Synthesis of thiophene based Macrocycle and Metal Dipyrrins

A thesis submitted towards partial fulfillment of

BS-MS dual degree programme

by

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Under the guidance of

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Indian Institute of Science Education and Research Pune

Certificate

This is to certify that this dissertation entitled " Synthesis and Characterization of thiophene based Macrocycle and Metal Dipyrrins" towards the partial fulfillment of the BS-MS duel degree programme at the Indian Institute of Science Education and Research Pune, represents original research carried out by Rakesh Gaur at IISER Pune under the supervision of Asst. professor V. G. Anand during the academic year 2010-2011.

Name and signature of the student : Rakesh Gaur

Supervisor: Dr. V. G. Anand **Head :Chemical Sciences**

Date: 15.04.2011 **Date : 15.04.2011**

Place: Pune **Place : Pune**

Dedicated to My Beloved Parents …….

DECLARATION

I hereby declare that the matter embodied in the report entitled **"Synthesis and characterization of thiophene base Macrocycle and Metal Dipyrrins "** are the results of the investigations carried out by me at the Department of Chemistry, Indian Institute of Science Education and Research-Pune (IISERP), Pune, under the supervision of Dr. V. G. Anand and the same has not been submitted elsewhere for any other degree.

Place: Pune **Rakesh Gaur**

April 2011

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"Beside a good researcher Anand sir is a good human being, friendly in nature, understanding and a perfect teacher. I must say I was lucky to get a project guide like him. The values which I got from him will stand with me throughout my life."

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Rakesh Gaur

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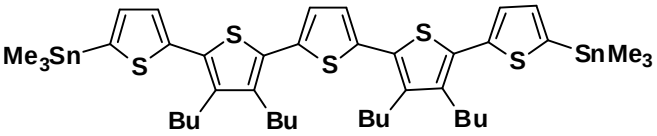
Introduction:

Macrocyclic compounds are attractive synthetic targets due to their topological features. The conjugated macrocycles, in particular, exhibit structure dependent electronic and chemical properties. This control over their physical properties increases their versatility for potential applications in supramolecular chemistry, molecular recognition, molecular electronics and material science.[1,2] Thiophene based oligomers and their analogous cyclic systems have gained significant research attention for their tunable optoelectronic properties.[3] In this regard, a few approaches to synthesize a variety of macrocyclic oligothiophenes have emerged recently. Bauerle and co-workers[4] have successfully synthesized cyclco[n]thiophenes, bearing ten to thirty five thiophene subunits. They have exploited a one-pot synthesis of platinum assisted cyclization /coupling reaction of stannyl substituted oligothiophenes, **1**. A metalla-macrocycle, **2**, is generated in this process of organometallic reactions involving ligand exchange reactions with platinum, to facilitate C-C bond formation by reductive elimination of the metal by thermal activation. The macrocycles were separated by size exclusion chromatography. The yields of the macrocycles varied from 1.5% to 25% depending on the size of the macrocycle. The thirty five membered macrocycle was found to form in major yields.



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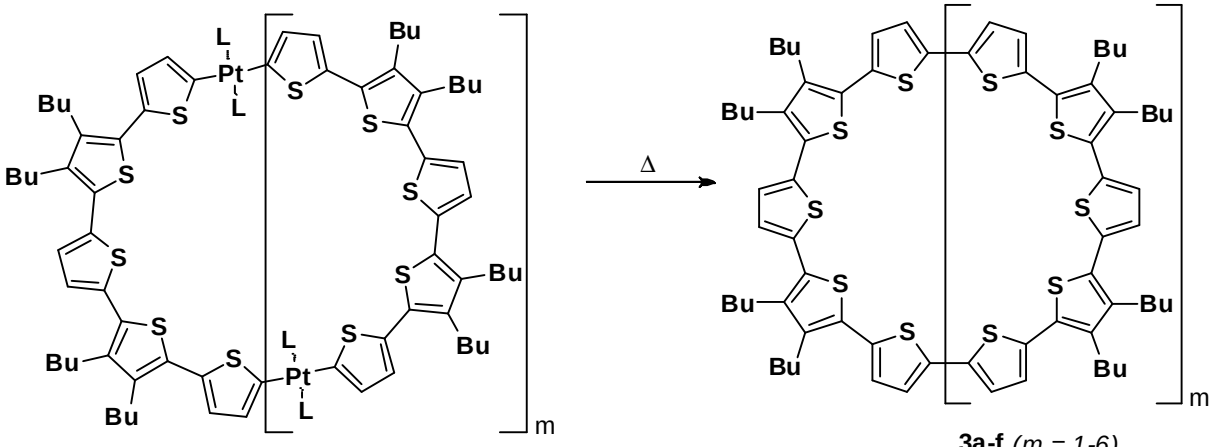
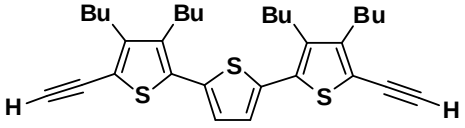


2 **3a-f** *(m = 1-6)*

In an earlier procedure they had directly made similar such macrocycles by employing Sonogashira-Hagihara coupling reaction between diiodo-oligothiophenes and

trimethylsilylacetylene to generate di-acetylene substituted oligothiopohene, **4**. This was followed by Glaser reaction of the corresponding deprotected acetylenes to synthesize macrocyclic oligothiophenes with two consecutive acetylenes in between the short oliothiophenes, **5**. The reaction of these macrocycles with sulfur nucleophiles in methanol converted the two acetylene bridges into an individual thiophene sub-unit. In this method they



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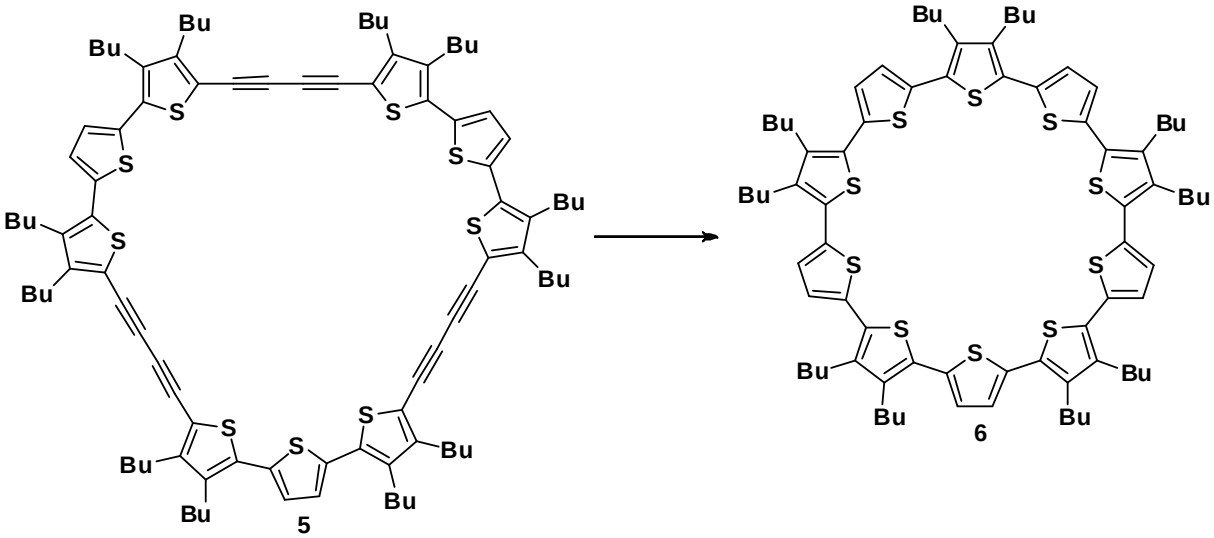


5 **6**

were able to create multiple thiophene sub-units upon the formation of the macrocycle, **6**.

