Chapter I

Introduction

"Corpora non agunt nisi fixata"[1]
"Molecules do not act if they do not bind"

I.1 Introduction: Self-assembly in Supramolecular Chemistry

Self-assembly chemistry has increasingly gained the interest of organic chemists since Pedersen's discovery that crown ethers complex with metal ions.[2,3] Originally a concept used by biologists and physicists, its principles and designs have now been applied to the new area of *supramolecular chemistry*.[4-6] To understand the conceptual ideas behind the design process, one must first understand the vocabulary of this relatively new chemical discipline.

The terms *self-assembly* and *self-organization* have sometimes been used interchangeably, but they are considered to be two different terms in the literature. The two terms are discussed in great detail in a review of *supramolecular chemistry* by Jean-Marie Lehn.[6] The reader is referred to this review for an extensive discussion of the definitions of several *supramolecular chemistry* terms. *Self-assembly* is defined as a means to "designate the evolution towards spatial confinement through spontaneous connection of a few/many components, resulting in the formation of discrete/extended entities at either the molecular, covalent or the supramolecular, non-covalent level." *Self-organization* is summarized as involving "interactions (between parts) and integration (of the interactions) leading to collective behavior, such as is found in a phase change or in the generation of spatial or temporal waves." *Self-assembly* appears to be the broader term, whereas *self-organization* appears to have as its purpose the formation of functional assemblies.

Several pioneering and intuitive investigators have defined *supramolecular chemistry*.[5,7-11] Lehn's definition is typically the most accepted one and essentially concurs with others. He defines *supramolecular chemistry* as "chemistry beyond the

molecule, bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces."[7] **Figure I-1** shows the evolution of *supramolecular chemistry*.

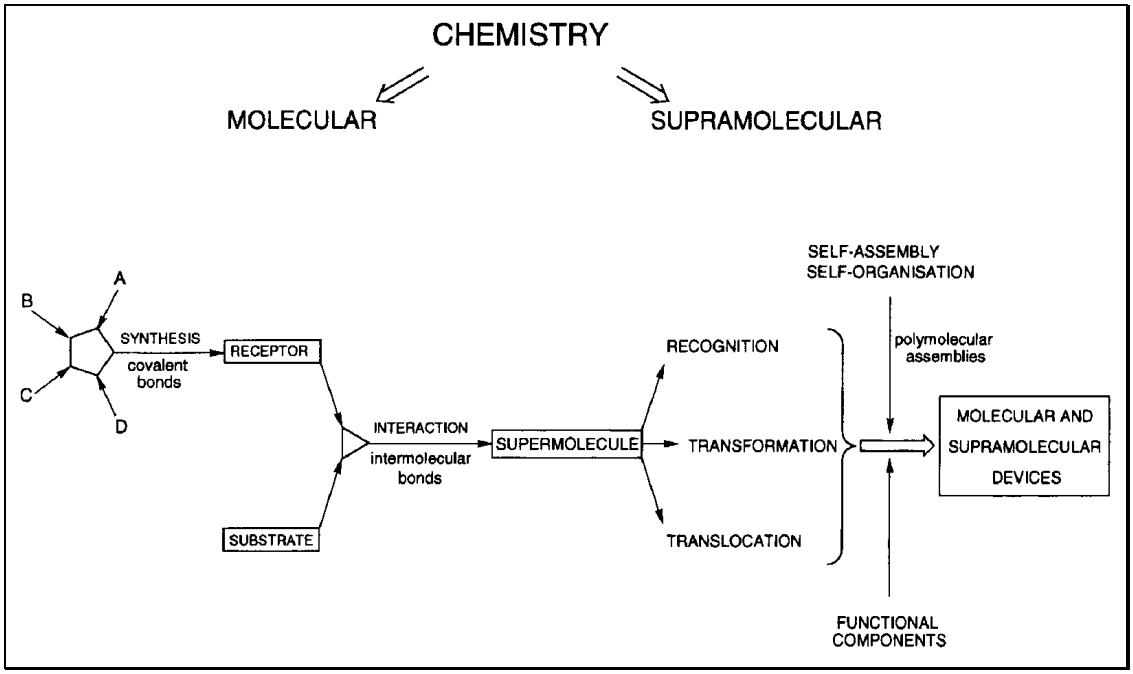


Figure I-1. The evolution of *supramolecular chemistry*.[6]

Lehn also discusses the differences between the use of the prefixes *super-* and *supra-*. Often times the terms *super*molecule and *supra*molecule are confused with one another. "The term '*super*molecular chemistry' would be restricted to the specific chemistry of the supermolecules themselves." Lehn proposes that "'*supra*molecular chemistry' be the broader term, concerning the chemistry of all types of supramolecular entities from the well-defined supermolecules to extended, more or less organized, polymolecular associations."[6] He further defines *supramolecular chemistry* by dividing the concept into two areas, which he cautions are broad, and sometimes overlapping. The two areas are: 1) *supermolecules*, well-defined, discrete *oligo*molecular species that result from the intermolecular association of a few components (a receptor and its substrate(s)) following a built-in "Aufbau" scheme based on the principles of molecular recognition;

and 2) *supramolecular assemblies*, *poly*molecular entities that result from the spontaneous association of a large undefined number of components into a specific phase having more or less well-defined microscopic organization and macroscopic characteristics depending on its nature (such as films, layers, membranes, vesicles, micelles, mesomorphic phases, solid state structures, etc.). The goal of *supramolecular chemistry* is to "gain control over the intermolecular bond. It is concerned with the next step in increasing complexity beyond the molecule towards the supermolecule and organized polymolecular systems, held together by non-covalent interactions."

