

**T.R.**  
**GEBZE INSTITUTE of TECHNOLOGY**  
**GRADUATE SCHOOL of ENGINEERING and SCIENCES**

**MOLECULAR MAGNETIC MATERIALS BASED ON**  
**PORPHYRIN MACROCYCLES**

**EMEL ÖNAL**  
**A THESIS SUBMITTED for THE DEGREE of**  
**DOCTOR of PHILOSOPHY**  
**CHEMISTRY DEPARTMENT**

**GEBZE**  
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**THESIS SUPERVISOR**  
**ASST. PROF. DR. CATHERINE HIREL**

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**GEBZE YÜKSEK  
TEKNOLOJİ ENSTİTÜSÜ**

## **DOKTORA JÜRİ ONAY FORMU**

GYTE Mühendislik ve Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 23/06/2014 tarih ve 2014/37 sayılı kararıyla oluşturulan jüri tarafından 30/06/2014 tarihinde tez savunma sınavı yapılan Emel ÖNAL 'ın tez çalışması KİMYA Anabilim Dalında DOKTORA tezi olarak kabul edilmiştir.

### **JÜRİ**

ÜYE

(TEZ DANIŞMANI) : Yrd. Doç. Dr. Catherine HIREL

ÜYE

: Prof. Dominique LUNEAU

ÜYE

: Prof. Makoto HANDA

ÜYE

: Prof. Vefa AHSEN

ÜYE

: Prof. Mustafa BULUT

### **ONAY**

GYTE Mühendislik ve Fen Bilimleri Enstitüsü Yönetim Kurulu'nun ..... tarih ve ...../..... sayılı kararı.

İMZA/MÜHÜR

## SUMMARY

The preparation of Molecule-Based Magnets is based on the assembling carriers of magnetic moment. These may be the metal ions only with diamagnetic linkers or the metal ions connected through open-shell organic molecule. The building of novel Molecule-Based Magnets architectures following the metal-radical approach relies on the design of innovative open-shell organic molecular blocks. In this regard, we focus our strategy on the synthesis of porphyrins incorporating free radicals. Indeed, porphyrins compounds are  $\pi$ -conjugated systems which should favor spin delocalization and the transmission of the magnetic interactions on the overall macrocycle and further over the all architecture.

Due to their excellent stability in a wide variety of chemical environments, and their abilities to coordinate with transition metal we focus our attention on nitroxide radicals. In this dissertation a series of porpyrin macrocycles were synthesized, bearing tBuNO, nitronyl and imino nitroxide covalently linked to the skeleton. Characterization was done by UV-Vis, Mass and EPR spectroscopy.

Moreover during this work some interesting synthetic intermediates were obtained with good yield and characterize for the first time. This was the case for *meso*-tetrakis(4-formylphenyl)porphyrin and its corresponding metallated derivatives by Cu(II) and Mn(II). Some novel promising tetrapyrrolic macrocycle precursors bearing nitronyl and imino nitroxides free radicals as 2-(3,4-dicyanophenyl)-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl, 2-(3,4-dicyanophenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl and 2-(4-benzaldehyde)-4, 4, 5, 5-tetramethylimidazoline-1-oxyl. To the best of our knowledge, these compounds represent the first example of nitronyl and imino nitroxide substituted porphyrin derivatives that have been unambiguously characterized by spectroscopic techniques.

**Key Words:** Porphyrin, molecular magnetic material, nitroxide free radical, EPR, synthesis.

## ÖZET

Molekül bazlı manyetler manyetik moment taşıyıcılarının birleştiriciliğine dayanmaktadır. Bunlar diyamanyetik bağlayıcı metal iyonları veya aktif organik moleküller boyunca bağlanmış metal iyonlarıdır. Metal-radical yaklaşım olarak bilinen son yaklaşım molekül bazlı manyetler için özellikle etkili olduğu kanıtlanmıştır.

Yeni molekül bazlı manyetlerin yapımı yeni tip organik moleküllerin dizaynına dayanan metal-radical yaklaşıma dayanmaktadır. Bu bağlamda çalışmamızdaki stratejimizi serbest radikaller içeren porfirin sentezleri üzerine odakladık. Nitekim porfirin bileşikler spin delokalizasyonunu sağlaması beklenen ve manyetik etkileşimin makromolekül boyunca ve tüm yapı üzerinde iletimini sağlaması beklenen pi-konjuge sistemlerdir. Çok geniş çeşitli kimyasal çevreler içindeki mükemmel kararlılıkları ve geçiş metalleri ile koordine olabilmeleri nedeni ile ilgimizi nitroksit radikalleri üzerine topladık.

Bu tez çalışmasında bir seri üzerinde kovalent bağlarla bağlı tBuNO, nitronil ve imino nitroksit radikalleri içeren porfirin makroyapıları sentezledik. Karakterizasyon çalışmaları UV-Vis, kütle ve EPR spektroskopisi ile yapıldı.

Dahası bu çalışma boyunca bazı ilginç sentetik ara ürünler iyi verimlerle elde edildi ve ilk kez karakterizasyonları yapıldı. Bu olgu *meso*-tetrakis(4-formilfenil)porfirin ve onun Cu(II) ve Mn(II) metal türevleri sentezi durumunda ve bazı yeni ümit verici tetrapirolik makrohalka olan üzerlerinde nitronil ve imino nitroksit serbest radikaller taşıyan başlangıç maddeleri olan 2-(3,4-disiyanofenil)-4,4,5,5-tetrametilimidazolin-3-oksit-1-oksil, 2-(3,4-disiyanofenil)-4,4,5,5-tetrametilimidazolin-1-oksil ve 2-(4-benzaldehit)-4, 4, 5, 5-tetrametilimidazolin-1-oksil dir. Bildiğimiz kadarıyla, bu bileşikler nitronil ve nitroksit süsstitüe porfirin türevlerinin açık bir şekilde spektroskopik tekniklerle karakterize edilmiş ilk örneklerini temsil etmektedirler.