Similar such macrocycles were also synthesized by Iyoda[5] and co-workers, in which the acetylene linked thiophenes were used as oligomers. Bisformylation of such oligothiophenes followed by McMurry coupling reaction yielded the ethylene bridged giant macrocyclic oligothiophenes bearing twelve to thirty subunits. They were separated by gel permeation chromatography. The presence of ethylene bridges gave rise to region isomers with respect to E and Z configurations. The macrocycle with twelve thiophene subunits was found to have three different isomers in the form of E, E; E, Z and Z, Z with respect to the ethylene bridges. Amongst these three, the E, E isomer was formed in highest yields and was also characterized by single crystal x-ray crystallography. Out of the twelve thiophenes in the macrocycle, two diagonally opposite thiophenes were found to be inverted such that the sulphur of these

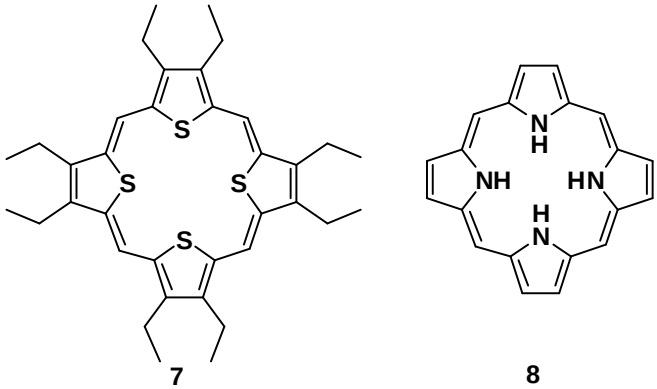
thiophene rings were pointing towards the outside of the macrocycle. The electronic properties of these macrocycles as measured by electronic spectroscopy shows a gradual red shift and they are found to absorb in the visible region between 450 – 500 nm. The ^{1}H NMR spectrum of these macrocycles do not show any significant ring current effects indicating the benzenoid nature of the macrocycles. This asserts the lack of effective π orbital overlap between adjacent thiophene unit and hence the absence global aromatic features for the macrocycles.

Objectives of this project:

The synthetic methodology adopted for the above mentioned macrocycles involved multiple steps and laborious in nature. Therefore, we attempted to design simpler synthetic methodology to for similar macrocycles from easy to make precursors. Apart from the synthetic view point, we envisaged the possibility of tuning electronic properties, like ring current effect, and the HOMO-LUMO gap depending on the number of the thiophenes present in the macrocycle. The macrocyclic systems described above do not show either paratropic or diatropic ring current effects in their respective ^{1}H NMR spectrum as expected of cyclic conjugated systems, clearly indicating the lack of effective π conjugation between adjacent thiophene units. A key priority was to have effective conjugation, which could enable the tuning of opto-electronic properties. Secondly, we wished to explore the design and synthesis of similar macrocycles with metal ions as connectors in the conjugated pathway. The role of metal ions in π conjugation is not well explored and hence encouraged us to investigate the possibility of engineering thiophene based metal complexes. We designed thiophene based dipyrrin metal complexes such that an alpha position of the thiophene is unsubstituted and can be reacted further for the formation of the macrocycle.

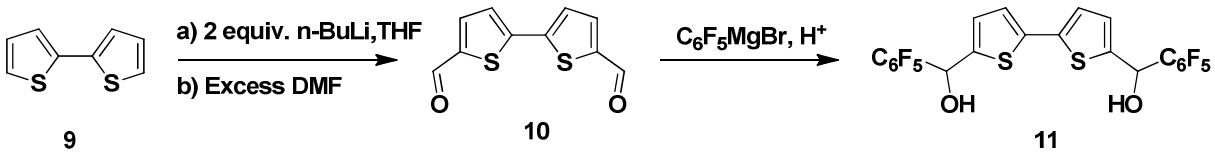
Synthesis:

Our idea for simple synthesis of the macrocycles stemmed from the fact that alcohols of thiophenes can undergo self condensation reaction leading to the formation of macrocyclic products. It was explored by Vogel and co-workers[6] in their attempt to synthesize tetrathia isophlorin, **7**. Isophlorin, **8**, was actually conceived as an anti-aromatic 20π macrocycle during the synthesis of chlorophyll.[7] In spite of being a synthetic challenge, its skeleton structure has inspired to synthesize a host of similar macrocycles with annulene like structure.[8] Expanding its π network has also been explored to synthesize a series of expanded isophlorins which exhibit paratropic or diatropic ring current effects depending on the number of the π electrons along the conjugated pathway.[9]



7 **8**

Invoking synthetic strategies similar to the synthesis of isophlorin and its expanded derivatives, we attempted to synthesize macrocycles starting from bithiophene precursors. Bithiophene, **9**, was synthesized by the Ni catalyzed Kumada coupling[10] of bromothiophene. This was further formylated to obtain the bisformyl bithiophene, **10**, which was further reduced to the corresponding dialcohol, **11**, using pentafluorophenyl Grignard reagent (scheme-1).

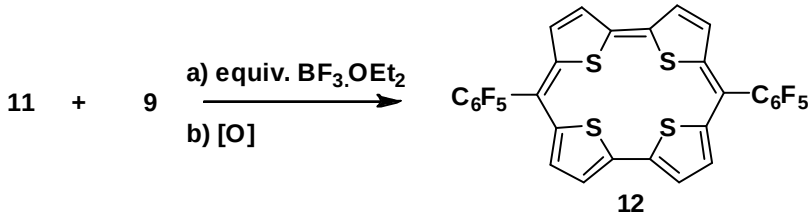


9 **10** **11**

Scheme-1: Synthesis of bithiophene diol

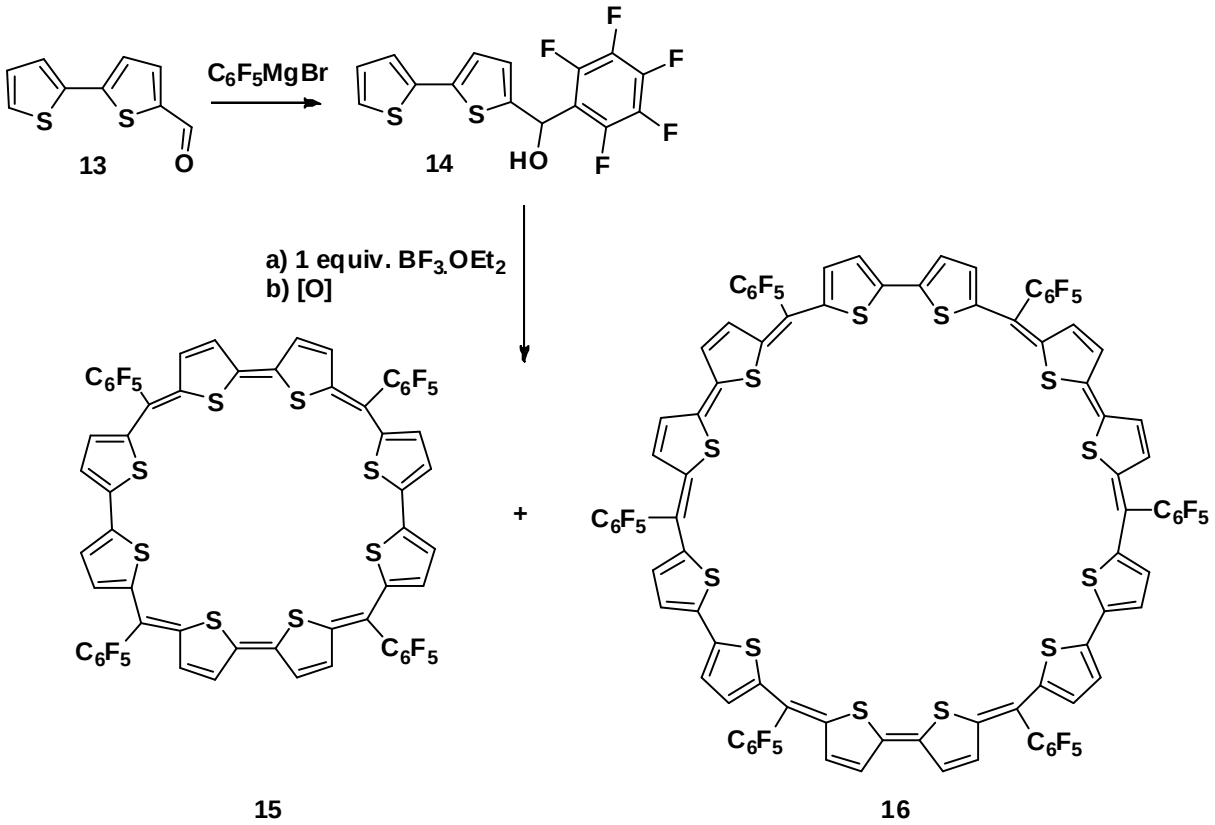
An equimolar concentration of **11** and **10** were subjected to acid catalyzed condensation reaction in dry dichloromethane under inert and dark atmosphere (scheme-2). This reaction mixture was

further oxidized to get the conjugated macrocycle. Only the 1:1 condensed product, **12**, was formed in trace yields in this reaction.