There are three foundations to *supramolecular chemistry*: 1) the *receptor* (first introduced by Ehrlich[1]), 2) *molecular recognition* (first introduced by Fischer[12]), and 3) *coordination* (first introduced by Werner[13]).[6] These three foundations are each essential parts of the design and creation of a *supermolecule* or *supramolecular assembly*. A *receptor* is simply a molecule capable of binding to another molecule, a *substrate*, through the acceptance of some intermolecular contribution from the *substrate*. A general example is Fischer's 'lock and key' model for steric fit;[12] the 'key' is the *substrate* and the 'lock' is the *receptor*. Lehn has also defined *molecular recognition* rather succinctly. It is defined by the "energy and the information involved in the binding and selection of substrate(s) by a given receptor molecule; it may also involve a specific function."[14] The term *coordination* is rather loosely applied to describe the intermolecular interactions of the host (ligand) and guest (core). Essentially, any non-covalent binding between a *substrate* and a *receptor* can be considered *coordination*.

I.1.1 Historical background: Self-assembly Origins and Methods

Nature is the quintessential ‘chemist’ of supramolecular self-assembly. DNA is a prime example of the self-assembly process. Base pairs of the backbone of DNA recognize each other and assemble to create a beautiful double helix. The process for the replication of the helices even involves error checking so as to minimize mistakes. The advantage of self-assembly is that there only need be a few subunits that are involved in the aggregation to result in the supramolecular structure.[15] Control results from reaction

condition control. During error checking, the molecules use cooperativity to rearrange themselves to fit. The aggregate is overall more stable! Another prime natural example of a supramolecular system is the cell membrane.[16] **Figure I-2** illustrates the similarities between the life science of a cell membrane and materials science. Valinomycin, **I-1**, and nonactin, **I-2**, use molecular recognition to transport antibiotics.[17-21] These natural macrocycles transport both sodium and potassium ions through biological membranes. **Figure I-3** shows the binding of the potassium ion in the solid-state.

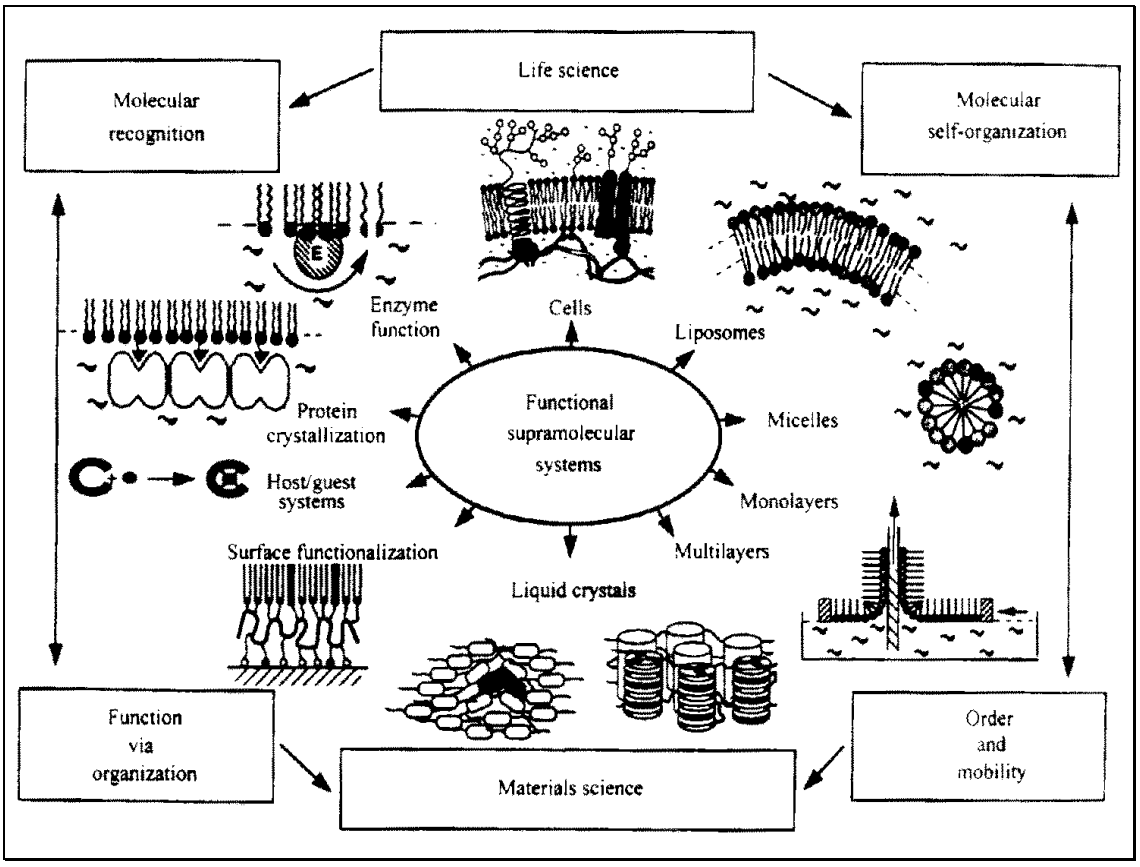
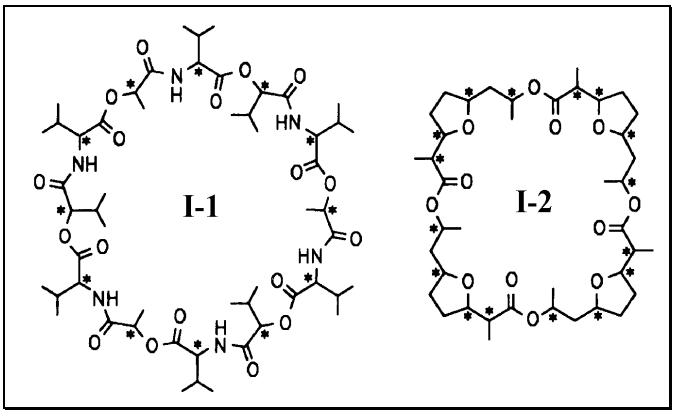


Figure I-2. Comparison of biological and material science supramolecular systems.[22]



