DESIGN AND SYNTHESIS OF FUNCTIONAL MOLECULAR SQUARES

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

HANDAN AKPINAR

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
DEPARTMENT OF CHEMISTRY

AUGUST 2006

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Hüseyin İşçi
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Prof. Dr. Engin U. Akkaya
Supervisor

Examining Committee Members

Prof. Dr. Mevlüt Ertan (HU, Pharm.) _____

Prof. Dr. Engin U. Akkaya (METU, CHEM) _____

Prof. Dr. Metin ZORA (METU, CHEM) _____

Assoc. Prof. Dr. Özdemir Doğan (METU, CHEM) _____

Assoc. Prof. Dr. Leyla Yıldırım (HU, Phys. Eng.) _____

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: Handan AKPINAR

Signature :

ABSTRACT

DESIGN AND SYNTHESIS OF FUNCTIONAL MOLECULAR SQUARES

AKPINAR, HANDAN
M.S., Department of Chemistry
Supervisor: Prof. Dr. Engin U. AKKAYA

August 2006, 51 pages

Self-assembly has big importance in synthesizing supramolecular structures. Highly fluorescent molecular squares with boradiazaindacene (BODIPY) building blocks were obtained via usage of metal driven self-asembly. The boradiazaindacene units were connected with the Pd(II) complex unit enforcing a near-90 degree angle between the building blocks. Thus, we believe we have the first example of BODIPY carrying fluorescent squares. With collective experience in BODIPY chemistry in our group, we may have the first example of functionalizable molecular square. Self-assembled light harvesting systems will be ultimate biomimetic example of photosynthetic reaction center.

Keywords: Self-assembly, molecular squares, metal coordination, BODIPY.

ÖZ

FONKSİYONEL MOLEKÜLER KARENİN DİZAYNI VE SENTEZİ

AKPINAR, HANDAN
Yüksek Lisans, Kimya Bölümü
Tez Yöneticisi: Prof. Dr. Engin U. AKKAYA

Ağustos 2006, 51 sayfa

Supramoleküler yapıları sentezlemede kendiliğinden biraraya gelme büyük önem arzeder. Metal yardımı ile oluşan kendiliğinden bir araya gelmeden faydalanılarak boradiazaindasen (BODIPY) yapı taşları içeren, oldukça floresan moleküler kareler elde edilmiştir. Boradiazaindasen birimleri Pd(II) compleksine yaklaşık 90 derecelik açı oluşturacak şekilde bağlanmıştır. Bu yüzden BODIPY içeren ilk floresan kareyi oluşturduğumuza inanıyoruz. Grubumuzda BODIPY kimyası üzerine olan müşterek tecrübemizle fonksiyonlandırılabilir moleküler karenin ilk örneğine sahip olabiliriz. Kendiliğinden bir araya gelerek oluşmuş ışık toplayan sistemler fotosentetik reaksiyon merkezinin nihai biyomimetik örneği olacak.

Anahtar Kelimeler: Kendilğinden biraraya gelme, moleküler kareler, metal koordinasyonu, BODIPY.

To my family

TABLE OF CONTENTS

LIST OF FIGURES

ACKNOWLEDGEMENTS

I would like to express my sincere thanks to my supervisor Prof. Dr. Engin U. Akkaya for his guidance, support and patience during the course of this research as well as his unlimited knowledge and experience that I have benefited from greatly.

Also, I would like to thank to members of Supramolecular Chemistry Group for their friendship and support.

My special thanks go to my family for their endless love, trust, support, and encouragement.

My gratitude to Cantürk for his helps and nice friendship.

I am grateful to my sweet friend, Aslı for her help, for sharing the troubles, and for the beautiful days we live.

CHAPTER 1

INTRODUCTION

1.1 Supramolecular Chemistry

It is an almost impossible task to write a useful definition of supramolecular chemistry. The field is ever changing as it advances, and researchers will have their own understanding and sets of terminology. In 1987, Jean-Marie Lehn introduced the modern concept of chemistry, which he defined as the "...chemistry of molecular assemblies and of the intermolecular bond [1]," although the term itself made a much earlier appearance (in *Webster's Dictionary* in 1903). Traditionally, phrases such as "chemistry beyond the molecule," "the chemistry of the non-covalent bond," and "non-molecular chemistry" or even "Lego chemistry" were also used to describe the field. In the beginning, supramolecules mainly comprised two components, a host and a guest, which interact one another in a noncovalent fashion (Fig. 1). The area rapidly evolved to encompass molecular devices and molecular assemblies. More recently (2002), Lehn added a further functional definition: "Supramolecular chemistry aims at developing highly complex chemical systems from components interacting by non-covalent intermolecular forces [2]." The current emphasis thus on increasing complexity and, hence increasingly sophisticated functionality, and on the information stored in the molecular components that allows this complexity to be achieved.

Fundamentally, supramolecular chemistry concerns the mutual interaction of molecules or molecular entities with discrete properties. This interaction is usually of a non-covalent type (an "intermolecular bond," such as a hydrogen bond, dipolar interaction or π-stacking). Key to many definitions of supramolecular chemistry is a sense of modularity. Supramolecules in the broad sense are aggregates in which a number of components (of one or more type) come together, either spontaneously or

by design, to form a larger entity with properties derived from its components. These aggregates can be of the host-guest type in which one molecule encapsulates the other, or they can involve mutually complementary or self complementary, components of similar size, in which there is no host or guest.

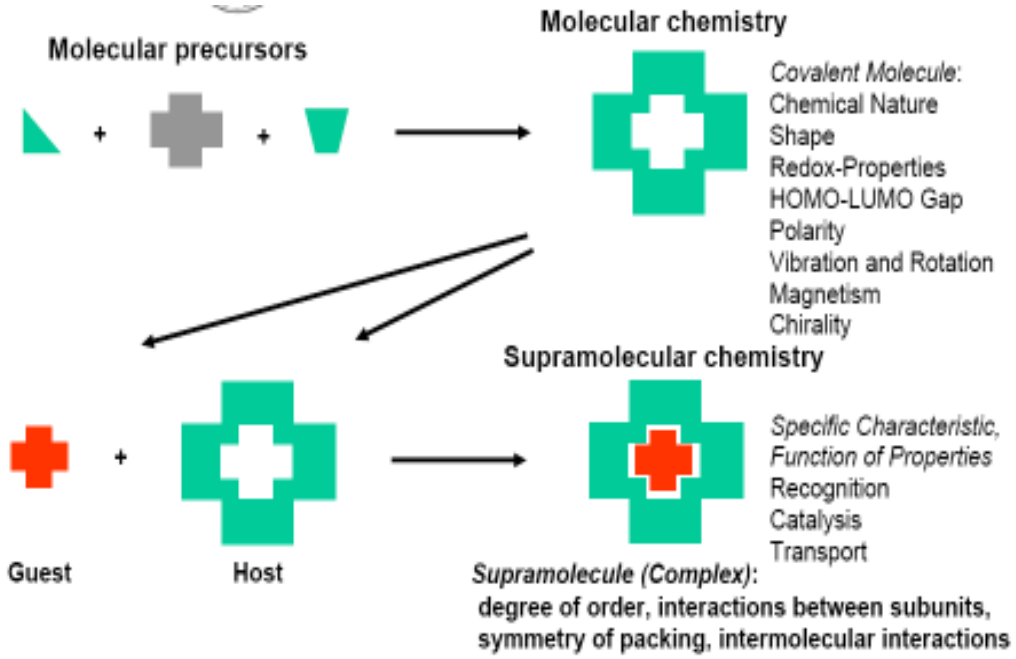


Figure 1 Comparison between the scope of molecular and supramolecular chemistry according to Lehn.

The broad general field of interactions between molecules is, in fact, of relevance to a number of loosely related disciplines, both within chemistry and at the interface of chemistry with biology, condensed matter physics, and material science [3].

1.2 Self-Assembly

Self-assembly is one of the core concepts of supramolecular chemistry. It is often defined as the spontaneous formation of the higher-ordered structures from molecular building blocks [3].

Self-assembly allows access to new molecular architectures that are inaccessible (or accessible in only very small yields) via traditional multi-step covalent bond making and bond breaking techniques. The new molecular architectures are produced by combining appropriately designed sub-units, which can be quite simple, and yet after the assembly process produce quite complex architectures. These assemblies have many potential uses ranging from information storage to drug delivery. Self-assembling systems that can self-replicate may give us insights into how life on earth started! It is the beauty of many of these systems, and their possible future uses (that can currently be dreamt of in the pages of a science fiction novel), that really excite the supramolecular chemists and push this area of research forward [4].

How are supramolecular assemblies formed? The most straightforward method is to use self-assembly techniques, which is to say that you mix your components under given set of conditions (solvent, temperature, pH etc.) then cross your fingers and hope for the best. Of course, most chemists try to approach things a little more rationally than this and attempt to design synthetic routes based on predicted interactions between the various components of the mixture. Happily, self-assembly processes often converge on a single product out of the countless possible combinations of your starting materials. This product is formed because it is the most thermodynamically stable arrangement of the constituent entities. Chemists get very excited about self-assembly, as they see it as being a very efficient and reliable method for the "bottom-up" synthesis of new materials (as opposed to current "top-down" methods for producing, for example, computer chips).

During the self-assembly process, inevitably some of your starting materials will go down the 'wrong track' towards other products. It therefore turns out to be very useful that the bonding interactions between the components of these assemblies are quite weak. This is because the 'wrong' products are easily dis-assembled and the components can quickly recombine in the 'right' way to form the most stable assembly. This 'reversibility' is one of the key features of supramolecular synthesis and it contrasts with the situation in conventional molecular synthesis involving covalent bonds. In molecular synthesis, a reaction which goes down the “wrong

pathway" often ends up at a dead end and the material which is formed must in the end be separated from the desired product.

1.2.1 Self-Assembly in Natural Systems

Self-assembly is everywhere in nature at both macroscopic and microscopic scales- for example, from the assembly of schools of fish in the ocean, flocks of birds in the sky, and herds of wild animals to oil droplets in water.

There are numerous examples of molecular self-assembly in nature. One of the well-known examples is silk assembly. The monomeric silk fibroin protein is approximately one micrometer long but a single silk worm can spin fibroins into silk materials over two kilometers in length, two billion times longer! Such marvelous engineering skill is hardly matched even by current technology. These building blocks are often on the nanometer scale. However, the resulting materials could be measured on meter and kilometer scales [5]. Likewise, the size of individual phospholipid molecules is approximately 1.5nm in length, but they can self-assemble into millimeter-size lipid tubules with defined helical twist, many million times larger, and a number of applications have been developed [6].

There are many examples of self-assembling biological systems. The formation of the DNA double helix from two complementary deoxyribonucleic acid strands is a striking example (Fig. 2). Under the right conditions, the thermodynamically stable double helix forms spontaneously and reversibly as the strands are mixed together and hydrogen bonds form between complementary base pairs. As a result of the reversibility of the process, any errors that may have occurred during assembly can be corrected (provided the reversibility is rapid).

Figure 2 DNA double helix.

The formation of cell membranes, multi-component enzymes, and viruses are paradigms of the way in which nature uses a simple, limited range of interactions to produce very complex molecular assemblies. A well-known example of a self-assembling system in nature is the tobacco mosaic virus (TMV). This rod-shaped particle is roughly 3000 Å long and 180 Å in diameter and is composed of over 2000 coat-protein subunits arranged into a right-handed helix conformation. Running along the core of a TMV is a single strand of RNA. What is remarkable about the virus, compared to a purely chemical entity, is that if it is decomposed into its component parts and these fragments are mixed under physiological conditions, then the virus particle is accurately self-assembled and regains full functionality. Under appropriate pH and ionic strength, the coat proteins (so named because they form a coat around the internal phase of the virus) aggregate to form small "lock-washer" helices known as protohelices. These protohelices specifically interact with the nucleotides of the RNA strand to drive the self-assembly of the final virus. In the absence of RNA, rapid assembly of the coat proteins (initiated by sharp changes in pH) causes the formation of a "nicked," incomplete helix, which, over a few hours' time, anneals to form continuous helical protein rods (Fig. 3) [7].

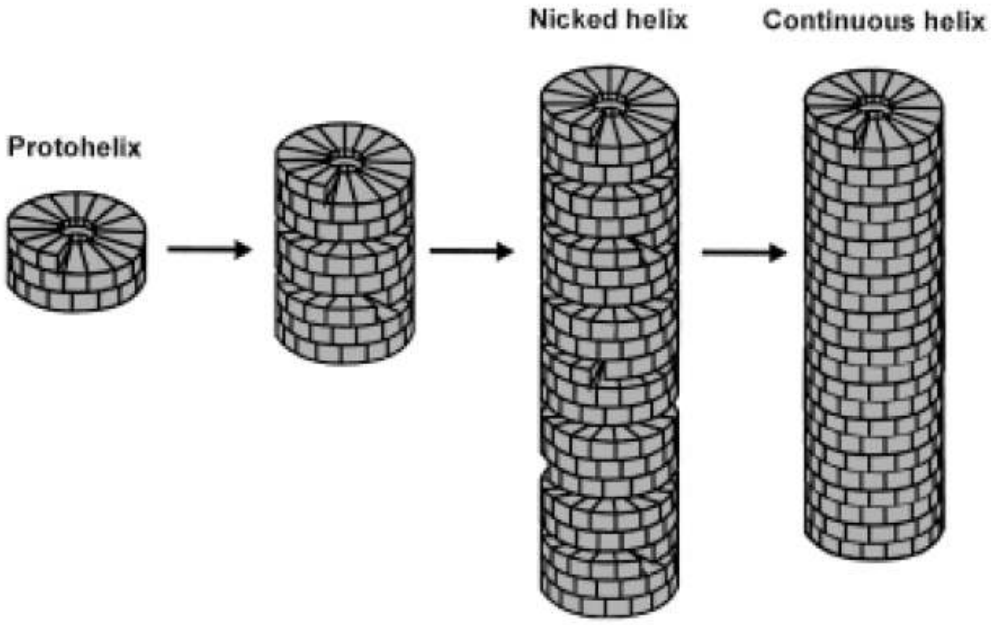


Figure 3 Self-assembly of tobacco mosaic virus coat proteins in the absence of RNA.

The assembly of TMV demonstrates the ability of biological systems to construct large, ordered molecular and supramolecular arrays from small, relatively simple subunits by a mechanism of self-assembly. Such processes are responsible for the wide diversity of structure and function observed at both the cellular and subcellular levels in Nature. The evolution of self-assembly pathways in natural systems can be rationalized in terms of the selective advantages conferred upon organisms that utilize such synthetic routes. The common feature of all biological self-assembly processes is the ability to take advantage of many, weak noncovalent interactions between preformed subunits or well-defined subassemblies to guide the formation of a structure. These noncovalent interactions are also responsible for the stability of the final structure. Since self-assembly involves the intermediacy of many weak and reversible interactions, the final structure formed represents a thermodynamic minimum for the stable subassemblies, which are then carried forward into the final structure, permits great synthetic efficiency; in chemical terms, the synthesis of the final structure is highly convergent [8]. The use of several identical subunits within a structure also requires that only a limited set of binding interactions is necessary to

form the structure correctly, minimizing the amount of information needed to describe the structure fully. In summary, biological self-assembly processes require assembling subunits to display complementarity in geometric shape and surface electronic properties. The result of this complementarity is a structure stabilized by many, relatively weak, noncovalent binding interactions, which may be shape-dependent (van der Waals/hydrophobic), or directed (hydrogen bonds/ electrostatic interactions), distributed over the whole molecular volume, rather than limited to a few strong, localized covalent bonds [9].