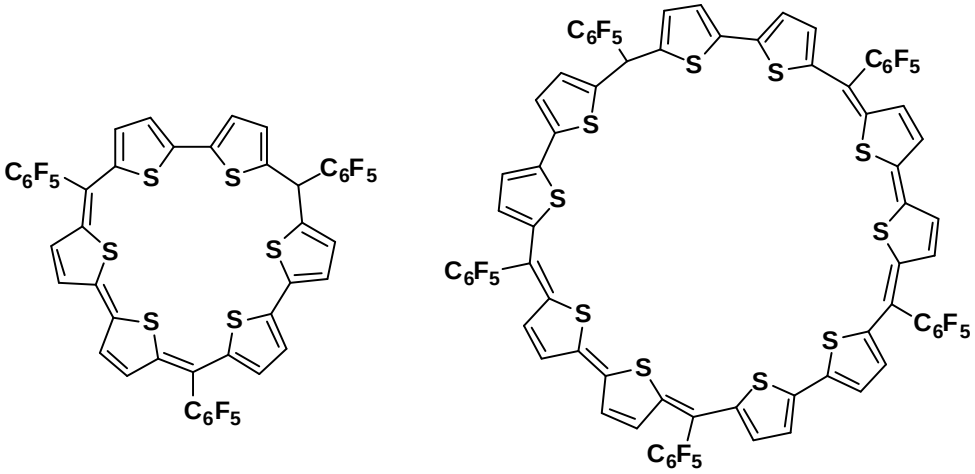
Scheme-2: Macrocyclization using **9** and **11**

This forced us to modify the synthetic strategy and we adopted a methodology similar to synthesis of **7**. The mono formyl bithiophene, **13**, was synthesized by mono lithiation of bithiophene, **9**, followed by addition of DMF at lower temperatures. The formyl bithiophene was further reduced by pentafluorophenyl Grignard reagent to obtain the alcohol, **14**, good yields. The alcohol, **14**, was subjected to acid catalyzed self condensation reaction (scheme-3) under similar conditions as described in scheme-2. The reaction mixture was purified by column chromatography to isolate the macrocyclic products **15** and **16**.



Scheme-3: Synthesis of **15** and **16**

Macrocylic products corresponding to two, three, four, five and six units of the bithiophene units could be detected in the MALDI-TOF mass spectrum of the reaction mixture. But all these macrocycles will not be completed conjugated as neutral molecules, and hence they were not isolated to be characterized at this point of time. As examples, the most probable structure for trimer and pentamer are shown in scheme-4. Only two macrocycles, **15** and **16**, could be isolated from column chromatography, while the higher congeners were found to be formed only in trace amounts.

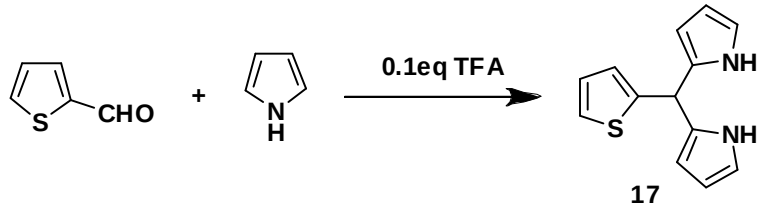


Scheme-4: Unconjugated macrocycles with odd number of bithiophene units

Both the macrocycles, **15** and **16**, were characterized by electronic absorption spectroscopy, 1H NMR and Mass spectrometry. MALDI-TOF mass analysis confirmed the composition of the macrocyles in terms of their m/z value. The eight thiophene macrocycle shows m/z value of 1372.2544 and the twelve thiophene macrocycle showed m/z value of 2058.3398 against the calculated values of 1371.87 and 2057.80 respectively. They were also characterized by ^{1}H NMR spectroscopy. They exhibit similar peak patterns, implying a similar structural feature in the solution state. Two quartets corresponding to equal number of protons were observed for **15** at δ 7.69 and 7.51 ppm. A similar spectrum bearing two multiplets corresponding to equal number of protons was observed for **16** at δ 7.69 and 7.51 ppm. A detailed analysis to confirm the solution state structure of these macrocycles is underway. Due to their extensive conjugation, they form colored solutions in common organic solvents. **15** forms a pink color, while **16** forms a bluish color in dichloromethane. **15** absorbs in the visible region of the electromagnetic spectrum having maximum absorption at 555 nm. **16** was found to have maximum absorption at 587 nm.

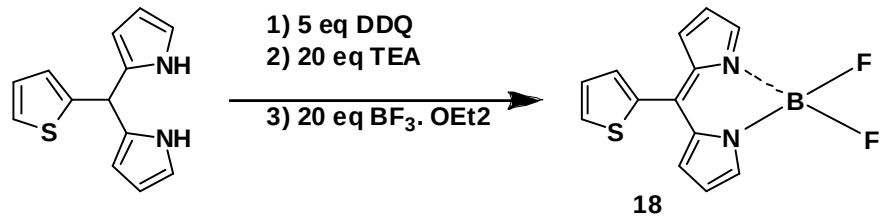
Synthesis of Thiophene Dipyrrins and its Complexes:

Dipyrrin[11] is a versatile ligand containing two pyrrole rings, which can complex with most of the metal ions. Its importance and applications are widely accepted in the form of boron complex which is commonly referred to as BODIPY.[12] Due to its extended conjugation in the oxidized state, it exhibits attractive photo physical properties which can be tuned depending on the nature of the substiutents or by replacing the metal ions. Since, two dipyrrin ligands are needed for the formation of a metal complex, we wished to explore the role of thiophene in making such metal complexes at either of its alpha position. It was synthesized by well established procedures using 2-formyl thiophene and pyrrole. In presence of acid, they react to for the dipyrromethane, **16**, at the second position of the thiophene (scheme-5).

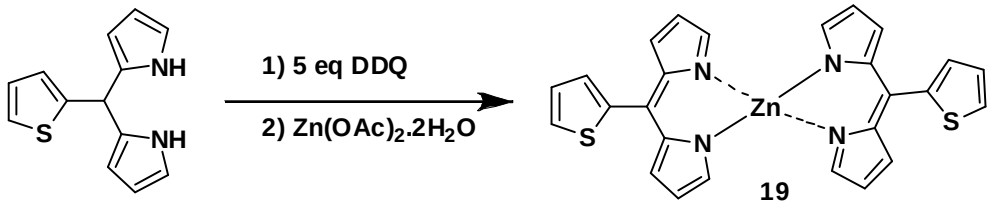


Scheme-5: Synthesis of 2-thienyl dipyrromethane

Further oxidation leads to the dipyrrin ligand, which is further used for the complexation reactions. It was first reacted (scheme-6) with boron trifluoride etherate to form the corresponding the BODIPY complex, **18**. Later the same dipyrrin ligand was reacted with Zn salts to form the Zi-Dipyrrin complex, **19** (scheme-7).



Scheme-6: Synthesis of 2-thienyl BODIPY



Scheme-7: Synthesis of 2-thienyl Zn-$(dipyrrin)_2$ complex

A similar reaction with a palladium salt also yielded a palladium complex analogous to the Zn(dipyrrin)$_2$ complex **19**. The structure of these molecules was determined by data obtained from various spectroscopic techniques. The formation of the dipyrromethane was evident from the significant change in the proton resonances for thiophene protons and the pyrrole NH (δ: 7.98 ppm, broad singlet corresponding to two protons) in the ^{1}H NMR spectrum. **17**. The formation of the boron dipyrrin complex was very much evident from the conspicuous absence of the pyrrole NH and the methylene proton signals in the proton NMR spectrum of 17. Similar absence of both the resonances (methylene proton and the pyrrole NH) in proton NMR spectrum of 19 confirmed the formation of zinc complex **19**. The formation of these molecules was also confirmed by mass spectrometry. The electronic absorption spectrum of the zinc complex showed a strong absorbance at 495 nm, while that of the boron complex was found to have an intense absorption at 512 nm.

The zinc complex, **19**, was also characterized by growing good quality single crystals from dichloromethane/hexane solvent system. It was found to have a monoclinic crystal system with P1 21/1 space group. The geometry around zinc was found to be a distorted tetrahedral structure with N-Zn-N bond angles varying from 94º to 122º (figure-1). Such severe distortion can attributed to the orientation of the two diyrrin units with respect to the central metal ion. The two pyrroles in the dipyrrin unit are found to coplanar in nature and the thiophene is found to make an angle of 45º with the planar system. Interestingly, the two dipyrrin units make an angle of 73º with each other, thereby making the whole unit non-planar in nature. The rigid planar nature of the dipyrrin ligands making arranged almost orthogonal to each other makes the geometry around the Zn to distort severely from regular tetrahedral structure.