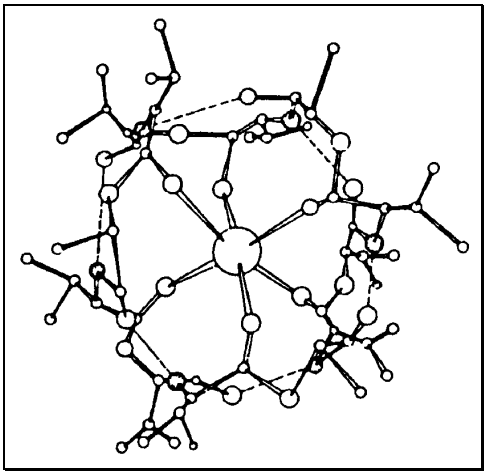
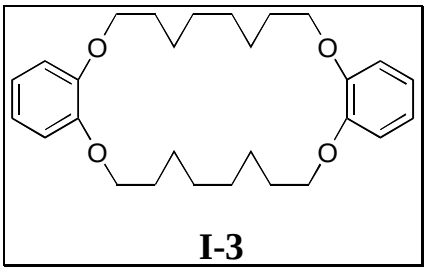


Figure I-3. Crystal structure of valinomycin binding a potassium ion.[6]

The oldest known inclusion complex involving molecular complexation was discussed in 1811 by Humphrey Davy upon his discovery of a chlorine hydrate (Cl_2-$6H_2O$) made by bubbling chlorine into cool water. It was later investigated by Michael Faraday, and the structure was determined in 1949 by Stackelberg.[5,23,24] In 1894, Fischer developed a 'lock and key' scheme for recognition of binding for proteins. It applied to substrates in enzymes, or to effectors generally, which then stimulate biologically important activities and responses. Lehn believes that his idea inspired chemists to use molecular recognition as a tool in chemistry.[6] Koshland extended Fischer's 'lock and key' by stating that the receptor (in this case a protein) changes

conformation to achieve optimal binding with a substrate.[25] In the early part of the 20th century, Braun and Tcherniac synthesized azamacrocyles that formed metal ion complexes with the phthalocyanines after pyrolyzing o-diaminobenzene and o-cyanobenzamide.[26] The cyclization process was due to a templated assisted synthesis of the azamacrocycles. In 1937, Lüttringhaus wanted to make molecules that concatenate, maybe having unusual properties. He made several macrocycles similar to **I-3**, but they lacked sufficient donor groups for complexation.[27-30]

Cramer, in 1952, defined an 'inclusion compound' as having in common the "ability to incorporate into the cavities of their own molecules, or within their lattices, other molecules of suitable size, spatially to enfold them, that is to hold them, though not by main or secondary valence forces, but mostly by physical imprisonment."[31] He later wrote: "the essential requirements are: 1) The enclosing substance must possess cavities. Such cavities may be present either in the molecule, in large rings, for instance, or in the crystal lattice of the host compound. The corresponding cavity-containing lattice need not be stable as such, but is, in many cases, only formed on incorporating the guest substances. 2) The substances to be incorporated must find enough space in the cavities present..."



I-3

The first reference to the use of supramolecular assemblies in chemistry was in 1978 by Lehn.[9,32] However, it was not until the late 1980s that he alluded to the use of self-assembly as a tool for the formation of supramolecular assemblies.[7,33,34] This conceptual discovery was prompted by work with the spontaneous generation of

inorganic double helices, a.k.a. the helicates. The organization was seen as a self-assembly process. As seen in **Figure I-4**, the 2,2'-bipyridine (bipy) groups of **I-4** spontaneously assemble into a helix to give the supermolecule **I-5** in the presence of Cu(I).

For his pioneering work and observations Jean-Marie Lehn is regarded as one of the forefathers of supramolecular chemistry. The other two pioneers were Charles Pedersen and Donald Cram. For their efforts all three received the Nobel Prize in chemistry in 1987. It is this point in history that synthetic chemists changed from a focus entirely centered on the covalent interactions of molecules and began to realize the potential and importance of intermolecular interactions.[35]

Pedersen demonstrated that dibenzo-18-crown-6 (**I-6**) formed a complex with alkali ions in that late 1960s.[2,3] His initial discovery was purely accidental (0.4% yield), although the synthetic strategy behind the discovery was creative and innovative. Pedersen's intention was to make the non-cyclic phenolic derivative **I-7** to complex divalent cations. He was particularly interested in the vanadyl group (VO). He expected the phenolic residues of **I-7** to dissociate under basic conditions. He noticed that 'charge-dense cations require charged donor groups for them to be bound most effectively.'[35] Pedersen named the class of compounds having structures similar to **I-6** as ‘crown ethers.’ In a manuscript he described the origin of the term: "I applied the epithet 'CROWN' to the first member of this class of macrocycle polyethers because its molecular model looked like one, and with it, cations could be crowned and uncrowned without physical damage to either, just as heads of royalty."[36] A review of crown ethers and their origins will be given in Chapter III.