1.2.1.1 Lessons to be learned from Biological Systems

Biological systems point the way forward to chemical systems capable of employing the advantages offered by synthetic routes incorporating self-assembly. The stunning diversity of structure and function found in biological systems, which rely on self-assembly for their genesis display four common themes for synthetic chemist to exploit:

- Self-assembly processes are economical by virtue of their high convergence
- Stable, structurally diverse assemblies can be rapidly, accurately, and efficiently synthesized from relatively simple subunits.
- The use of identical subunits within an assembly enables the lexicon of interactions employed to be kept to a minimum, economizing on the amount of information required to describe a structure.
- Molecular recognition by means of many, weak noncovalent bonding interactions leads to a dynamic, reversible, and “intelligent” synthetic pathway, which is self-checking and self-correcting and affords a product representing a thermodynamic minimum [9].

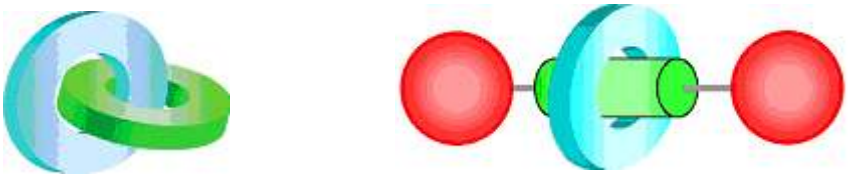
1.2.2 Self-Assembly in Chemical Systems

Non-covalent interactions such as metal coordination, hydrogen bonding, anion coordination or charge transfer are used to drive (or template) the formation of the supramolecular assemblies.

1.2.2.1. π-Electron Donor-Acceptor Systems

1.2.2.1.1. Catenanes and Rotaxanes

The synthesis of assemblies in which two molecular components are interlinked, but not physically joined by covalent bonds presents a considerable challenge to the supramolecular chemist. The catenanes and rotaxanes (Fig. 4) illustrate this challenge most clearly.



(a) **(b)**

Figure 4 Schematic representation of a [2]catenane **(a)** and a rotaxane **(b).**

[n]Catenanes (from Latin: catena (chain)) consist of n interlocked macrocyclic species. For example a [2] catenane refers to two interpenetrating macrocycles (Fig. 4 (a)). Once a catenane has formed, the only way in which the rings can be removed from one another is by breaking one of the rings open. One can regard the catenane as being held together by a topological bond. One of the forces used to drive the formation of such structures is the self-assembly of aromatic π-donor and π-acceptors.

Stoddart and co-workers discovered that bisparaphenylene-[34]crown-10 (BPP[34]C10) will bind a paraquat dication forming a reasonably strong 1:1 complex **1** in acetonitrile and acetone solution (Fig. 5). This complex is stabilized by hydrogen bonding between the acidic aromatic hydrogen atoms of the paraquat and the oxygen atoms of the crown ether and also by a charge transfer π-π stacking interactions from the electron rich crown ether to electron poor paraquat cation. Similarly electron poor macrocycles have been synthesized which will encapsulate electron rich guests. This type of interaction has been used to synthesize a wide range of rotaxanes and catenanes.

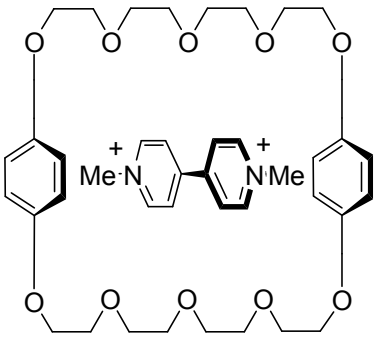


Figure 5 Paraquat-bisparaphenylene-[34] crown-10 complex

The synthesis of a [2]catenane from BPP[34]C10 and compound **2** is shown in Fig. 6. The pyridine nitrogen of compound **2** acts as a nucleophile, displacing a bromine from 1,4-bis(bromomethyl)benzene. The resultant tricationic strand **3** assembles with the crown ether present in the reaction mixture, threading through it to form a complex that is stabilized by hydrogen bonding and π-π stacking. This complex is then trapped by a ring closing intramolecular nucleophilic attack to form a [2] catenane **4** (isolated as the hexafluorophosphate salt). The crown ether may be regarded as a template around which the pyridinum box forms. This template effect is reflected in the high yield (70%) of the reaction.

Rotaxanes (from Latin: *rota* (wheel) and *axis* (axle)) are compounds of a macrocyclic component through which an axle or rod is threaded. The ends of the axle are stoppered with bulky groups that prevent the macrocycle slipping off. Therefore the individual components are permanently joined together, but are not

linked by an actual covalent bond. The nomenclature [n]rotaxane refers to the total number of non-covalently linked components present in the rotaxane. Thus a [2]rotaxane consists of one macrocycle and one axle. Strategies for rotaxane synthesis are illustrated in Fig. 7.

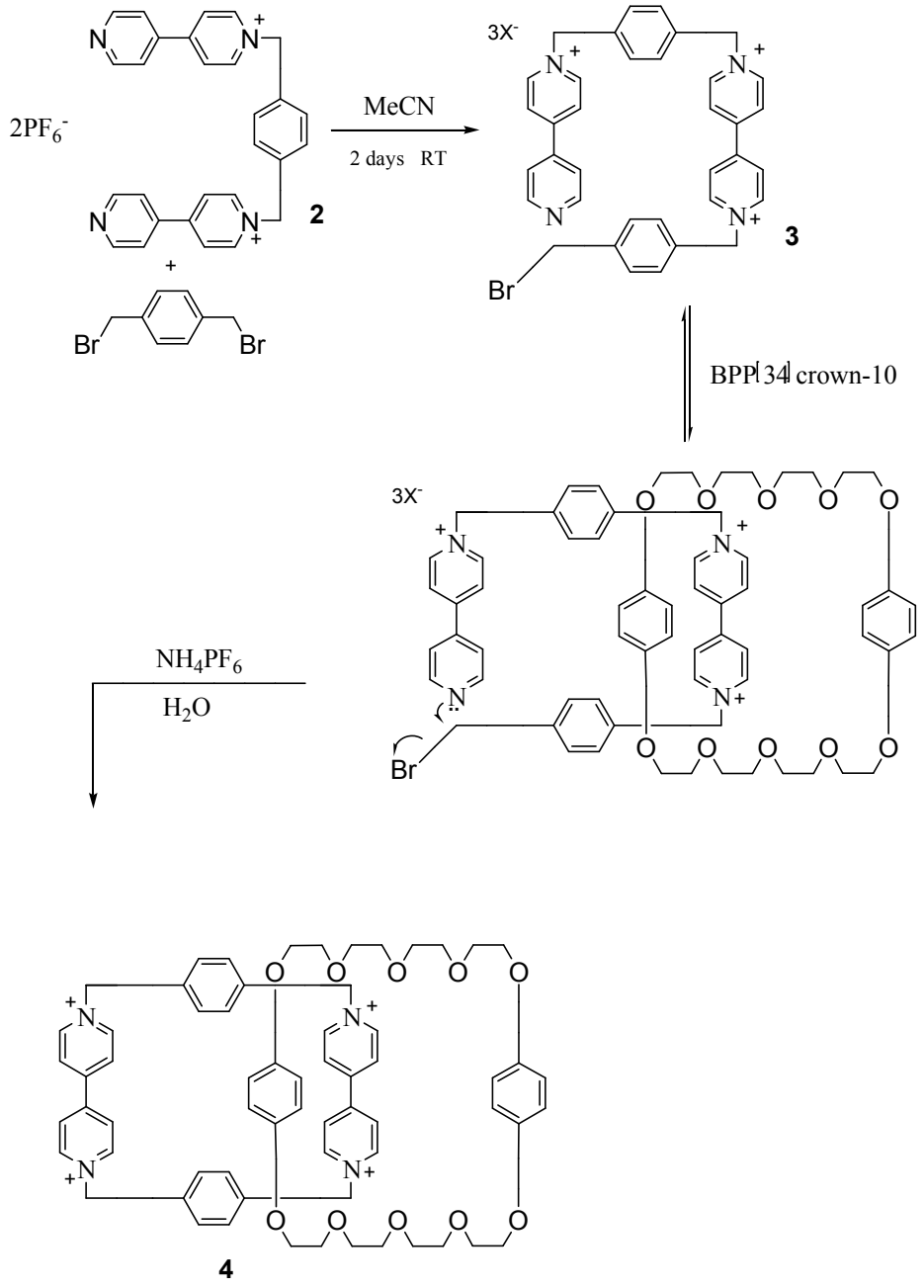


Figure 6 [2]catenane formation.

There are two main approaches: threading and clipping. Threading involves mixing self-assembling linear and macrocyclic components to form a pseudorotaxane. The ends of the linear component are then stoppered to prevent the wheel slipping of the axle, producing a [2]rotaxane. For clipping, a "pre-stoppered" linear component may be mixed with a self-assembling component which undergoes macrocyclic ring closure around the axle. Fig. 7 shows the synthesis of rotaxane **9** via both of these routes.

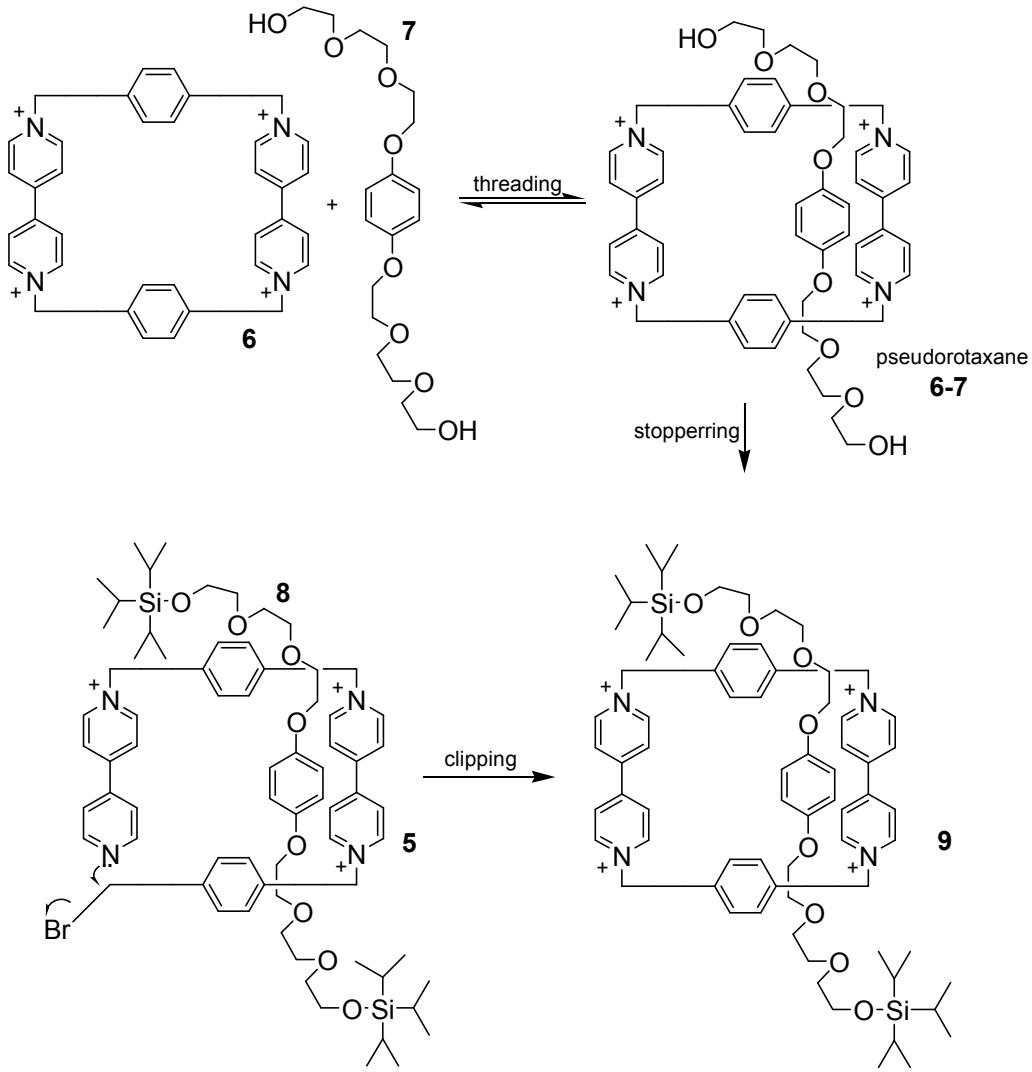


Figure 7 Synthesis of a rotaxane **9** by two different routes: threading and clipping.

A third approach to rotaxane synthesis has also been developed by Stoddart's research group. They reasoned that if the stoppers are not too large then at high

temperatures, the macrocyclic component may be able to slip over them. The rotaxane is thermodynamically stable compared to unassembled component parts due to the favorable π-donor–π-acceptor interaction and hydrogen bonding interactions.

More complicated rotaxane systems have been produced, for example [3]rotaxanes (one axle with two macrocycles). Axles containing positions (stations) for one macrocyclic component have been produced and can be considered as molecular shuttles, with the position of the macrocycle on the rod being variable and controllable [4].

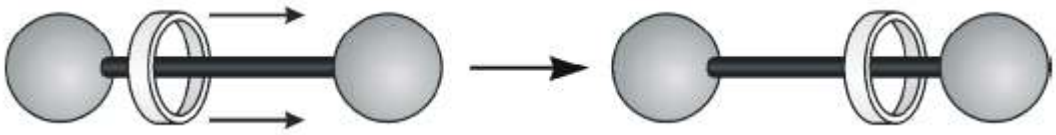


Figure 8 Shuttling motion in rotaxane.

1.2.2.2. Transition Metal Directed Assemblies

Metal directed supramolecular self-assembly is a rapidly growing field, and recent years have witnessed enormous research activity in this area [10]. The use of transition metal ions to direct molecular assembly has two major advantages. Firstly, metal-ligand dative bonds are thermodynamically strong interactions, but have varying degrees of lability (providing the supramolecular chemists with a range of kinetic stabilities). They can therefore provide stabilisation energy for a range of different structures. Secondly, due to ligand field effects, transition metal ions often have very specific geometric requirements in their coordination sphere. This gives metal ions the ability to control the geometry of molecular assembly very precisely [4].

One of the earliest examples of molecular self assembly was provided by the field of metal coordination chemistry [11]. In 1960 Curtis reported the one pot synthesis of a yellow crystalline product **10** from the reaction of $[Ni(en)_3]^{+2}$ (en= ethylenediamine) in dry acetone (Fig. 9). Although the precise mechanism of this self-assembly process is not clear, it may involve repetitive imine formation with subsequent attack

of an acetonyl carbonion on the Ni-coordinated imine; in other words, the Ni^{+2} cation acts as the template around which the macrocycle is assembled [12].

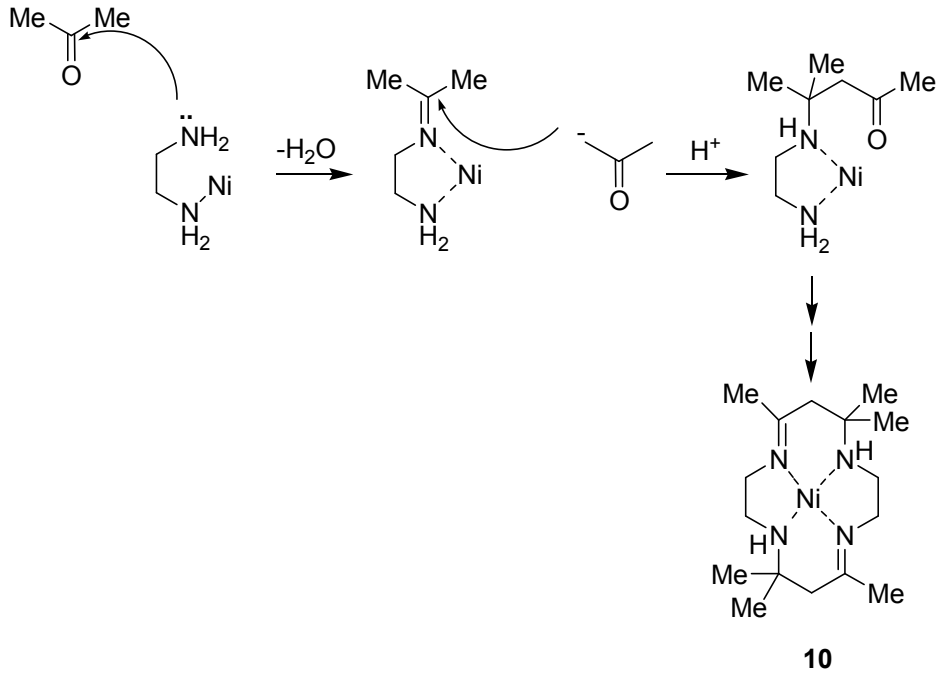


Figure 9 The self-assembly of a macrocycle around a Ni^{+2} ion.