**Anahtar Kelimeler: Porphirin, moleküler manyetik malzeme, nitroksit serbest radikal, EPR, sentez.**

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## LIST of ABBREVIATIONS and ACRONYMS

| <u>Abbreviations</u> | <u>Explanations</u>                                        |
|----------------------|------------------------------------------------------------|
| <u>and Acronyms</u>  |                                                            |
| $\beta$              | : Boltzmann constant                                       |
| $J$                  | : Dipole-dipole exchange interactions                      |
| $T_c$                | : Curie temperature                                        |
| $M$                  | : Magnetization                                            |
| $H$                  | : Magnetic field strength                                  |
| $\chi$               | : Magnetic susceptibility                                  |
| $C$                  | : Curie constant                                           |
| $B_o$                | : Applied magnetic field                                   |
| $AB_3BrP$            | : 5-(4-bromophenyl)-10-15-20-triphenylporphyrin            |
| $AB_3AP$             | : 5-(4-formylphenyl)-10,15,20-phenylporphyrin              |
| $ATPP$               | : <i>meso</i> -tetrakis(4-formylphenyl)porphyrin           |
| $ATPPCu(II)$         | : <i>meso</i> -tetrakis(4-formylphenyl)porphyrinato Cu(II) |
| $ATPPMn(II)$         | : <i>meso</i> -tetrakis(4-formylphenyl)porphyrinato Mn(II) |
| $BDPA$               | : $\gamma$ -bis(diphenylene)- $\beta$ -phenylallyl         |
| $BF_3 \cdot Et_2O$   | : Boron trifluoride diethyl etherate                       |
| $BHA$                | : 2,3-bis(hydroxylamino)-2,3-dimethylbutane                |
| $BM$                 | : Bohr magneton                                            |
| $BPNO$               | : Tert-Butylphenylnitroxide                                |
| $CNPh$               | : Benzonitrile                                             |
| $DCM$                | : Dichloromethane                                          |
| $DDQ$                | : 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone                |
| $DEER$               | : Electron-electron double resonance                       |
| $DHB$                | : 2,5-Dihydroxybenzoic acid                                |
| $DMF$                | : N,N'-dimethylformamide                                   |
| $DMSO$               | : Dimethyl sulfoxide                                       |
| $EPR$                | : Electron Paramagnetic Resonance                          |
| $ESI-MS$             | : Electro Spin Ionisation Mass Spectroscopy                |
| $EtOAc$              | : Ethylacetate                                             |
| $FT-IR$              | : Fourier Transform Infrared                               |

|                |                                                 |
|----------------|-------------------------------------------------|
| IMI            | : Imino                                         |
| MeOH           | : Methanol                                      |
| MBM            | : Molecule-Based Magnet                         |
| MALDI-MS       | : Matrix-assisted laser desorption/ionization   |
| NA             | : Avogadro's number                             |
| n-BuLi         | : n-Buthyllithium                               |
| NIT            | : Nitronyl                                      |
| PELDOR         | : Pulsed electron–electron double resonance     |
| PDT            | : Photodynamic therapy                          |
| PNN            | : <i>p</i> -nitrophenyl nitronylnitroxide       |
| <i>p</i> -TsOH | : <i>p</i> -Toluenesulphonic acid               |
| QTM            | : Quantum Tunnelling of the Magnetisation       |
| SQUID          | : Super conducting quantum interference device  |
| SMM            | : Single-Molecule Magnet                        |
| TBrPP          | : <i>meso</i> -tetrakis(4-bromophenyl)porphyrin |
| tBuNO          | : N- <i>tert</i> -butyl-N-oxyamino              |
| TEA            | : Triethylamine                                 |
| TFA            | : Trifluoroacetic acid                          |
| THF            | : Tetrahydrofuran                               |
| TMEDA          | : <i>N,N,N,N</i> -tetramethylethylenediamine    |
| TPP            | : Tetraphenylporphyrin                          |
| TREPR          | : Time-resolved electron paramagnetic resonance |
| UV-Vis         | : Ultra-Violet Visible                          |
| ZFS            | : Zero Field Splitting                          |

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# 1. INTRODUCTION

## 1.1. The outline of the thesis

The intention of the thesis was construction of novel bricks for molecular magnets in solid state. All the dedicated efforts were focused on synthesis, structural and magnetic studies of porphyrin macrocycles including different spin carriers at the periphery, preferentially nitroxide free radicals and also metal ions. The biggest challenge was building organic spin carrying ligands such as tBuNO, nitronyl and imino nitroxide free radicals on targeted porphyrin derivatives with multi step synthesis work. This principally essential work based on radical-radical interaction approach;