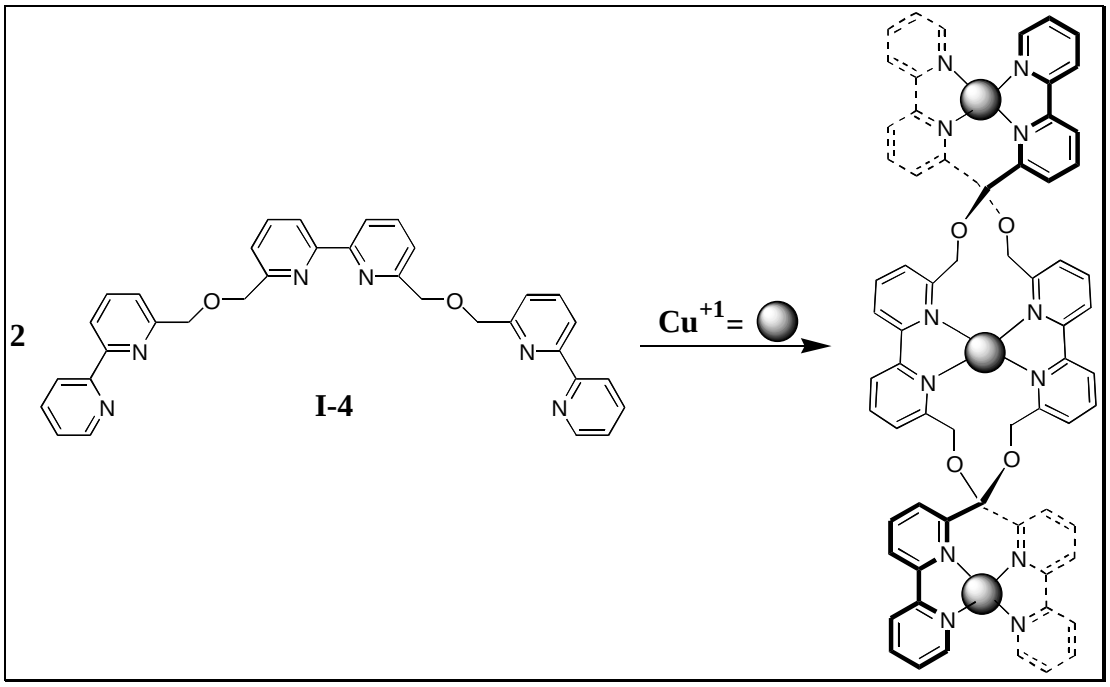
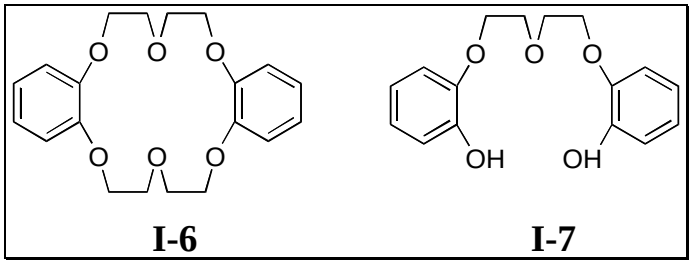
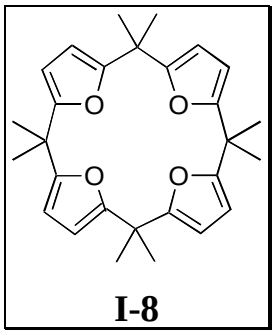


Figure I-4. Self-assembly of helicates.[6]

Cram had noticed that carbanions have aggregate states and he reasoned that the chemical activity of the carbanion might be increased if the cation and anion were separated.[35] His intention was to use a cyclic polyether to fully solvate the cation. Efforts in the mid-1960s to solvate a lithium cation with macrocycle **I-8** did not occur, however. Once he noticed the discovery by Pedersen he turned his attention to the synthesis of chiral crown ethers and their ability to differentiate stereochemically optically active primary ammonium salts.





I-8

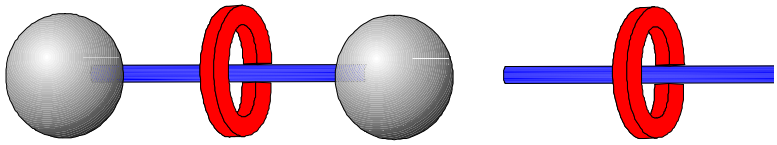
The origins of supramolecular chemistry began with crown ethers and have diverged greatly from there, to include, e.g., nanotubes, linear arrays, and self-assembled monolayers. Supramolecular chemistry is the essence of interdisciplinary science. One must attempt to design, construct, and characterize a supramolecular system using as many tools as are available. This requires the understanding of the chemical and physical aspects of chemistry, biology, and physics as well as the analytical and design aspects of each discipline. The next century will bring an age of a new chemical discipline, *supramolecular chemistry*, an age where the chemist will have a better understanding of how molecules interact with one another.

I.2 Rotaxanes and Pseudorotaxanes

An excellent example of a supermolecule is a rotaxane. The term rotaxane comes from Latin for "wheel" and "axle."[37,38] As illustrated in **Figure I-5** a rotaxane, **I-9**, contains a minimum of two molecular components one of which is a cyclic component and the other a linear component. The cyclic component is threaded through its opening by the linear component, much like a bead threaded on a string. The interaction between the two components is purely mechanical and the two components are assembled through non-covalent forces. A rotaxane has traditionally been further defined as containing bulky end groups on the linear component to prevent the dethreading of the cyclic component. A pseudorotaxane, **I-10**, is similar to a rotaxane but lacks the bulky end-groups on the linear component to prevent dethreading. The definition is actually a misnomer, since the

prefix *pseudo*- implies that the pseudorotaxane is not a true rotaxane even though it meets the initial basic requirements.[39]

The nomenclature used in the literature for rotaxanes[40], which resembles the closely related catenanes, is slightly misleading. Rotaxanes having *n* components are designated as [*n*]rotaxanes. For instance, the rotaxane **I-9** is called a [2]rotaxane which is easily envisioned as a two component rotaxane, the simplest rotaxane. However, for a three component rotaxane, [3]rotaxane, there is no indication if there are two linear units and one cyclic unit or there are one linear unit and two cyclic units. The author suggests that a new nomenclature system be used, one in which two numbers are used as the prefix. Further, the number of cyclic units should be first since most rotaxane and pseudorotaxane systems are considered host-guest systems and the host is usually the cyclic unit. This is purely a historical choice. Therefore, as an example, the rotaxane **I-9** should be named a [1.1]rotaxane. A rotaxane comprised of one cyclic unit and two linear units should be name a [1.2]rotaxane, and the opposite case a [2.1]rotaxane.