1.2.2.2.1. Catenates and Catenands

Metal directed assembly also provides an approach to interlocked structures complementary to that described in Section 1.2.2.1.1..Sauvage and his research group have investigated the assembly properties of 2,9-disubstituted 1,10-phenathroline molecules with copper(I) ions. Fig. 10 shows the synthesis of a [2]catenate by a metal directed route starting from a 2,9 phenol-substituted 1,10-phenathroline unit. Copper(I) has a d^{10} electronic configuration and prefers a tetrahedral coordination environment. When phenanthroline **11** is mixed with 0.5 equivalents of copper (I), the two phenanthroline units are locked together forming the tetrahedral complex **12**. The subsequent nucleophilic substitution reaction with

pentaethylene glycol diidiode forms the interlocked catenate **13** in 27 % yield. This structure is called a catenate rather than a catenane because it contains a metal ion. Demetallation of the catenate is possible by addition of CN^- yielding the [2]catenand **14** [4].

1.2.2.2.2. Double and Triple Helices

The formation of the double and the triple helices presents many challenges to the supramolecular chemist. The helicates are polynuclear metal complexes of helical shape, in which two or three ligand strands wrap around a set of linearly disposed metal ions, thus forming inorganic double or triple helices, respectively [13]. The helices described in this section consist of ligands containing multiple binding sites that self-assemble around metal ions. The formation of helices is permitted in assemblies containing more than one metal ion. As will be illustrated, both the arrangement of the binding sites on the ligand and the preferred coordination geometry of the metal ion are crucial to successful helicate synthesis [4].

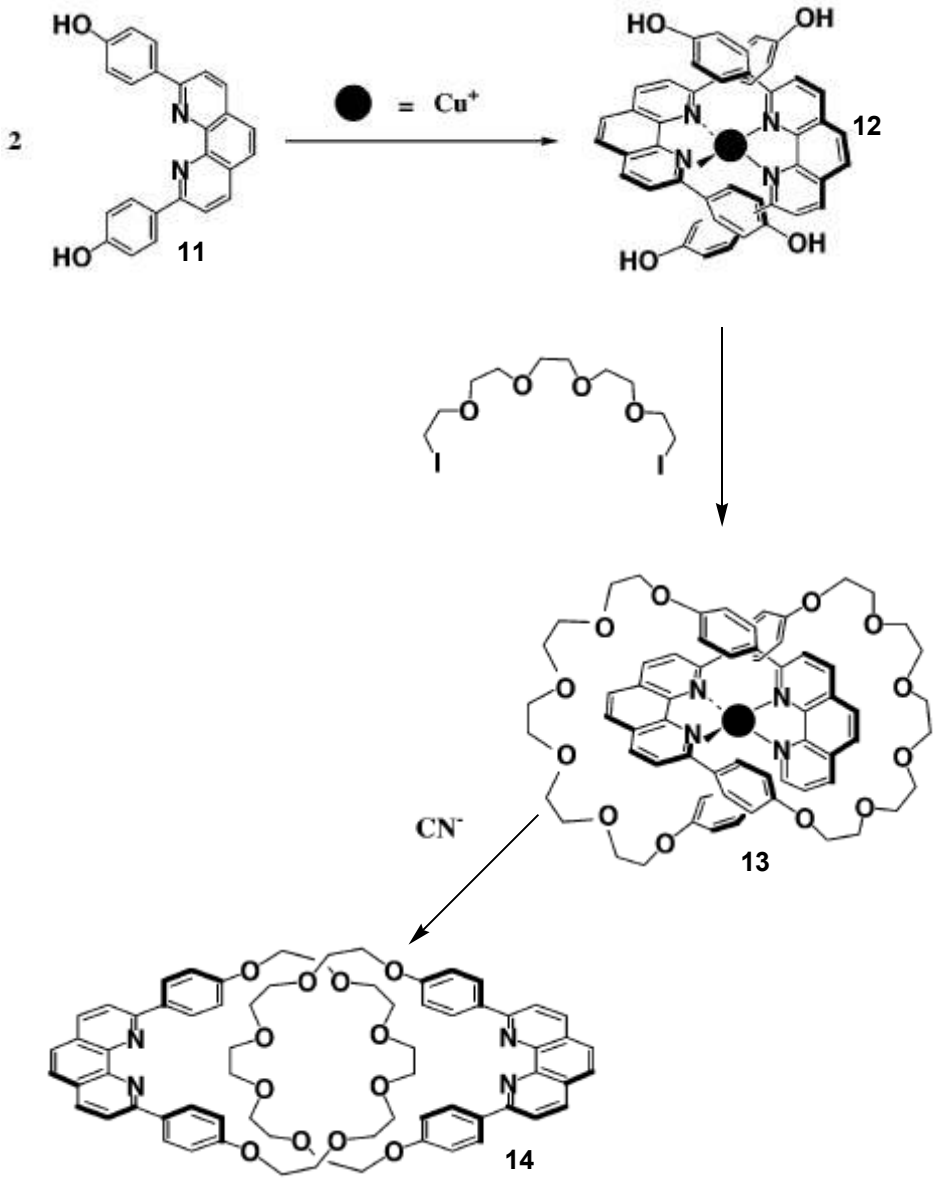


Figure 10 Preparation of the copper (I) catenane and subsequent demetallation to the catenand.

Jean-Marie Lehn's group at Strasbourg produced a series of polymetallic double helices based on poly-bipyridine ligand strands with ether linkages between each bipyridine subunit. An example containing three copper (I) ions is shown in Fig. 11. Once again copper (I) ions enforce a tetrahedral coordination geometry that causes

the assembly of the helical structure. Helicates with up to five copper ions were produced.

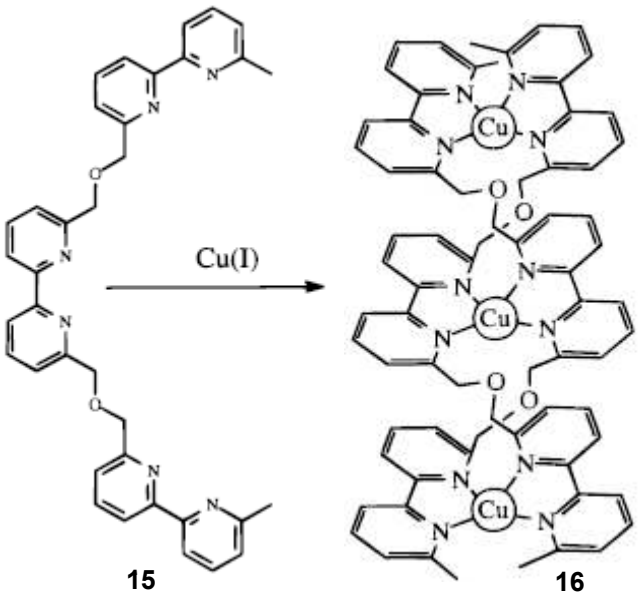


Figure 11 Self-assembly of the trinuclear double-stranded helicate.

Lehn found that if poly-bipyridine strands containing two, three, four, and five bipyridine units were mixed together then, in the presence of copper (I) ions, only helices containing two strands of the same length would form. Lehn termed this remarkable process "self-recognition".

Benzimidazole-pyridine ligands (**17**) form different types of helicate depending upon the metal ion used to template the self-assembly process. The arrangement of nitrogen atoms in **17** provides two metal binding sites, while the inflexibility of the strand forces the formation of dimetallic complexes. The addition of copper (I) ions causes the assembly of a double helical structure (**18**), with four coordinate metal ions. However, addition of cobalt (II) ions causes the assembly of a triple helicate (**19**) (because only then can the metal ions achieve their preferred six-coordinate octahedral geometries (Fig. 12)). This illustrates how metal ion coordination geometry requirements can control the structure of the assembly [4].

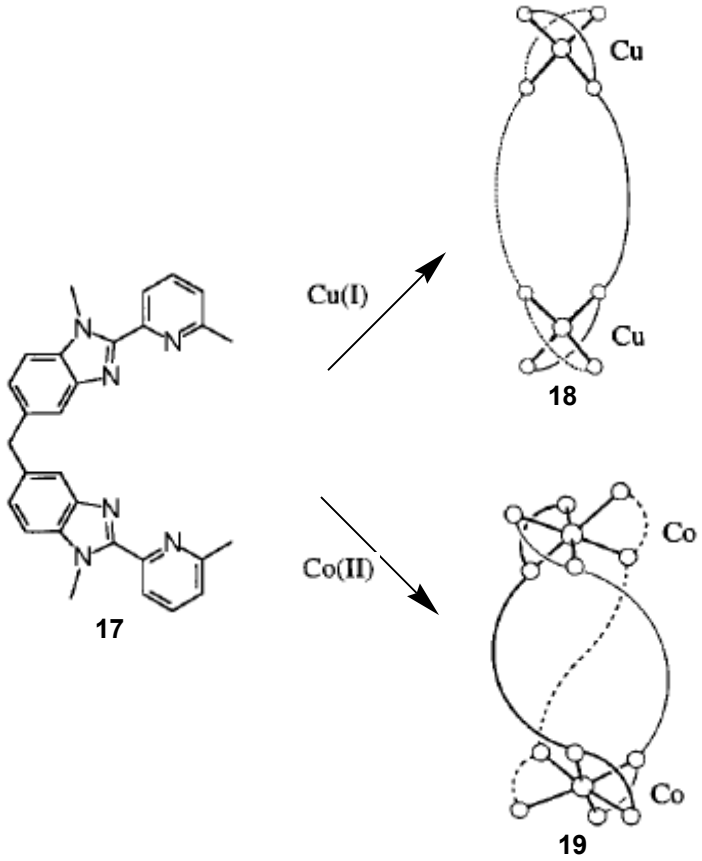


Figure 12 Self-assembly of double-stranded **18** and triple-stranded **19** helicates according to tetrahedral (Cu(I)) or octahedral (Co(II)) reading of the molecular information stored in **17**.

1.2.2.2.3. Molecular Squares and Boxes

Molecular squares are termed for discrete cyclic assemblies that possess per definition 90^{o} turns in the assembly. Because of the constraints imposed by the coordinative bonding, metallosupramolecular squares usually exhibit considerable conformational rigidity, which leads to remarkable stabilities and unique properties. It is well known that coordination bonds are relatively weak interactions which impart the features of flexibility, directionality and complementarity. The energies of coordination bonds range from 40 to 120 kJ mol^{-1} per interaction, which lie between the strong organic covalent bonds (ca. 400 kJ mol^{-1}) and other weak noncovalent interactions such as hydrogen bonding (< 40 kJ mol^{-1}). Therefore, this kind of

interaction is most suitable for sewing ligand components into well-ordered entities with appropriate stability and topology. In principle, coordination bonds can posses kinetically inert or kinetically labile metal-ligand interactions. The former types of metal bonds behave like conventional organic covalent bonds and are kinetically stable with respect to ligand displacement. However, in systems with kinetically labile metal-ligand interactions, ligands may exchange readily. So that associations through such interactions are reversible and allow facile interconversion to the favorable formation of thermodynamically most stable products [14].

For the formation of square macrocycles in high yield, the proper selection of metal corner units and bridging ligands is crucial. Since it is rather difficult to control the coordination number and direction in the self-assembly process of ligands by "naked" metal ions, the latter are not properly suited for the preparation of molecular squares in high selectivity [15]. In most cases, some of the metal ions' coordination sites are protected with strongly coordinated organic ligands whereas other coordination sites are either free or only occupied by weakly coordinating ligands, allowing a thermodynamically and kinetically feasible exchange by more strongly coordinating ligands such as aromatic aza ligands.

Transition metals with square planar coordination geometries, in which the four coordination sites are separated by about 90^{o} from the adjacent one, are most suitable as metal corner building blocks for the square formation. *Cis*-metal corner units with 90^{o} angle may be easily derived from such metal species by blocking two adjacent coordination sites with strong chelating reagents, but keeping the other two sites accessible for further coordinative interactions. Indeed, the readily available *cis*-protected Pd(II) and Pt(II) corners have proven to be versatile metal building blocks for molecular squares [14].

Fujita, Yazaki, and Ogura have reported the first square self assembly **22a** that contains *cis*-protected palladium corner (Fig. 13) [16]. The structurally predefined metal corner $[Pd(en)(NO_3)_2]$ **(21a)** provides two vacant coordination sites of a 90 degree angle, while the rigid 4,4'-bipyridine ligand **(20)** possesses two lone pairs of 180 degree divergence. These structural features of metal and ligand contribute

convergently to the formation of a square framework of assembly **22a** at room temperature in water. When $[Pd(en)(NO_3)_2]$ is treated with 4,4'-bipyridine, a cyclic tetrameric macrocycle **22a** —a molecular square— is formed as the thermodynamic product. The mechanism presumably involves stepwise displacement of the nitrate ligands by bipyridine. Notably, whilst 4,4'-bipyridine precursor is insoluble in water, square **22a** dissolves in water up to high concentration. This novel concept, pioneered by Fujita, has been abundantly applied for the construction of various metallosupramolecular squares [14].

In contrast to Pd(II) complex **21a** that produced quantitatively the square **22a** on mixing with stoichiometric amounts of the 4,4'-bipyridine ligand under ambient conditions, the treatment of the Pt(II) complex **21b** with 4,4'-bipyridine gave initially the kinetically distributed oligomeric products, which could be converted to the thermodynamically favorable square species **22b** by heating at 100 ^{o}C for more than four weeks [16]. Molecular square **22b** is more stable than **22a** under ordinary conditions due to the relative inertness of platinum-pyridine bond, which is also responsible for the required long reaction time. Accordingly, this represents a convincing example of kinetically stable macrocycles, which could be obtained in high yield under the conditions of thermodynamic control.

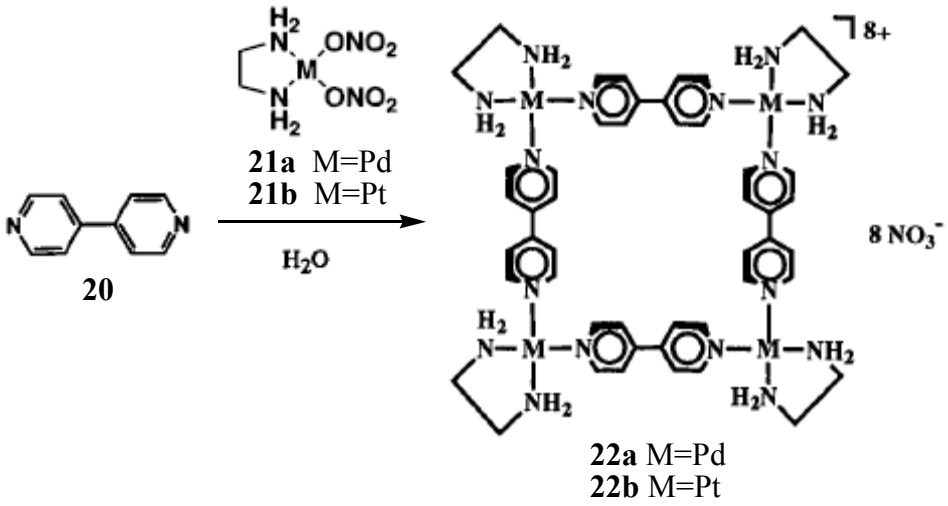


Figure 13 Tetrameric bipyridine macrocycles are formed readily through metal directed self-assembly.