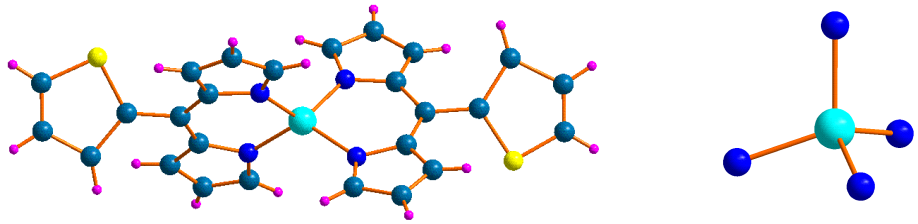
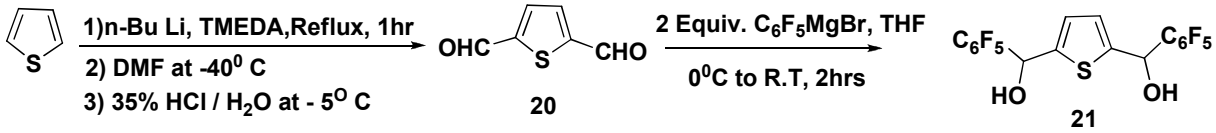
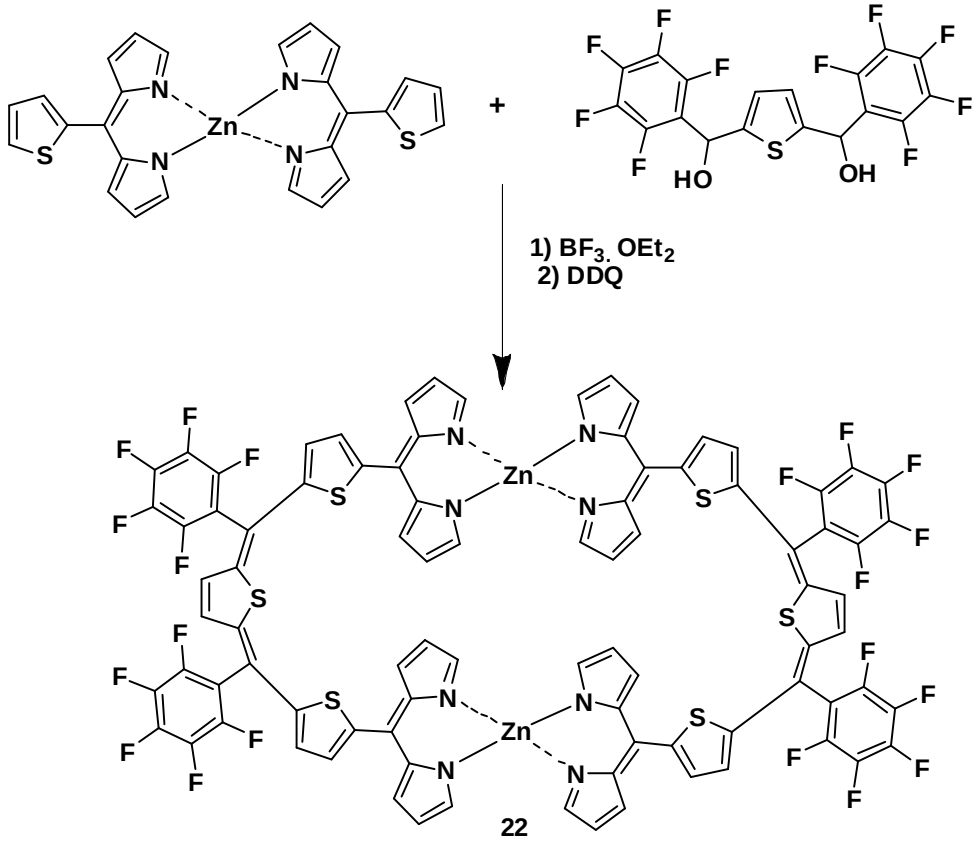


Figure – 1: Molecular structure of **19** (left). The tetrahedral geometry around Zn (right) in **18**. Color Codes: Blue-C, Yellow-S, Pink-H and Cyan-Zn

The zinc complex of the dipyrrin, **19**, has two thiophenes that are diagonal to each other. Since they have an unsubstituted alpha position, they could be used as precursors for condensation reactions. We envisaged that condensation of **19** with an alcohol such as thiophene diol, **21**, should yield a novel macrocycle, **22**, wherein a metal ion will be a covalent bridge to construct the macrocycle. The thiophene diol, **20**, was synthesized by the reduction of 2,5-diformylthiophene, **20**, by pentafluorophenyl Grignard reagent (Scheme-8). This diol was condensed with **19** (scheme-9) under conditions similar to that described in scheme-2. The metallo-macrocycle, **22**, was formed only in poor yields as detected from MALDI-TOF spectrum and hence could not be isolated for completely characterization.

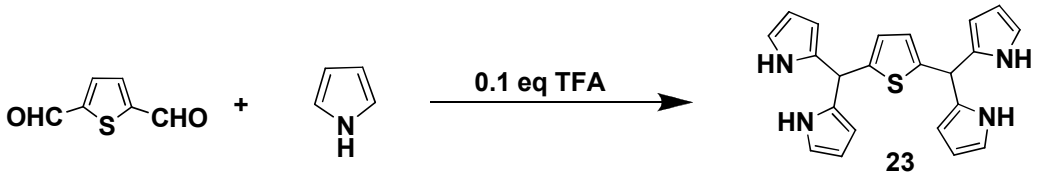


Scheme-8: Synthesis of thiophene dio from thiophene

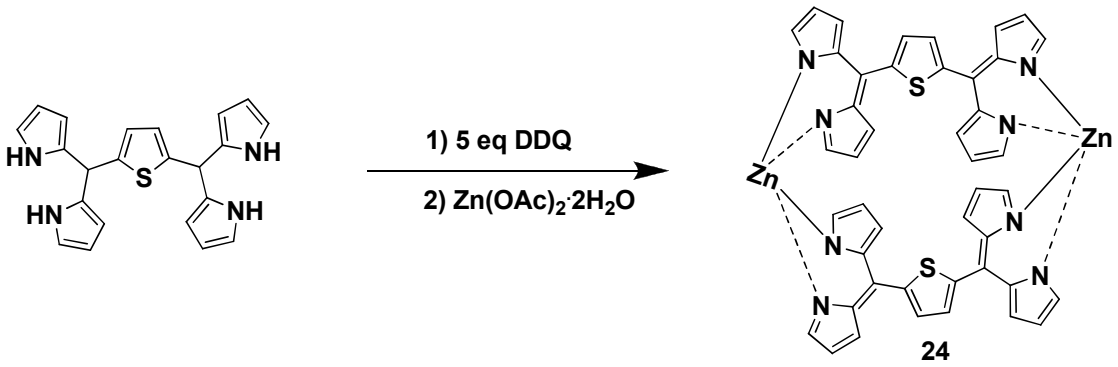


Scheme-9: Condensation reaction of thiophene dio with thienyl zinc(dipyrrin)$_2$

Since the product formed from the scheme-9 were found to be very poor, we modified the synthetic pathway to synthesisze the metalla-macrocycles such that formation of the metal complex will lead to the cyclized product, **24**. 2,5-diformylthiophene, 20, was reacted with pyrrole (scheme-10) to obtain 2,5-bis(dipyrromethane)thiophene, **23**. This was reacted with the zinc salt (scheme -11) as described in scheme-7 to obtain the metal complex. But the reaction was unsuccessful and lead to polymeric like product, which could not characterized completely.



Scheme-10: Synthesis of 2,5-bis(dipyrromethane)thiophene



Scheme-11: Synthesis of cyclic Zn(dipyrrin)$_2$

Summary:

This thesis describes our efforts to explore novel and simple synthetic strategies for macrocyclic compounds. Our idea to use thiophene as the starting material to synthesize macrocyclic products is ably supported by the number of reactive precursors that could be generated by simple reactions. The key goal in our synthesis was to design simple synthetic steps with easy to make precursors. The cyclic product from bithiophene could be achieved from the acid catalyzed self condensation of its corresponding alcohol. Two different macrocycles **15** and **16** were obtained in just two steps starting from bithiophene in comparison to the multistep reactions know so far. Suitable modifications such as reaction time, solvent polarity and dilution effects may enable us to synthesize much larger size macrocycles.

The dipyrrins are known to act as ligands for various metals. For the first time, we have explored the possibility that it can be developed as ligand to suitably link metal ions to form metallo-macrocycles. Even though the reactions were did not fetch the desired products, but the formation of macrocycle **22** in trace amount certainly hints at the feasibility for the formation of such macrocycles. Research is underway to explore the possible synthetic approach to synthesize such macromolecules in good yields.