I-9 **I-10**

Figure I-5. A rotaxane, **I-9**, and pseudorotaxane, **I-10**.

The polymeric analog of the rotaxane is the polyrotaxane. The simplest polyrotaxane is **I-11** in **Figure I-6**. The absence of blocking groups in the polyrotaxane defines a polypseudorotaxane, **I-12**, often misnamed as a pseudopolyrotaxane. The use of a polymer chain allows several different topologies to exist for the polyrotaxanes, e.g. side-chain polyrotaxanes, main-chain polyrotaxanes, mechanically crosslinked polyrotaxanes, etc…, some of which are shown in **Figure I-6** (structures **I-13** through **I-22**).

The first evidence for the synthesis of a pseudorotaxane was reported by Lüttringhaus *et al.* in 1958,[41] although the host-guest complex between one cyclodextrin molecule and dithiol terminated linear component was not labeled as a pseudorotaxane at the time. In 1961, Frisch and Wasserman, published the first suggestion of rotaxanes.[42] They did acknowledge that there was anecdotal evidence of the first rotaxane as early as 1900. Both the groups of Harrison and Harrison[43] and Schill and Zöllenkopf[37] simultaneously reported the first conclusive evidence for the existence of rotaxanes in 1967. Since their initial groundwork there has been an abundant amount of research on rotaxanes. Each new discovery has caught the attention of the chemical community and involved new investigators and disciplines of science each year. Several reviews of the subject have been published that highlight the evolution of the remarkably novel area of rotaxane chemistry.[39,44-49]

There are some geometric or steric parameters that are to be met when considering the threading process. These requirements were established by both Harrison[50,51] and Schill and co-workers.[52,53] The size of the cyclic unit must be of at least 22 carbon, oxygen, and/or nitrogen atoms to be threaded by the simplest organic linear component, namely a polymethylene chain, having a cross-sectional backbone of 4.5 Å. Out of the previously mentioned cyclic molecules above as examples, structures **I-1, I-2,** and **I-3** are a suitable candidate for making a rotaxane with polymethylene.

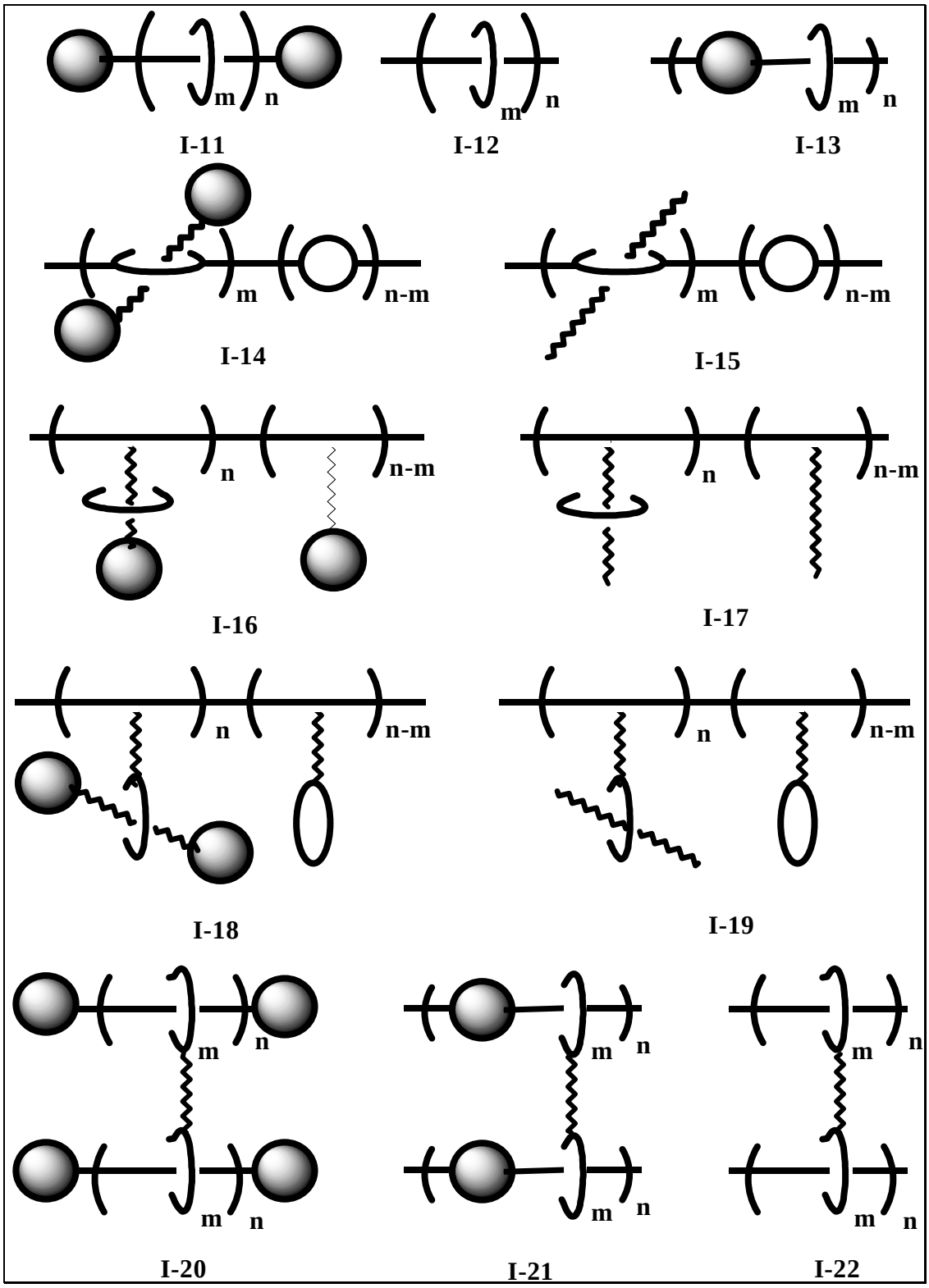


Figure I-6. Various polyrotaxanes and polypseudorotaxanes.