Recently it was reported that the formation of square **22b** was brought to completion with 10 min simply by grounding a powdered 1:1 mixture of **21b** and 4,4'-bipyridine under ambient conditions [17]. Despite dramatic acceleration of the reaction rate in the solid state, the reaction course is identical to that of self-assembly in solution, that is, initial formation of linear oligomeric intermediates followed by conversion to square scaffold. This solid state reaction is facilitated by efficient molecular interactions through physical friction. The self-assembling process under solvent free conditions offers attractive opportunities for simplified synthesis of coordination assemblies.

An even more effective route to palladium and platinum containing molecular squares was developed by Stang *et al*. by employing metal corners with chelating bisphosphino ligands that are well-soluble in organic media [18]. Representatively, molecular squares **24a,b** were made accessible by self-assembly of 4,4'-bipyridine with the phosphine complexes **23a,b** in dichloromethane at room temperature. While Fujita's squares **22** are water soluble, metallosupramolecular squares **24** are highly soluble in various polar organic solvents, including chloroform, acetone, and nitromethane.

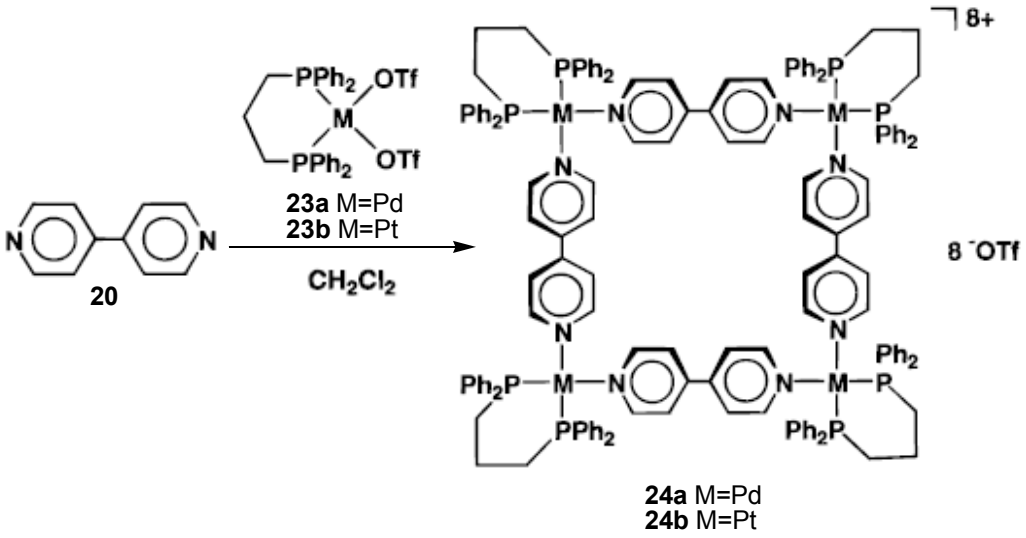


Figure 14 Phosphino metal corner-containing metallosupramolecular square constructed by Stang et al**.**

X-Ray analysis of square **24b** revealed that the high degree of π-stacking between one of the phenyl groups of the phosphine ligand and the pyridine rings imposes considerable rigidity on the corner unit and fixes the angle between the two adjacent coordination sites. These favorable interactions between the ditopic ligand and chelated bisphosphine, on the one hand, promote square formation and, on the other hand, contribute to the stability of the square. The fortunate choice of phosphine complexes as corner units by Stang's group led to distinct advancement in the area of metallosupramolecular squares. Thus, self-assembly between numerous linear and right-angle bidentate aromatic aza ligands with phosphine complexes afforded diverse metallosupramolecular squares [17].

Jeremy Sanders' group have pioneered the use of self-assembly in the synthesis of boxes containing porphyrin binding sites. A series of interesting hexagons have been formed by irreversible, directed self-assembly involving the linkage of alkyne groups between three monomers containing zincated porphyrins [19]. For example, the hexagon **27** was obtained by a copper coupling reaction in dichloromethane of the substituted porphyrin **25** in the presence of tris(4-pyridyl)triazine (**26**) (Fig. 15). In coordinating solvents or in the absence of **26**, the hexagon did not form [20]. In the presence of 4,4′-bipridine, the corresponding distorted square was instead formed. Thus, the coordination of the amines to the Zn (II) ions of the porphyrins templated the formation of the resulting motif. Once formed, these structures were also able to act as artificial receptors of guest complexes containing pyridines in a spatial arrangement suitable for the coordination of the porphyrin Zn (II) ions [21]. Other molecular squares, hexagons, octagons, and linear coordination oligomers, formed in similar ways and incorporating zincated porphyrins, have also been reported by the same researchers [19].

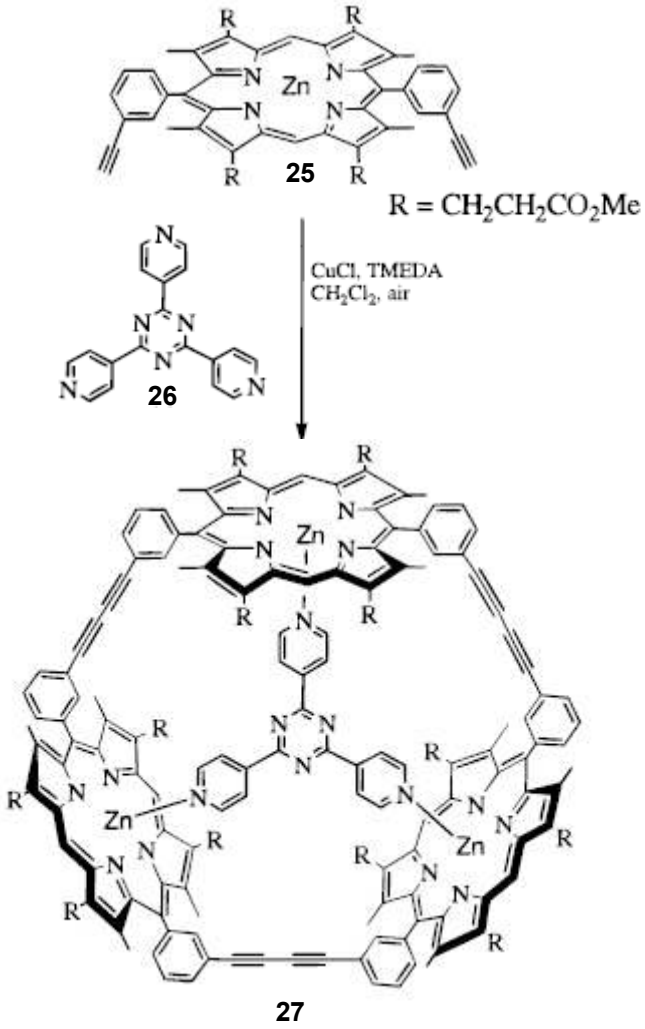


Figure 15 Tris(4-pyridyl)triazine can act as an efficient template for the formation of a macrocyclic porphyrin array.

Attractive features of molecular squares and boxes are their suitability for various functional applications. On the other hand, functionalities can be readily introduced onto metallosupramolecular squares and boxes by employing functional ligands or/and metal corners in the assembly processes. Upon square formation these functions may interact leading to a higher level of functionality. Additionally, cavities are created which may accommodate guest molecules. On the other hand, macrocycles containing transition metals are generally more sensitive and responsive on electro- and photochemical stimuli compared to metal-free organic macrocyclic molecules. Therefore, the employment of metallosupramolecular squares and boxes

may open up new opportunities to develop novel molecular switches and devices. Molecular squares and boxes have been applied in various fields of science and technology [14].

1.2.2.2.4 Racks, Ladders and Grids

Metal directed assembly allows the formation of increasingly complex molecular superstructures. A number of these structures are shown schematically in Fig. 16.

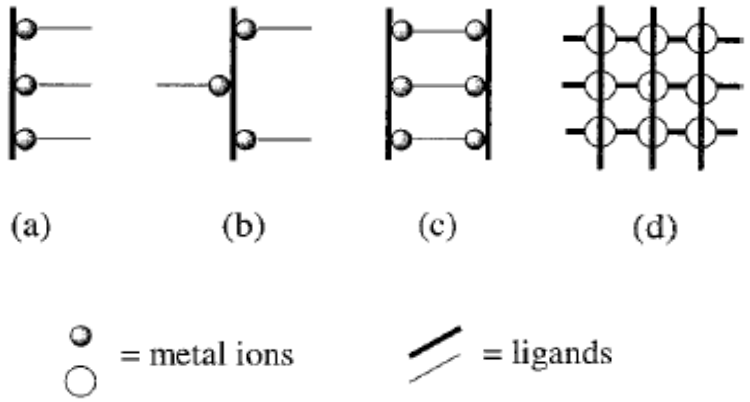


Figure 16 Racks, ladders, and grids. Schematic illustrations of (**a**) syn-rack, (**b**) trans rack, (**c**) ladder, and (**d**) grid architectures.

A rack structure (Fig. 17) is formed when the tris-bipyridine strand **28** is mixed with the 1,10-phenanthroline cown ether **29** in the presence of copper (I) ions. This rock like complex **30** is actually a pseudo-rotaxane with three macrocycles bound to the central axle via three copper (I) metal ions.

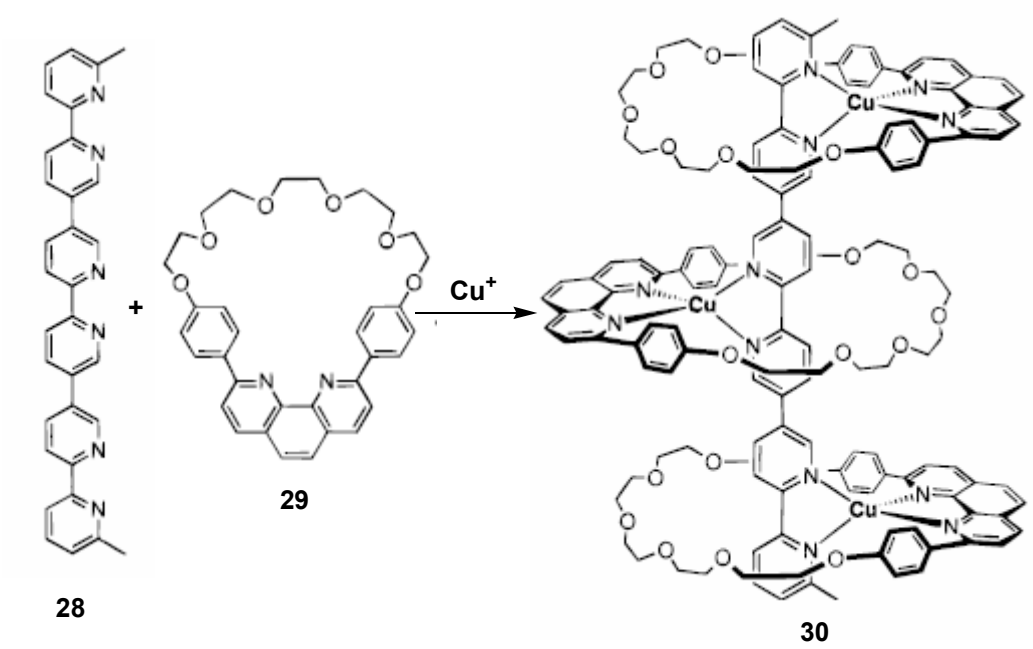


Figure 17 Metal directed assembly of a rack.

However when a bipyridine strand is mixed with six copper (I) ions and three bispyrimide units **31** a ladder forms **32** (Fig. 18).

Spectacular complexes such as 3x3 molecular grid **34** may be produced by mixing the linear ligand **33** with nine silver (I) ions (Fig. 19). Lehn has suggested that arrays of metals, such as that present in **34**, may be used in the future for information storage. One could imagine each metal ion as corresponding to a "bit" of information (for example one oxidation state could correspond to "on" another to "off"). Such arrays would allow the storage of large amount of information in very small volumes of material, however we need to find a way of addressing (reading and writing information from and to) the individual metal ions first! This type of approach to functional materials is often termed a nanoscale approach.

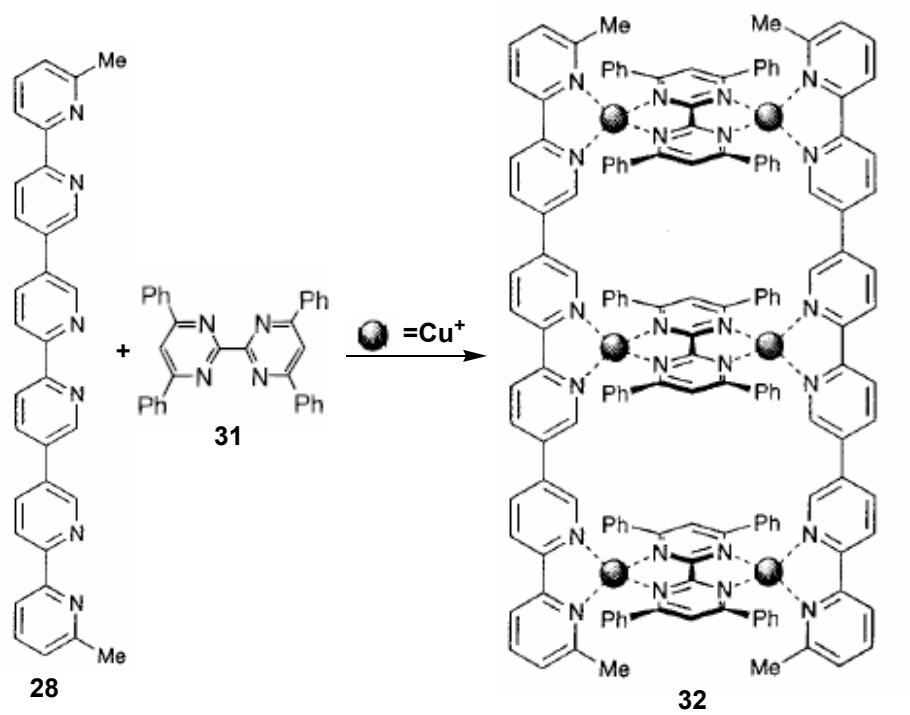


Figure 18 Metal directed assembly of a ladder.

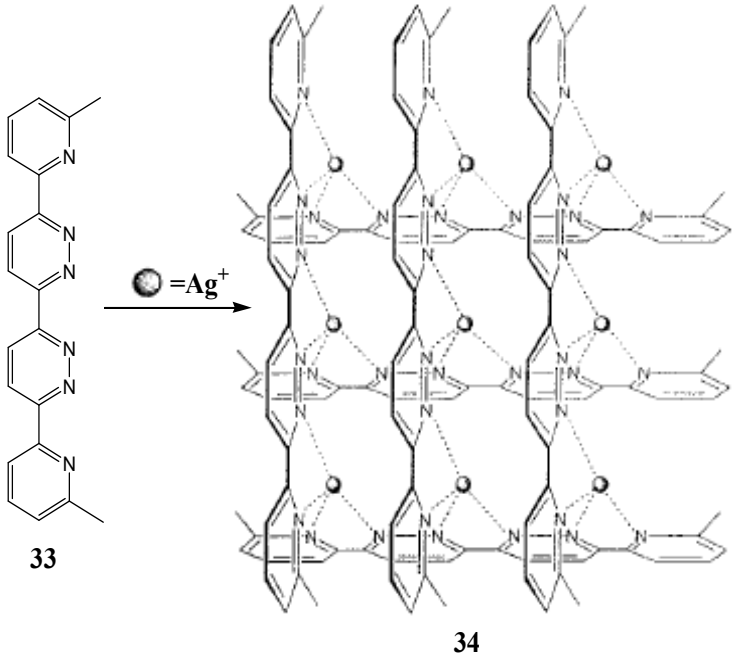


Figure 19 Metal directed assembly of a grid.

