DESIGN AND SYNTHESIS OF NEW SUPRAMOLECULAR BUILDING BLOCKS BASED ON OLIGO-BODIPY DYES

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

BY

BORA BİLGİÇ

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

FEBRUARY 2008

Approval of the thesis

DESIGN AND SYNTHESIS OF NEW SUPRAMOLECULAR BUILDING BLOCKS BASED ON OLIGO-BODIPY DYES

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ABSTRACT

DESIGN AND SYNTHESIS OF NEW SUPRAMOLECULAR BUILDING BLOCKS BASED ON OLIGO-BODIPY DYES

Bilgiç, Bora

M.S., Department of Chemistry

Supervisor: Prof. Dr. Engin Umut Akkaya

February 2008, 54 pages

We have designed and synthesized a fluorescent, self-assembled molecular square containing a highly fluorescent well known flurophore boradiazaindacene (BODIPY) dye. Pt(II) complexes were used to hold together BODIPY derivatives and give the right angle to form the square structure. Usage of BODIPY fluorophore is very important on such structures because its variety of superior properties. BODIPY is a well studied fluorophore in our group and it is known that this self assembled square can be easily modified to any area of use it is needed.

Keywords: BODIPY, Self-Assembly, Supramolecular Building Blocks, Metal Coordination

ÖZ

OLIGO-BODIPY İÇEREN YENİ SÜPRAMOLEKÜLER YAPI TAŞLARININ TASARIM VE SENTEZİ

Bilgiç, Bora

Yüksek Lisans, Kimya Bölümü

Tez Yöneticisi: Prof. Dr. Engin Umut Akkaya

Şubat 2008, 54 sayfa

Floresan boradiazaindasen (BODIPY) içeren ve kendiliğinden biraraya gelen moleküler kare tasarlanıp sentezlendi. BODIPY türevlerini birarada ve uygun açıyla tutmak için Pt(II) kompleksleri kullanıldı. BODIPY nin bu tarz yapılarda kullanılmasındaki önemi benzerleri arasında sahip olduğu üstün özelliklerinden kaynaklanmaktadır. BODIPY laboratuvarımızda çok yönlü çalışılmış ve iyi bilinen bir florofordur ve bu sebeple sentezlenen kendiliğinden biraraya geln moleküler kare kullanım alanına gore kolaylıkla modifiye edilebilir

Anahtar Kelimeler: BODIPY, Kendiliğinden biraraya gelme, Süpramoleküler yapı taşları, Metal Koordinasyonu

Dedicated to my family and my grandmother . . .

ACKNOWLEDGEMENTS

I would like to express my profound gratitude to my advisor, Prof. Dr. Engin U. Akkaya ,for his guidance, support and patience during the course of this research as well as his unique imagination and great experience that I have benefited from. I wish to express my sincere appreciation to Ö. Altan BOZDEMİR and Serdar ATILGAN, Ali COŞKUN for their support and guidance to improve my skills in the field of supramolecular chemistry during my study at Middle East Technical University.

I am obliged to each and every member of Supramolecular Chemistry Laboratory for the great atmosphere in the laboratory and for being easy targets at CS:). They (of course including Kadir!) had a very hard job to remain as the smartest group of all.

I was extraordinarily fortunate in having such a wonderful mother, Gülay ASLAN and a brother, Mustafa BİLGİÇ. I could never have succeeded all of this without their support.

Words fail me to express my appreciation to my lovely fiancée Oya ERTUNÇ whose dedication, love and persistent confidence in me, has taken the load off my shoulder. I would also thank her family for accepting me as a member of the family, warmly.

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INTRODUCTION

1.1. What is Supramolecular Chemistry?

The term supramolecular chemistry refers to the branch of chemistry where intermolecular forces are used to hold the components together reversibly. Chemists working in this area can be thought of as architects combining individual covalently bonded molecular building blocks, designed to be held together by intermolecular forces, in order to create functional architectures [1].

Jean-Marie Lehn introduced the modern concept of chemistry, which he defined as the "...chemistry of molecular assemblies and of the intermolecular bond", in 1987, 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. Supramolecular chemistry, originated from Paul Ehrlich's receptor idea, Alfred Werner's coordination chemistry and Emil Ficher's lock-and-key image, may be defined as "chemistry beyond the molecule". Its development requires the use of all resources of molecular chemistry combined with the desired manipulation of noncovalent interactions [2].

It's the biological systems that provide inspiration and organic and inorganic chemistry allows the artificial synthesis of the inspired systems. The role of the

physical chemistry is to fully understand their properties and a degree of technical expertise can lead to functioning devices ready for application to the real world. The breadth and especially the unifying power of the concept became progressively more and more apparent, so that recent years have seen an explosive growth as measured by the increasing number of laboratories that join the field and whose work has been reported in a vast range of publications, books, journals, meetings and symposia. Supramolecular chemistry has thus developed into a coherent and extremely lively body of concepts and objects, progressively generating and incorporating novel areas of investigation [1].

1.1.1. Molecular Recognition

Molecular recognition can be defined as the specific interaction between two or more molecules through noncovalent bonding such as hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π stacking, and/or electrostatic effects. In biological systems molecular recognition is observed in many cases like between receptor-ligand, antigen-antibody, DNA-protein, sugar-lectin, RNA-ribosome.

Molecular recognition covers geometrical and interactional complementarity between the interacting partners; optimal information content of a receptor with respect to associating partners, optimal information content of receptor with respect to a given substrate. This idea was first described by Emil Fischer in 1894. The name ‘lock and key’ was used to describe this complementarity. Every lock can only be opened by a specific key. The juts on the key should be in a perfect allignment with the dents on the lock. This rule is also valid for molecular recognition.

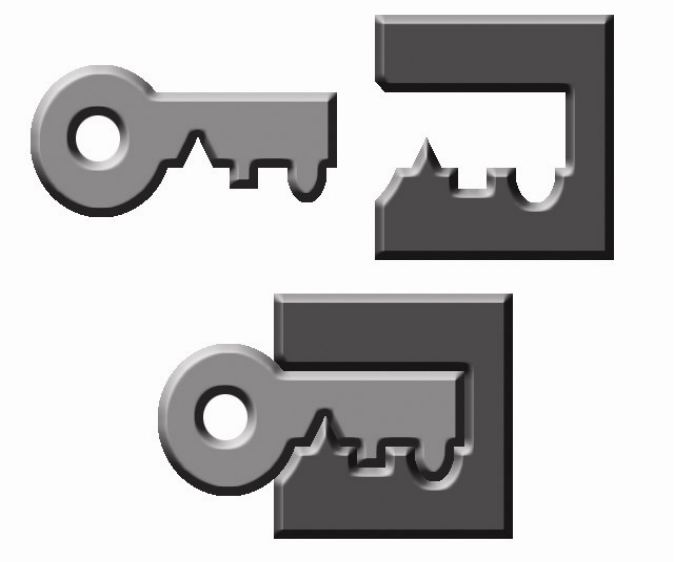


Figure 1. Lock and Key Model

The arrangement of binding sites in the host (lock) is complementary to the guest (key) both sterically and electronically.

Having a control on these types of recognitions also develops the abilities of scientists on livings. The aim of the chemists working on this area is to learn about the main idea behind the molecular recognition in living systems and to develop artificial systems. Up to now chemists demonstrated many artificial examples of molecular recognition systems. One of the earliest examples of such a system are crown ethers which are capable of selectively binding specific cations.

This type of recognition can be either a static recognition or dynamic recognition. Static recognition is most likely the lock and key example. Key molecule interacts with the suitable site on the lock molecule and forms a complex molecule. There may be one or more connecting sites ready for the key molecules on the lock molecule.

In dynamic recognition the interacting molecules are not stay in perfect geometrical conformation and should be rearranged before the partners interact. The binding of the first guest to a the first binding site of a host (Figure 2, a). affects the association constant of a second guest with a second binding site (Figure 2, b).

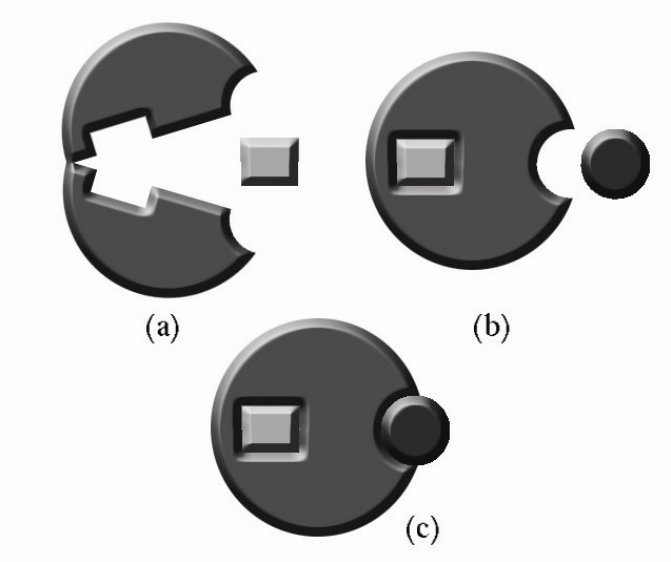


Figure 2. Dynamic Recognition

1.1.2. Intermolecular Interactions

The bond energies of typical single covalent bonds range between 350 $kJmol^{-1}$ and 942 $kJmol^{-1}$ for the very stable triple bond in N_2. The strengths of many of the non-covalent interactions used by supramolecular chemists are generally much weaker ranging from 2 $kJmol^{-1}$ for dispersion force, through to 20 $kJmol^{-1}$ for a hydrogen

bond to 250 kJ/mol for ion-ion interaction. Supramolecular chemistry uses the combination of these interactions to get stable, rigid structures.

Ion-Ion Interactions

The logic behind the ion ion interactions is the attraction between the opposite charges. Ionic bonding is comparable in strength to covalent bonding (bond energy = 100 - 350 $kJmol^{-1}$). When two oppositely-charged particles flying in a vacuum come closer they will be attracted toward each other, and the force becomes stronger and stronger as they approach until eventually they will stick together and a considerable amount of energy will be required to separate them.

Ion – Dipole & Dipole-Dipole Interactions

The charge separation on polar molecules give the molecule enough charge to get into an attraction with an ion or another polar molecule. This attraction is also a strong one but not as strong as an ion-ion interaction.

Hydrogen Bonding

Hydrogen bonding is a special case of dipole-dipole interactions, which has a certain amount of covalent character and directionality. It is valid in a relatively short range about 2.5-3.5 Å. The energy of the bond (12-30 kJ/mol) can be significantly stronger then typical dipole-dipole interaction. It forms when a hydrogen atom is positioned between two electronegative atoms, i.e. O, N, F (but not C). Arrays of hydrogen bonds, such as those employed in biological systems (i.e. the DNA double helix), have been utilized in receptors designed to coordinate neutral organic species such as barbiturates, short chain alcohols and amides, and also anions [5].

π –π Stacking

π-π stacking interactions occur between systems containing aromatic rings. The attractive interactions may be an ''edge to face'' interaction as well as a ''face-to-face'' interaction. Those attractions are relatively weak attractions (0 – 50 kJ/mol).

Some very elegant receptors have been synthesized employing π-π interactions including a receptor for benzoquinone [6].

van der Waals (Dispersion and Induction) Forces

van der Waals type Interactions exists between almost all atoms and molecules. van der Waals type interactions are the interactions between the fluctuating induced dipoles due to instantaneous and short-lived vibrational distortions. During these distortions molecule acts as a dipole instantaneously and the poles of the molecules interacts with the charges around them and this phenomena exist between all atoms and molecules. The energy between the interacting molecules is very weak (0.1-3 kJ/mol). This is what drives molecules to eliminate spaces or vacuums and makes it difficult to engineer porous or hollow structures.

Hydrophobic Interactions

The hydrophobic effect is the specific driving force for the association of apolar binding partners in aqueous solution. Water molecules around the apolar surfaces of a hydrophobic cavity arrange themselves to form a structured array. With guest complexation water molecules are released and become disordered. This result in a favourable increase in entropy. In addition, there is believed to be an enthalpic component to the hydrophobic effect. Receptors containing hydrophobic interior cavities designed to encapsulate organic guest molecules in aqueous solution include the cyclophanes and cyclodextrins.

1.2. Studies On Supramolecular Chemistry

1.2.1. Chemosensors

In supramolecular concept, recognition sites can be coupled to certain groups that are capable of "reporting" the coordination of target molecule. Molecular receptors that are specifically designed for sensing purposes are generally called chemosensors. A

receptor may be used as a sensor if it can report the presence of the guest by some physical means. Sensor should ideally be selective for a particular guest and not only report the presence of the guest molecule, but should also allow the chemist to monitor its concentration. This is important medically (for monitoring indicators of physical function) and enviromentally (monitoring pollutant levels)[7].

Optical sensors uses the fluorescence phenomenon. Fluorescence is the emmision of the photon at longer wavelengths, absorbed by the fluorescent molecule (fluorophore).

The most widely used mode of fluorescence signalling is the decrease or increase of fluorescence intensity at a single emission wavelength upon analyte binding. With intrinsic fluorescent chemosensors, where donor atoms of the ligand is a part of the fluorophore, the comploexation of target molecule results in either fluorescence enhancement or decrease in fluorescence.

Optical sensors are more preferred because the output can be directly observed, most of the time with naked eye. The most important issue about the optical sensors is the sensitivity of the fluorophore. Rapid detection or the detection of small changes in the target molecules' concentration may not be very important for every media but a scientist dealing with the living organisms must come up with a rapid and highly sensitive fluorophore. Simple optical sensors can determine concentrations only as low as several tenths of a micromolar. However by using fluorescence techniques one can accurately measure concentrations in pico and even femtomolar. The main disadvantage of this technique are the solubility of the fluorophore in aquous media as well as in the organic media.

1.2.2. Photodynamic Therapy

Photodynamic therapy (PDT) is a noninvasive method of treating malignant tumors and age-related macular degeneration,[8] and particularly promising in the treatment

of multidrug-resistant (MDR) tumors[9]. The logic behind the PDT is the localization of certain photosensitizers in tumor tissues selectively. Then after the excitation of the photosensitizer in red or NIR region reactive oxygen species (ROS) including singlet oxygen (1O2) are produced which starts to damage the tumor cells. Up to last few years the photosensitizers used in PDT is limited to a few porphyrin derivatives, however these compounds are not considered to be ideal drugs for use in PDT [10]. Also nonporphyrin photosensitizers, texaphyrins, phthalocyanines, squaraines, chalcogenopyrylium dyes, azadipyrromethenes and perylenediimides have been suggested for PDT. However nowadays boradiazaindacene (BODIPY) sensitizers showing superior properties among the others. In addition to its long wavelength excitability, singlet oxygen generation capacity and good solubility and non-toxicity of unexcited form characteristics are the superior properties of BODIPY derivates. A well modified example of a BODIPY derivative designed for PDT was introduced to literature by Akkaya and his co-workers [38].