In solid state, crystal phase very important for magnetic behaviour and for organic compounds design of solid state structure is not easy because of crystal packing based on weak bonds like hydrogen bond or Wan Der Waals interactions. Porphyrin macrocycles were great choice because of their highly polarizable  $\pi$ -conjugated system that will favor the spin delocalization all over the molecule skeleton favoring the spin coupling between the radical-radical and the metal-radical interaction. As a spin carriers tBuNO nitroxide, imino nitroxide and nitronyl nitroxide free radicals were chosen because of their high stability, solubility, exhibiting structural versatility and multifunctionality among the building blocks in literature. According the radical-radical interaction approach it was necessary to combining of spin carrier nitroxide stable free radical on highly polarizable  $\pi$ -conjugated porphyrin system. For this aim the biggest challenge was synthesis of *meso*-tetrakis(4-formylphenyl)porphyrin which was the key intermediated molecule for creation of nitronyl and imino nitroxide substituted porphyrins. To compare the contribution of different number nitroxide radicals on porphyrin macrocycle for the high spin magnetic material, it was necessary to start to synthesis tetra radicals( targeted molecules **1**, **2**, **3**) which is the maximum number for *meso*-pistion on porphyrin macrocycle and also mono radical substituted porphyrins ( molecule **4**, **5**, **6**) which will help to understand the spin contribution to magnetic behaviour.

In addition, obtaining well-resolved ESR spectra with isotropic proton hyperfine structure were necessary to understand of the type of the radicals if they

are tBuNO, nitronyl or imino nitroxide free radicals and also to control the number of the radical on the porphyrin macrocycles.

Using crystal engineering as a tool to prove structural characterization, it was challenging to obtain single crystals X-ray structures of maximum number of molecules. Good magneto-structural correlation was necessary in order to find an explanation for the different magnetic behaviors. This had to be done by correlating solution ESR data and the bulk magnetic susceptibility data with the crystal structures.

## 2. BIBLIOGRAPHY

### 2.1. Porphyrins

#### 2.1.1. General Background

Porphyrins are a large class of deeply colored compounds that is one of the most exiting stimulating and rewarding research are for scientists in the files of chemistry, physics, biology and medicine. They owe their bright colors to intense absorptions in the near ultraviolet and visible regions. Porphyrins have been described as “the pigments of life” because they perform a variety of fundamental biological functions that lie at the very core of life as we understand it[1]. The word porphyrin is actually derived from the Greek word for purple, porphura.

The best-known natural porphyrin is probably the heme cofactor (iron porphyrin), which is responsible for O<sub>2</sub>-transport and storage (as hemoglobin and myoglobin), electron transport (as cytochromes b and c), O<sub>2</sub> activation and utilisation (cytochrome P<sub>450</sub> and cytochrome oxidase) and sensing (as the NO-sensor soluble guanylate cyclase, the O<sub>2</sub> sensor, and the CO sensor)[1].

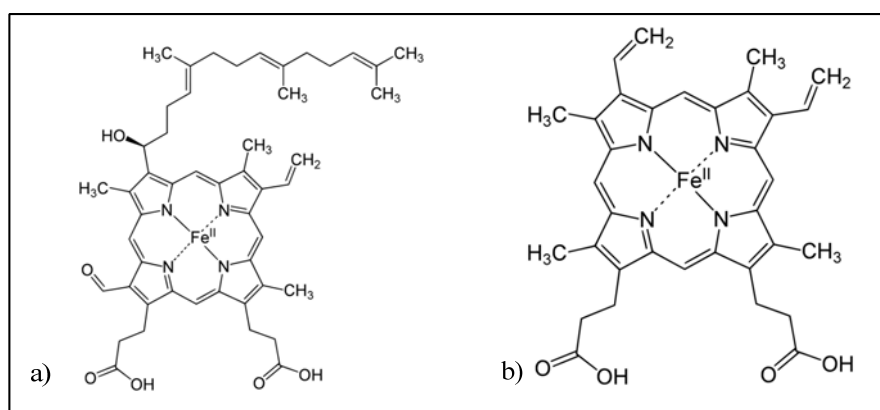


Figure 2.1: a)The hemoglobin a, b) hemoglobin b.

The porphyrin skeleton is made by four pyrrole units linked together by four methine bridges. The common structural feature of porphyrins is a tetrapyrrole

macrocyclic ring that consists of an 18  $\pi$ -electron system. Examples of porphyrin structures are showed in Figure 2.2.

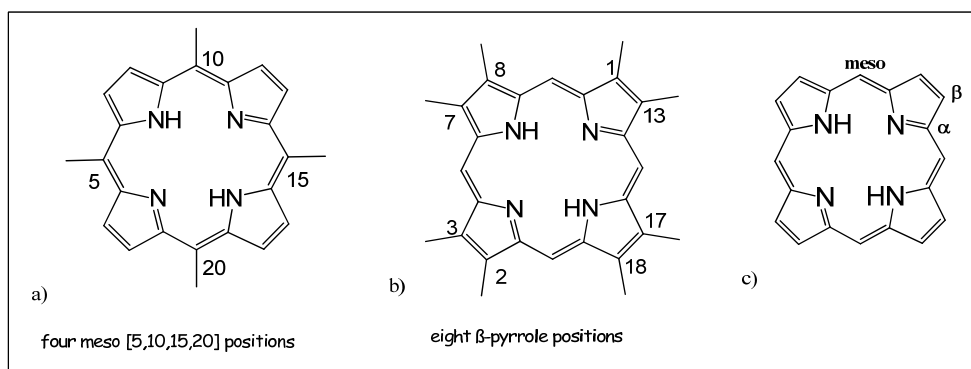


Figure 2.2: Positions of the a) C $\alpha$ , b) C $\beta$ , c) C $m$  of free base porphyrin.