1.2.2.3. Hydrogen Bond Directed Assemblies

The highly selective and directional nature of hydrogen bond makes it ideal for use in the construction and stabilization of large noncovalently linked molecular and supramolecular architectures [9]. Indeed hydrogen bonding is key to the assembly of perhaps the most beautiful natural supramolecule, the DNA double helix (Fig. 16 and Fig.2).

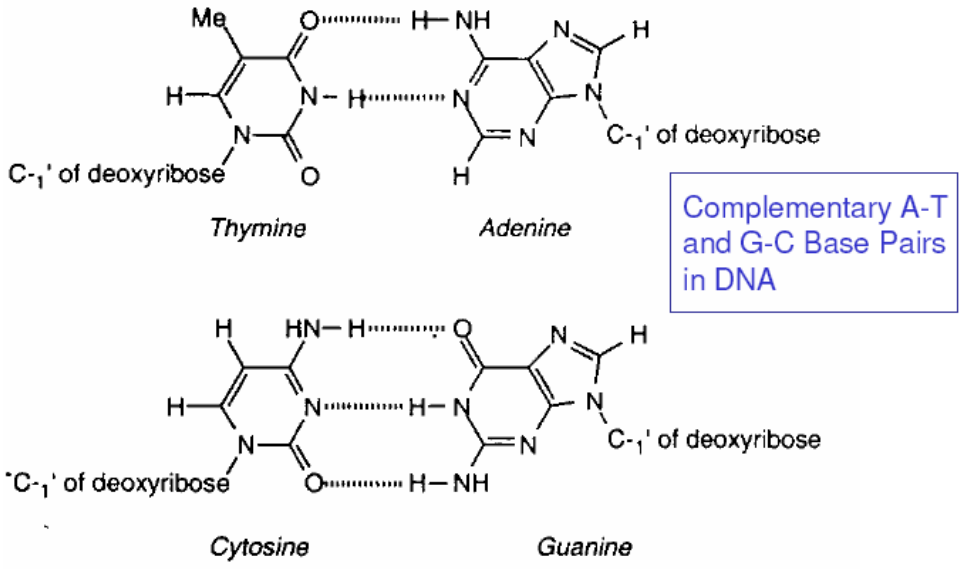


Figure 20 H-bonding in DNA.

1.2.2.3.1. Rosettes and Ribbons

Hydrogen bonds have been used to produce supramolecules incorporating melamine and cyanuric acid derivatives. Melamine **35** can be regarded as having three faces each with a donor-acceptor-donor (DAD) triad of hydrogen bonding groups. This is a complementary arrangement to that of cyanuric acid **36** which possesses an ADA triad. When these two species are mixed together in solution, an insoluble polymeric

complex with a “rosette-like” arrangement of sub-units **37** precipitates (Fig. 17). This complex is held together by multiple hydrogen bonds between adjacent heterocycles [4].

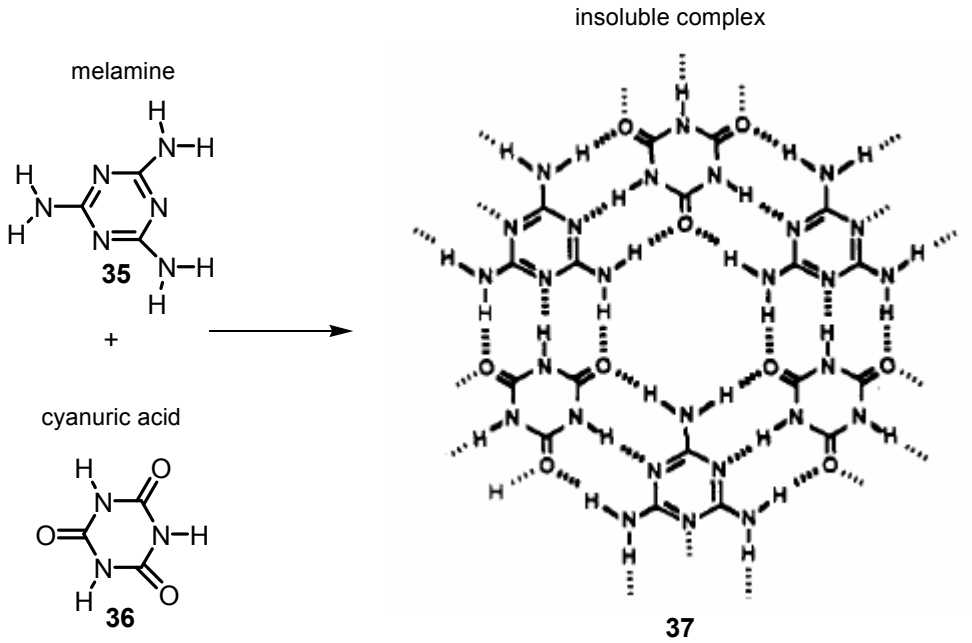


Figure 21 Formation of cyanuric acid-melamine complex.

A variation on this hydrogen bonding motif was used by Lehn and coworkers to synthesize molecular ribbons. Compound **38** is a barbituric acid derivative that is similar to compound **36** except that one of the hydrogen bonding faces of the molecule has been blocked by two alkyl groups. Compound **39** is similar to melamine except that a butyl group prevents hydrogen bonding on one face of the heterocycle. **38** and **39** produces a molecular ribbon **40** with the bulky blocking groups protruding from each side of the linear array (Fig. 18). This type of ribbon can be considered as a supramolecular polymer, with length of the aggregate dependent on the strength of the hydrogen bonding interaction [4].

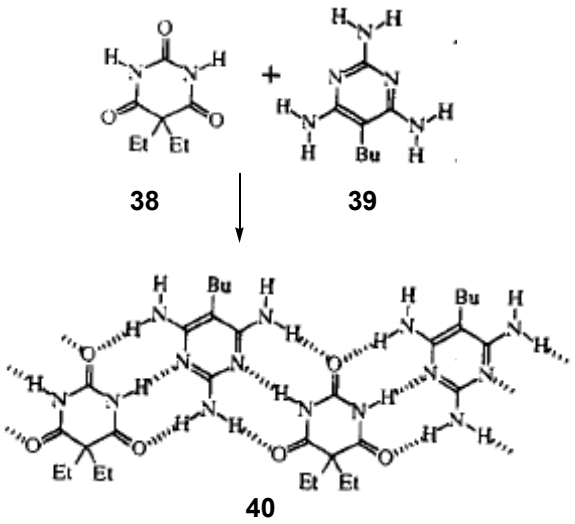


Figure 22 Formation of a molecular ribbon (supramolecular polymer).

1.3. Boradiazaindacene (BODIPY)

Boradiazaindacene dyes (aka, BODIPY, BDP, BDPY, or dipyrromethene dyes) are well-known compounds that possess highly desirable qualities as fluorophores such as high quantum yield and extinction coefficient, solubility, being amenable to structural modification, etc [22]. Interactions of fluorophores with DNA bases can be used for the specific detection of DNA or RNA sequences at the single molecule level [23,24]. BODIPY fluorophores span the complete visible spectrum, and when used in automated DNA sequencing, they offer improved spectral characteristics compared with conventional fluorescein and rhodamine dyes.

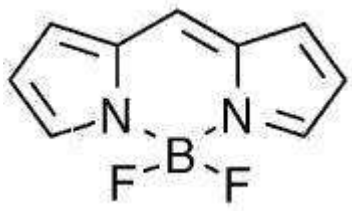


Figure 23 Structure of boradiazaindacene (BODIPY) .

1.4. Sonogashira Coupling

Reactions that form carbon-carbon bonds are of great importance in synthetic chemistry. Transition metals catalysts have developed into excellent reagents in organic synthesis to form carbon–carbon and carbon-heterocyclic bonds for simple and complex stereo controlled reactions. The Sonogashira reaction is the palladium-catalyzed cross-coupling reaction between terminal alkynes with aryl and vinyl halides in the presence of an aliphatic amine or inorganic base under mild conditions [25-27]. The proposed catalytic cycle is shown in Fig. 20 [28].

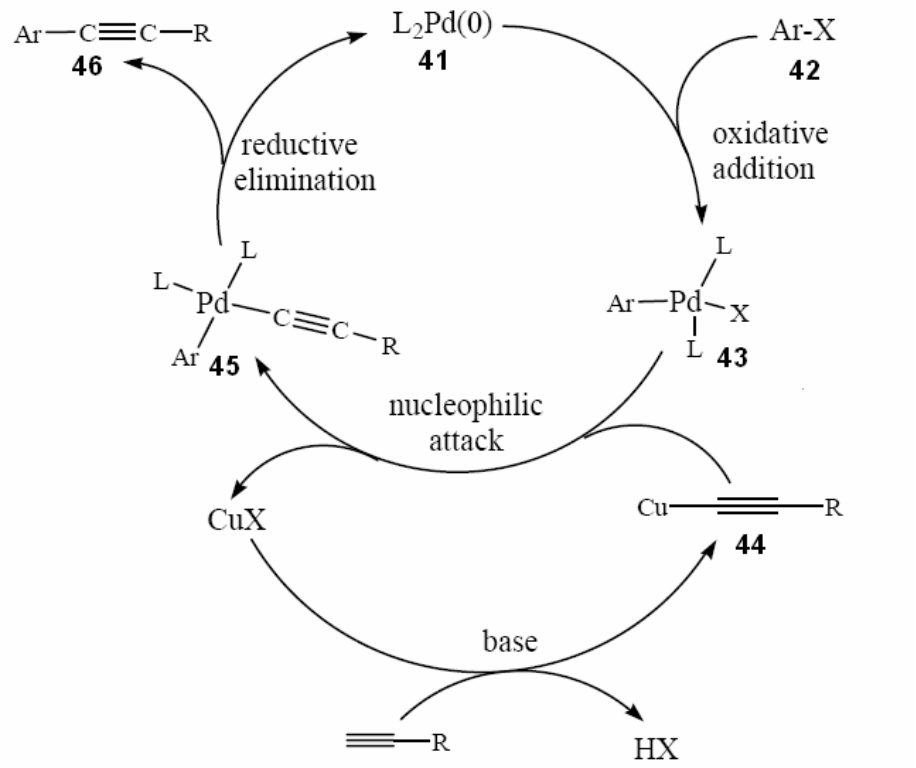


Figure 24 Catalytic cycle of the Sonogashira coupling.

CHAPTER 2

EXPERIMENTAL

2.1 Instrumentation

In this study ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Instruments Avence Series-Spectrospin DPX-400 Ultra shield (400 MHz) High Performance digital FT-NMR spectrometer (METU, NMR Laboratory). All chemical shifts are referenced to residual signals previously referenced to TMS and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (qartet), m (multiplet), p (pentet) and br (broad).

Electronic absorbtion spectra were recorded on a Varian spectrophotometer. Varian Eclipse spectrofluorometer was used for recording the fluorescence emission spectra. All instrumental parameters were controlled by Flourescence Data Manager Software (FLDM). Measurements were conducted at 25^{o}C using a 1x0.5 cm rectangular quartz cuvette.

Mass spectrometry measurements were done at the Ohio State University Mass Spectrometry and Proteomics Facility, Ohio, U.S.A., Kent Mass Spectrometry Laboratory, Kent, U.K.

Chemicals and solvents were purchased from Aldrich and used without further purification. Column chromatography of all products were performed using Merck Silica Gel 60 (particle size: 0.040-0.063 mm, 230-400 mesh ASTM) pretreated with

the eluent. Reactions were monitored by thin layer chromatography using Merck Silica Gel 60 Kieselgel F_{254} TLC Aluminum Sheets 20x20 cm.

2.2 Synthesis of 4,4-difluoro-8-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (1)

Benzoyl chloride (2.63 mmol, 369 mg) and 2,4-dimethylpyrrole (5.25 mmol, 500 mg) were refluxed for 3 h in CH_2Cl_2. The reaction was monitored by TLC (eluent $CHCl_3$), after 3h, Et_3N (3 ml) and $BF_3.OEt_2$ (3 ml) were added. Immediately after the addition of $BF_3.OEt_2$ bright yellowish fluorescence was observed. Crude product washed three times with water, dried over Na_2SO_4 and concentrated *in vacuo*. Then crude product was purified by silica gel column chromatography (eluent: $CHCl_3$). The orange fraction which has bright yellow fluorescence was collected [29]. Orange solid (320 mg , 19 %)

^{1}H NMR (CDCl3) :δ (ppm) 1.31 (s, 6H), 2.50 (s, 6H), 5.92 (s, 2H), 7.15-7.25 (m, 2H), 7,35-7,45 (m, 3H).

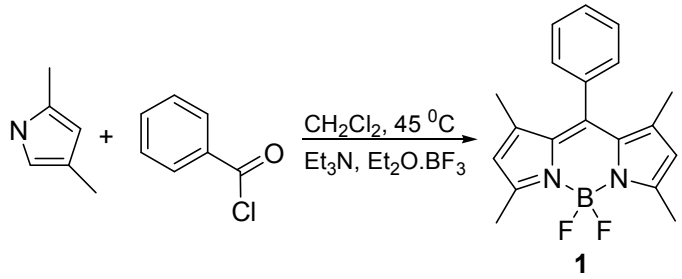


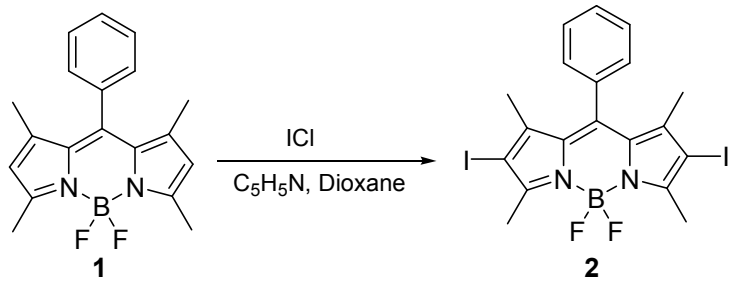
Figure 25 Synthesis of BODIPY derivative **1**.

2.3 Synthesis of 4,4-difluoro-2,6-diiodo-8-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (2)

4,4-difluoro-8-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene **(1)** (0.62 mmol, 200 mg) in 4 ml pyridine at 0 ^oC was treated with ICl (1.24 mmol, 200 mg) in 5 ml dioxane and kept 60 hours. The solvent was removed *in vacuo* . After dissolving the crde product in CH_2Cl_2 it was washed three times with $NaHSO_3$ solution and then

with water. The residue dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography (eluent 2 Hexane: 1 $CHCl_3$). The red fraction which has bright red fluorescence was collected. Red solid (214 mg , 60 %)

^{1}H NMR ($CDCl_3$) :δ (ppm) 1.31 (s, 6H), 2.58 (s, 6H), 7.16-7.21 (m, 3H), 7,40-7,50 (m, 2H).



1 **2**

Figure 26 Synthesis of diiodo-BODIPY derivative **2**.

2.4 Synthesis of 2,6-bis[4-pyridylethynyl]-4,4-difluoro-8-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (3)

A mixture of 4,4-difluoro-2,6-diiodo-8-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene **(2)** (0.35 mmol, 200 mg), [$Pd(PPh_3)_4$] (0.02 mmol, 20 mg), and 4-ethnylpyridine hydochloride (1.05 mmol, 147 mg) was stirred at 60 ^oC under argon for overnight. The mixture was diluted with EtOAc (100 ml), washed with water, dried over Na_2SO_4 and evaporated to yield crude product. This was purified via silica gel chromatography (eluent EtOAc) to afford 120 mg of **3.** Yield 65 % [30].