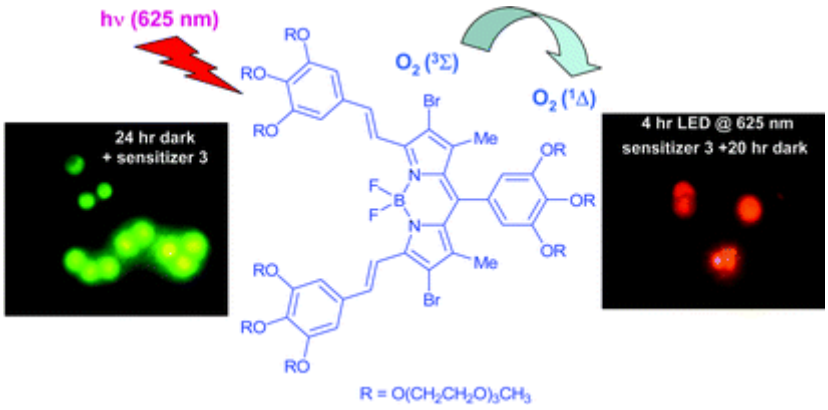


Figure 3. An example of PDT reagent

1.2.3. Solar Cells

A solar cell or photovoltaic cell is a device that converts light energy into electrical energy by the photovoltaic effect. To produce a good solar cell one needs a good charge carrier and a light absorbing material. Photons in sunlight hit the solar panel and are absorbed by semiconducting materials. Energy of the photons are transferred to the atoms on the surface and the electrons leave the atoms and flow through the charge carrier material. This flow of electrons is current, and by placing metal contacts on the top and bottom of the PV cell, we can draw that current off to use externally. Although the most efficient silicon based solar cells has an efficiency of 42.8% commercially used ones has an efficiency of about 14-16% because of the very high cost of the high efficient ones. Dye-sensitized solar cells uses dyes instead of silicon surfaces.

These cells are extremely promising because they are made of low-cost materials and do not need elaborate apparatus to manufacture. In bulk they should be significantly less expensive than older solid-state cell designs. Although their conversion efficiency is a bit less than the best thin-film cells, their price/performance ratio should be high enough to allow them to compete with the traditional solar cells. Also an efficiency of 11% was achieved by the founder of dye-synthesized solar cells; Michael Grätzel [11].

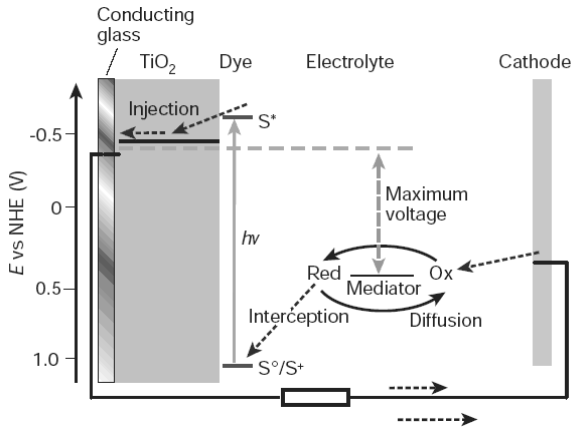


Figure 4. Working Mechanism of a Dye-Synthesized Solar Cell (DSSC)

1.2.4. Logic Gates

Logic gates are the 'brain' substituents of digital circuits in where data input, analysis and the first output is occurred. Most logic gates have two inputs and one output. Only two types of entries and two types of outputs is seen in logic gates (0) for low and (1) for high according to different voltage levels. The production of smaller and effective logic gates has great importance in all areas of circuit technology. However as they become smaller the substances start to loose their properties where the molecular interactions become important.

Nanotechnology and Supramolecular chemistry comes with help in this point. Different from the traditional methods supramolecular chemistry uses "bottom to up" production technique where molecular interactions have greatest importance. That's how the construction of simple electronic or photonic driven systems and network that function as molecular level devices which are working by logic gates become possible [12].

The main idea of computing is based on bits that can be written and read as 0 or 1. This is achiavable in molecules as in many ways, but the most common are based on switching the optical properties of the molecule. Photon absorption is used as the input and the luminescence is used as the output. Using the photons instead of electrons reduces the connection problem also.

Fluorescent chemosensing is useful in biomedical research and it has been very recently developed into chemical logic [13]. In the chemical logic system, the binding of a guest molecule to a host compound corresponds to the logic input and the resulting physical property change such as absorbtion and/or fluorescence spectra corresponds to the logic output.

There are seven basic logic gates: AND, OR, XOR, NOT, NAND, NOR, and XNOR. And all of this logic gates were achieved by molecules. All these gates are shown with a specific symbol and their working principles can be simply showen by using tables called “truth tables”.

Summary for all 2-input gates							
Inputs		Output of each gate					
A	B	AND	NAND	OR	NOR	EX-OR	EX-NOR
0	0	0	1	0	1	0	1
0	1	0	1	1	0	1	0
1	0	0	1	1	0	1	0
1	1	1	0	1	0	0	1

Figure 5. Truth Table for all 2-Input Logic Gates

1.2.5. Self Assembly

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 [2]". Actually the term "Self-assembly" can be used for the formation of structural organization on all scales from molecules to galaxies. It is defined as reversible processes in which pre-existing parts or disordered components of a preexisting system form structures of patterns. There are several reasons for interest in self assembly. First, from the first appearance of mankind humans are always attracted by the appearance of order from disorder. Second, self assembly is the working principle of living cells. To understand the truths of life the good understanding of self-assembly is a must. Third, because of the many disadvantages of "up to bottom" designing techniques in nanotechnology, self-assembly comes up with good solutions for making ensembles of nanostructures. Fourth self-assembly is common to many dynamic, multicomponent systems, from smart materials and self-healing structures to netted sensors and computer networks. Finally, the focus on spontaneous development of patterns bridges the study of distinct components and the study of systems with many interacting components. It thereby connects reductionism to complexity and emergence.

Scientists are trying to learn about the secrets of self assembly and try to copy the formation mechanisms of self assembled molecules most of which are very critical for the continuity of life.

There are two basic classes of self-assembly; static and dynamic. Static self-assembly is when the ordered state occurs when the system is in equilibrium and does not dissipate energy. However dynamic self-assembly is when the ordered state requires dissipation of energy and thus reconformation of the self assembling units. Examples of self-assembling system include weather patterns, solar systems, histogenesis and self-assembled monolayers and of course the most well-studied subfield of self-assembly is molecular self-assembly.

Molecular self-assembly involves noncovalent or weak covalent interactions (van der Waals, electrostatic, and hydrophobic interactions, hydrogen and coordination bonds). In the self-assembly of larger components— meso- or macroscopic objects interactions can often be selected and tailored, and can include interactions such as gravitational attraction, external electromagnetic fields, and magnetic, capillary, and entropic interactions, which are not important in the case of molecules. Metal ligand corrdinations are also another field of molecular self assembly that uses metalic interactions to hold units together.

1.2.5.1. 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, non-covalently linked, molecular and supramolecular architectures [14].

Hydrogen bonding is also the key to the assembly of the double helix structured DNA molecule which is perhaps the most important natural supramolecule.

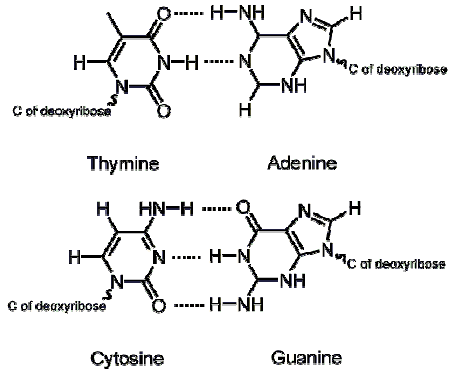


Figure 6. Hydrogen Bond Directed Self Assembly of DNA

Some of the most clear examples of hydrogen bond directed assembled supramolecules are melamine and cyanuric acid derivatives.

Melamine has three nitrogens interacting with the hydrogens of cyanuric acid and the hydrogens of amine groups interact with the oxygens on the cyanuric acid. This high interaction makes rigid, strong and insoluble polymeric complex with a “rosette-like” arrangement of sub-units precipitates [15].

Hydrogen bond directed assembly was also used by Lehn and coworkers to synthesize molecular ribbons. Sub-units (a barbituric acid derivative and melamine) are very similar but this time one of the hydrogen bonding faces of the molecule has been blocked by two alkyl groups. This time with two hydrogen bonding faces the formed molecule is a molecular ribbon.

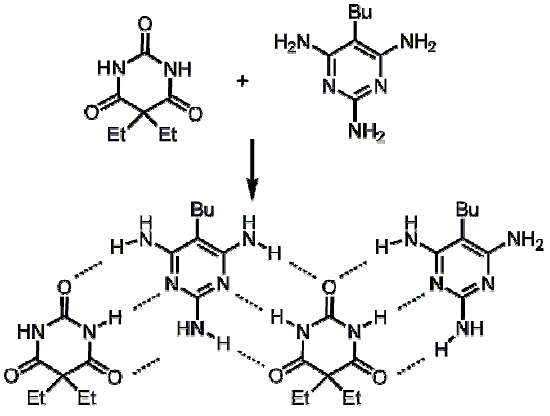


Figure 7. Molecular Ribbon

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 [15].

1.2.5.2. 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 [16]. 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 [15]. One of the earliest examples of molecular self assembly was provided by the field of metal coordination chemistry [17].

In 1960 Curtis reported the one pot synthesis of a yellow crystalline product from the reaction of $[Ni(en)_3]^{+2}$ (en= ethylenediamine) in dry acetone.

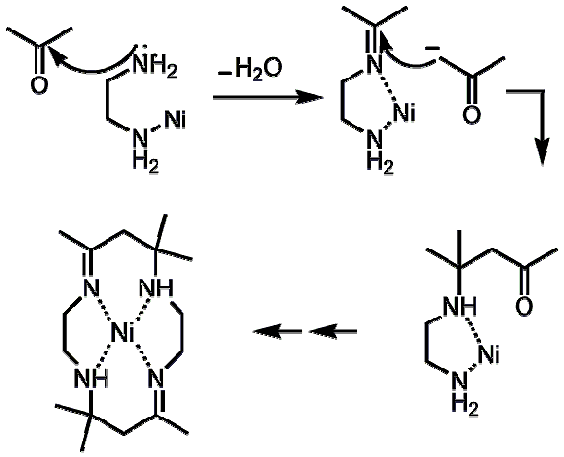


Figure 8. Transition Metal Directed Self Assembly

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 [18].

1.2.5.2.1. Catenanes, Ladders, Grids, Helices

Almost every of the hardest structural organizations form by self assembly in biological systems. The most important example of them is of course DNA molecule having the detailed explanation of every step in living organisms. It is a long polymer of simple units called nucleotides and has a strong backbone made of sugars and phosphate groups joined by ester bonds. Attached to each sugar is one of four types of molecules called bases. The formation of the double helix structure forms spontaneously and reversibly as the strands are mixed together and hydrogen bonds form between complementary base pairs.

Formation of helix structures is a problem for scientists because of the confusing and diversity nature of the hydrogen bonding. Instead supramolecular chemists use 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 [19].

The metal directed formation of catenates and catenands can be regarded as the first steps of helix type structural assemblies.

One of the well known examples of catenates is the one which was introduced to literature by Sauvage and his research group. The formation of helix type of a structure needs a ligand having a multiple bonding sites. Each of them interact with a different metal ion and the second ligand interacts with the same metal ions. Of course, a further modification is needed because by this way one can only get a

ladder type structure. Also a single sided ladder called rack or a gird structure can be obtained by similar modified ligands.

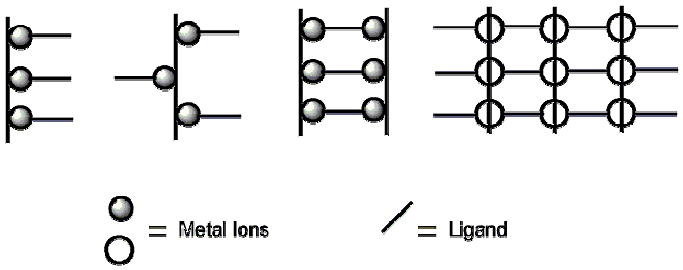


Figure 9. Formation of Molecular Grids and Ladders

To from a rack structure after the combination of the first ligand with the metal ions the second type of the ligand interacts with the coordinated metal ion-ligand complex.

To obtain a ladder structure the ligand should have two binding sides. After the formation of metal ligand complex another metal ion connects to the other side of the ligand and a second ligand1 molecule binds to them.

Formation of a grid structure is a relatively easier procedure. This time only one type of a ligand and a one type of a metal ion is needed. As soon as the metal ions connected to the ligand another ligand molecule interacts with the same metal ions in a suitable geometry and forms a grid like structure.

1.2.5.2.2. Rotaxanes

In Latin rota means wheel and axis means axle. The combination of these gives the name of molecular structures having two mechanically-interlocked units. The axle unit have two stopper parts larger than the internal diameter of the ring on each side just to prevent deslipping of rota unit. Difference between rotaxane and pseudo-rotaxane is only the stopper groups. A pseudorotaxane is formed when noncovalent forces bind an axle inside a macrocyle without help of stoppers.

One can use different types of interactions to build a rotaxane or a pseudo-rotaxane. J.P Sauvage and his coworkers introduced metal coordinated rotaxanes to the literature [20].

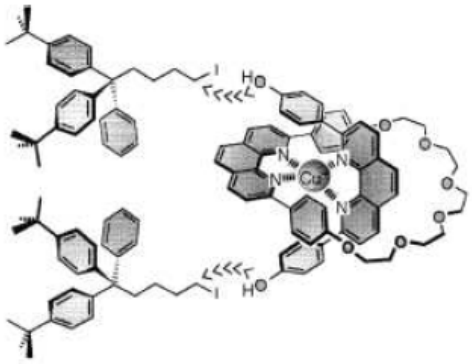


Figure 10. Metal Coordinated Rotaxane [20]

Another different type of coordinated rotaxane was synthesized in Stoddart's group. They used the π-donor, π-acceptor interaction between electron poor paraquat and electron rich hydroquinone moieties in order to preorganize a rotaxane [21].

Figure 11. π-π Interaction Based Rotaxane [21]

Hydrogen bonding also could be used a nonionic template in rotaxane synthesis. The first examples of this idea is actualized by Vogtle and his group [22].

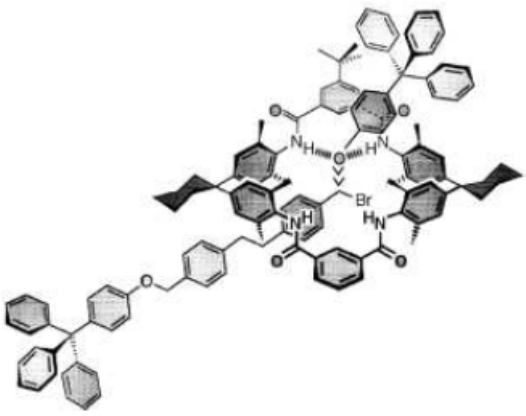


Figure 12. Hydrogen Bond Assisted Rotaxane [22]

1.2.5.2.3. Molecular Squares and Boxes

In supramolecular chemistry molecular squares and boxes have a special place. All among the others the most rigid and surprising units are them. The rigidity of their structures make them great units for molecular architecture. The cavities inside them are multifunctional. The same square or box can be used as a solar cell, as a PDT agent, as a chemosensor or as an energy transfer cassette just making small modifications. They also catalyze some reactions but most of their catalyzing effects can not be predicted and found surprisingly.