Although far from complete, this introduction aims to highlight the diversity of the available *meso*-porphyrin ligands and the principal advances in the field over the past decades. It is hoped that this chapter will provide a useful underpinning for the research work reported by the author in the ensuing chapters of this Dissertation and it will allow the readers to obtain a glimpse into the *meso*-porphyrin chemistry that remains to be explored.

### 2.1.2. *meso*-Substituted Porphyrins

Synthesis of porphyrins involves the arrangement of diverse substituents in specific patterns about the periphery of the macrocycle. synthetic control over the molecular entities attached at the porphyrin periphery enables porphyrins to be designed and tailored for specific applications. The  $\beta$ -substituted porphyrins closely resemble naturally occurring porphyrins. The *meso*-substituted porphyrins have no direct biological counterparts but have found wide application in material chemistry. The popularity of *meso*-substituted porphyrins comes from their easy synthesis. One-flask synthetic methods can be used to prepare a *meso*-substituted porphyrin from an aldehyde and pyrrole. The wide availability and ease of manipulation of aldehydes enables diverse porphyrins to be constructed without extensive multistep synthesis of precursors. The substituents at the *meso*-positions can include alkyl, aryl, heterocyclic or organometallic groups, as well as other porphyrins. In particular *meso*-substituted tetraarylporphyrins provide versatile building blocks for creating 3-D

architectures that incorporate porphyrins. The challenge of creating more refined structures led to development of variety of methods for *meso*-substitution. The best known synthetic methods for *meso*-substituted porphyrins were summarized below.

- P. Rothmund Method

Meso-substituted porphyrins have been synthesized by the method, using pyrrole and one of the following aldehydes: formaldehyde, acetaldehyde, propionaldehyde, nbutyraldehyde, benzaldehyde and a-furaldehyde in methanol, pyridine, one-flask reaction in sealed vessel in 1935-1936. In most of his work, careful examination of each reaction product showed the presence of a second porphyrinic substance at the 10-20 % level which was isolated by chromatography and shown to be chlorin. The chlorin can be converted by oxidation to the corresponding porphyrin[2]-[4]. In a summary for features of Rothmund method reactions were at high concentration and high temperature in a sealed vessel in an absence of an added oxidant[5],[6].

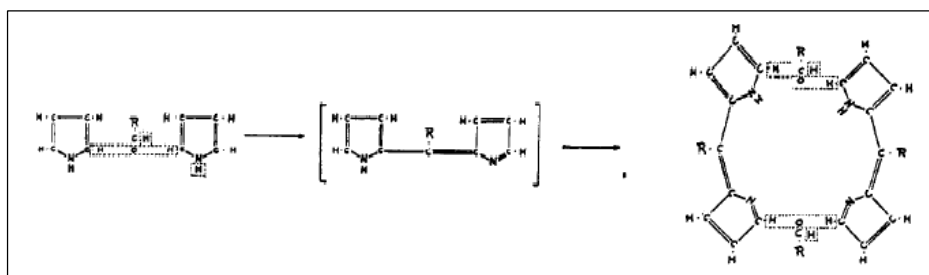


Figure 2.3: P. Rothmund method.

- Adler method

Condensation of pyrrole with aldehyde in acidic conditions open to the atmosphere, one-flask reaction[7].

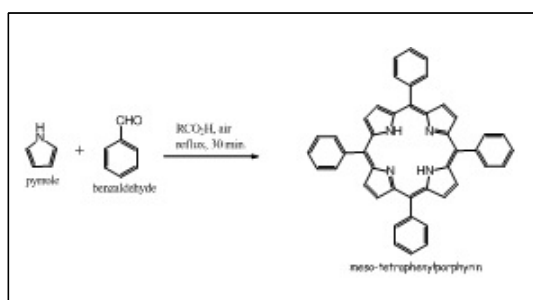


Figure 2.4: Adler method.

### •Lindsey Method

A one-step synthesis of porphyrins has been investigated where aldehyde, pyrrole, acid catalyst, and oxidant are present simultaneously. Also the room-temperature synthesis of meso-porphyrins has been investigated at aldehyde and pyrrole, using the two-step process of acid-catalyzed condensation followed by quinone[8], [9].

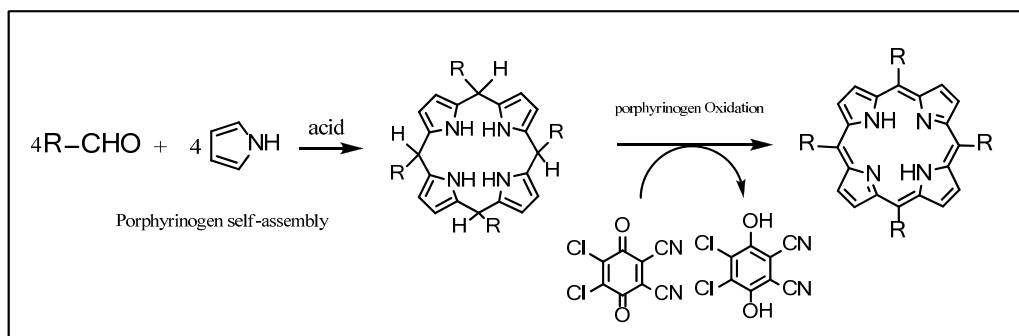


Figure 2.5: Lindsey method.