^{1}H NMR ($CDCl_3$) :δ (ppm) 1.47 (s, 6H), 2.66 (s, 6H), 7.18-7.63 (m, 9H), 8.46-8.55 (m, 4H).

^{13}C NMR ($CDCl_3$) :δ (ppm) 13.5, 13.7, 87.2, 94.1, 125.3, 127.7, 128.4, 128.5, 129.5, 129.7, 131.9, 132.1, 132.2, 149.1

ESI-MS (m/z); 527.2217 [M+H], calc. 527.2219 [M+H] (Figure 32).

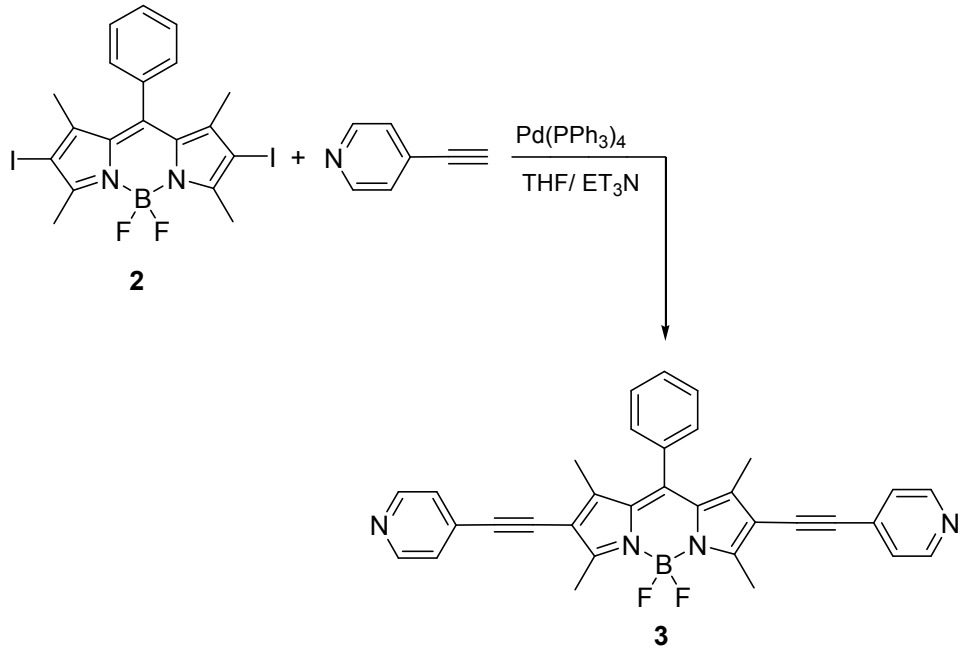


Figure 27 Synthesis of bis-pyridylethynyl-BODIPY derivative **3**.

2.5 Synthesis of [1,3-Bis(diphenylphosphino)propane]dichloropalladium(II) (4)

Anhydrous palladium(II) chloride (1.14 mmol, 200 mg) and dppp (1.14 mmol, 471 mg) were heated under reflux in $CHCl_3$ (40 ml) for 3 h. The product was precipitated from the hot solution on addition of n-hexane. The product remained solvated with both chloroform and hexane, even after prolonged heating *in vacuo* [31].

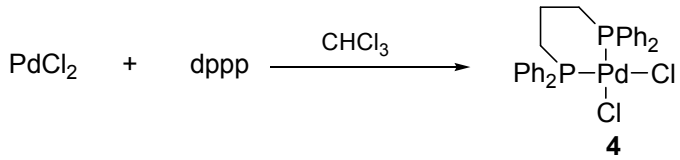


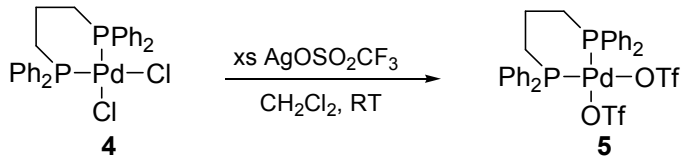
Figure 28 Synthesis of [$PdCl_2$ (dppp)] (**4**).

2.6 Synthesis of Pd bis(triflate) complex (5)

AgOTf (8.46 mmol, 2.17 g) is added to a solution of $PdCl_2$(dppp) **(4)** (1.05 mmol, 620 mg) in CH_2Cl_2 (60 ml). The reaction mixture was stirrred at 25 ^oC for 12 h. The

heterogeneous mixture was filtered and concentrated to 10 ml under reduced pressure. After addition of diethyl ether precipitate of halogen-exchanged metal triflate complex was formed. Collection and drying under vacuum gave 800 mg (93%) of yellow powder **(5)** [32].

^{1}H NMR ($CDCl_3$) :δ (ppm) 2.26-2.34 (m, 2H), 2.66-2.75 (m, 4H) 7.40-7.60 (m, 20H).



4 **5**

Figure 29 Synthesis of [Pd(OTf)$_2$(dppp)] (**5**).

2.7 Synthesis of molecular square (6)

To a solution of Pd bis(triflate) complex **(5)** (0.19 mmol, 155 mg) in CH_2Cl_2 (70 ml) was added bis-pyridylethynyl bodipy (0.19mmol, 100mg) to give an immediate precipitation of light-brown solid. The resulting heterogeneous reaction mixture was alowed to stir for 1 hour at room temperature. The reaction mixture is then collected and washed with diethyl ether to give 918 mg (90%) of **6** [32].
^{1}H NMR (DMSO-d_6): δ (ppm) 1.38-1.53 (br s, 24H), 1.85-2.12 (br, 16H), 2.54-2.63 (m, 24H), 2.85-3.19 (br 16H), 7.29-7.79 (br m, 116 H), 8.58-8.75 (br m, 16H).

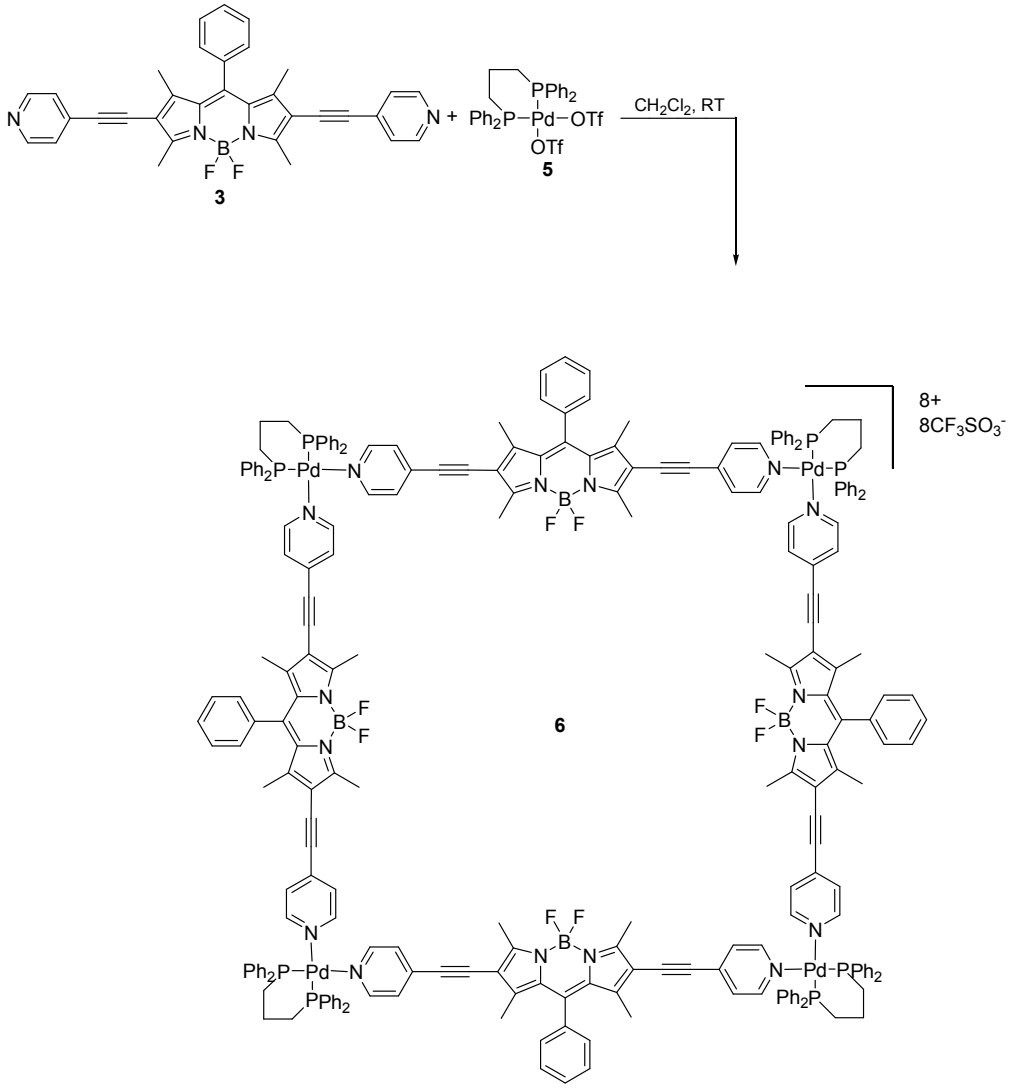


Figure 30 Synthesis of molecular square **(6)**.

CHAPTER 3

RESULTS AND DISCUSSION

There is no doubt that self-assembly can be used to construct a wide range of structural forms with obvious ease. Use of metals and dative bonding coordination is a very different approach for the formation of supramoecular species via spontaneous self-assembly of precursor building blocks. Metal-ligand bonds can be strong, lending stability to a structure, yet kinetically labile, allowing reorganization to occur. Another advantage is that this bond is directional which helps us to design a wide diversity of structural types. Molecular squares are one of the important structural forms which we can get with the usage of metal-ligand interactions. Formation of a molecular square requires two types of building blocks: linear units of two-fold symmetry, which contain reactive sites with a 180° orientation relative to each other and angular units, containing 90^{o} turn and possessing reactive sites with other desirable angles. The proper selection of metal corner units (angular units) and bridging ligands (linear units) is very crucial for the formation of square macrocycles in high yield. It is very difficult to control the coordination number and direction in the self-assembly process of ligands with "naked" metal ions. Thus it is better to protect some of the coordination sites of the metal ions with strongly coordinated organic ligands whereas other coordination sites are either free or only occupied by weakly coordinating ligands. By this way thermodynamically and kinetically feasible exchange by more strongly coordinating ligands becomes possible.

To synthesize, characterize and functionalize a flourescent molecular square with boradiazaindacene (BODIPY) building blocks was our aim in this study. The angular unit chosen in our study is a *cis*-protected Pd (bis)triflate complex. This complex has a square planar shape. Two of the coordination sites are protected with bisphosphino ligands which are strongly coordinated to Pd metal. Other two coordination sites are occupied by weakly coordinating triflate ions. This allows exchange of these triflate

ligands by more strongly coordinating bridging ligands during the formation of molecular square. The bridging ligand chosen in our study was a bis-pridyl-ethynyl-BODIPY derivative. In this bridging ligand lone pairs on the nitrogen atom can coordinate to Pd metal more strongly than the triflate ions do. As a result of this, by metal assisted self-assembly two types of building blocks could assemble together to form the molecular square we designed.

3.1 Synthesis of Molecular Square (6)

Reaction path way starts with the synthesis of standard boradiazaindacene dye **1.** Electrophilic aromatic iodination at 2 and 6 positions using ICl results in a red fluorescent dye **2** with 60% yield. Sonogashira coupling of 2,6-diiodo-BODIPY with 4-ethynyl pyridine in the presence of a palladium catalyst results, following purification using silica gel column chromatography, the desired derivative **3** in 65 % yield. Fluorescence lost in previous step was regained with synthesis of BODIPY dye **3.** Compound **3** serves as the ligand part in self-assembled formation of molecular square. This ligand possesses two lone pairs of 180 degree divergence. The presence of an ethynyl unit is important to relieve any potential steric problem that might hinder the formation of a molecular square. The structurally predefined metal corner $[Pd(OTf)_2(dppp)]$ **(5)** provides two vacant coordination sites of 90 degree angle. These structural features of metal and ligand contribute convergently to the formation of the square framework assembly **6** (with 90 % yield) at room temperature in dichloromethane.

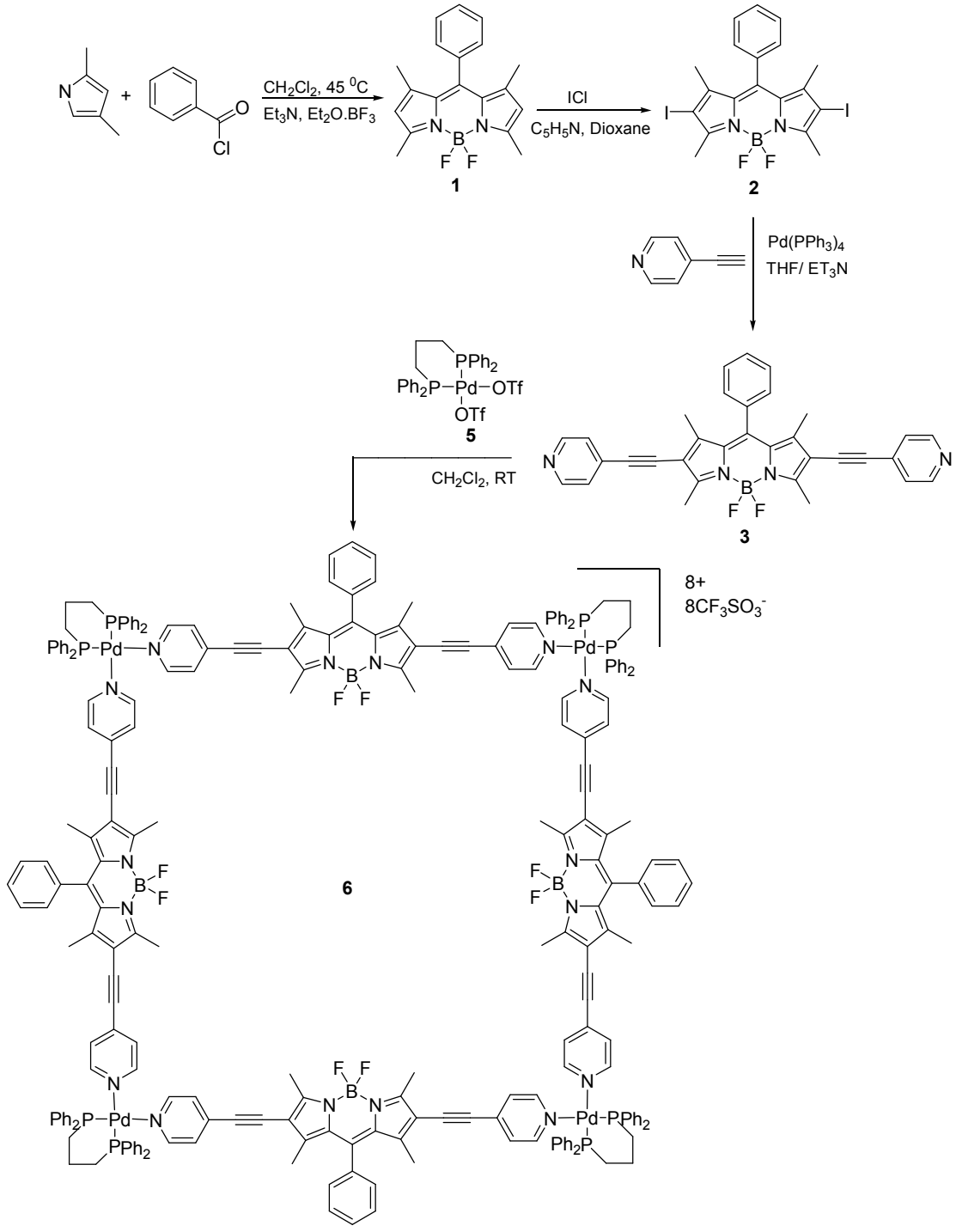


Figure 31 Reaction series for the synthesis of molecular square **(6)**.