Supramolecular architecture uses all molecular interactions like electrostatic interactions, hydrogen bonding, π-π stacking, van der Waals forces, hydrophobic interactions, and metal-ligand coordination. However while designing a molecular square or a box metal-ligand coordinationis the best choice because of the rigid geometry of the bonding orbitals of metals. 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 [24].

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.

The most suitable metals used for this type of production are decided to be transition metals with square planar coordination geometries. They have four coordination sites which are all separated by about 90° from the adjacent one. Mono-units are found at the sides of the square or box and transition metals are placed at the corners.

Cis-metal corner units with 90° 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 cisprotected Pd(II) and Pt(II) corners have proven to be versatile metal building blocks for molecular squares [25].

The first self assembled square was introduced to the literature by Fujita, Yazaki, and Ogura that contains cis-protected palladium corner [26].

The structurally predefinedmetal corner $[Pd(en)(NO_3)_2]$ provides two vacant coordination sites of a 90 degree angle, while the rigid 4,4'-bipyridine ligand possesses two lone pairs of 180 degree divergence.

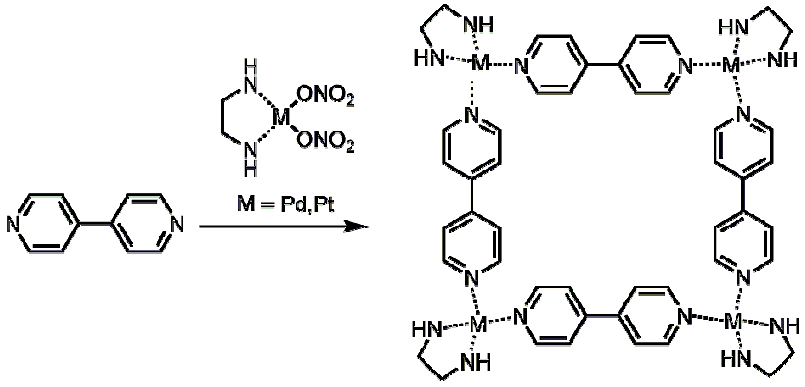


Figure 13. Metal Coordinated Molecular Square [26]

These structural features of metal and ligand contribute convergently to the formation of a square framework of assembly at room temperature in water. When $[Pd(en)(NO_3)_2]$ is treated with 4,4'-bipyridine, a cyclic tetrameric macrocycle -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 dissolves in water up to high concentration. This novel concept, pioneered by Fujita, has been abundantly applied for the construction of various metallosupramolecular squares [25].

Usage of Pt(II) complex instead of Pd(II) complex needs longer procedures but more advantageous. The kinetically distributed oligomeric products were initially observed when the Pt(II) complex was treated with 4,4'-bipyridine. However these kinetic oligomeric products could be converted to the thermodynamically favorable square species by heating at 100° C for more than four weeks [26]. This complex is more stable than Pd complex under ordinary conditions due to the relative inertness of platinum-pyridine bond.

The importance of the phosphine groups on the metal complexes can be understood with the X-Ray analysis of final square. The considerable rigidity of the corner units is due to the high degree π-stacking between one of the phenyl groups of the phosphine ligand and the pyridine rings. These favorable interactions between the ditopic ligand and chelated bisphosphine, not only promote square formation but also 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 [27].

Another binding unit 'porphyrin' was introduced to the literature by Jeremy Sanders' group. The group showed the formation of interesting hexagons by irreversible, directed self-assembly involving the linkage of alkyne groups between three monomers containing zincated porphyrins [28]. For example, the hexagon in figure 19 was obtained by a copper coupling reaction in dichloromethane of the substituted porphyrin in the presence of tris(4-pyridyl)triazine (2). In coordinating solvents or in the absence of tris(4-pyridyl)triazine, the hexagon did not form [29].

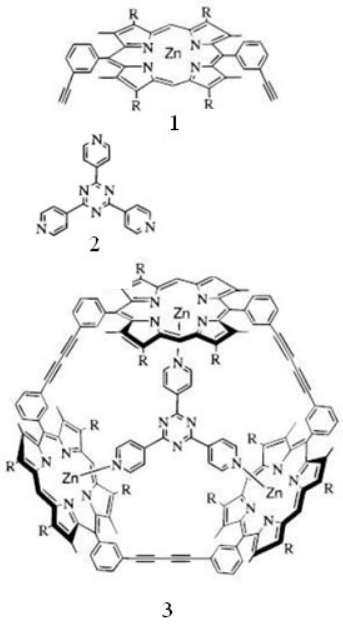


Figure 14. Molecular Hexagon [29]

In the presence of 4,4-bipyridine, the corresponding distorted square was instead formed. Thus, the coordination of the amines to the Zn (II) ions of the porphyrins template the formation of the resulting structure. 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 [30].

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[28].

The importance of molecular cages on some chemical reactions was well exampled by Fujita's research group. They found that an aqueous organopalladium cage induces highly unusual regioselectivity in the Diels-Alder coupling of anthracene and

phthalimide guests, promoting reaction at a terminal rather than central anthracene ring.

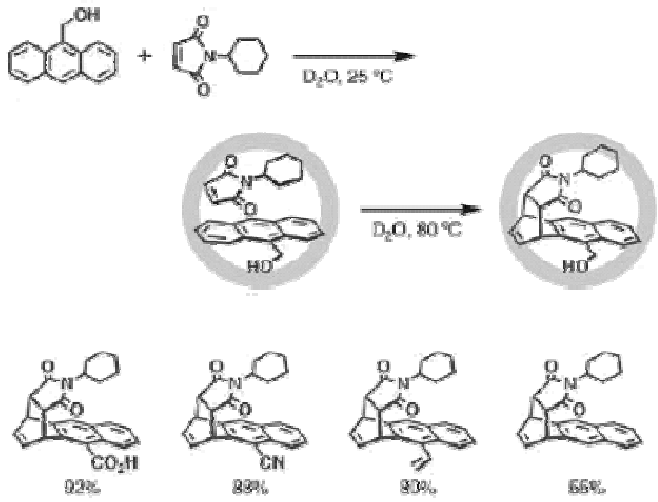


Figure 15. Regioselective Diels Alder [31]

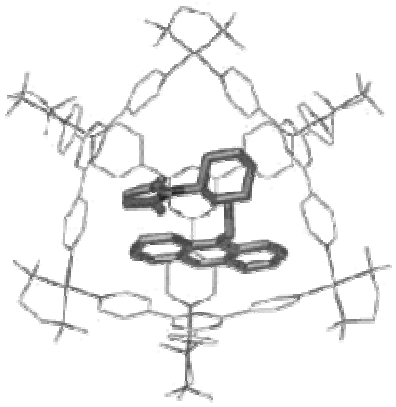


Figure 16. Catalytic Molecular Cage [31]

The Diels-Alder reaction of anthracenes in the absence of hosts is extremely well studied and generally yields an adduct bridging the center ring (9,10-position) of the anthracene framework as a consequence of the high localization of p-electron density at that site. They found that an appropriately designed cage structure can alter this well-established selectivity to favor adduct formation at a terminal ring (1,4-position). This unusual regioselectivity likely stems from topochemical control induced by the proximity of the 1,4-position of the anthracene to the dienophile in the cage [31]. 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 [25].

1.3. Coupling Reactions

1.3.1. Suzuki Coupling

Suzuki reaction is the coupling of an aryl- or vinyl-boronic acid with an aryl- or vinyl-halide catalyzed by a palladium(0) complex [32]. The widest usage area of this reaction is the synthesis of poly-olefins, styrenes, and substituted biphenyls. However this reaction mechanism also works with pseudo halides instead of halides, and also with boron-esters instead of boronic acids. The mechanism gets its name from the scientist Akira Suzuki in 1979. The first reaction was the coupling of a

boronic acid (containing an organic part) to a halide. Key part of the reaction is the usage of a palladium catalyst such as tetrakis(triphenylphosphine)palladium(0) to effect part of the transformation. The palladium catalyst (more strictly a pre-catalyst) is 4-coordinate, and usually involves phosphine supporting groups.

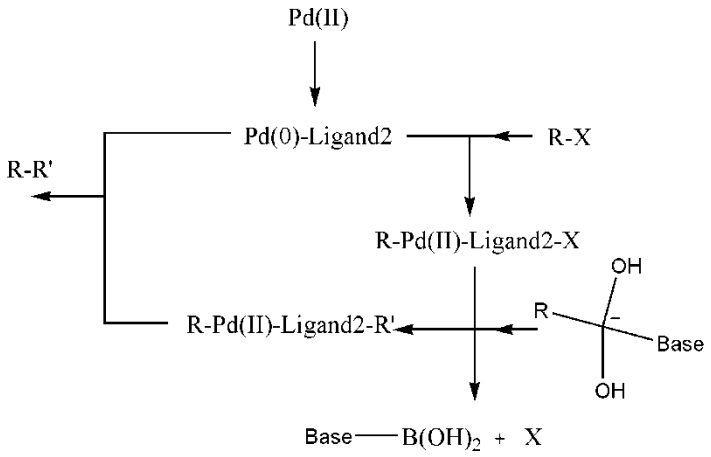


Figure 17. Mechanism of Suzuki Coupling Reaction

1.3.2. Sonogashira Coupling

The specialty of Sonogashira reaction comes from the great importance of carbon-carbon bond formation reactions in chemistry. Most of these types of reactions are metal catalyzed. Actually Sonogashira coupling is a modification of the Castro-Stephens coupling reaction. Sonogashira reaction is the cross-coupling reaction between terminal alkynes with aryl and vinyl halides in the presence of an aliphatic amine or inorganic base under mild conditions [33].

In a typical Sonogashira coupling reaction, two catalysts are needed for this reaction: a zerovalent palladium complex and a halide salt of copper (I). The palladium complex activates the organic halides by oxidative addition into the carbon-halogen bond.

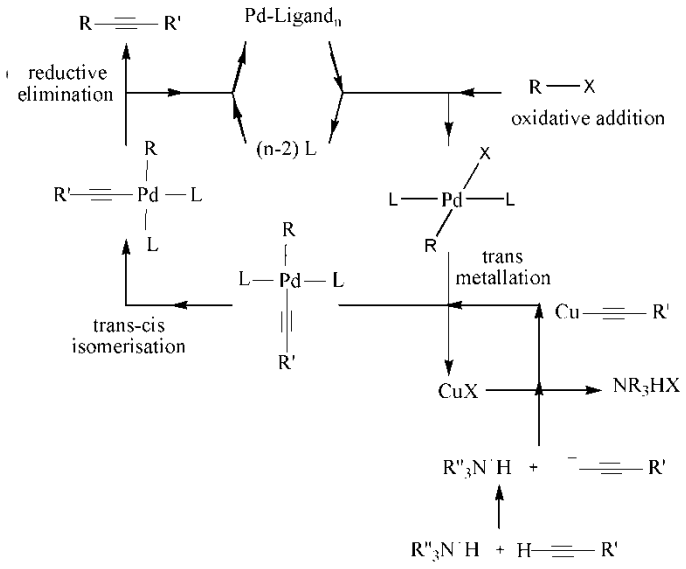


Figure 18. Mechanism of Sonogashira Coupling Reaction

Phosphine-palladium complexes such as tetrakis(triphenylphosphine)palladium(0) are used for this reaction, but palladium(II) complexes are also available because they are reduced to the palladium(0) species by the consumption of terminal alkynes in the reaction medium. In contrast, copper(I) halides react with the terminal alkyne and produce copper(I) acetylide, which acts as an activated species for the coupling reactions. The proposed catalytic cycle is shown in the figure below [34].

CHAPTER 2

EXPERIMENTAL

2.1. Instrumental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Instruments Avance 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 refenced to TMS and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), p (pentet), dt (doublet of triplet) and br (broad).

Chemicals and solvents were purchased from Aldrich and used without further purification. Column chromatography of all the products were performed using Merck Silica Gel 60 (particle size: 0.040-0.063 mm, 230-400 mesh ASTM) pretreated with eluent. Reactions were monitored by thin layer chromatography using Merck Silica Gel 60 Kiesegel F_{254} TLC Aluminum Sheets 20x20 cm.

2.2. Synthesis of 2,4-Dimethyl Pyrrole

2.2.1. 2,4-Dimethyl-3,5-Dicarboethoxypyrrole

Synthesis of this molecule was done according to literature; in a three-necked, round-bottomed flask, fitted with a liquid-sealed mechanical stirrer and dropping funnel, were placed 390 g (3 moles) of ethyl acetoacetate and 900 ml. of glacial acetic acid. The solution was cooled in an efficient freezing mixture to 5°, and a cold solution of 107 g (1.47 moles) of 95% sodium nitrite in 150 ml of water was added dropwise with vigorous stirring at such a rate that the temperature remains between 5° and 7°. With efficient cooling about one-half hour was required to add the nitrite. The mixture was stirred for one-half hour longer and then allowed to stand for four hours, during which time it warms up to room temperature. The separatory funnel was replaced by a wide-bore condenser, and the third neck of the flask was fitted with a stopper. The solution was stirred and portions of 196 g of zinc dust were added quickly through the third neck of the flask until the liquid boils and then frequently enough to keep it boiling. After the addition had been completed, the mixture was refluxed for one hour. While still hot the contents of the flask were decanted from the remaining zinc into a crock containing 10 l of water which was being vigorously stirred. The zinc residue was washed with two 50 ml portions of hot glacial acetic acid which were also decanted into the water. After standing overnight, the crude product was filtered by suction, washed on the filter with two 500 ml portions of water, and dried in air to constant weight. The yield was 195 g (60% of the theoretical amount) of material melting at 126–130°. On recrystallizing a 50 g portion from 100 ml. of 95% alcohol and washing twice with 20 ml portions of cold alcohol, there was obtained 35 g. of pale yellow crystals [39].