For the comparison of One-flask synthetic methods for preparing porphyrins some generalisation can be conserved wieved in Table 2.1.

Table 2.1: Porphyrin synthetic methods.

|                        | Porphyrin Synthetic Methods |                                        |                                                                     |
|------------------------|-----------------------------|----------------------------------------|---------------------------------------------------------------------|
|                        | Rothmund                    | Adler                                  | Lindsey                                                             |
| Solvent                | Pyridine                    | (I) Propionic acid<br>(II) Acetic acid | Dichloromethane<br>Chloroform                                       |
| Temperature            | 220 °C                      | (I) 141 °C<br>(II) 120 °C              | 25 °C                                                               |
| Catalyst               | -                           | Same as solvent                        | TFA<br>BF <sub>3</sub> etherate<br>BF <sub>3</sub> etherate/ethanol |
| Oxidant                | -                           | O <sub>2</sub>                         | DDQ or p-chloranil                                                  |
| Reactant concentration | 3.6 mol.dm <sup>-3</sup>    | 0.3 – 1.0 mol.dm <sup>-3</sup>         | 0.001 – 0.1 mol.dm <sup>-3</sup>                                    |
| Time of reaction       | 48 h                        | 0.5 – 1.0 h                            | 1 h                                                                 |
| Procedure              | One step                    | One step                               | Two steps                                                           |
| Purification (work up) | Crystal separation          | Filtration                             | Chromatography**                                                    |
| Yield                  | < 10%                       | ~ 20%                                  | Up to 40%                                                           |
| Method range           | Restrict                    | Medium                                 | Large                                                               |

Following wonderful explanation in the Porphyrin Handbook[10] one can have genaral picture of the conditions employed in different methods. From Table 2.1 it is clear that the Rothmund method does not have any advantages.

The Adler method is prevailing method for synthesizing porphyrins for preparative scale from stable aldehydes. The limitaion of this method ; refluxing propionic acid condition is can be very strong condition for not stable aldehydes, many 2,6-disubstituted aryl aldehydes, some aliphatic aldehydes and some of aldehydes do not crystalize from propionic acid.

But also quick and easy crystallisation led to 20 % reaction yield makes this method attractive.

The Lindsey method has the strongest reaction conditions but broadest scope of application. The yields are generally higher than Adler method. The best part of the method is very sensitive aldehydes can be used in this method. The disadvantage of the method is for the reaction from 0.01M to 0.1M requires and removal of large amount of solvent. During this dissertation work chiefly Adler method was used.

### **2.1.3. Literature Survey of Nitroxides Directly Substituted to Porphyrin**

In the area of purely organic materials, radicals are still under active investigation. Among the radicals Nitroxides are the most well-known class of stable radicals. The molecular skeleton of these stable neutral free radicals has two important features i) the good stabilization of the spin and ii) the modulation and control of electronic structure by N-O group with one unpaired electron in a  $\pi^*$  orbital equally shared by the nitrogen and oxygen atoms. Thus nitroxides are one of the best ligands have potential in many different research area. In porphyrin chemistry there are limited reports describing the synthesis and properties of porphyrin-bound nitroxides since the attaching nitroxide radical directly to porphyrin macrocycle is still challenging synthetic point of view.

Kamachi et al [11] reported polymers of acrylate and methacrylate containing paramagnetic piperidinyl and verdazyl side chain groups on porphyrin rings to demonstrate a magnetic ordering of the paramagnetic species through an exchange interaction of unpaired electrons is possible in the polymers. For this reason they used stable macrocycle porphyrins as a spin carrier conjugate system. A polymer effect on the magnetic ordering was found in those systems, but the exchange interactions between these organic radicals were too weak for the polymers to function as magnetic materials.

The coordination chemistry approach is essential in the field of molecular-based magnets. Shultz prepared free radical substituted Zn porphyrins for construction of coordination polymers. The phenylnitroxide radical is attached to the *meso*-position of three porphyrins: directly through a single bond ; through an ethenyl group and

through an ethynyl group to investigate conjugative effectiveness of the fragment that links the porphyrin because the aryl group is critical for sufficient spin-spin communication.

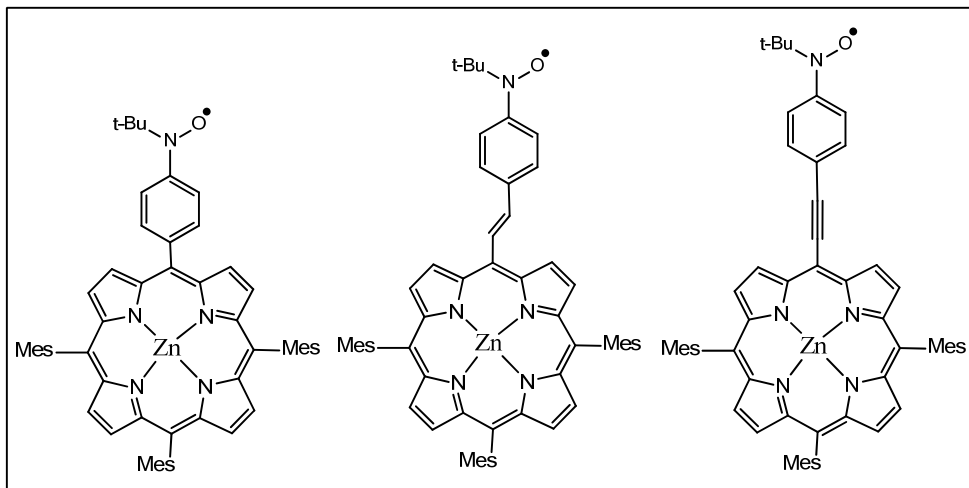


Figure 2.6: Phenyl nitroxide substituted porphyrins.