Experimental Techniques:

Chemicals used for Syntheses:

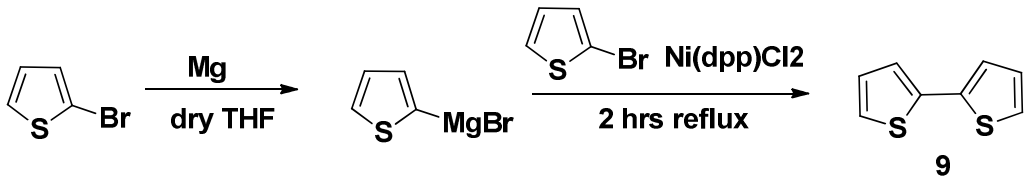
Common solvents used for syntheses were purified according to known procedures. Thiophene and Pyrrole was procured from Aldrich chemicals USA, and was distilled before use. Deuterated solvents for NMR measurements were used as received. n-Butyllithium (15% in hexane) were procured from E. Merck, Germany or Lancaster, UK. Anhydrous sodium sulfate and anhydrous calcium chloride were obtained from RanKem Fine chemicals, India. Aluminum oxide (basic) and silica gel (100-200 and 230-400 mesh) were purchased from Acme chemicals, India. 2-Bromothiophene and pentafluoro benzaldehyde were used as received from Aldrich chemicals USA.

Physico-chemical techniques:

Instruments used for characterization and evaluation of spectroscopic data are discussed below. Electronic spectra were recorded on a Perkin Elmer-Lambda 20 UV-Vis spectrophotometer. The data analyses were done using the UV-winlab software package. ^{1}H and ^{13}C NMR spectra were obtained either from 500 MHz Bruker Advance DPX spectrometer or from 400 MHz Jeol machine either in $CDCl_3$ or in CD_2Cl_2. Chemical shifts are expressed in parts per million relative to residual $CHCl_3/CH_2Cl_2$. MALDITOF was carried out on Voyager-De-STR (Applied Biosystems). Single crystals were diffracted on Bruker Apex Duo single crystal x-ray diffractometer. The data was solved using Apex-2 software.

Synthesis:

Bithiophene: (**9**)



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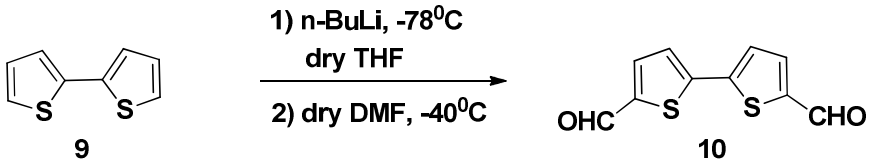
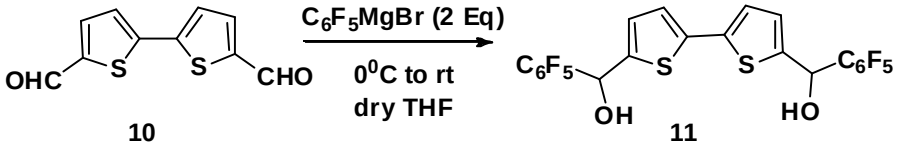
Activated Mg (1.5 g, 62 mmol) and dry THF (around 40 ml) and pinch of iodine was stirred for 5-10minutes and color of solution changed to light brown. Then, 2-thiophene bromide (6ml, 62mmol) was added slowly and after sometime color of solution became colorless. Vigorous bubbling was observed and color changed to dark brown and most of the Mg turnings were found to be dissolved. Thiophene bromide (5.01ml, 51.6mmol) was added at 0^0C and temperature was maintained. After that Ni(dpp)Cl_2 (0.336gm, 0.62mmol) was added as slowly as possible, as a suspension in THF. The solution mixture was allowed to come to room temperature and was refluxed at 90^0C for 3hrs. The reaction was quenched with dil. HCl while keeping it in ice cold conditions as lot of heat was released. The organic layer was separated and the aqueous layer extracted with Et_2O (4 x 100 ml), dried over Na_2SO_4, and evaporated under reduce pressure. Then resulting mixture was chromatographed on silica (hexane). The desired product **12** was obtained as colorless viscous liquid. Yield 8.54 g (83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, 5.7 Hz, 2H), 7.20 (d, 3.6 Hz, 2H), 7.03 (dd, 2H).

2,2'-Bithiophene-5,5'-dicarbaldehyde: (**10**)



A solution of *n*-BuLi (1.6 M in hexanes, 25 ml, 40 mmol) was added drop wise at –78 °C under Ar to a stirred solution of bithiophene (1.66 g, 10 mmol) in 100 ml of dry THF. During the whole addition, the reaction temperature was kept at –78 °C and then was allowed to gradually rise to –40 °C. At this temperature, DMF (6.1 ml, 80mmol) was slowly added and the reaction mixture allowed to warm to room temperature. The mixture was poured into a 2 M aqueous solution of ammonium chloride and extracted with $CHCl_3$ (5x50 ml). . The combined extracts were washed with water (3x50 ml), saturated brine, dried over Na_2SO_4, and evaporated under reduce pressure. The residue was recrystallized twice from CH_2Cl_2 to give 1.25 g (56 %) of desired product as yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 2H), 7.73 (d, 4.0 Hz, 2H), 7.42 (d, 4.0 Hz, 2H).

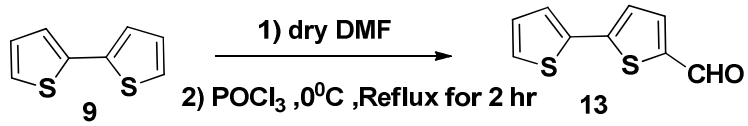
2,2'-bithiophene-5,5'-diylbis((perfluorophenyl)methanol): (**11**)



Dry THF (25ml) and activated Mg (0.169 g, 6.95 mmol) and pinch of iodine was stirred for 2 minutes. After that pentafluorobromide (0.859 ml, 6.7 mmol) was added slowly and color of solution became dark brown and was allowed to stir for two hours. To the Grignard of pentaflorobromide was added the aldehyde dissolved in THF at 0^{0}C and allowed to reach room temperature. Then TLC was checked and dipped in DNPH to check if any aldehyde is left or not. Then reaction mixture was quenched after 3 hours and the organic layer was extracted with Et_2O and combined organic layer was washed with water and brine solution. After drying over

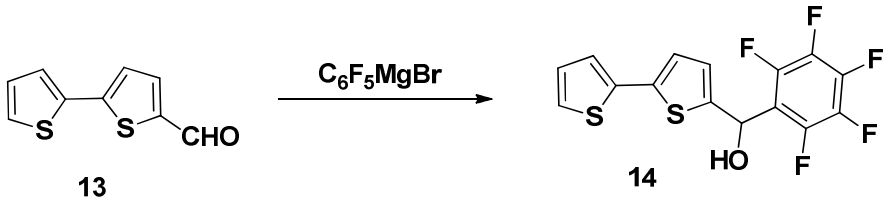
Na_2SO_4, the solvent was evaporated under vacuum to yield the pure compound**,** as white solid. Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, 5.7 Hz, 2H), 7.20 (d, 3.6 Hz, 2H), 7.03 (dd, 5.0, 3.6 Hz, 2H) .

2,2'-Bithiophene-5-carboxaldehyde: (**13**)



POCl3 (0.95 ml, 10 mmol) was added at 0 °C to a stirred solution of 2,2'-bithiophene (0.83 g, 5 mmol) and dry DMF (1.2 ml, 15 mmol) in 20 ml of 1,2-dichloroethane under Ar. After 2h of refluxing, the mixture was cooled to room temperature and neutralized with 10 ml of a 1M aqueous solution of sodium acetate. The organic layer was separated and the aqueous layer extracted with 3x15 ml of CH2Cl2. The combined extracts were washed with water, dried over Na2SO4, and evaporated under reduce pressure. The residue was purified by column chromatography (silica gel, CH2Cl2) to give 0.87 g (89 %) of product as a yellowish solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.85(s,1H), 7.66(d, 4Hz, 1H), 7.37-7.35(m, 1H), 7.34(s,1H), 7.23(s,1H) ,7.07-7.05(m,1H)

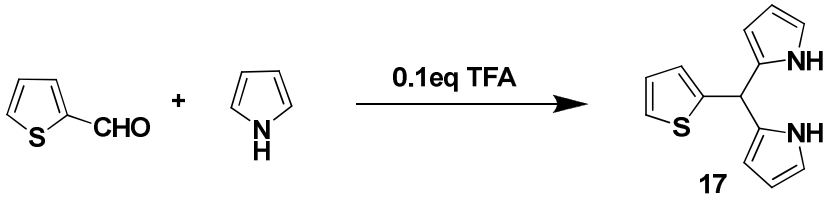
Bithiophene diol: (**14**)



Dry THF (25ml) and activated Mg (0.169 g, 6.95 mmol) and pinch of iodine was stirred for 2 minutes. After that pentafluorobromide (0.859 ml, 6.7 mmol) was added slowly and color of solution became dark brown and was allowed to stir for two hours. To the Grignard of pentaflorobromide was added the aldehyde dissolved in THF at 0^0C and allowed to reach room temperature. Then TLC was checked and dipped in DNPH to check if any aldehyde is left or not. Then reaction mixture was quenched after 3 hours and the organic layer was extracted with Et_2O and combined organic layer was washed with water and brine solution. After drying over Na_2SO_4, the solvent was evaporated under vacuum to yield the pure compound**,** as white solid.