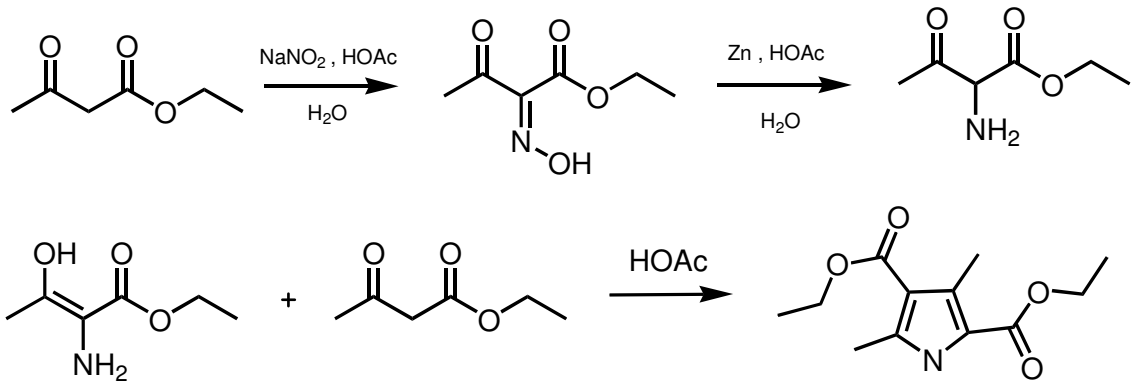


Figure 19. Synthesis of 2,4-dimethyl-3,5-dicarboethoxypyrrole

2.2.2. Decarboxylation of 2,4-Dimethyl-3,5-Dicarboethoxypyrrole

Synthesis of this molecule was done according to literature; a solution of 270 g. (4.8 moles) of potassium hydroxide in 150 ml. of water was prepared in a 3-l. round-bottomed flask, 120g. (0.5 mole) of crude 2,4-dimethyl-3,5-dicarbethoxypyrrole were added, and the whole was mixed thoroughly by shaking. The flask was fitted with a reflux condenser, and the mixture was heated in an oil bath at 130°C for two to three hours with occasional shaking until the thick paste had become partially liquified owing to the formation of dimethylpyrrole. The flask was next fitted for distillation with superheated steam and with a separatory funnel for the introduction of water into the center of the flask. A 3-l. round-bottomed flask fitted with a vertical condenser was used as a receiver. The temperature of the oil bath was raised to 160°C, and superheated steam at 220–250°C was introduced. The temperature of the oil bath was then gradually raised to 200°C .Steam distillation is continued until no more dimethylpyrrole comes over. This took two hours, and the distillate amounts to 2.5–3 l. The distillate was extracted once with 200 ml. of ether and three times with 100 ml. portions, and the extract was dried for two hours over 20 g. of anhydrous potassium carbonate. The ether was removed by distillation from a 100 ml. flask

having a 15-cm. fractionating side arm, the solution being added gradually through a separatory funnel. After the ether was removed the residue was distilled and the fraction boiling at 160–165°C is collected. The yield is 22 g. (42% of the theoretical amount) [39].

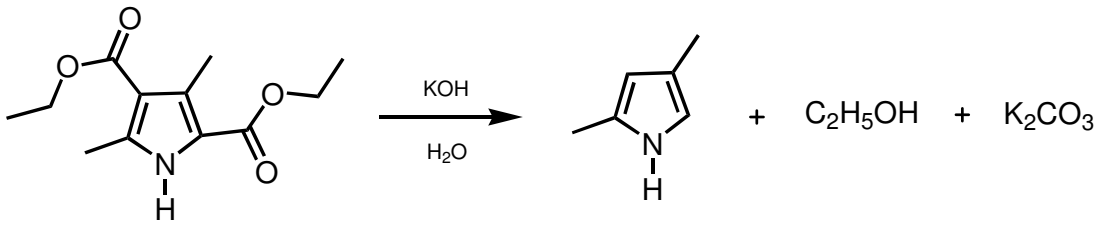


Figure 20. Decarboxylation of 2,4-dimethyl-3,5-dicarboethoxypyrrole

2.3. Synthesis of Platinum Complex

2.3.1. Synthesis of [1,3-Bis(diphenylphosphino)propane]dichloroplatinum(II) (1)

Anhydrous platinum(II) chloride (0.501 mmol, 133 mg) and dppp (0.501 mmol, 752 mg) were heated under reflux in CH_2Cl_2 (40 ml) overnight. The product was precipitated from the hot solution and purified by column chromatography (%5 $CHCl_3/CH_3OH$, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.8 (m, 8H), 7.5 (m, 12H), 2.7 (br.s, 4H), 1.8 (br.t,2H)

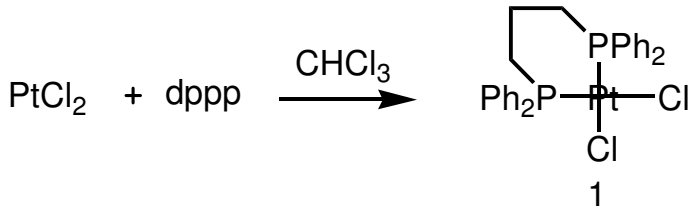


Figure 21. Synthesis of dichlorinated Platinum complex (1)

2.3.2. Synthesis of Pt bis(triflate) complex (2)

$AgOSO_2CF_3$ (1.94 mmol, 500 mg) is added to a solution of $PtCl_2$(dppp) (1.94 mmol, 440 mg) in CH_2Cl_2 (60 ml). The reaction mixture was stirrred at 25°C 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 yellowish powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.8 (m, 8H), 7.7-7.5 (m, 12H), 3.0 (br.s, 4H), 1.9 (br.t,2H)

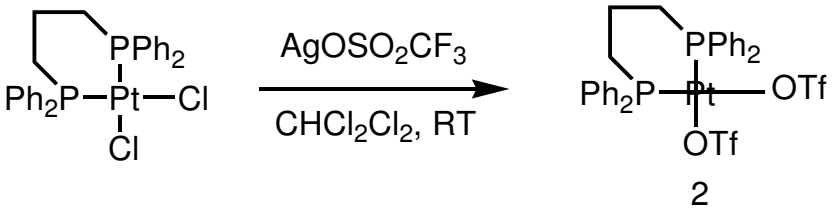


Figure 22. Dechlorination of Platinum Complex (2)

2.4. Synthesis of Square Complex

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

Benzoyl chloride (3.94 mmol, 553.5 mg) and 2,4-dimethyl-3-ethylpyrrole (7.87 mmol, 968 mg)were refluxed overnight in CH_2Cl_2. The reaction was monitored by TLC (eluent $CHCl_3$), Et_3N (5 ml) and $BF_3.OEt_2$ (5 ml) were added after night. 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 [4].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 3H), 7.21-7.17 (m, 2H), 2.45 (s, 6H), 2.22 (q, J= 7.5 Hz ,4H), 1.20 (s, 6H), 0.90 (t, J= 7.5 Hz , 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 140.2, 138.4, 135.8, 132.7, 130.8, 128.9, 128.7, 128.3, 17.1, 14.5, 14.1, 12.5, 11.6

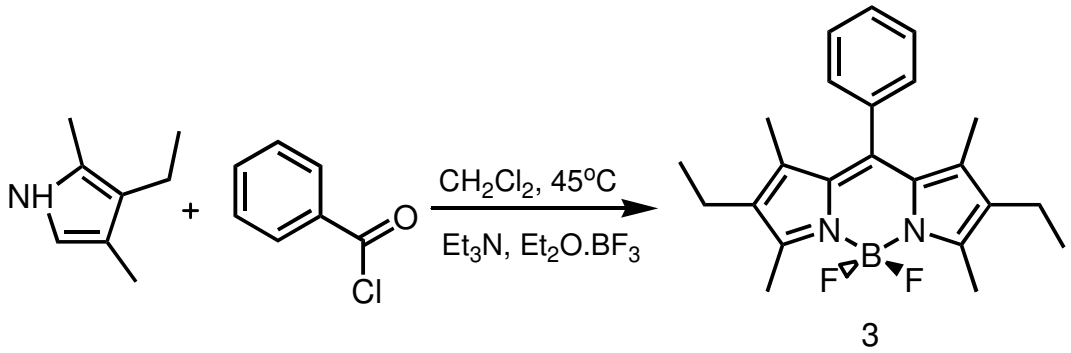
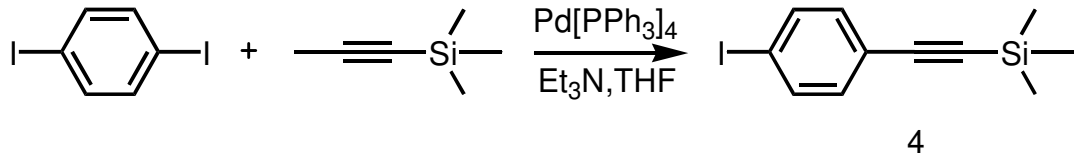


Figure 23. Synthesis of Phenyl BODIPY Unit **(3)**

2.4.2. Sythesis of (2-(4-iodophenyl)ethynyl)trimethylsilane (4)

Diiodo benzene, was dissolved in a mixture of Et_3N(9 ml) and THF(15 ml). Then $Pd[PPh_3]_4$ (0.8 mmol) was added to the mixture and argon bubbled through the solution for 30 min. After 30 min. trimethylsilylacetylene (22 mmol) was added. The mixture mixed overnight at room temperature and purified by column chromatography(hexane).



4

Figure 24. Synthesis of molecule **(4)**

2.4.3. Synthesis of 4-(2-(4-(2-(trimethylsilyl)ethynyl)phenyl)ethynyl)pyridine (5)

Ethynyl pyridine(0.66 mmol, 293 mg) was dissolved in a mixture of Et_3N (5 ml) and THF(30ml). Then $PdCl_2$ (0.13 mmol, 23.6 mg), CuI (0.26 mmol, 49.9 mg) and PPh_3(0.52 mmol, 136.4mg) was added to the mixture and argon bubbled through the solution for 30 min. After 30 min. (2-(4 iodophenyl)ethynyl)trimethylsilane (0.66 mmol, 200 mg) was added. The mixture mixed overnight at room temperature and purified by column chromatography (EtOAc) [3].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8,52 (d, 2H, J= 5,4 Hz), 7,4 (s, 4H), 7,28 (d, 2H, J=5,5 Hz), 0,2 (s,9H)

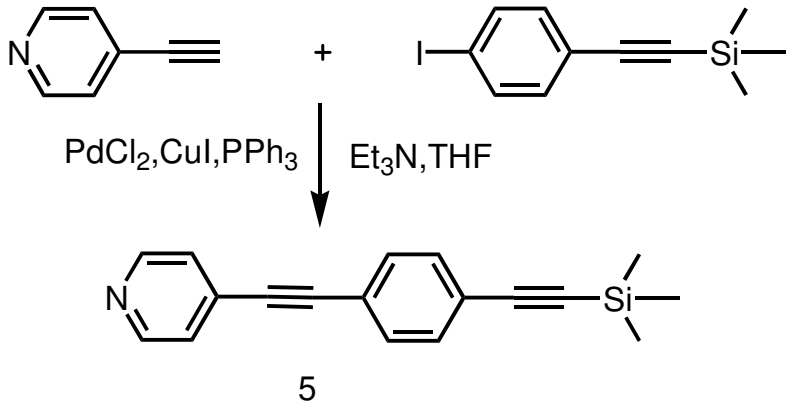


Figure 25. Synthesis of molecule **(5)**

2.4.4. Deprotection of 4-(2-(4-(2(trimethylsilyl)ethynyl)phenyl)ethynyl)pyridine (6)

4-(2-(4-(2-(trimethylsilyl)ethynyl)phenyl)ethynyl)pyridine (0.363 mmol, 100 mg) was dissolved in MeOH/CH_2Cl_2 (5/10 ml). Another solution of NaOH (1.8mmol, 72 mg) in 5 ml MeOH was added to the solution of 4-(2-(4-(2-(trimethylsilyl)ethynyl)phenyl)ethynyl)pyridine. The solution was stirred at r.t. for 1 hour, until the complete consumption of the starting material was observed by TLC ($CHCl_3$/Hex 1:1). Water (30 ml) was added and the solution was extracted with CH_2Cl_2 (30 ml). After evaporation, the organic layer was purified by column chromatography on silica (eluent: EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8,55 (d, 2H, J= 5,6 Hz), 7,42 (s, 4H), 7,3 (d, 2H, J=5,9 Hz), 3.1 (s,1H)

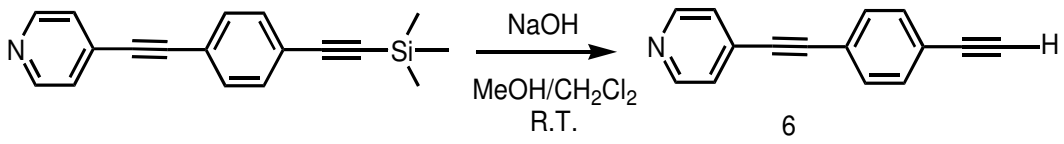


Figure 26. Synthesis of molecule **(6)**

2.4.5. Synthesis of 4,4-di-(4-(2-(4-ethynylphenyl)ethynyl)pyridine)-8-phenyl-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene (7)

In a Schlenk flask, n-Butylithium (2.1 mmol, 135 mg) was added at -78°C, to a stirred degassed solution of the 4-(2-(4-ethynylphenyl)ethynyl)pyridine (2.1 mmol, 425 mg) in anhydrous THF. The mixture was stirred at -78°C for 1h and at room temperature for half an hour. The resulting anion was then transferred to a degassed solution of the BODIPY dye (1 mmol, 380 mg) in anhydrous THF. The solution was stirred at room temperature until the complete consumption of the starting material was observed by TLC. Water was added, and the solution was extracted with CH_2Cl_2. After evaporation, the organic layer was purified by column chromotography (EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8,6 (d, 4H, J= 4,2 Hz), 7,5-7,3 (m, 17H), 2,9 (s, 6H,), 2.4 (q, 4H, J=7,5), 1,3 (s, 6H), 1,0 (t, 6H, J=7,4)

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.63, 149.56, 140.35, 136.70, 132.95, 131.61, 131.53, 129.16, 128.94, 128.63, 128.50, 126.60, 125.52, 120.42, 94.23, 87.73, 17.42, 14.74, 14.02, 11.81

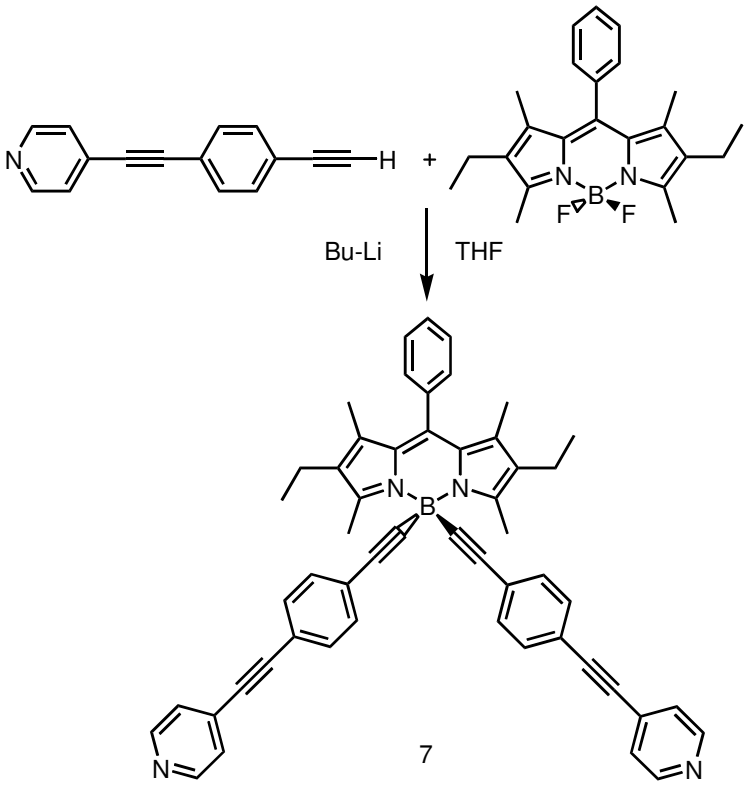


Figure 27. Synthesis of molecule **(7)**

2.4.6. Synthesis of Square Complex (8)

Molecule [7] (0.4 mmol, 300mg) was dissolved in $CHCl_3$(200ml). Then Pt-bis(triflate) complex (0.4 mmol, 330 mg) was added to the solution and as soon as the addition is done white crystals were formed. After 24 hours white crystals were filtered and dried under vacum.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8,9 (d, 8H, J= 4,4 Hz), 7,5-7,2 (m, 34H), 2,9 (s, 12H,), 2.3 (q, 8H, J=7,7), 1,2 (s, 12H), 0,9 (t, 12H)