Another interesting application area of porphyrins in magnetic file is possibility to switch (on/off) the magnetism under light irradiation as reported by Herges [12]. report on individual molecules in homogeneous solution that are switched between the diamagnetic and paramagnetic states at room temperature by light-driven coordination-induced spin-state switching (LD-CISSS). Switching of the coordination number (and concurrently of the spin state) was achieved by using Ni porphyrin as a square-planar platform and azopyridines as photodissociable axial ligands. The squareplanar Ni porphyrin is diamagnetic (low-spin,  $S = 0$ ), and all complexes with axial ligands are paramagnetic (high-spin,  $S = 1$ ).

K. Ishii et al. reported, nitroxide-porphyrin system where a nitroxide radical is directly substituted to the meso position of a porphyrin ligand. They succeeded in observing the excited multiplet state and examined the photo-physical properties with TREPR and transient absorption measurements. It was the first excited doublet (D1) and quartet (Q1) observation in a system where the nitroxide is directly substituted to a porphyrin ligand. The free radical substituted porphyrin exhibited the longest lifetime of any nitroxide-porphyrin systems in the lowest excited state, indicating a relatively weak electron exchange interaction between triplet ZnP and doublet nitroxide [13].

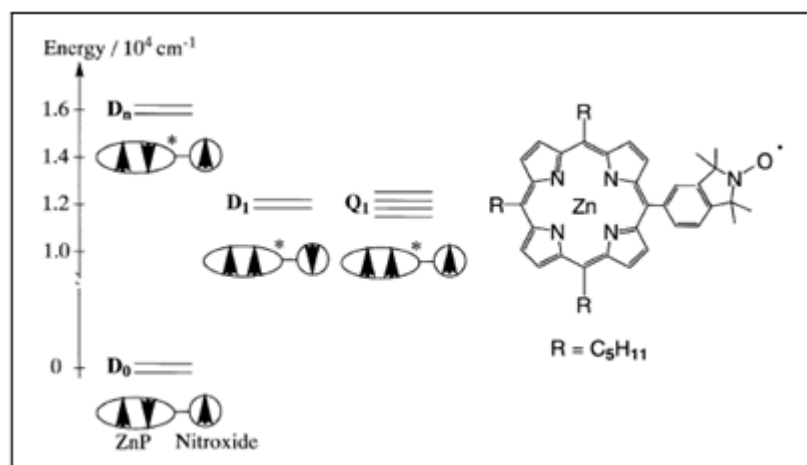


Figure 2.7: Isoindoline nitroxide substituted porphyrin.

Some porphyrins and their metal complexes play important roles in magnetic resonance imaging (MRI), photodynamic therapy (PDT), anticancer drugs, and fluorescence imaging because of their preferential selective uptake and retention by tumor tissues. Steven E. Bottle and colleges synthesised spin-labeled porphyrins containing isoindoline nitroxides and their manganese complexes as spin prob. The interest was on stable free radicals can be administered as imaging agents, and following their fate in the body can give useful insights into organ function and tissue status. Nitroxides provide a key modality for EPR studies in viable systems, as they are sensitive to other free radicals, to the redox state, and to oxygen levels. Moreover, nitroxides are remarkably stable free radicals that have been used as spin probes for many years, giving characteristic three-line signals readily detected by EPR [14].

Development of novel molecular materials for electronics and energy production is very important, thus understanding of spin polarization and the ability to control spin transport through organic molecules is still attractive. Colvin et al [15] synthesised tert-Butylphenylnitroxide (BPNO•) and R, $\gamma$ -bisdiphenylene- $\beta$ -phenylallyl (BDPA•) stable radicals attached to zinc *meso*-tetraphenylporphyrin (ZnTPP) at a fixed distance using one of the ZnTPP phenyl groups. Following photoexcitation of them transient optical absorption spectroscopy was used to observe excited state quenching of porphyrin by the radicals and time-resolved electron paramagnetic resonance (TREPR) spectroscopy was used to monitor the spin dynamics of the paramagnetic product states. The presence of BPNO• or BDPA• accelerates the intersystem crossing rate of porphyrins about 10- to 500-fold in radical porphyrins depending on the structure compared to that of ZnTPP itself.

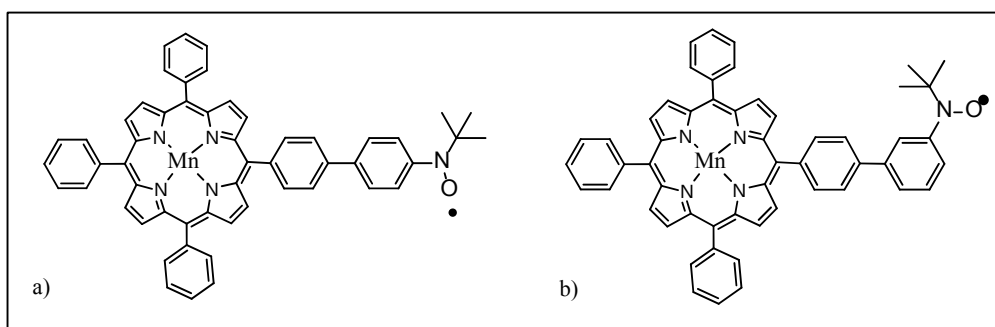


Figure 2. 8: a)BPNO•, b) BDPA• stable radical substituted Zn porphyrins.