There are three main categories for the synthetic approaches to rotaxane formation: 1)'*directed*' or '*chemical conversion*', 2) *statistical threading*, and 3) *thermodynamic* control or design. The later case has acquired tremendous attention, whereas the first two approaches have historically been abandoned due to either their low yields or difficult syntheses. **Figure I-7** illustrates the '*directed*' or '*chemical conversion*' approach Schill and co-workers utilized.[37,38,53] It has had little attention due to the low yield, multistep synthesis of rotaxane precursor **I-25** and the statistical threading and dethreading equilibrium that exists between the topological isomers **I-23** and **I-24** of the first reaction.

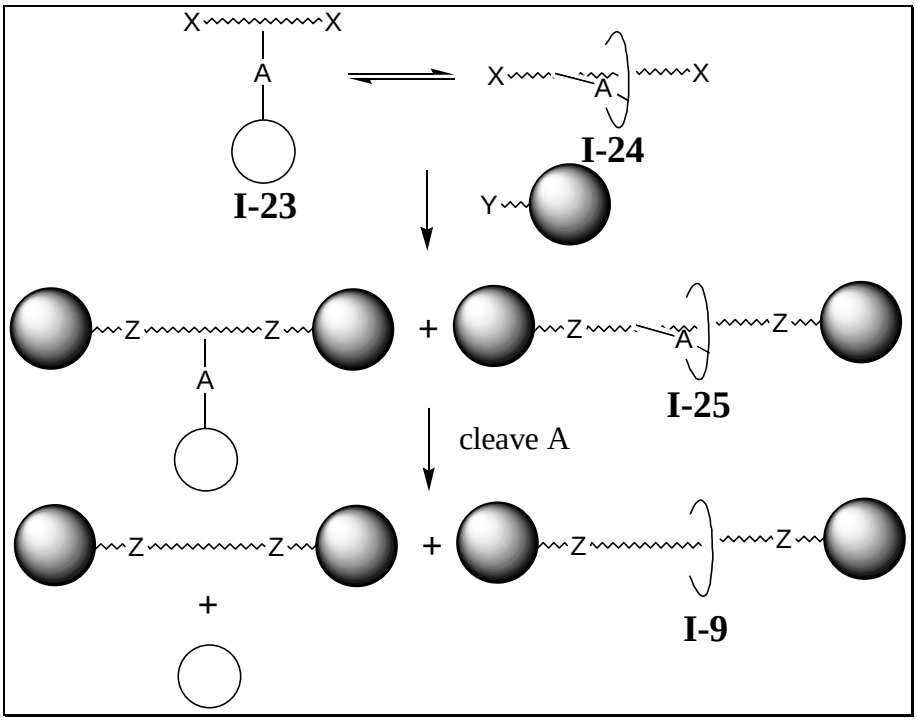


Figure I-7. '*Directed*' or '*chemical conversion*' approach for rotaxane synthesis.

The *statistical threading* and *thermodynamic* control approaches are similarly related. Both approaches can be depicted as in **Figure I-8**, but in the *statistical threading* approach the ΔH term is either only slightly negative (attractive forces such as van der

Waals forces), positive (entropy driven), or zero. The *statistical threading* approach can be manipulated by the application of Le Châtelier's principle. Under the *thermodynamic* control approach the ΔH term is always negative and in some cases highly negative. This method uses *molecular recognition* and *coordination* between the *receptor* and *substrate* through intermolecular interactions. The first and second step are often referred to as the 'threading' and 'end-capping' steps respectively.

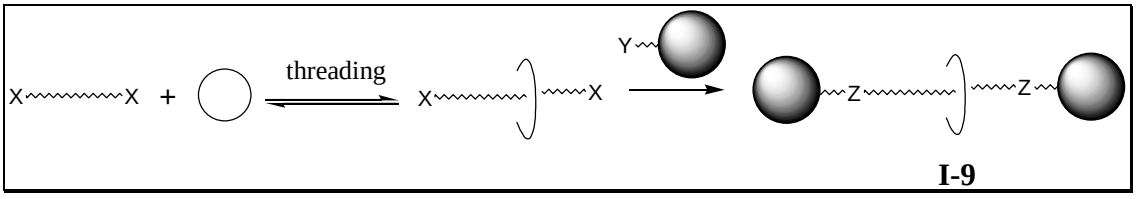


Figure I-8. *Statistical* and *thermodynamic* control approaches to rotaxane synthesis.

There are typically three methods for the self-assembling of rotaxanes. These are illustrated in **Figure I-9** as the *clipping*, *threading*, and *slipping* approaches.[40] In the clipping approach the linear component **I-28** acts as a template for the cyclization step through some intermolecular complexation with macrocycle precursor **I-27**. The cyclic is then formed between **I-26** and **I-27** to give rotaxane **I-9**. The threading approach is analogous to **Figure I-8**. It is actually a two-step process. A preformed pseudorotaxane is created between the cyclic component **I-29** and the linear component **I-30** and this is followed by the covalent attachment of two stopper groups **I-31** to form **I-9**. The slippage approach involves the introduction of sufficient thermal energy to allow slippage of the cyclic component **I-29** over the linear component **I-28** to form **I-9**.

Under the *thermodynamic* control approach there are several types of intermolecular driving forces for the formation of rotaxanes. These include 1) hydrogen bonding, 2) hydrophopic-hydrophilic interactions, 3) metal complexation, 4) charge-transfer, 5) other weaker forces, such as π–π aryl stacking. Some systems involve more than one of the forces. Two reviews by Gibson[39] and Gibson and Mahan[54] give an

excellent summary of examples of these forces in action for both low molar mass rotaxanes and polyrotaxanes.