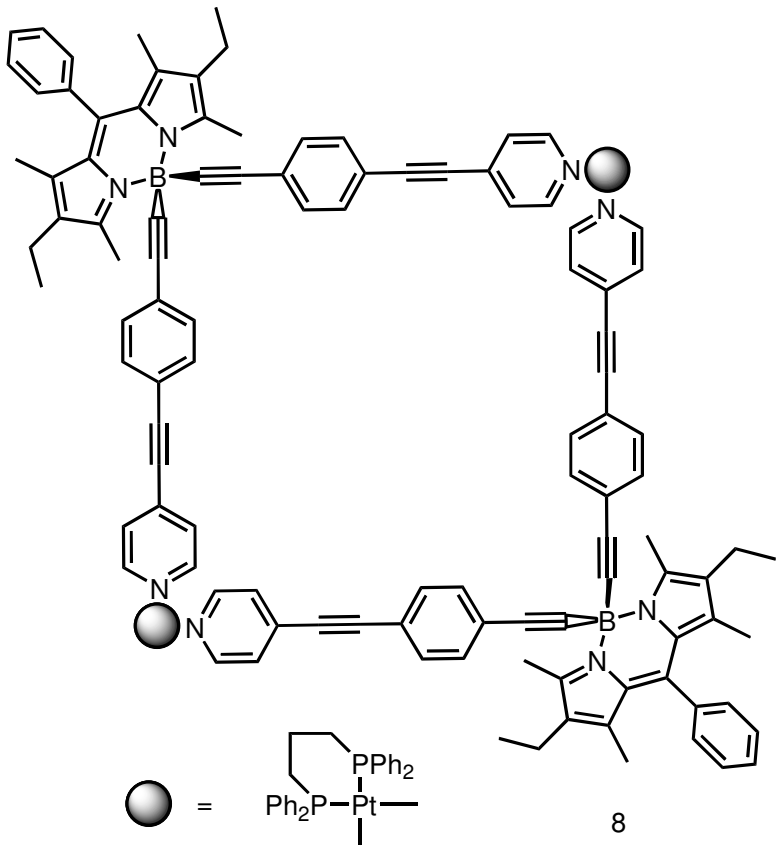
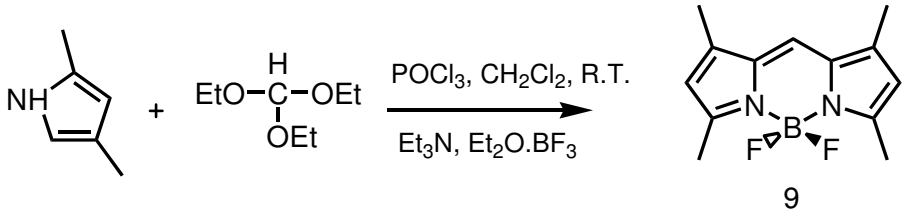


Figure 28. Full Square Complex (8)

2.5. Synthesis of the sub-unit of Cage Complex (12)

2.5.1. Synthesis of 4,4-difluoro-1,3,5,7-tetramethyl -4-bora-3a,4a-diaza-s-indacene (9)

Triethyl-ortho-formate (14.6 mmol, 2.52 g), $POCl_3$ (16.1 mmol, 2.5 g) and 2,4-dimethyl-pyrrole (29.1 mmol, 2.7 g) were stirred at room temperature for 1.5 h in previously argon bubbled CH_2Cl_2. The reaction was monitored by TLC (eluent $CHCl_3$), Et_3N (15 ml) and $BF_3.OEt_2$ (15 ml) were added and stirred 1h more. 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: $CHCl_3$).

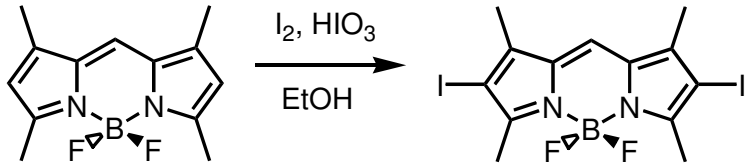


9

Figure 29. Synthesis of BODIPY derivative **(9)**

2.5.2. Synthesis of 4,4-difluoro-2,6 diiodo-1,3,5,7-tetramethyl -4-bora-3a,4a-diaza-s-indacene (10)

BODIPY (1.5 mmol, 372 mg), was dissolved in 200 ml EtOH. HIO_3(1.5 mmol 263.8 mg) was dissolved in min. amount of water and added to BODIPY solution with I_2 (2.5mmol, 634,5mg). The mixture was stirred at 60°C for 20 min. Then the reaction mixture was extracted with water/CH_2Cl_2. Organic layer was evaporated and the redish solid was collected.



9 10

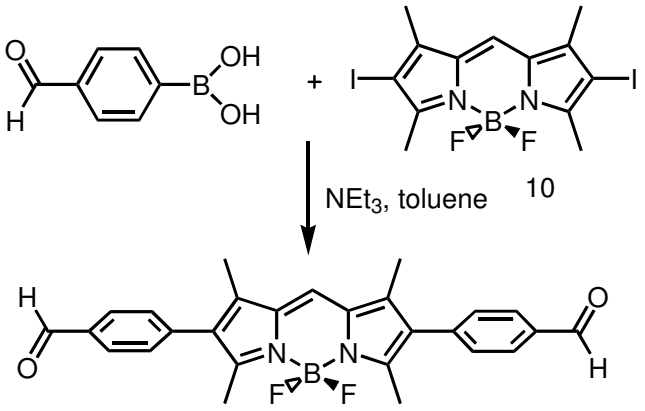
Figure 30. Synthesis of molecule **(10)**

2.5.3. Synthesis of 4,4-difluoro-2,6 bis(4-formylphenyl)-1,3,5,7-tetramethyl -4-bora-3a,4a-diaza-s-indacene (11)

4-formylphenylboronic acid (1.2 mmol, 180 mg) and 2,6-diiodo BODIPY (0.6 mmol, 346 mg) and [$Pd(PPh_3)_4$] (0.05 mmol, 60 mg) were heated reflux in toluene (10 ml) and triethylamine (5ml) for 3h. The mixture then was cooled to 25°C and diluted with EtOAc (20 ml). The mixture was washed with water/ CH_2Cl_2 and dried with

Na_2SO_4 and evaporated to yield crude product. Then purified with silica gel chromotography ($CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10,0 (s, 2H), 7,9 (d, 4H, J=8.1 Hz), 7,4 (d, 4H, J=7,9 Hz), 7.2 (s,1H), 2.5 (s, 6H), 2.2 (s, 6H)



11

Figure 31. Synthesis of molecule (11)

2.5.4. Synthesis of tri-BODIPY unit (12)

Compound [12] (1 mmol, 455 mg) and 2-4 dimethylpyrrole (2 mmol, 195 mg) was mixed in CH_2Cl_2(argon bubbled) overnight. Tetrachloro-p-benzoquinone (1 mmol, 245 mg) was added and mixed for 30min. Et_3N (3 ml) and $BF_3.OEt_2$ (3 ml) were added to the mixture. After 1h mixture extracted with water and dried with Na_2SO_4 and purified with column chromatography (MeOH/$CHCl_3$ %3, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3 (m, 8H), 7,2 (s, 1H), 5,9 (s, 4H), 2.5 (s,18H), 2.2 (s, 6H), 1.4 (s, 12H)

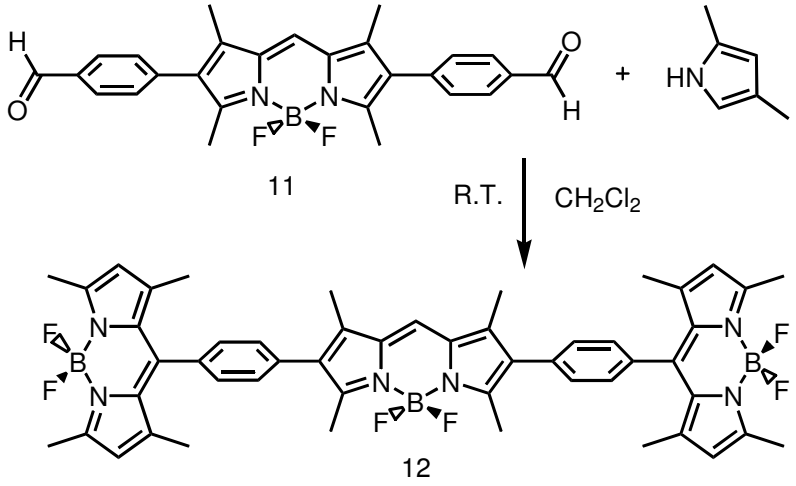


Figure 32. Synthesis of molecule (12)

2.6. Synthesis of the Sub-Unit For Wire Complex

2.6.1. Synthesis of 2,4,6-trimethylbenzene-1,3,5-tricarbaldehyde (13)

NaOH (10 mmol, 400 mg) was dissolved in isopropanol (20 ml). Then 2-nitropropane (10 mmol, 900 mg) was added. After 20 min. 2,4,6-Tris(bromomethyl)mesitylene (1.25 mmol, 500 mg) was added to the mixture and stirred at room temperature under argon for 4h. The mixture was extracted with water/$CHCl_3$ and dried with Na_2SO_4. No further purification was needed.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10,5 (s, 3H), 2,6 (s, 9H)

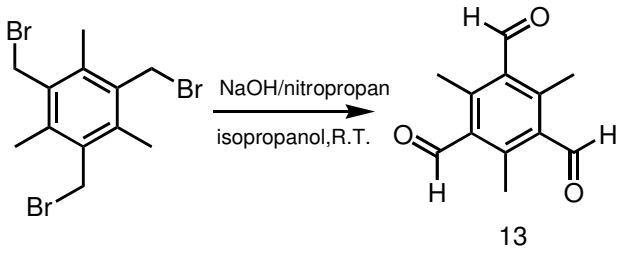


Figure 33. Synthesis of molecule **(13)**

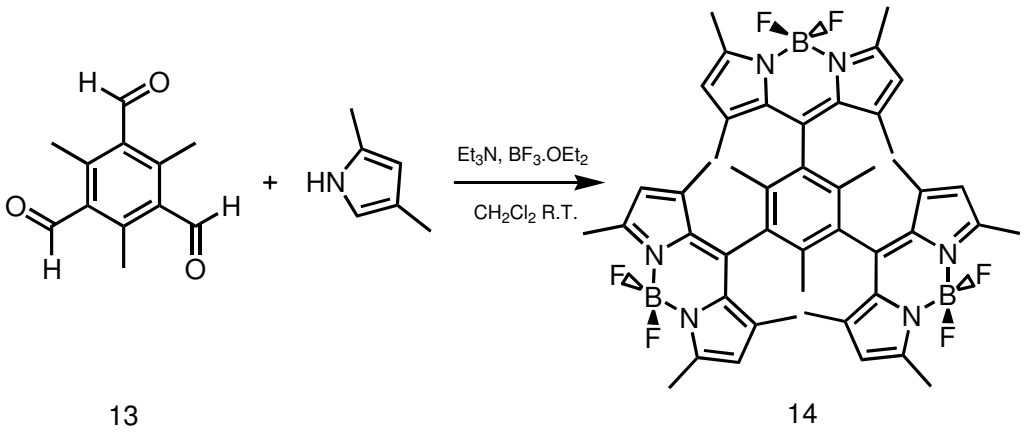


Figure 34. Synthesis of molecule (14)

2.6.2. Pilot synthesis reaction of 2,4,6-trimethylbenzene-1,3,5-tri-(4,4-difluoro-8-phenyl-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene) (14)

2,4,6-trimethylbenzene-1,3,5-tricarbaldehyde (0.618 mmol, 330 mg) was dissolved in previously argon bubbled CH_2Cl_2 (300 ml). Then 2-4dimethylpyrrole (6.18 mmol, 570 mg, 0.63 ml) and 2 drops of trifluoroacetic acid was added. The mixtured was stirred over night at room temperature. Then washed with water and dried with Na_2SO_4. The product was purified with column chromotography ($CHCl_3$).

CHAPTER 3

RESULTS AND DISCUSSION

To synthesize, characterize and functionalize a flourescent molecular square, cage and tube with boradiazaindacene (BODIPY) building blocks was our aim in this study. The angular unit chosen in our study is a cis-protected Pt (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 Pt 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 Pt 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 all three molecular blocks we designed.

3.1. Synthesis of Molecular Square

Reaction pathway starts with the synthesis of standard boradiazaindacene dye. The coupling of ethynyl pyridine and (2-(4 iodophenyl)ethynyl)trimethylsilane yields a unit that can be replaced with the fluorine atoms. All the steps of this unit's synthesis are about100% efficient. The replacement of fluorine atoms was also not a competing step and about 90% yield. The fluorine atoms on the BODIPY unit are located originally 90° to each other. This alignment was also preserved after the

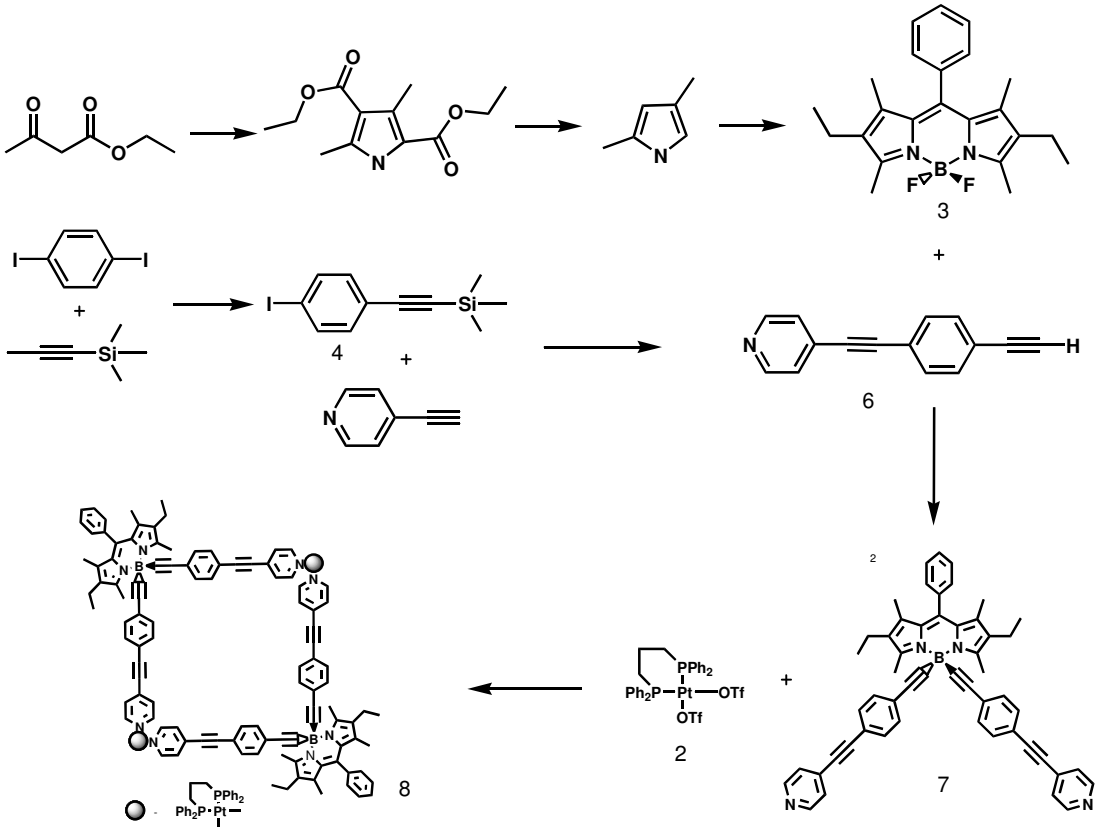


Figure 35. Synthesis Pathway of Molecular Square

replacement and pyridine derivates are also located 90° to each other. Especially this configuration makes it possible to form a square complex from a BODIPY unit.