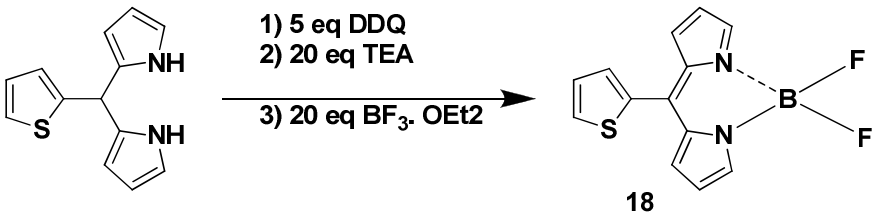
Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, 4 Hz, 1H), 7.12 (d, 4 Hz, 2H), 7.01-6.99(m, 1H), 6.98 (d, 4Hz, 1H),6.80(d, 4Hz, 1H),6.35(d, 4Hz, 1H), 3.89(d, 4Hz,1H)

Thiophene Dipyrromethane: (**17**)



Mixture of Pyrrole (436 mmol, 30.24 ml) and thiophene 2-aldehyde (21.8 mmol, 2 ml) was degassed by bubbling with nitrogen for 10min. TFA (2.18 mmol, .14 ml) was added and the mixture was stirred for 30 minutes at room temperature. It was diluted with dichloromethane (50 ml), and then washed with 0.1N NaOH, followed by water washing. The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the unreacted pyrrole was removed by applying high vacuum. The resulting viscous dark brown liquid was purified by colomn chromatography(silica gel 100-200 mesh) using 5% ethylacetate in petroleum ether as eluant. Product isolated as white solid in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98(s, 2H), 7.2 (dd, 1H), 6.95-6.93(m, 1H), 6.88(d, 4Hz, 1H), 6.70-6.69(m, 2H), 6.17-6.14(m, 2H), 6.05-6.03(m, 2H), 5.74(s, 1H).

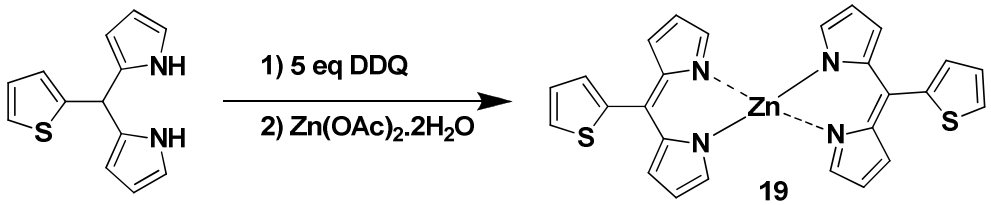
Thienyl Borondipyrrin: (**18**)



Solution of thiophenedipyrromethane (0.5 g, 2.19 mmol) in 10ml and DDQ (1 g, 4.2 mmol) in 10 ml THF was prepared, which was added drop wise to oxidized thiophenedipyrromethane with constant stirring as this reaction is a very exothermic, under atmospheric pressure and at room temperature for 1hr. Then it is thoroughly washed with water after evaporating THF. Then anhydrous sodium sulphate is added to remove water if present .After that solvent is removed,

then 5 ml DCM is added to residue after which TEA (4.3ml, 30.89 mmol) was added under nitrogen at room temperature with constant stirring and then Boron trifluoride etherate (4 ml, 31.8 mmol) was added drop wise and reaction is left for 8 hr. The above was washed with water thoroughly to separate dark brown organic viscous liquid and then sodium sulphate is added. After that filtration, column chromatography of the residue was done in 10% ethyl acetate in petroleum ether using 100-200 silica. Product was isolated as an orange solid with greenish shine.Yield :30%. ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.92 (s, 2H), 7.72-7.70 (m, 1H), 7.57-7.56 (m, 1H), 7.27-7.25 (m, 3H), 6.57 (d, 4Hz, 2H).

Bis(dipyrrinato)zinc complexes: (**19**)



19

A mixture of thiophenedipyrromethane (500 mg, 2.15 mmol) and Zn(OAc) O (2.4 mg, 1.1 mmol) in THF (10 mL) was treated all at once with DDQ (621 mg, 2.5 mmol). TLC (silica, $CHCl_3$) showed no dipyrromethane remained after stirring for 1 hr at room temperature. Solvent was removed, and the residue was dissolved in DCM. The organic phase was washed with aqueous $NaHCO_3$ and dried with sodium sulphate. Chromatography purification [silica, 80% DCM in pet ether] afforded a shining needle shaped fibres after crystallization. Yield : 72%.^{1}H NMR (400 MHz, $CDCl_3$): δ:7.53-7.50 (m, 3H), 7.40-7.39 (m, 1H), 7.16-7.14 (m, 1H), 7.04 (d, 4Hz ,2H), 6.43-6.42 (m, 2H).

Synthesis of macrocycles **15** and **16**:

Bis-thiophene -mono-ol (500 mg, .34mmol) was prepared in 200 ml of DCM under very dry condition and in absence of light $BF_3.OEt_2$ (0.12 ml, 97mmol) was added by micro syringe and left for constant stirring for 2 hr at room temperature. DDQ was added , left open for 1hr and basic workup was done by passing reaction mixture through Basic Alumina .Column chromatography was done but macromolecule could not separated. The formation of this macrocycle is confirmed by MALDI –TOF.

(**15**): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70-7.68 (m, 8H), 7.52-7.50 (m, 8H). Uv-Vis (CH_2Cl_2) λ_{nm} (ε x 10^{-4}): 464 (0.906), 555 (1.7) MALDI-TOF: Obsd.: 1372.2544; Calcd: 1371.87.

(**16**) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70-7.68 (m, 8H), 7.53-7.50 (m, 8H). Uv-Vis (CH_2Cl_2) λ_{nm} (ε x 10^{-4}): 458 (1.41), 587 (2.78). MALDI-TOF: Odsd.: 2058.3398; Calcd.: 2057.80.