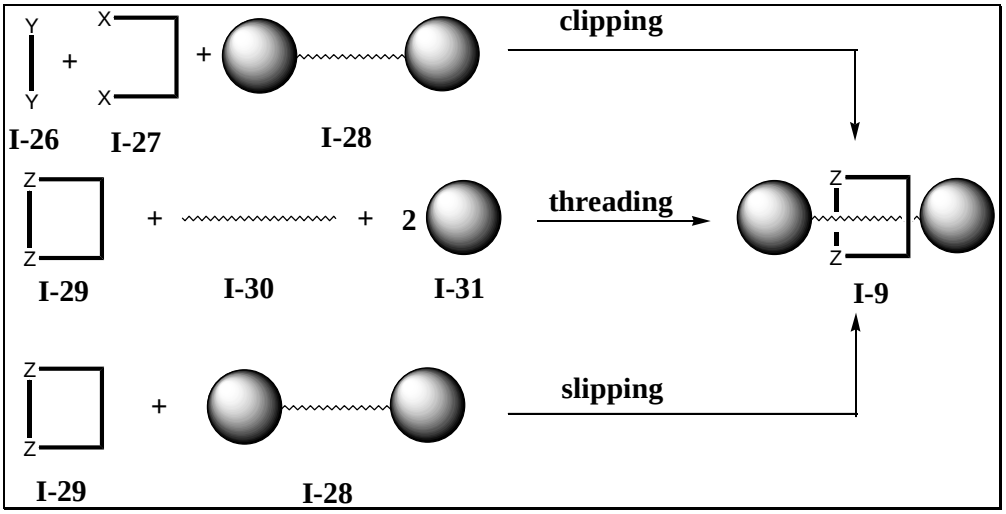
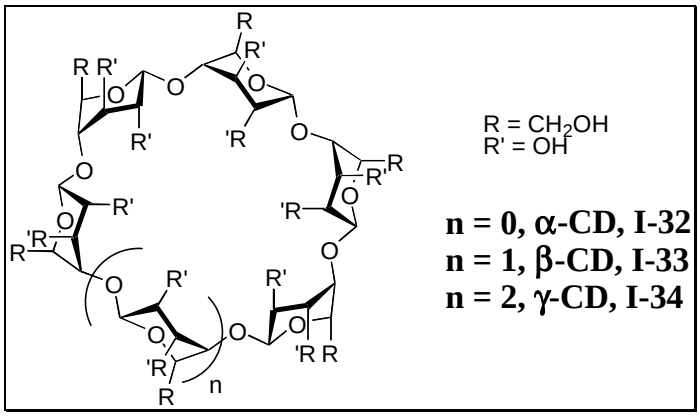


Figure I-9. Self-assembling approaches to rotaxanes.[40]

Historically the first report of using hydrogen bonding for rotaxane formation may have been from Agam *et al*. in 1976.[55,56] Although there was no acknowledgement of a hydrogen bond driving force, the yields of the rotaxanes were relatively higher than expected for the claimed statistical threading system. Hydrogen bonds may have formed between the crown ethers and oligo(ethylene glycol)s' hydroxyl endgroups during the end-capping step. Since 1995, the Busch,[57,58] Stoddart,[59-67] and Takata[68] groups have reported numerous self-assembled rotaxanes and pseudorotaxanes based on secondary ammonium ions and bisphenylene crown ethers. The principle driving force for these rotaxanes is the hydrogen bond formation between the ether oxygens of the crown ethers and the hydrogens of the secondary ammonium ions. Secondary stabilization is achieved through π–π aryl stacking in some of the systems.

Hydrophobic-hydrophilic complexation to form rotaxanes is primarily based on the use of cyclodextrins (CD). The three most used CDs are α- (**I-32**), β- (**I-33**), and γ-

CD (**I-34**), having 6, 7, and 8 saccharide repeat units, respectively. The first report of a rotaxane using CD was from Ogino in 1981.[69-71] He found that eight methylene groups were needed to reach from one end of the CD cavity to the other. Since the hydroxy groups are on the exterior of the CDs and the cavities are primarily hydrocarbon in nature the macrocycles are able to form inclusion complexes with hydrocarbon-like linear units in polar (usually water) solution environments. The interiors of the CDs are hydrophobic and the exteriors are hydrophilic. Several reviews[72-77] of the progress of CD rotaxanes have been published since Ogino's breakthrough.



Sauvage and Dietrich-Buchecker[78] reported rather elegant research in 1983 using the metal complexation approach to rotaxanes. Their approach involves using the Cu(I) tetrahedral geometry that results from the use of 1,10-phenanthrolines as ligands. An example is shown in **Figure I-10**. Both the cyclic and the linear component have a 1,10-phenanthroline ligand present. The linear unit can be end-capped and the copper can be removed to give the rotaxane. An excellent review[79] of their rotaxane chemistry as well as catenanes, molecular knots and more elegant supramolecular assemblies has recently been published.

Rotaxanes have also been assembled using charge-transfer complexation. Most of the research has involved complexation between linear or cyclic components containing the 2,2'-bipyridinium and 4,4'-bipyridinium moieties with bisphenylene crown ethers or

linear units containing ethylene-oxy moieties. The first example of this approach was reported in 1987 by Stoddart *et al*.[80,81] Although the main driving force for the rotaxane formation is hydrogen bonding, charge-transfer is an important secondary stabilizing factor. Other secondary stabilization occurs due to π-π aryl stacking and dipole-dipole interactions. A review of their work has also appeared recently.[40] More recent work by Loeb and co-workers has demonstrated complexation between 1,2-bis(pyridinium)ethane linear components and several crown ethers to create rotaxanes.[82,83] Again, hydrogen bonding is the primary driving force for the rotaxane formation and π–π aryl stacking is a secondary stabilizing factor.