In the interaction between nitrogens on the pyridine unit and platinum complex weakly coordinated triflate ions on the metal corner are exchanged with the more strongly coordinated lone pairs of the nitrogen atom. That's the reason of the thermodynamically stability of the product. The metal-ligand coordination is reversible. Thus the formation of other macrocyclic or polymeric by-products are eliminated. During the formation of molecular squares the reaction parameters of the possible side products should also be recorded for further structural designs. By simply changing the reaction conditions one can easily switch between the other possible products and the desired square unit. Such an exchange also 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 Molecular Square (6)

The BODIPY dye [3] and molecular square [6] were characterized by spectral means as detailed in Experimental Section. ^{1}H and ^{13}C NMR spectra agree with the structures. Supramolecular units are connected via intermolecular interactions. That's why no new or missed proton information is found on the NMR spectrum of the square unit. But the formation of the square is also be proved still by the chemical shifts of the protons. The peaks of the protons on the two neighbour carbons of nitrogens are shifted to downfield. Electron density on the pyridine decreased due to the interaction with platinum. ^{1}H and ^{13}C NMR spectra are good proofs but the most useful piece of evidence for the structure will be the mass spectrometry data. 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. Like the previous examples this molecular square is also very fragile on ionizing conditions.

3.3. Synthesıs of Molecular Cage Sub-Unit And Molecular Tube Sub-Unit

Reaction pathway starts with the synthesis of a simple derivative of standard boradiazaindacene dye 1. Electrophilic aromatic iodination at 2 and 6 positions using ICl results in a red fluorescent dye 2 with 100% yield. After iodination a Suzuki coupling reaction was performed. BODIPY is a pH sensitive molecule. In basic media it quickly dissociate. The most important problem in this coupling was this sensitivity of the dye. The suitable base was chosen as triethylamine because it was known that triethylamine was also used during the synthesis of BODIPY. After a relatively low yielded coupling reaction a second BODIPY reaction was performed on the same molecule. A three BODIPY containing structure was obtained which will be further modified to another sub-unit of a molecular cage.

The last part of the study was the pilot syntheis reaction of a molecular unit, again a tri BODIPY containing one. First a three aldehyde containing phenyl structure was obtained with a reaction of 99% yield. Then all these aldehydes are forced to form a seperate BODIPY.

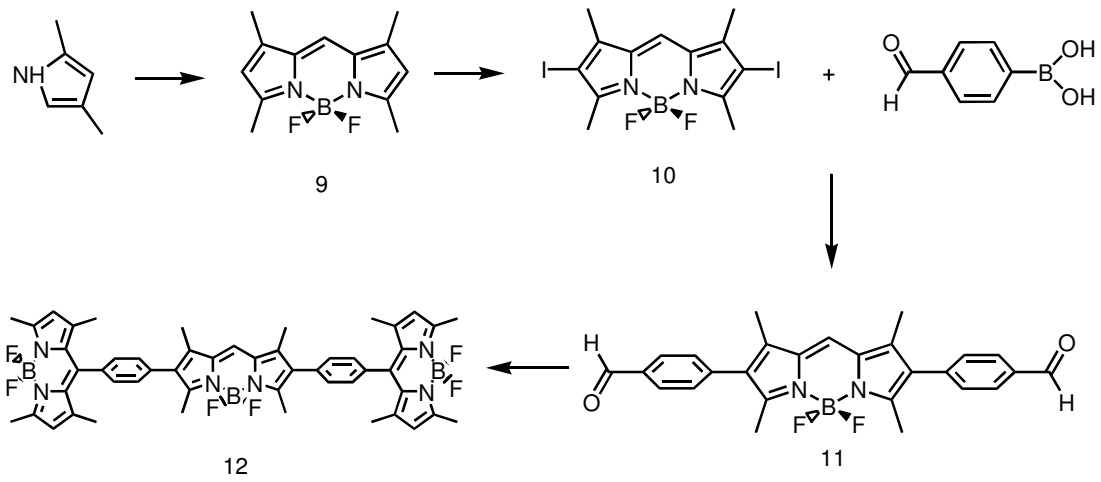


Figure 36. Synthesis Pathway of Molecular Cage-Unit

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° 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 multioxidation 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. It is not suprizing that the square complex is obtained in relatively large yield. NMR data suppports the formation of the complex. 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.

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APPENDIX A

^{1}H and ^{13} C NMR SPECTRA OF

SYNTHESIZED COMPOUNDS

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Instruments Avance 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 refenced to TMS.