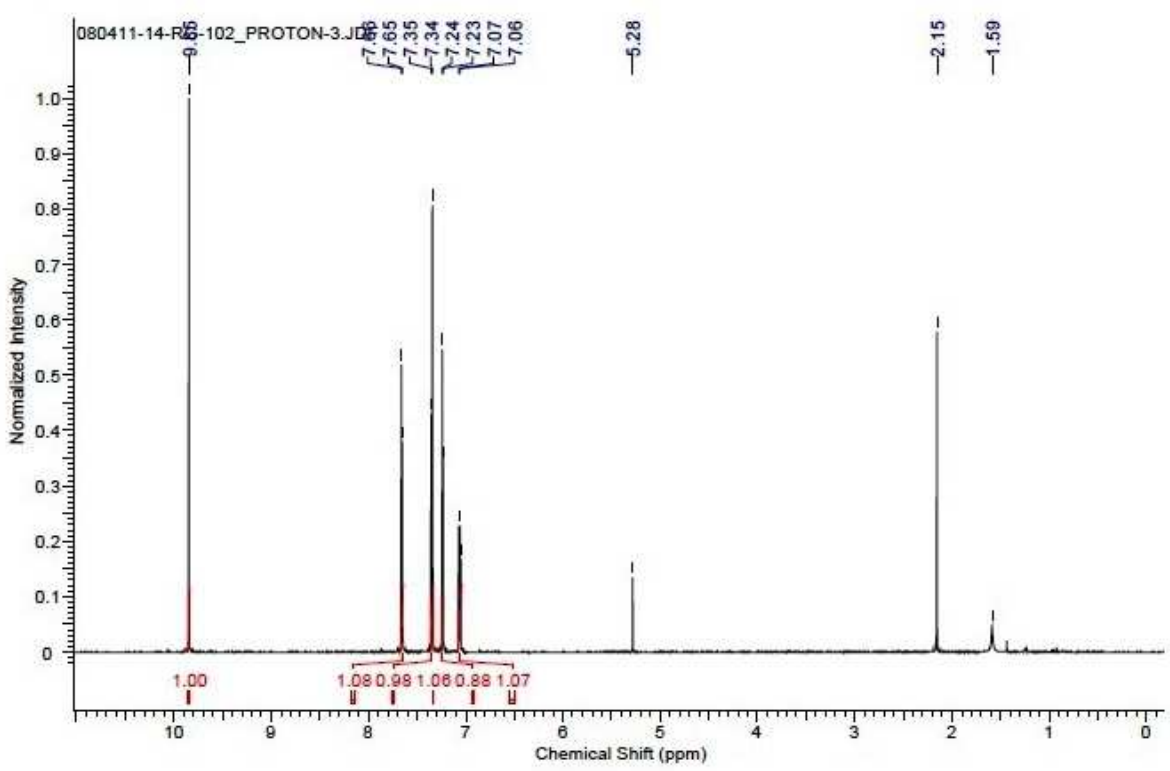


Figure – 1: ^{1}H NMR spectrum of **13**

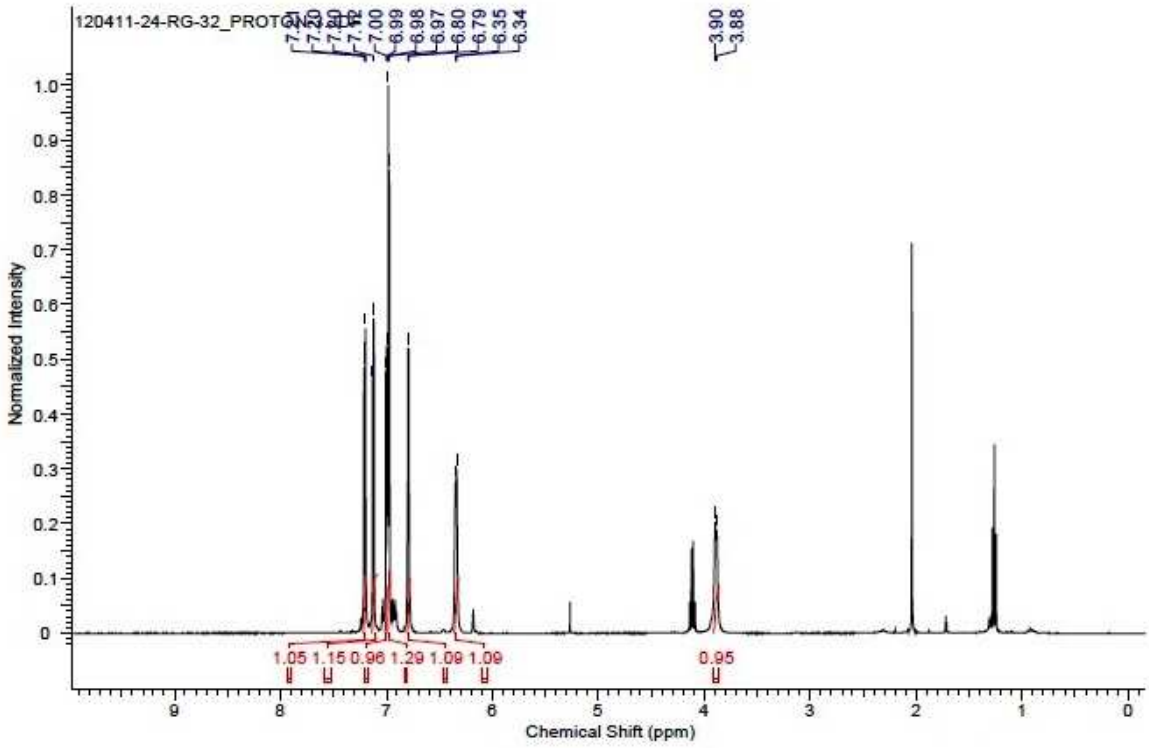


Figure – 2: ^{1}H NMR spectrum of **14**

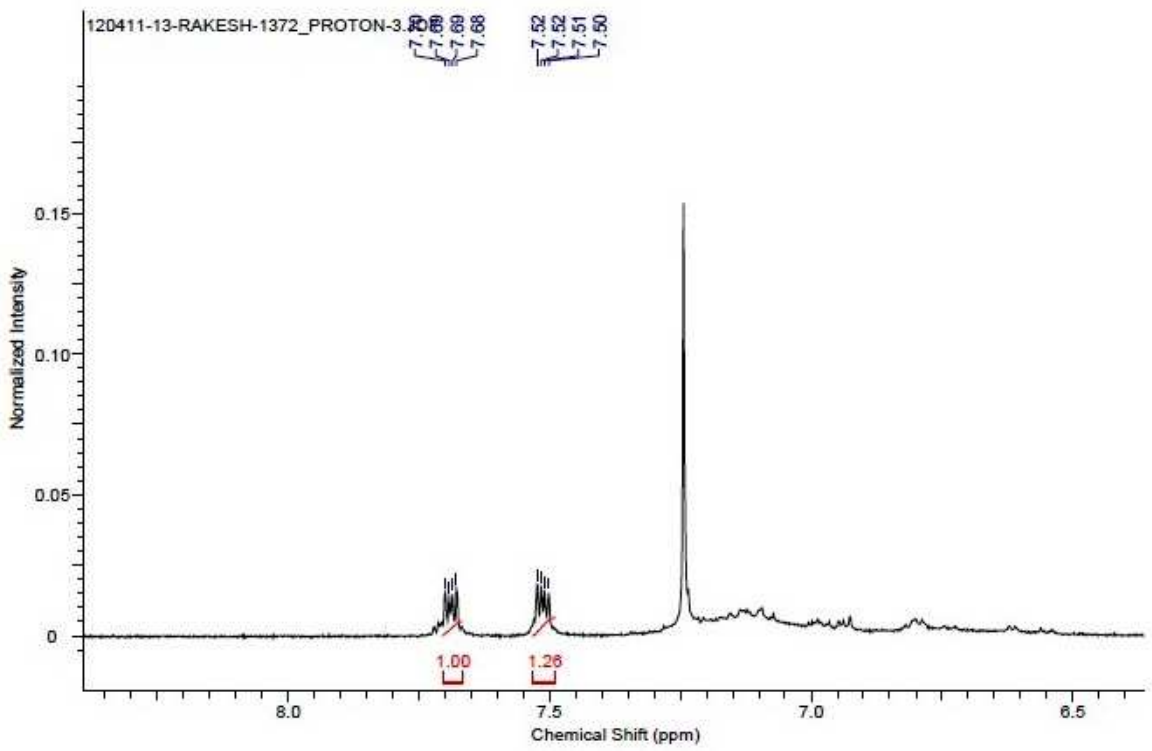


Figure – 3: ^{1}H NMR spectrum of **15**

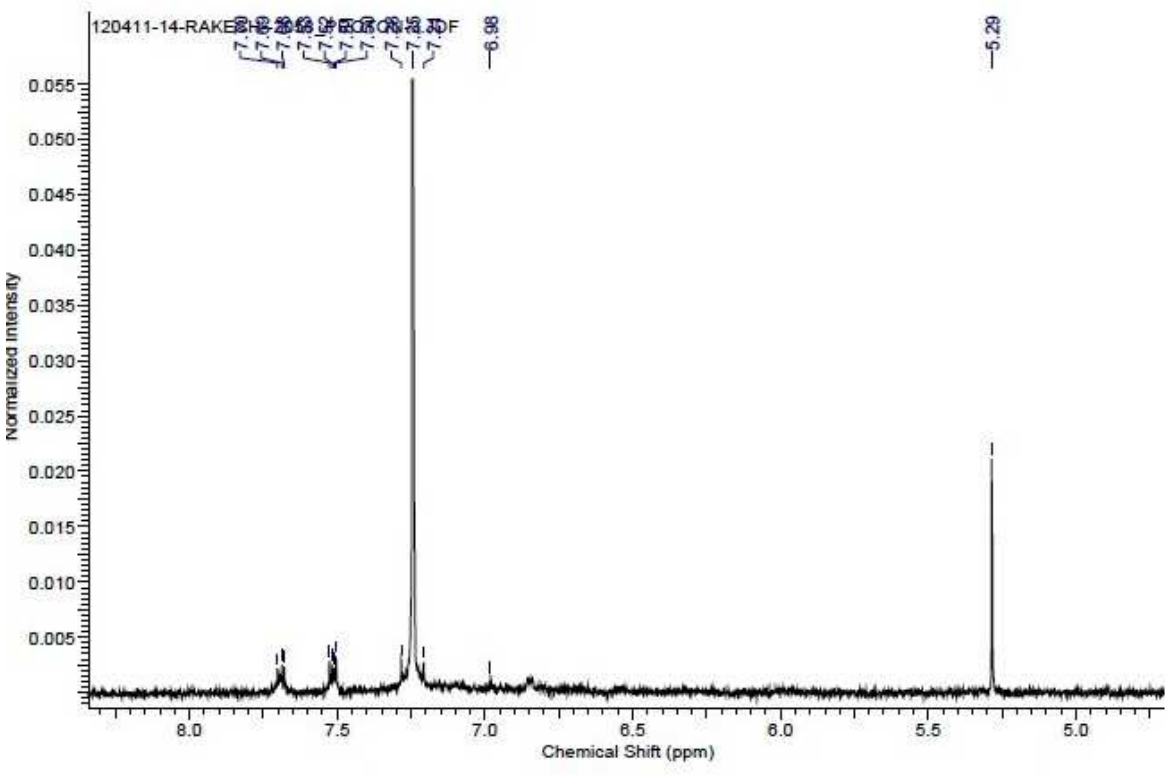


Figure – 4: ^{1}H NMR spectrum of **16**