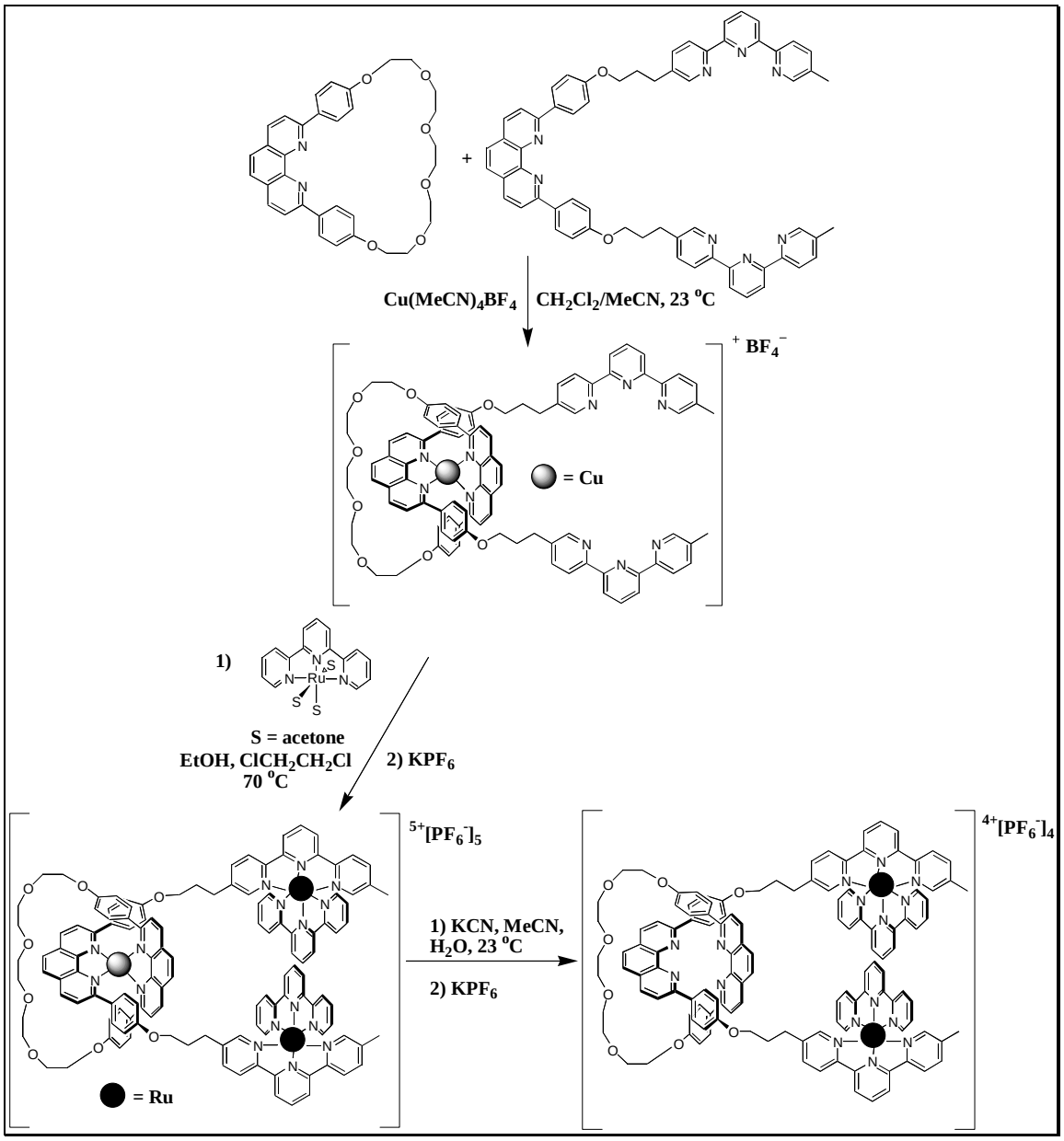


Figure I-10. Example of a rotaxane synthesis using metal complexation.

I.3 Thesis Statement

The research discussed in this thesis will involve the formation of *supermolecules* through the use of *self-assembly*. Care has been taken in designing suitable *receptors*, and *substrates*, to use *molecular recognition* for the *coordination* of the assemblies through intermolecular interactions of the molecular components.

The research was inspired by the discovery by Stoddart *et al*. that secondary ammonium ions form pseudorotaxanes with bisphenylene crown ethers.[59,60] Not discussed was the use of *meta*-substituted bisphenylene crown ethers. In the present work several crown ethers having *meta*-substituted bisphenylene groups were synthesized and their suitability as receptors for the formation of pseudorotaxanes with several secondary ammonium ions was investigated.

Substituted *meta*-phenylene crown ethers, due to their symmetric nature, can be prepared as pure compounds without isomer separation and have simpler NMR spectra than their substituted bis(*ortho*-) and bis(*para*-) analogs. They are also better suited for incorporation into polymer backbones or side chains due to the same reasons. Although no polyrotaxanes were made, the ultimate goal here was to design suitable systems to make polyrotaxanes involving secondary ammonium ion linear moieties and bisphenylene crown ether cyclics containing *meta*-substitutions.

The effects of *meta*- and *para*-substituted centers of benzylic diammonium ions on complexation with dibenzo-24-crown-8 were examined. The model compound investigation was done because the synthetic route to the benzylic secondary ammonium polymer involves the synthesis of a benzylic poly(imine), which are typically insoluble materials if the repeat unit contains *para*-substitution. The use of a *meta*-substituted repeat unit creates a more soluble polymer easily convertible to the polyammonium salt.

Also discussed is the synthesis of two new cryptands and their complexation with several different organic ions. The use of cryptands instead of crown ethers as receptors was investigated due to the "pre-organization" associated with these receptors. Cryptands have relatively lower degrees of freedom than crown ethers; therefore, the ΔG of complexation for complexes with cryptands is more negative than for complexes with

crown ethers. The understanding of the binding of the cryptands with the secondary ammonium ions will also give valuable information for the design of polymeric materials using cryptand moieties.

I.4 References

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