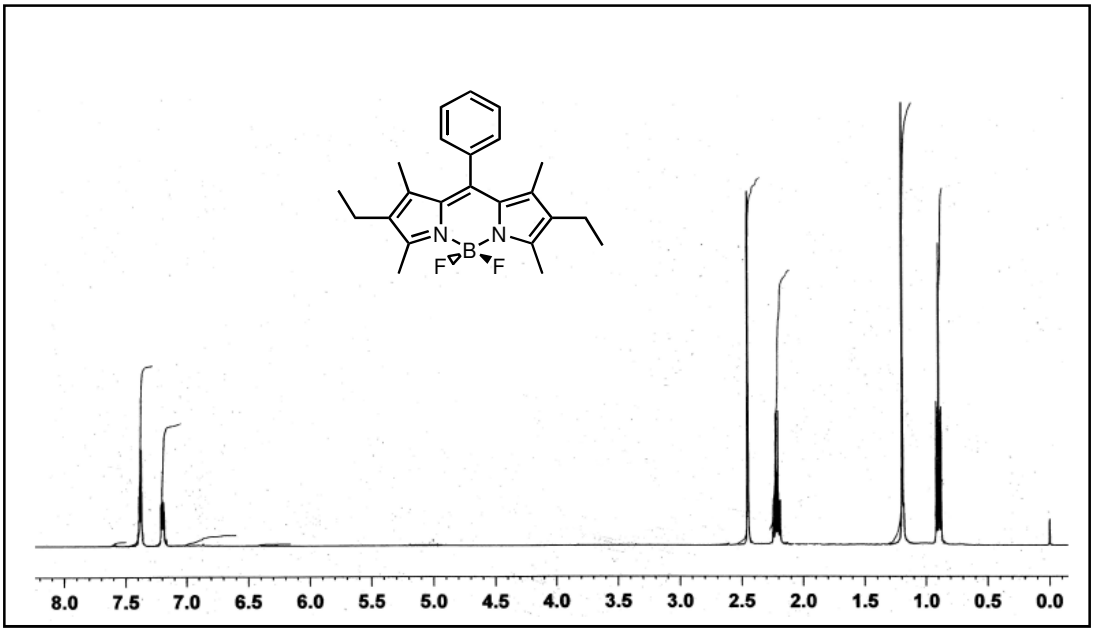

Figure A. 1. ^{1}H NMR Spectrum of Compound **(3)**

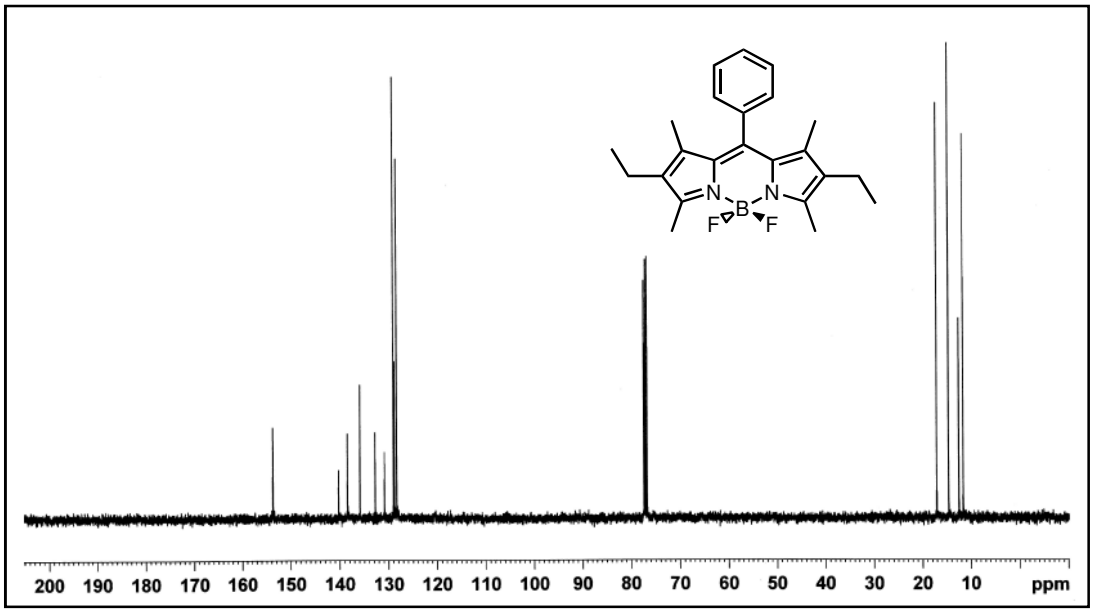

Figure A. 2 ^{13}C NMR Spectrum of Compound **(3)**

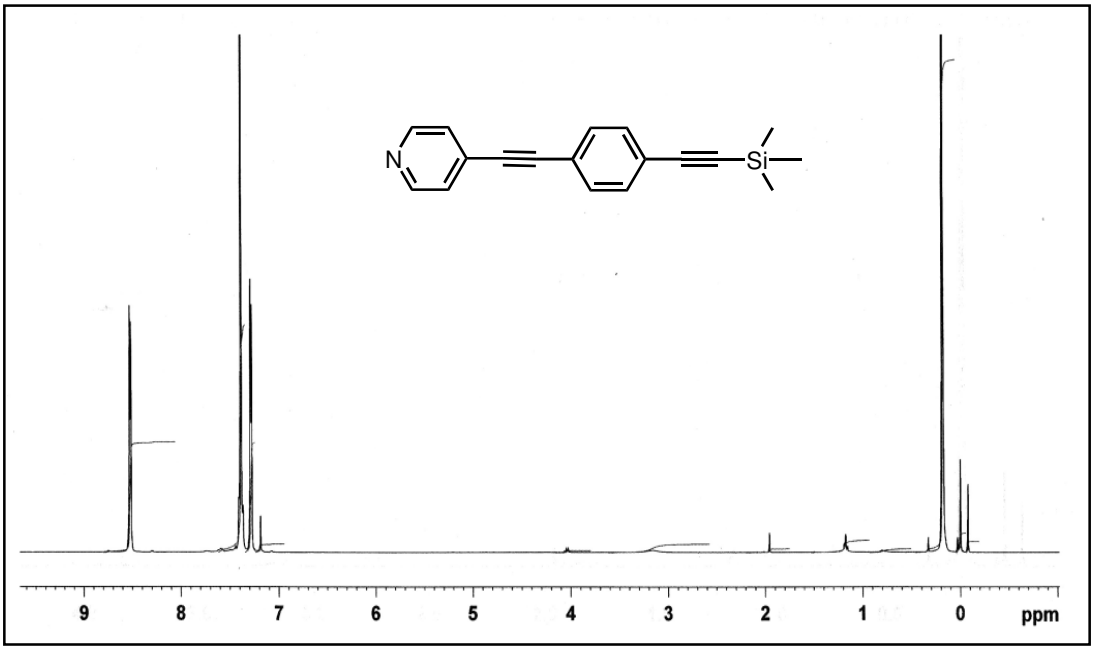

Figure A. 3. ^{1}H NMR Spectrum of Compound **(4)**

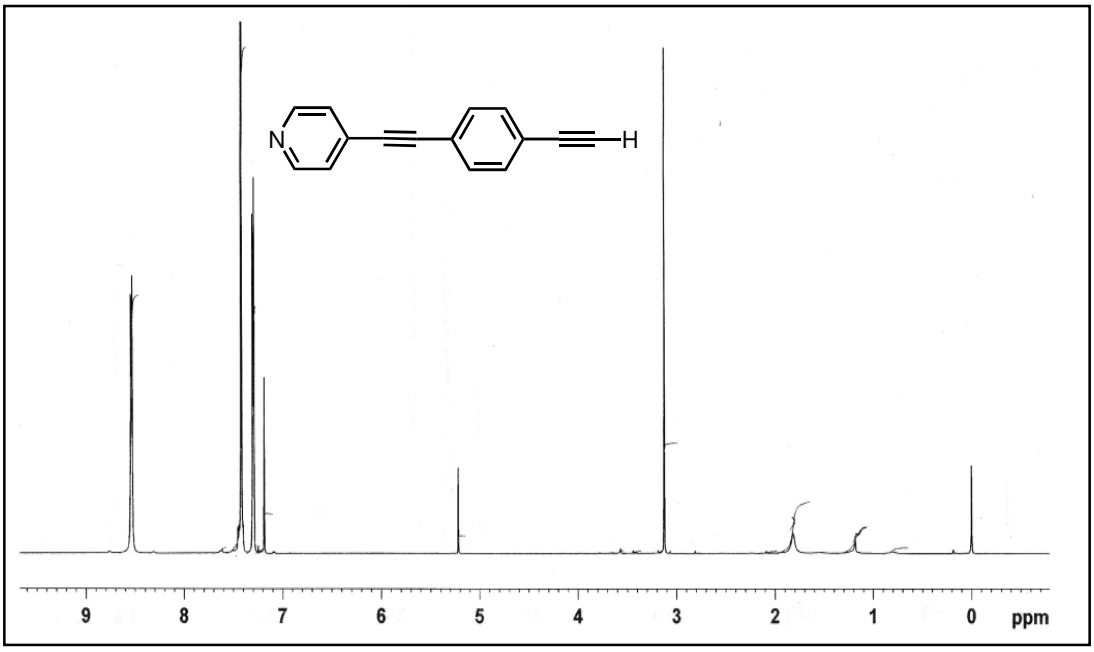

Figure A. 4. 1H NMR Spectrum of Compund **(5)**

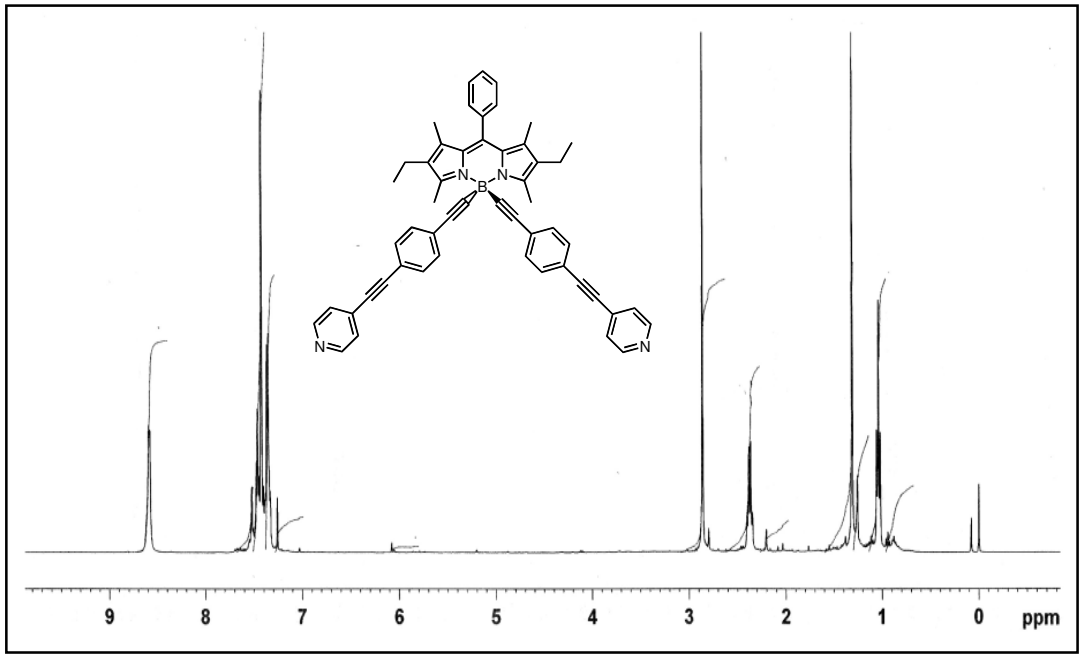

Figure A. 5. ^{1}H NMR Spectrum of Compound **(7)**

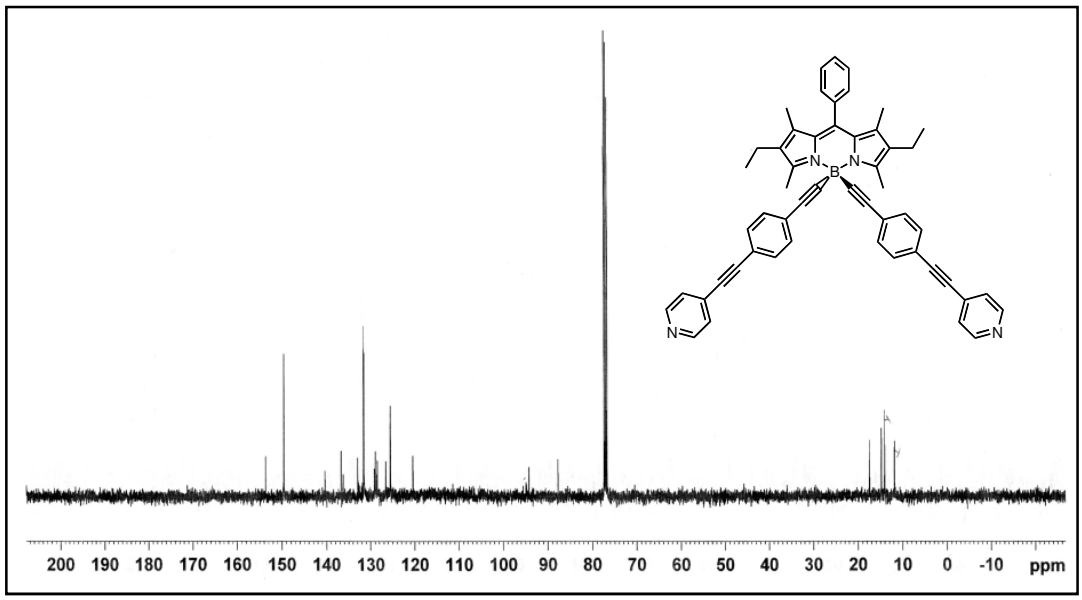

Figure A. 6. ^{13}C NMR Spectrum of Compound **(7)**

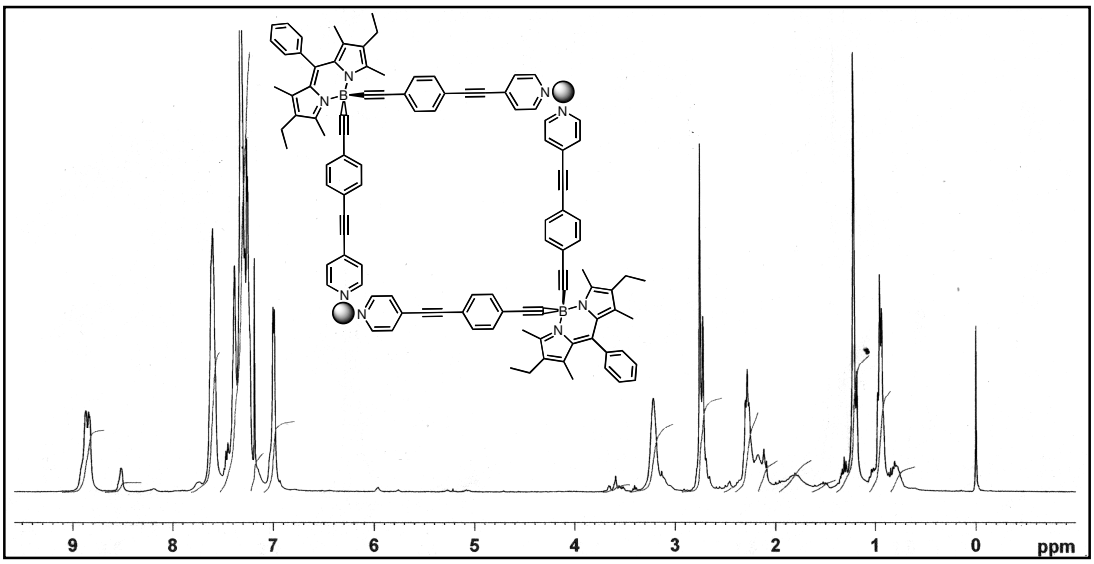

Figure A. 7. ^{1}H NMR Spectrum of Compound **(8)**

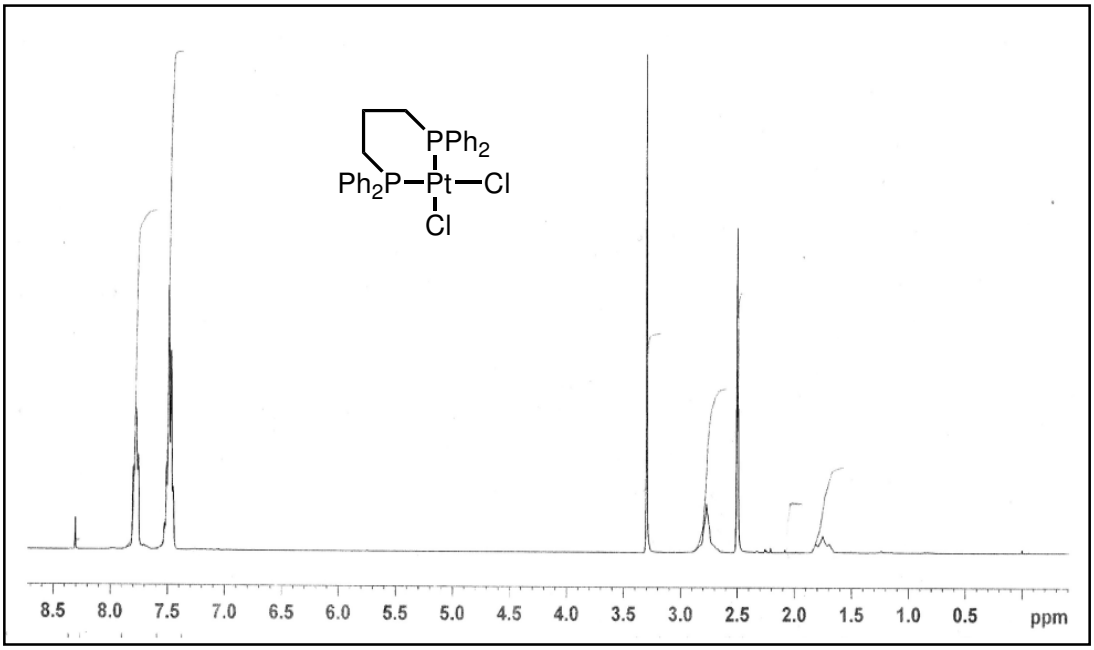

Figure A. 8. ^{1}H NMR Spectrum of Platinum Complex1

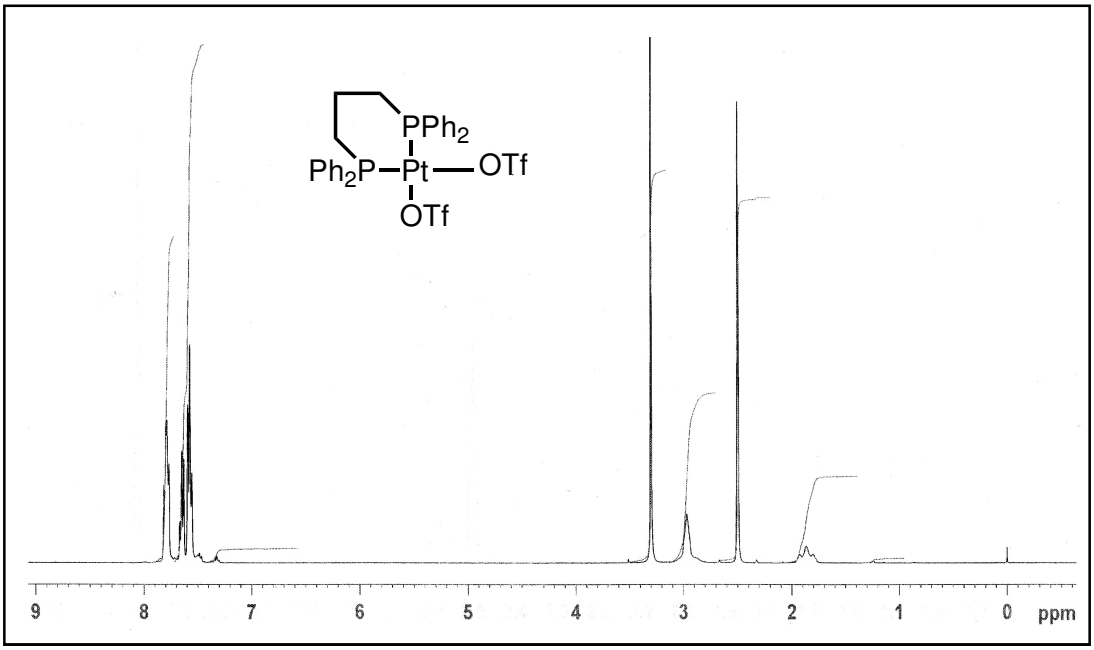

Figure A. 9. ^{1}H NMR Spectrum of Platinum Complex2