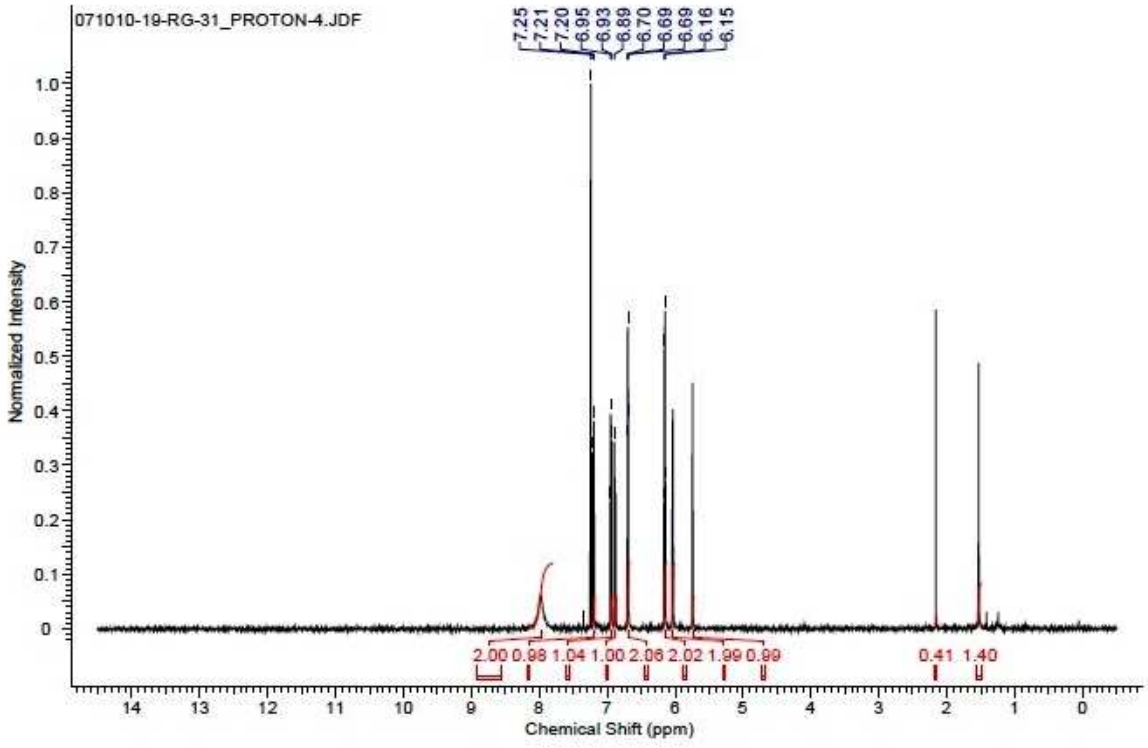


Figure – 5: ^{1}H NMR spectrum of **16**

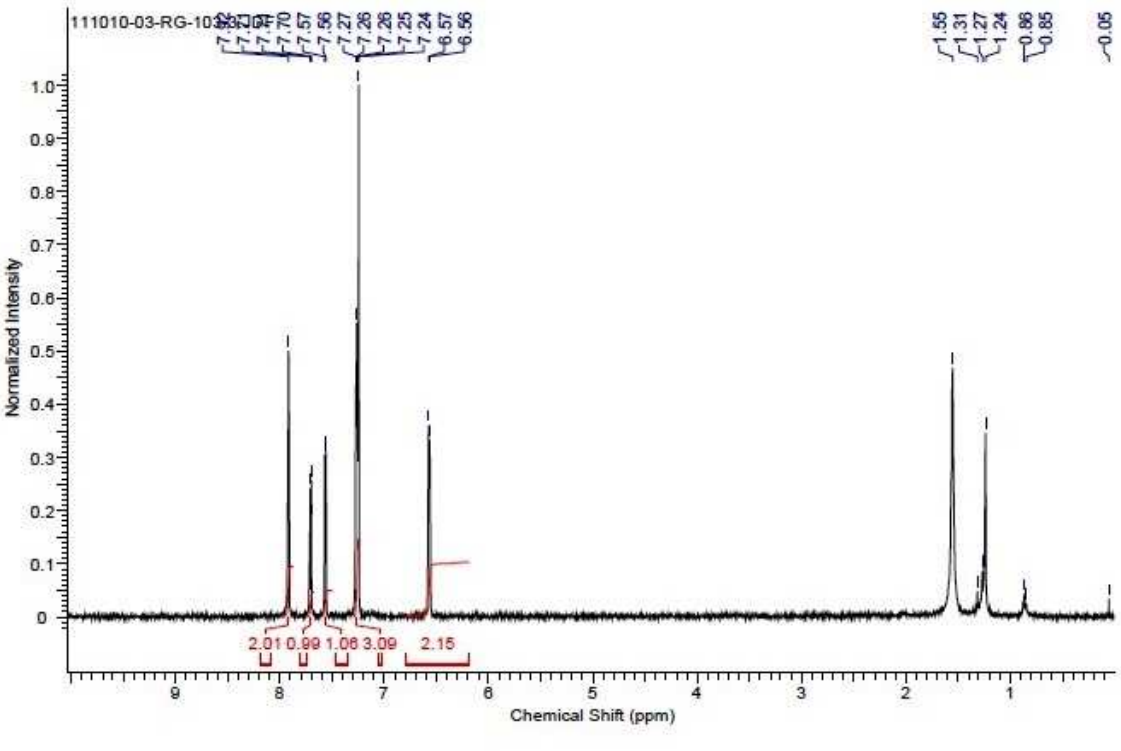


Figure – 6: ^{1}H NMR spectrum of **17**

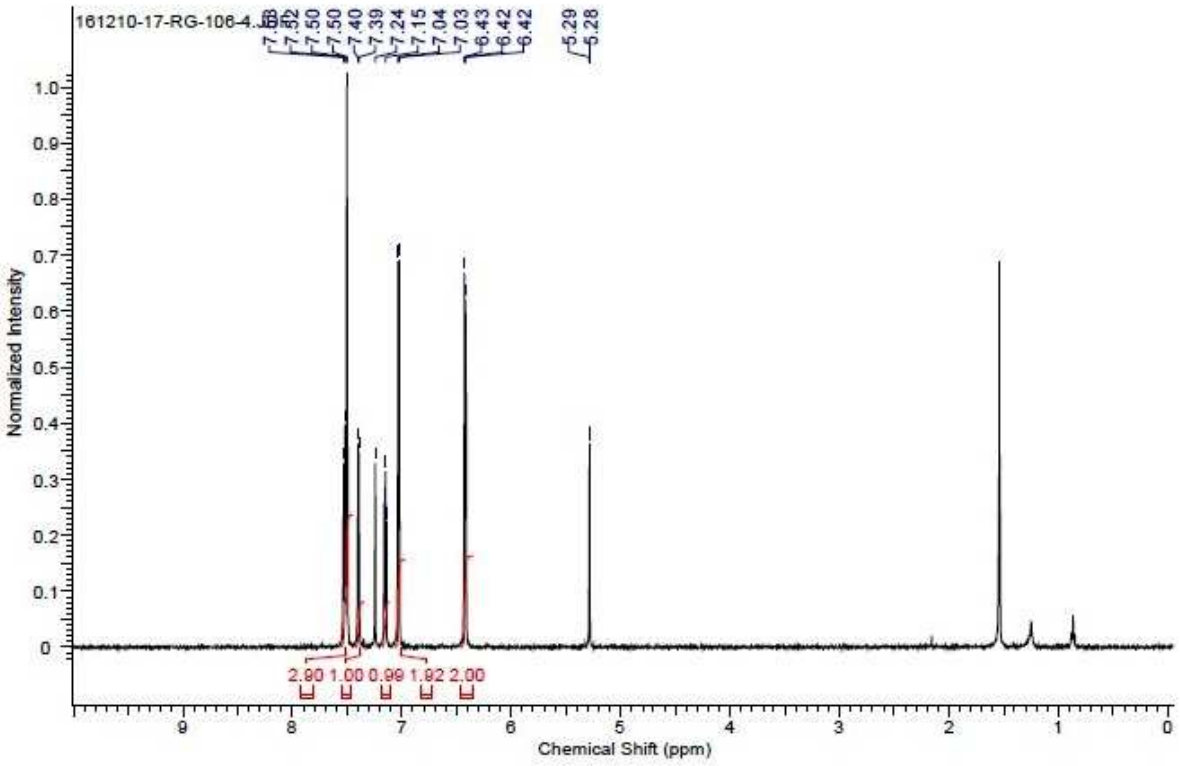


Figure – 7: ^{1}H NMR spectrum of **18**

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