The self-assembly of the molecular square **6** was achieved via the interaction of four bidentate angular units **(5)** with four linear components **(3)**. In this interaction weakly coordinated triflate ions in metal corner are exchanged with the more strongly coordinated lone pairs of the nitrogen atom in compund **3.** This is why the resultant product **(6)** is thermodynamically most stable product (Fig. 31).

The reversibility of metal-ligand coordination plays a pivotal role in the formation of metallosupramolecular squares in high yields by avoiding other macrocyclic or polymeric by-products. Based on rapid chemical exchanges among starting materials, intermediates (*e.g.* oligomers and polymers) and final ensembles during the coordinative assembling processes, the composition of the final products depends primarily on the thermodynamic parameters of the possible products and intermediates. Such exchange provides an efficient mechanism for error correction, which may result in the conversion of the thermodynamically unfavorable intermediates into a single final product.

3.2 Characterization of BODPY Dye (3) and Molecular Square (6)

The BODIPY dye **(3)** and molecular square **(6)** were characterized by spectral means as detailed in Experimental Section. Absorption, emission, ^{1}H and ^{13}C NMR spectra agree with the structures but most useful piece of evidence for the structure will be the mass spectrometry data. Figure 32, Figure 33, Figure 34 and Figure 36 illustrate the ESI-MS results for BODIPY dye **(3)**. The signal observed at *m/z* 527.2217 can be assigned to the M+H species in excellent agreement with the calculated mass of compound **3** (Fig. 32). The structure and stability of coordination squares are critically dependent on various factors such as ligand itself, metal ions, solvent, concentration, temperature and even counterions. Molecular squares are very fragile on ionizing conditions. The molecular square we synthesized is also not stable enuogh to make a proper characterization by ESI-MS technique. One of the mass spectrometry result is shown in Figure 36. There is a +2 charged peak at *m/z* 1031.3 which may be assigned to a large fragment which corresponds to a molecular mass of 2062.6.

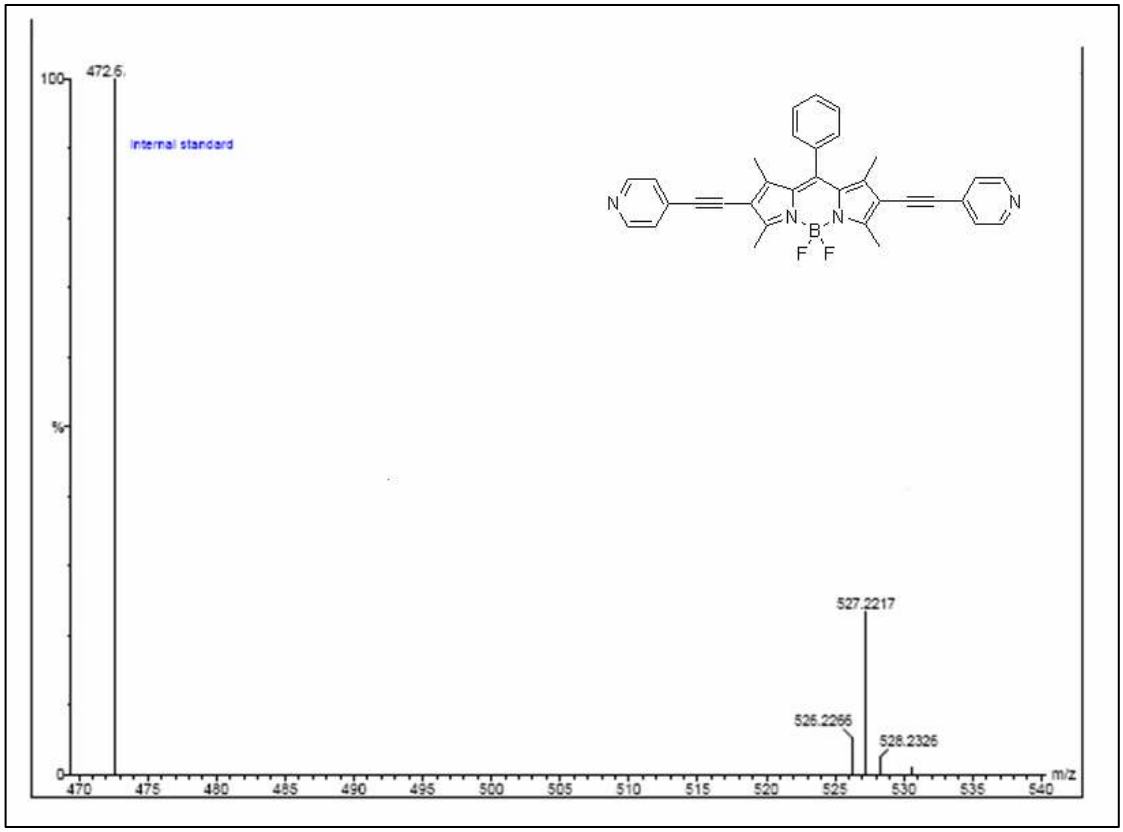


Figure 32 ESI-MS spectrum of compound **3**.

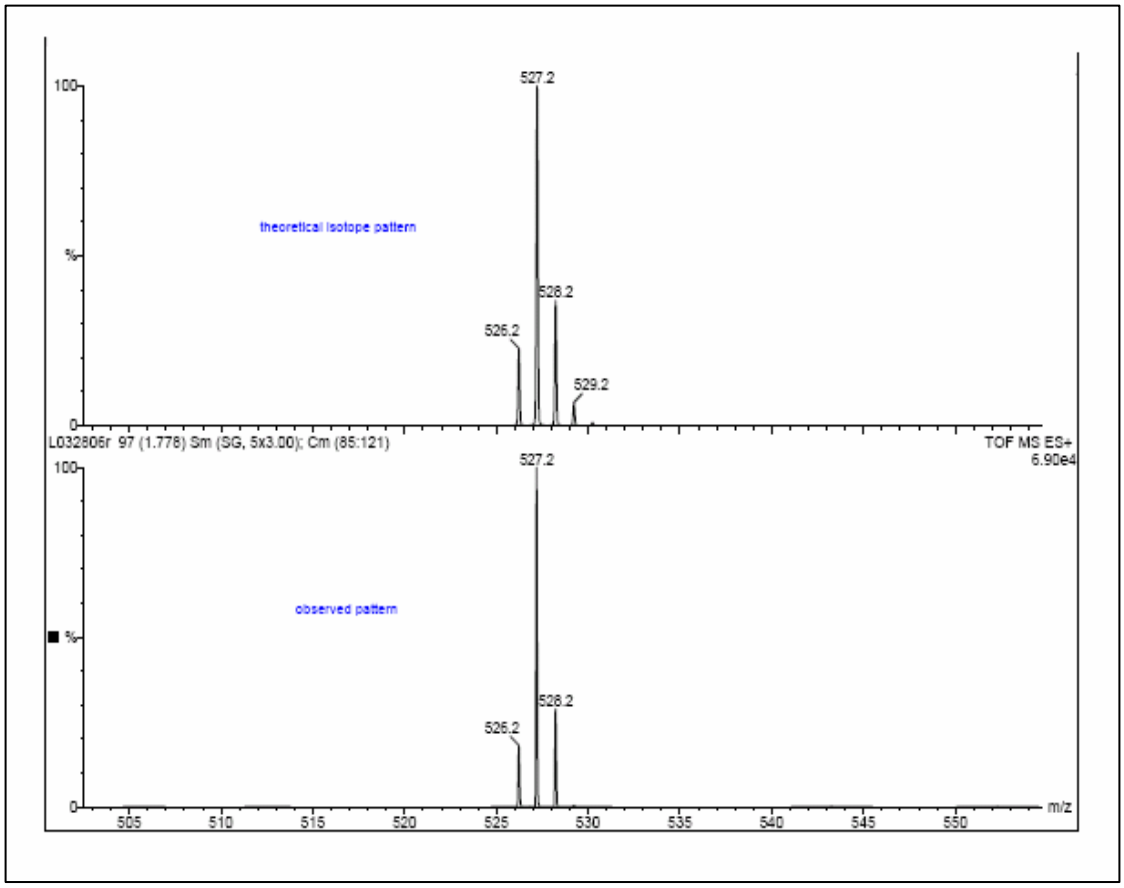


Figure 33 ESI-MS spectrum of compound **3**.

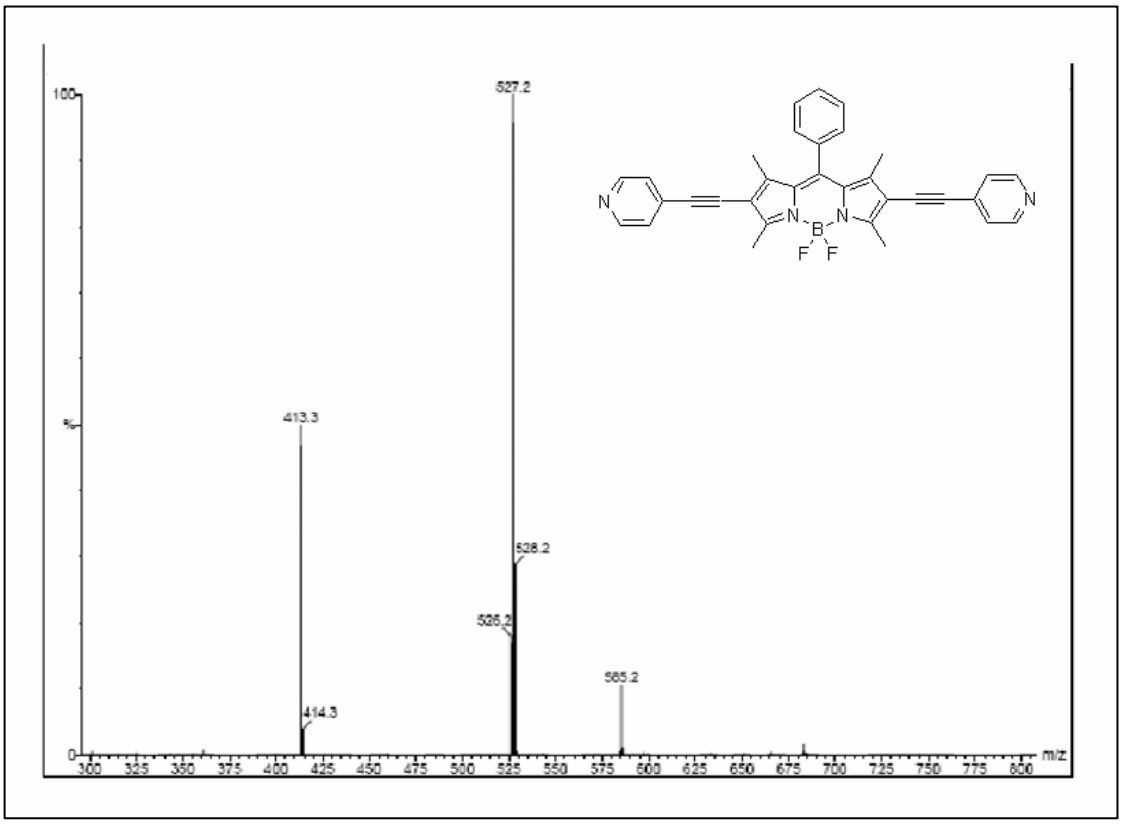


Figure 34 ESI-MS spectrum of compound **3**.

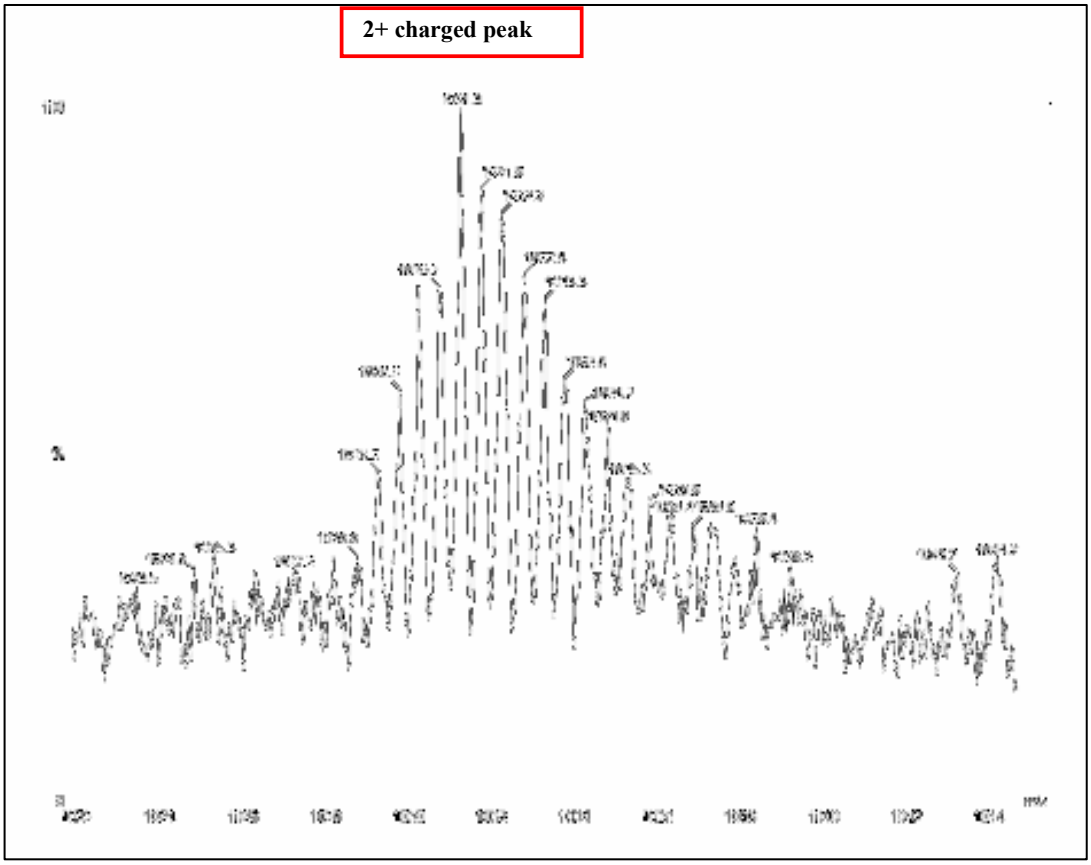


Figure 35 ESI-MS spectrum of compound **6**.

3.2.1 Photophysical Properties of BODPY Dye (3) and Molecular Square (6)

The BODIPY dye **3** was synthesized in 65 % yield by Sonogashira Coupling of diiodo BODIPY dye **2** with 4-ethnylpyridine. The fluorescence of the dye is restored at this step. After mixing BODIPY dye **3** with Pd bis(triflate) complex **(5)** molecular square **(6)** was formed and we observed no change in fluorescence. Spectrophotometric studies of the molecular square **(6)** have given us the same results with the BODIPY dye **3**. Figure 37 illustrates the emission spectra for BODIPY dye **3** (it is linear unit so it is also called as edge) and molecular square **(6)**.