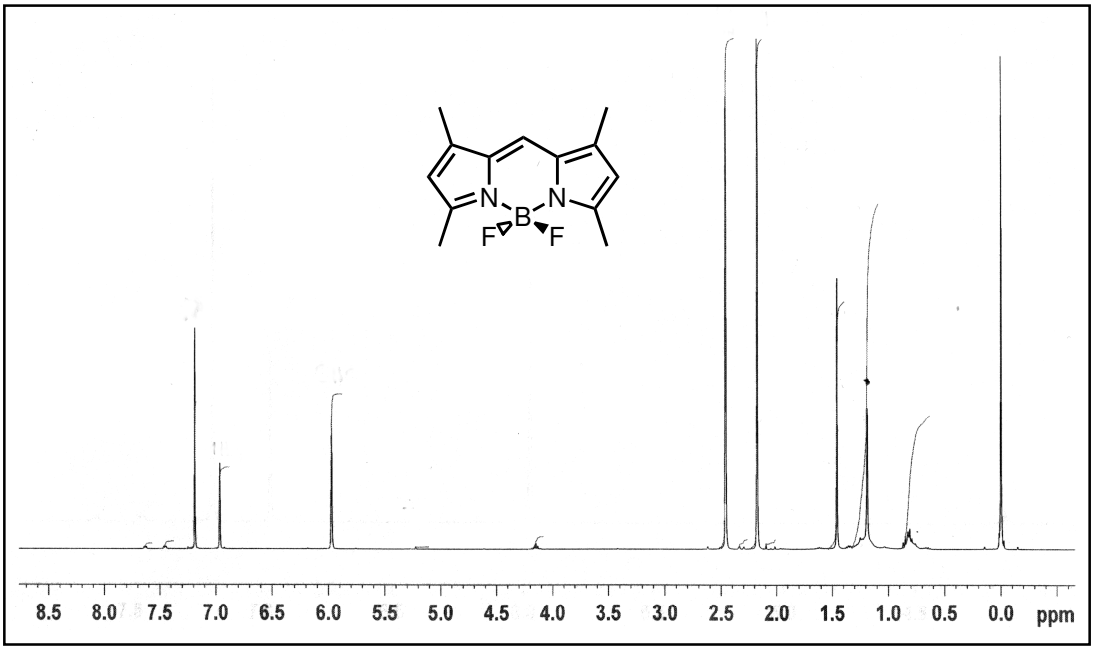

Figure A. 10. ^{1}H NMR Spectrum of Compound **(9)**

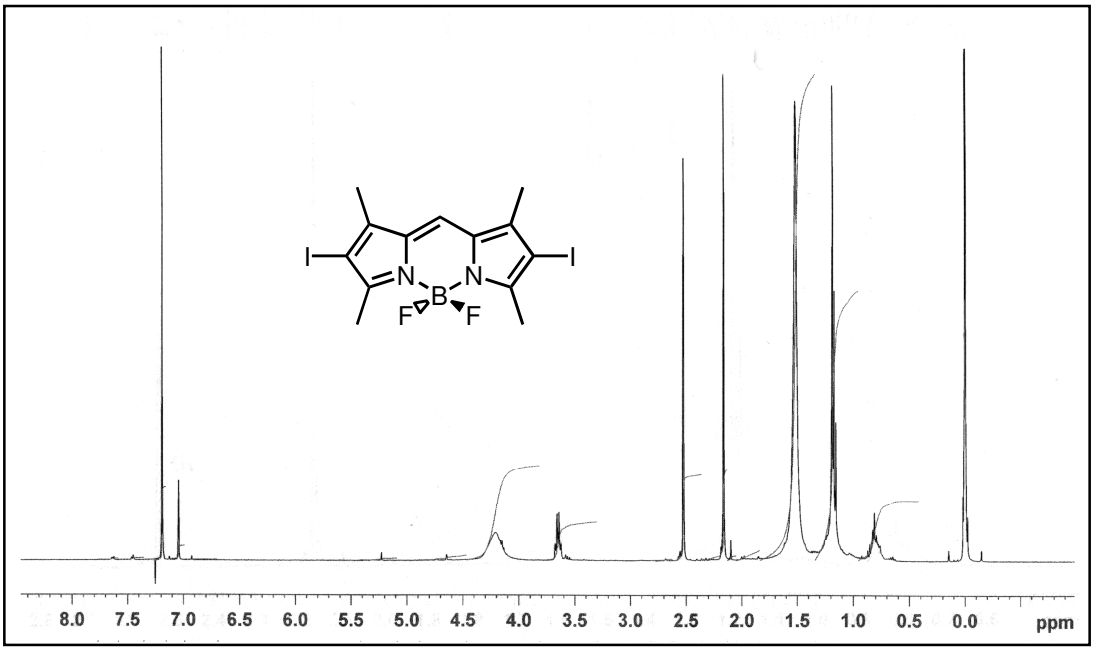

Figure A. 11. ^{1}H NMR Spectrum of Compound **(10)**

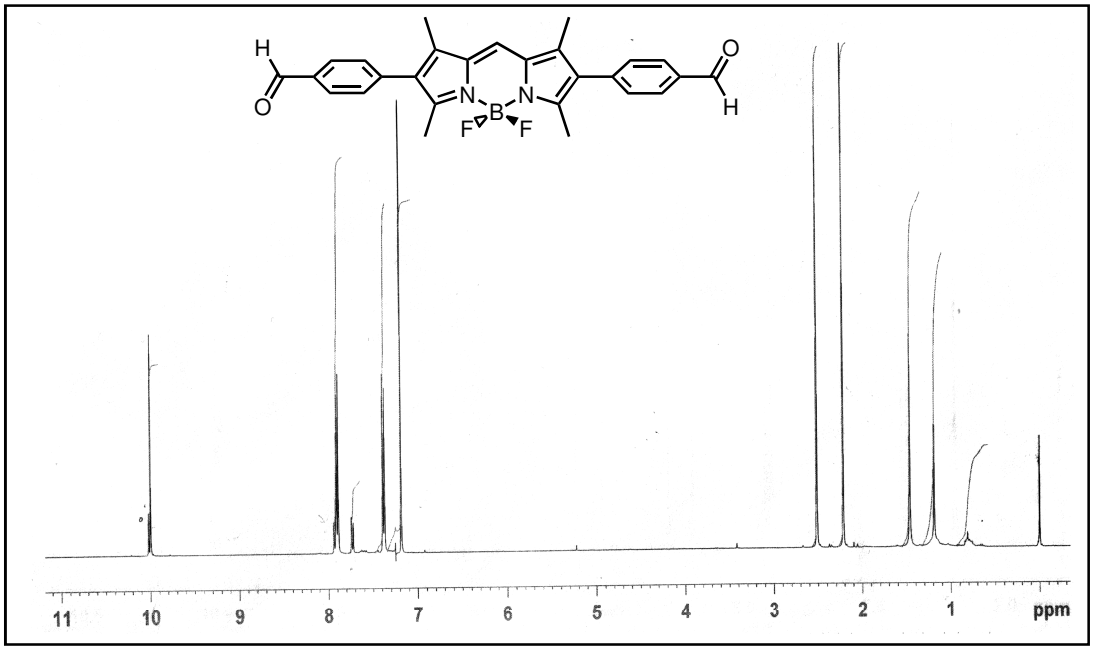

Figure A. 12. ^{1}H NMR Spectrum of Compound **(11)**

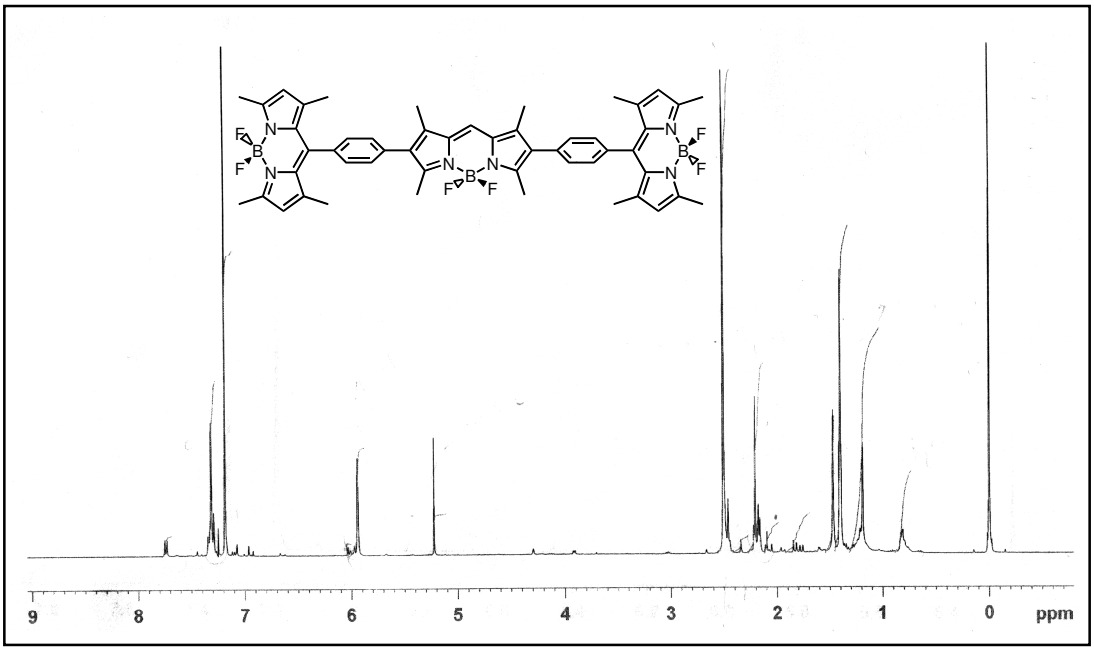

Figure A. 13. ^{1}H NMR Spectrum of Compound **(12)**

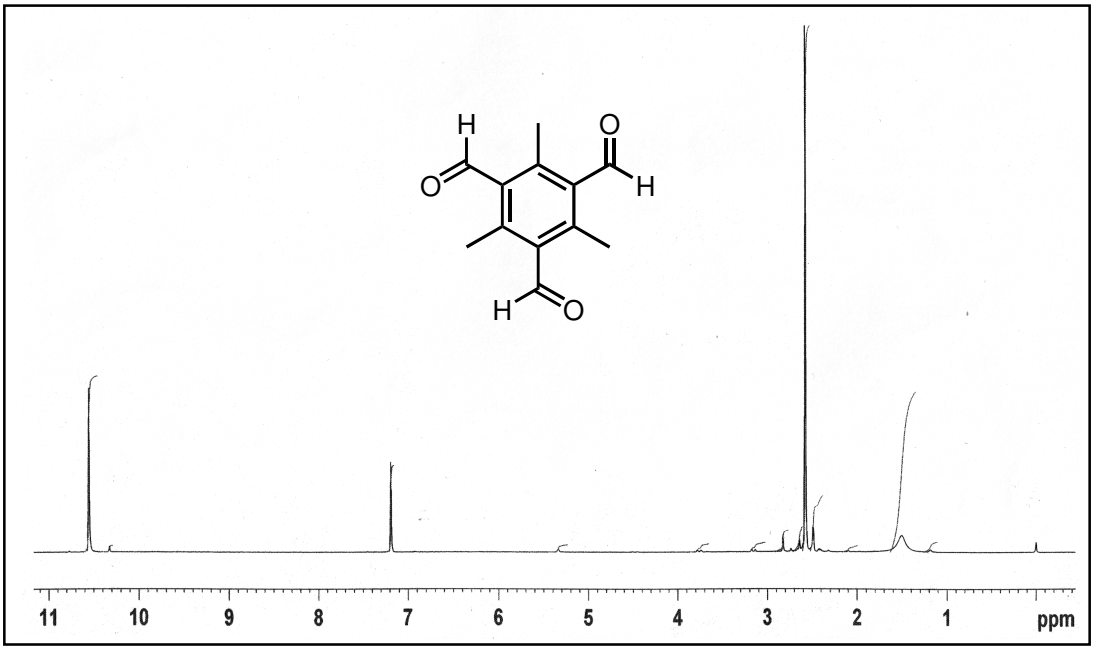

Figure A. 14. ^{1}H NMR Spectrum of Compound **(13)**

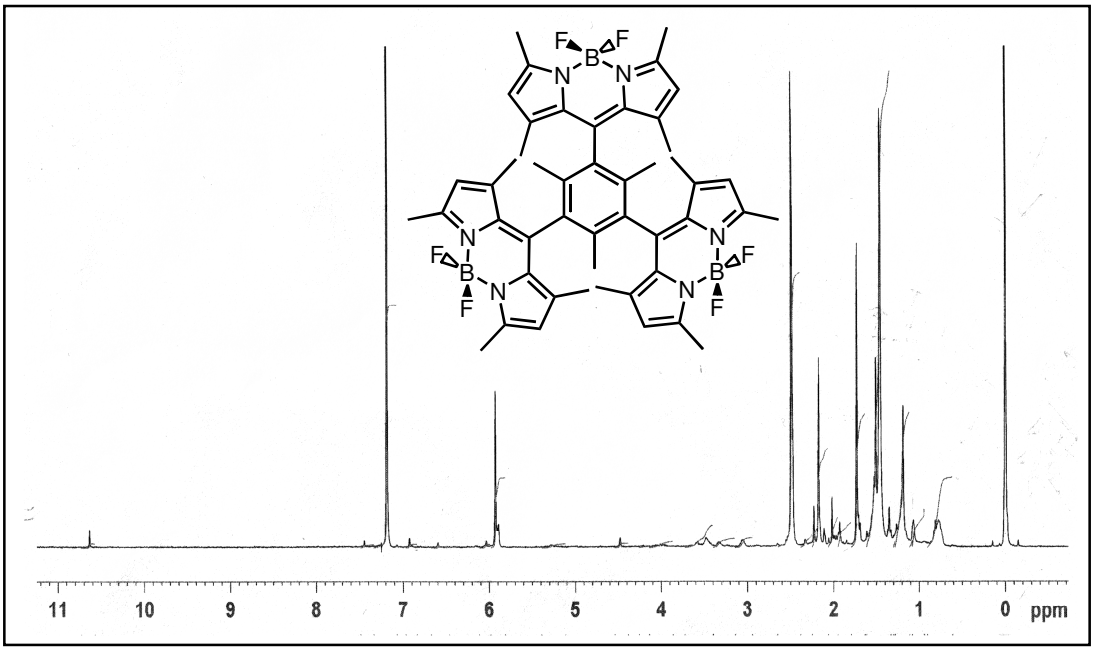

Figure A. 15. ^{1}H NMR Spectrum of Compound **(14)**

APPENDIX B

MASS SPECTRA OF

SYNTHESIZED COMPOUNDS

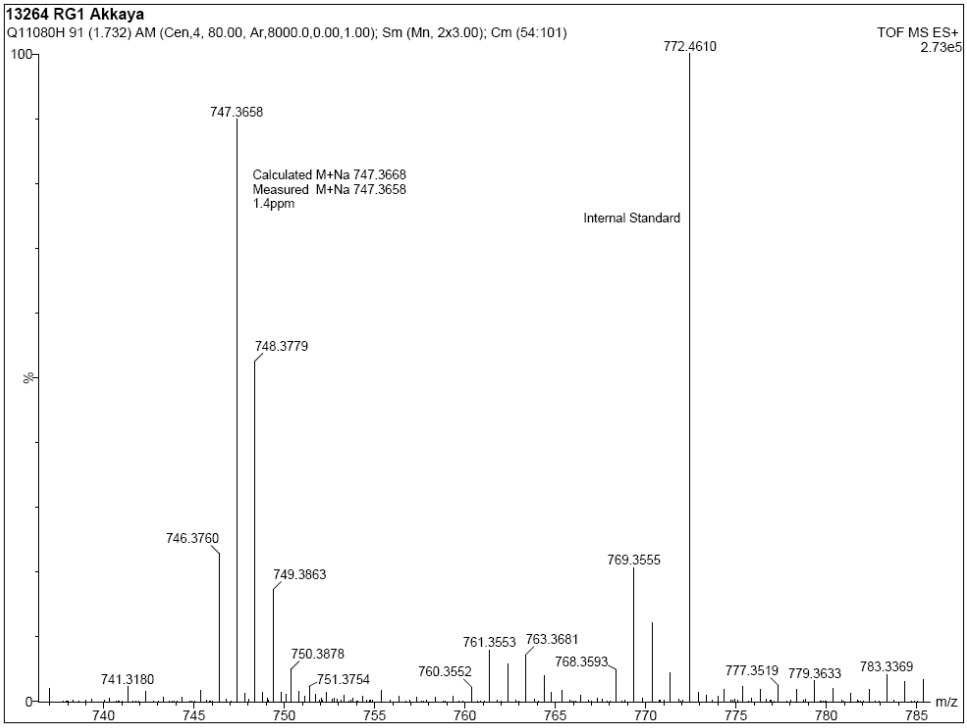

Figure B. 1 Mass Spectrum of Compound **(7)**

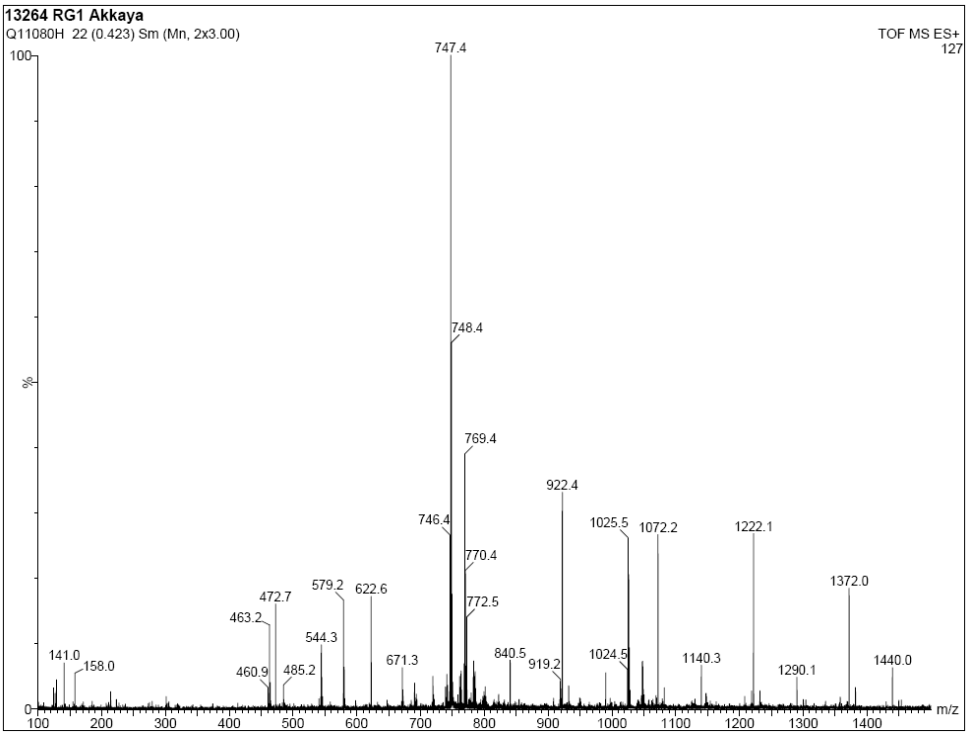

Figure B. 2 Detailed Mass Spectrum of Compound (7)