely within the three internal cavities and provide sufficient electrostatic stabilization of this tetra-metallic assembly.

A similar structure can be formed with the slightly larger tetrafluoroborate counter anions, however in much reduced yields due to lower encapsulation affinity and



SCHEME 10.9 Anion-controlled formation and disassembly of quadruply interlocked assembly **16**.

less anion–cavity complementarity. For the even larger triflate, no interlocked product is possible. Moreover, when the nitrate anions within the interlocked assembly are exchanged for 2-naphthalenesulfonate, which exhibits higher affinity for the palladium(II) centers but cannot fit within the interlocked cavities, the dimer spontaneously disassembles into monomer **15** with two encapsulated sulfonate anions. This highly selective control of interlocked assembly is based on the powerfully simple concept of size complementarity between the cationic framework and its exchangeable counter anions and is a feature of such coordination cages and their interpenetrated dimers.³¹

10.2.3 Traceless Ion Pair Templation

Receptors that bind both cations and anions can be employed for interlocked structure formation using a strategy best described as *traceless* ion pair templation. In this approach, such a receptor binds a reactive ion pair to produce a neutral product that retains neither of the templating ion pair partners. The product—interlocked if appropriately designed components are used—does, however, retain its ion pair binding ability.

Traceless ion pair templation of an interlocked molecule was first used by Smith in 2000 and focused on macrobicycle **17** that contains both cation and anion binding motifs in the forms of crown ether and isophthalamide groups (Figure 10.6).^{32,33} As a result, this receptor binds salts including potassium chloride as solvent separated ion pairs. Such binding is synergistic, for example, the presence of potassium in the crown ether section was shown to enhance the binding of chloride to the isophthalamide cleft by a factor of seven (1:1 association constants of 50 and 350 M⁻¹ for the binding of chloride in 3:1 d₆-DMSO:CD₃CN in the absence and presence of potassium, respectively).³³ The synthesis and investigation of ion pair receptors is of special interest due to a variety of important applications as salt extraction, salt solubilization, and membrane transport agents.

To exploit this ion pair receptor for rotaxane formation, Smith utilized a discrete potassium template bound within the crown ether group of **17** to aid the association of an anionic phenolate half-axle **19** in the adjacent isophthalamide cleft (Scheme 10.10). Successive esterification reactions between this complex, isophthaloyl dichloride (**18**), and a further equivalent of the half-axle **19** are necessary to form a fully stoppered axle component. The templated arrangement promotes formation of this axle within the macrocycle, yielding uncharged rotaxane **20**.

The cooperative behaviors of both the anionic and cationic templates are vital for efficient interlocked molecule formation. The anion templation component of this approach, in which the phenolate anion is held within an isophthalamide macrocycle and consumed in the reaction, was pioneered by Vögtle in 1999.³⁴ However, the macrobicycle design and presence of the bound alkali metal enabled rotaxane **20** to be synthesized in the polar solvent medium of 5:1 THF:DMF in a yield of 20%. Furthermore, the direct templating action of the potassium was demonstrated by the fact that no equivalent reaction occurred in its absence or with the larger cesium cation that was not able to bind efficiently in the crown ether.



FIGURE 10.6 Anion-controlled formation and disassembly of quadruply interlocked assembly 16.



SCHEME 10.10 Synthesis of salt binding rotaxane **20** using macrocycle **17** and ion pair templation.

Unsurprisingly, the presence of the bulky interlocked axle within rotaxane **20** was found to have a substantial effect on the salt binding properties of the component macrocycle. First, the rotaxane displayed considerably stronger chloride binding compared to macrocycle **17** (300 and 50 M⁻¹, respectively, in the same d_6 -DMSO:CD₃CN media).³³ This difference was attributed to DMSO complexation inside free macrocycle **17** that inhibited chloride binding. This DMSO competition cannot occur to the same extent in rotaxane **20** due to the presence of the interpenetrating axle.

Second, the same steric shielding effect in **20** is also responsible for a lack of observed cooperativity in ion pair binding. No enhancement in chloride affinity occurred upon potassium complexation to the adjacent crown ether ($K_a = 300 \text{ M}^{-1}$ with or without potassium cations present). Hence, the axle induced an insulating effect on the through-space electrostatic interaction between the bound potassium and chloride ions, resulting in deviation away from the synergistic behavior of macrocycle **17**.

Additional studies showed that ion pair binding has its own influence on the intercomponent dynamics of rotaxane **20**. In polar solvents such as d_6 -acetone and d_6 -DMSO, the broad ¹H NMR spectrum revealed dynamic co-conformational behavior between the axle and macrocycle components, most likely pirouetting and shuttling motions. Upon potassium binding, however, only one co-conformation existed in solution, with one of the axle carbonyl groups thought to coordinate to the bound alkali metal, halting the dynamic motion.

In contrast, chloride complexation to the macrocycle isophthalamide cleft had no apparent effect on the system's dynamics, presumably due to the absence of any potential axle–anion interactions to lock the rotaxane co-conformation. Overall, the work shows that effective traceless ion pair templation can produce uncharged mechanically interlocked molecules with ion-dependent switchable dynamic properties.

10.3 CONCLUSIONS

Since research into the templated synthesis of interlocked structures began over three decades ago, many strategies have been employed to produce, in remarkably high yields, a multitude of diverse architectures with increasing complexity and supramolecular functionality. In this chapter we described three successful ion pair templation strategies, specifically the use of integrated cationic and anionic components, discrete ion templates, and reactive ion pairs bound by macrocyclic receptors, all to mediate interlocked structure formation.

As the supramolecular chemistry of interlocked structures progresses and researchers begin applying these elegant systems to a broad range of technologies, the focus on synergistic functional behavior will increase. Crucially, ion pair templation looks promising for achieving this goal. Mainly through the ability to exchange discrete ion templates, the templating ion pair interaction can be removed, and as a result the overall energy state of a system is perturbed.

This behavior can be exploited for the fabrication of spring-like devices in which a return to the ion paired state is highly favorable. for example, in the synthesis of

interlocked molecules that exhibit strong and selective ion recognition properties through cavity binding and those capable of controllable ion-induced molecular motion.

The continuing development of such systems exhibits great potential in the areas of sensing, molecular switches, and nanoscale machines capable of doing work. Realization of these ambitious goals will likely require new synthetic methods to construct more complex hierarchical ion pair networks containing multiple aligned mechanically interlocked assemblies for amplified functionality and macroscopic device incorporation.

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