Another interesting spectroscopic investigation was on spin labelling, pulsed electron–electron double resonance (PELDOR or DEER) which are good methods for characterisation and localization of metal ions. Bode et al [16] reported synthesis and full characterization of a copper(II) and nickel(II) porphyrin/nitroxide model system bearing an extended p-conjugation between the spin centres and demonstrate the possibility to disentangle the dipolar through space interaction from the through bond exchange coupling contribution even in the presence of orientational selectivity and conformational flexibility.

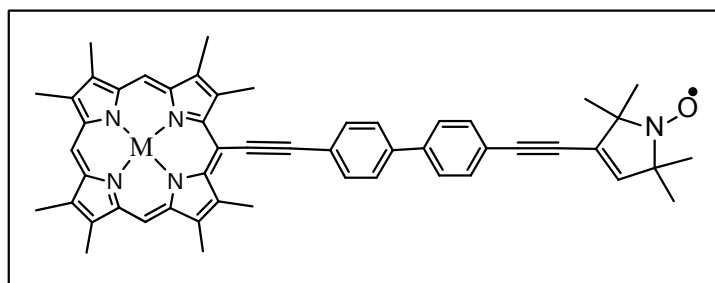


Figure 2. 9: Copper(II), nickel(II) porphyrin/nitroxide model system.

Since nitroxides have redox- and radical-trapping properties, nitroxides have been extensively used as electron paramagnetic resonance (EPR) spin labels for proteins, enzymes, nucleotides and other biological systems [17]-[19]. They exhibit low fluorescence due to electron exchange interactions between the excited molecule and the nitroxide radical (enhanced intersystem crossing from first excited singlet state to triplet state). A series of spin-labeled porphyrin containing isoindoline nitroxide moieties were synthesized and characterized as potential free radical fluorescence sensors by Australian group [20]. They reported synthesis of free-base mono radical and biradical porphyrins and free-base biradical porphyrins exhibited highly

suppressed fluorescence about three times greater than the monoradical porphyrins. The observed fluorescence-suppression was attributed to enhanced intersystem crossing resulting from electronexchange between the doublet nitroxide and the excited porphyrin fluorophore.

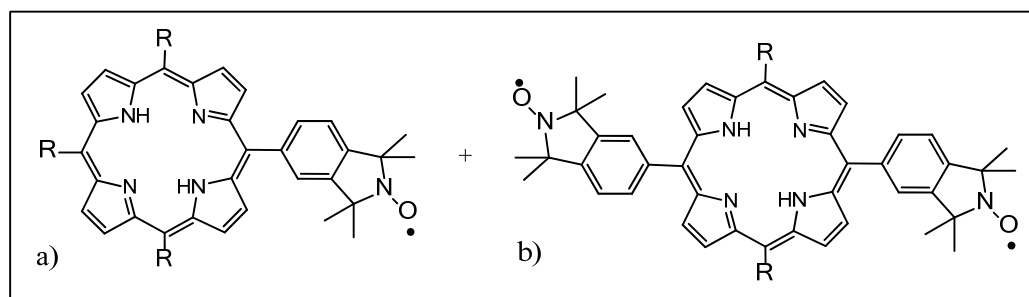


Figure 2.10: Porphyrins containing a) mono, b) diisoindolin nitroxide moieties.

Functionalized porphyrins are now relatively easily accessible and well studied compounds. Especially, their ease of functionalization is of particular interest as it has been clearly demonstrated that tailoring the nature of the substituent or the central metallic ion allows fine-tuning the properties of these metalloligands. Particularly, since the 1990s, many attempts have been reported in order to build up open coordination frameworks based on linkers derived from porphyrins. Thank to porphyrin chemistry richness, there are numerous work extensively explored for their numerous applications in molecular devices and molecular magnets is one of the promising area. Although many works in this field, researches in the literature for molecular magnetic materials shows the lack of new molecular building blocks and the sufficiency of the metal-radical approach. in this situation our study proposes the synthesis of porphyrins decorated with free nitroxide radicals as a novel building blocks which may be used for the building of *molecule-based magnets* (MBM) or in *single-molecule magnets* (SMM).

## 2.2. Nitroxide Free Radicals

### 2.2.1. Stable Radicals

There are many scientific work in chemistry of systems containing stable organic radicals because many kinds of radicals are stable enough to isolate, can be stored without any special technique and can be used effectively. They have one less bond than expected based on simple valency considerations. They are highly reactive that dimerization, hydrogen abstraction, disproportionation reaction can occur with little to no activation barrier. Many radicals exist with unpaired electrons that have sufficiently long lifetimes to be observed by conventional spectroscopic methods and some of them can be isolated as pure compounds, and a few of these are even unreactive to air and water. In chemistry there are many areas that use advantage of specific combination of open-shell configuration and chemical stability. For example, stable radicals have been used for a long time to obtain structural, dynamic, and reactivity information using electron paramagnetic resonance (EPR) spectroscopy and spin labelling[21] and spin trapping[22]-[25]. More recently EPR imaging [26] is very useful technique to get definite information from the systems that include stable radicals. Magnetism and conductivity are another technological area that many efforts aimed for developing new materials with relevant properties and stable radicals are excellent building blocks simply by virtue of having unpaired electrons [27], [28].