It can be easily seen that the emission graph of the molecular square is very similar to that of the dye (ligand). The absorbance spectra of these compounds are shown in Figure 38. The absorbance graph of the molecular square has very similarities with the absorbance graph of the dye. As a result it can be said that the optical properties of the BODIPY ligand **3** remain almost unchanged upon formation of the molecular square **6.**

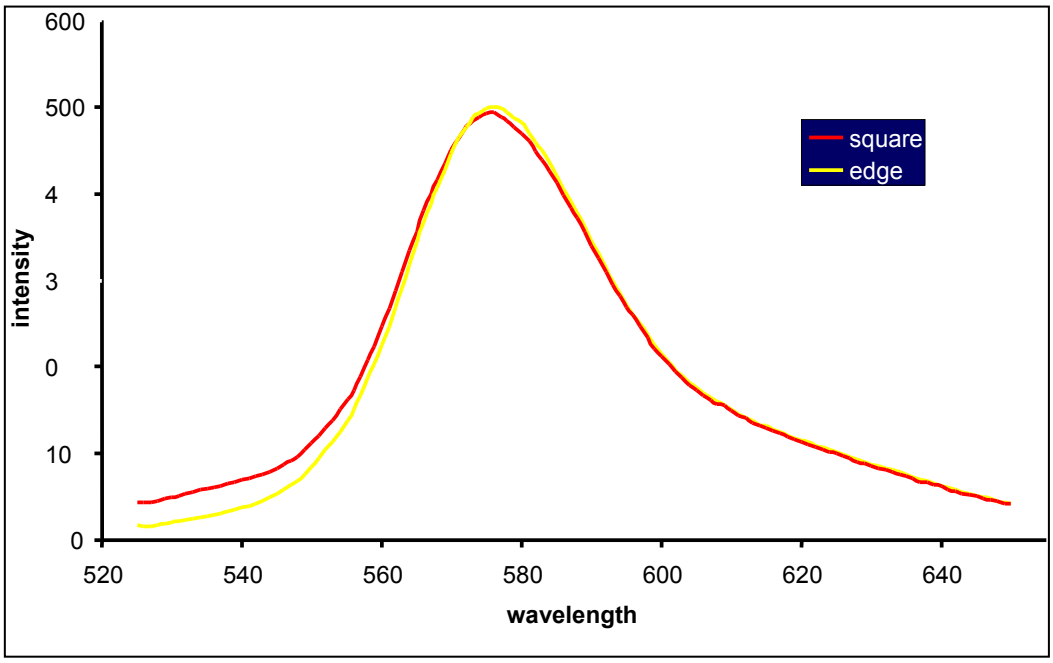


Figure 36 Emission spectra of BODIPY dye **3** (edge) and molecular square (**6**) (square).

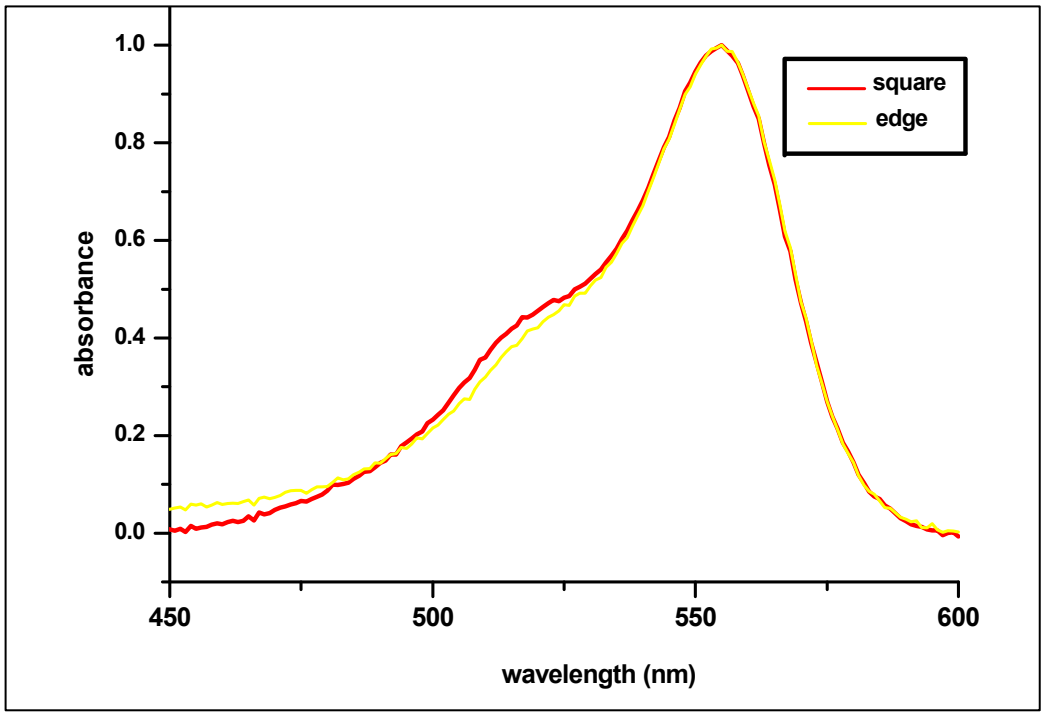


Figure 37 Absorbance spectra of BODIPY dye **3** (edge) and molecular square (**6**) (square).

3.3 Future Work

As a future work, we plan to functionalize the molecular square to obtain a light harvesting system. This will be carried out by introducing one dimethyl amino styrl group to one of the edges of the molecular square. After one of the edges is functionalized it will have different photophysical properties than the other three edges such as having longer wavelength absorbtion and emission. In this case excitation of the three edges (L_1) may follow energy transfer to the edge L_2.

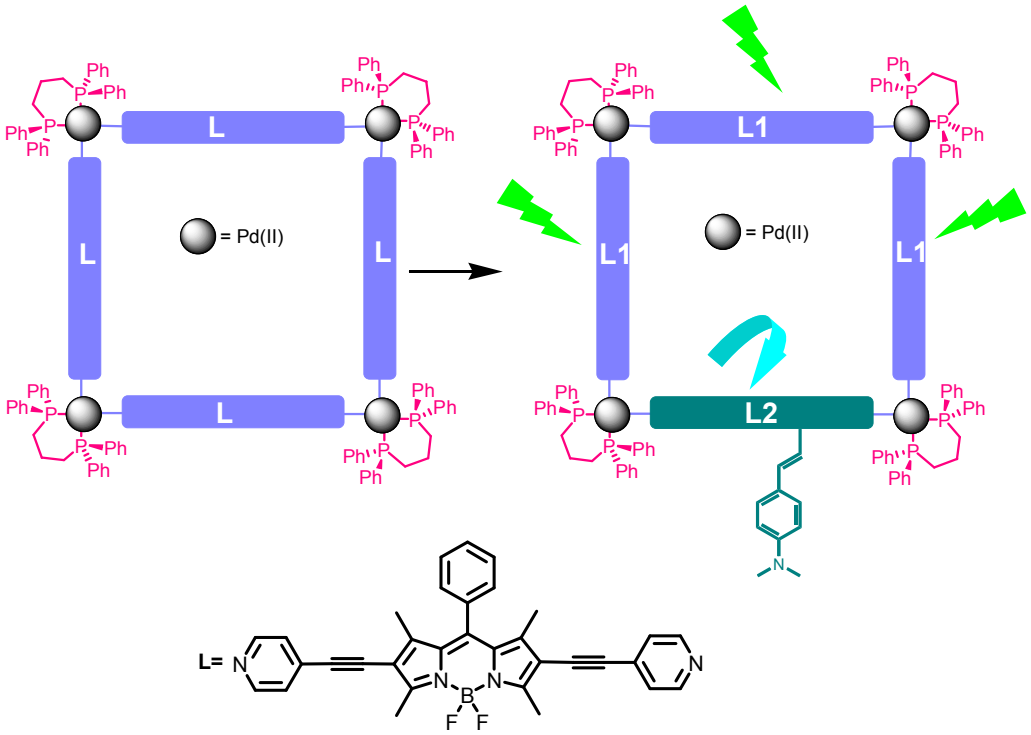


Figure 38 Functionalization of molecular square (**6**) to obtain a light harvesting system.

CHAPTER 4

CONCLUSION

Self-assembly is one of the hottest fields of research in supramolecular chemistry. Nature makes use of self-assembly in large number of biological systems, structural and functional. In natural systems hydrogen-bonding and shape complementarity (London dispersion) play a very important part. Metal-ligand interactions, with their highly predictable nature are the dominant kind of interactions found in synthetic supramolecular systems.

Square-planar cis-complexes of Pt(II) and Pd(II) have proved themselves to be very useful in the synthesis of the so-called "molecular-squares". Earliest examples based on diphosphino-platinum(II) and palladium(II) complexes linked together at 90^{o} angle were reported by Fujita and Stang. Crystallographic studies, clearly established "square-like" geometry of the tetrametallic complexes as predicted. The next goal is to obtain "functional" molecular squares, boxes, rectangles etc. This "function" could be catalysis, binding and/or signaling the presence of a particular analyte.

To that end, fluorescent molecular squares have to be synthesized. One potential problem, is the likely quenching of fluorescence in close proximity to multi-oxidation state "open-shell" metal ion, once the molecular square structure is assembled. Recently there has been a report of a perylenediimide bis-pyridinyl derivative which retains its florescence characteristics in molecular square structure. We targeted the use of bis-pyridylethynyl-BODIPY derivatives as fluorescent modules, because BODIPY is not only a well-known fluorophore with high quantum yields and extinction coefficients, but as it was recently demonstrated in our group and by Rurack, Ziessel, Boens, BODIPY fluorophore is amenable to further

functionalized in many ways to modify its photophysical properties including emission wavelength, quantum yield, and solvent sensitivity. Thus, we targeted the molecular square **6**. Considering the fact that the thermodynamically favored product is the tetrameric square complex, we concluded that the material we isolated was indeed the molecular square **6**. It has been reported that mass spectrometry including ESI only provides circumvential evidence to the (structure) Pd(II) based molecular squares. The Pd(II) squares are apparently too unstable to yield M^+ or $(M - 4OTf)^{+4}$ peaks. ESI mass spectrometry of **6** shows only one multiply charged species which corresponds to a mass of 2062.6 amu. Absorbtion spectrum of the molecular square clearly shows the presence of the BODIPY dye. Excitation near absorbtion λ_{max} (550 nm) results in a sharp emission band at 580 nm. Compared to compound **3**, fluorescence spectrum is not significantly altered.

Thus, we have demonstrated that appropriate modification of boradiazaindacene dyes could transform them into binucleating ligands which can be used for the construction of molecular squares, which retain important fluorescence characteristics of the boradiazaindacene dyes. Exploiting rich chemistry of boradiazaindacenes it is very likely that molecular devices based on BODIPY units would emerge work to that end is in progress.

REFERENCES

[1] Lehn, J.M., *Angew. Chem., Int. Ed. Eng*., **1988**, *27*, 89-112.

[2] Lehn, J.M., Supramolecular Chemistry and self-assembly special feature: Towards complex matter: Supramolecular chemistry and self-organization. Proc. Natl. Acad. Sci. U. S. A. **2002**, 99, 4763-4768.

[3] Atwood, J.L, Steed, J.W., Encyclopedia of Supramolecular Chemistry, Marcel Dekker, Inc., New York, **2003**, 1401-1411.

[4] Beer, P., Gale, P., Smith, D., Supramolecular Chemistry, Oxford University Press Inc., New York, **1998**, 61-81.

[5] (a) Feltwell, J., The Story of Silk. Sutton, Phoenix Mill, UK, **1990**. (b) Winkler, S., Szela, S., Avtges, P., Valluzzi, R., Kirschner, D. A., Kaplan, D., *Int. J. Biol. Macromol.* **1999**, *24*, 265-270.

[6] Schnur, J. M., *Science*, **1993,** *262*, 1669-1676.

[7] Kazmaier, P., Chopra, N., *Mrs Bulletin*, **2000**, 30-35.

[8] (a) Corey, E. J., Cheng, X.M., The Logic of Chemical Synthesis, Wiley, New York **1989**. (b) Corey, E. J., *Angew. Chem*., **1991**, *103*, 469; *Angew. Chem., Int. Ed. Eng.*, **1991**, *30*, 455. (c) Nicolau, K.C., Sorensen, E.J., Classics in Total Synthesis, VCH, Weinheim, **1996.**

[9] Philp, D., Stoddart, J.F., *Angew. Chem., Int. Ed. Eng*., **1996**, *35*, 1154-1196.

[10] Radhakrishnan, U., Schweiger, M., Stang, P.J., *Org. Lett*., **2001**, *3,* 3141-3143.

[11] (a) Curtis, N.F., *J. Chem. Soc*., **1960**, 4409. (b) Curtis, N.F., House, D.H., *Chem. Ind*. **1961**, 1708. (c) Curtis, N.F., Curtis, Y.M., Powell, H.K. *J. Chem. Soc. A*, **1996**, 1015.

[12] Hay, R.W., Lawrance, G.A., Curtis, N.F., *J. Chem. Soc. Dalton Trans*. **1975**, 591.

[13] Hasenknopf, B., Lehn, J.M., Boumediene, N., Dupont-Gervais, A., Dorsselaer, A.V., Kneisel, B., Fenske, D., *J. Am. Chem. Soc*., **1997,** *119*, 10956-10962.

[14] Würthner, F., You, C.-C., Saha-Möller., C.R., *Chem. Soc. Rew.*, **2004**, *33*, 133-146.

[15] Gianneschi, N.C., Mirkin, C.A., Zakharov, L.N., Rheingold, A.L., *Inorg. Chem*., **2002**, *41*, 5326-5328.

[16] (a) Fujita, M., Yazaki, J., Ogura, K., *J. Am. Chem. Soc*., **1990**, *112*, 5645-5647. (b) Fujita, M., Yazaki, J., Ogura, K., *Chem. Lett*., **1991**, 1031-1032.

[17] Orita, A., Jiang, L., Nakano, T., Ma, N., Otera, *J., Chem. Commun*., **2002**, 1361-1362.

[18] Stang, P.J., Olenyuk, B., *Acc. Chem. Res*., **1997**, *30*, 502-518.

[19] Swiegers, G.F., Malefetse, T.J., *Chem. Rev.* **2000,** *100*, 3483-3537.

[20] Anderson, H.L., Sanders, J.K. M., *Angew. Chem., Int. Ed. Engl*. **1990**, *29*, 1400.

[21] Mackay, L.G., Anderson,H.L., Sanders, J.K. M., *J. Chem. Soc., Perkin Trans. 1*, **1995**, 2269.

[22] Turfan, B., Akkaya, E.U., *Org. Lett*., **2002**, *4*, 2857-2859.

[23] Knemeyer, J.P., Marme´, N., Sauer, M., **2000**, *Anal. Chem*., *72,* 3717-3724.

[24] Piestert, O., Barsch, H., Buschmann, V., Heinlein, T., Knemeyer, J. P., Weston, K. D., and Sauer, M., **2003** *Nano Lett*. *3*, 979-982.

[25] Sonagashira, K., Tohda, Y., Hagihara, N., *Tetrahedron Lett*., **1975**, *17*, 4467-4470.

[26] Rossi, R., Carpita, A., Belina, F., *Org. Prep., Proc. Int*., **1995**, *27*, 129-160.

[27] Negishi, E., Anastasia, L., *Chem. Rev*., **2003**, *103*, 1979-2017.

[28] Yin, L., Synthesis of new calcineurin inhibitors via Pd-catalyzed cross-coupling reactions, Doctor of Philosophy Thesis in Chemistry, Humboldt-Universität zu Berlin, **2005**.

[29] Coskun, A., Akkaya, E.U., *J. Am. Chem. Soc*., **2005**, *127*, 10464-10465.

[30] Wan, C.-W., Burghart, A., Chen, J., Bergström, F., Johansson, L.B.-A., Wolford, M.F., Kim, T.G., Topp, M.R., Hochstrasser, R.M., Burgess, K., *Chem. Eur. J*. **2003**, *9*, 4430- 4441.

[31] Appleton, T.G., Bennett, M.A., Tomkins, I.B., *J. Chem. Soc. D*, **1976**, *439*.

[32] Stang, P.J., Cao, D.H., Saito, S., Arif, A.M., *J. Am. Chem. Soc.*, **1995**, *117*, 6273-6278.