Another good reason to work with stable radical is their rich chemistry which is much more selective and controllable nature than the reactivity of reactive radicals. They are widely used as (co)catalysts for the oxidation of alcohols to carbonyl compounds [29]-[31]. Their transition metal coordination chemistry is an active area of interest to inorganic chemists for three decades[32]-[35] Radical reactions are implicated in a huge range of biological processes, and stable radicals are often key players from simple inorganic radicals such as NO and O<sub>2</sub> to tyrosyl[36], [37] based radicals. Triphenylmethyl discovery was the beginning of organic free radical chemistry [38] phenalenyl[37] and Phenoxyls[39]-[41] are still venerable stable radicals in class of hydrocarbon-based radicals.

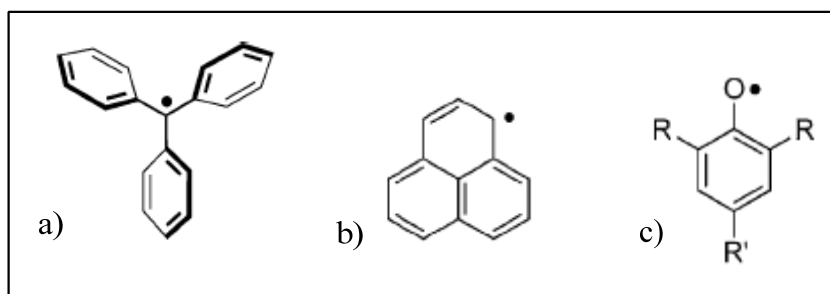


Figure 2.11: a)Triphenylmethyl, b)phenalenyl, c)phenoxyls.

### 2.2.2. Nitroxides

A considerably portion of spin density of many stable radicals on nitrogen and/or oxygen. Simple inorganic radicals such as  $O_2$ ,  $NO$ , and  $NO_2$  can be viewed as prototypes of the many different organomain group radicals[42]. Among stable radicals Nitroxide chemistry has a long and rich history, and there are many derivatives which are stable with respect to air, water, dimerization, and other radical-involving reactions. The versatility of these radicals is further enhanced by the fact that a fairly diverse range of organic chemistry can be carried out on remote sites of molecules carrying a nitroxide group without affecting the radical site itself. In coordination chemistry studies aimed at synthesizing new magnetic materials, metal-radical interaction must not result in diamagnetic compounds and it is generally achieved by control of redox potential through appropriate chosen substituents. for this aim among the bridging ligands, such as nitronyl- (2a) and imino- (2b) nitroxides [43]-[45] and polynitroxides, where nitroxyl groups are *m*-substituents of a phenyl ring (2e) are particularly attractive [46]-[48]. They all possess several oxyl groups and unsaturated structures allowing correlation of the unpaired spin density over the different coordination sites. Toward molecular magnets, they are the keystone of the metal–radical approach [34], [49], [50].

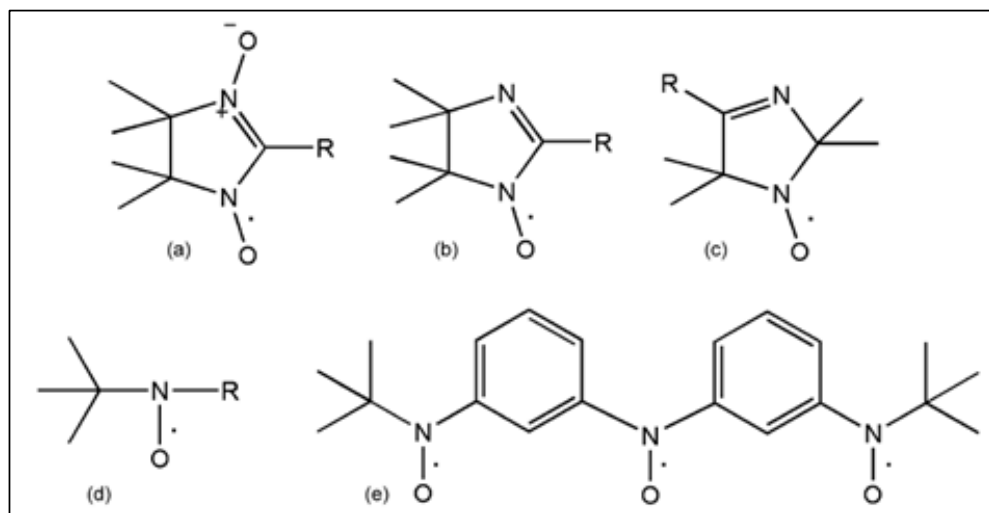


Figure 2. 12: Examples of nitroxide ligands a) nitronyl b) imino c) 3-imidazolynyl d) aminoxyls e) aromatic polyaminoxyl.

To control the intermolecular exchange interactions and the resultant magnetic behavior of the compounds, one should be able to arrange molecules in a predictable fashion. Therefore, much interest in the field of organic-based magnetic materials was focused on studying the magneto-structural correlations and finding the way to adjust them.

The oxygen atom of the nitroxide group exhibits weak basicity; therefore, it demonstrates coordinating ability with respect to transition metal ions, which allows assembling metal ions and nitroxide radicals in low dimensional materials in order to obtain bulk magnets[51]-[59]. Iwamura has described tert-butyl nitroxide radicals functionalized pyridines and imidazoles (Figure 2.13), which were used for the preparation of a number of metal complexes [60], [61].

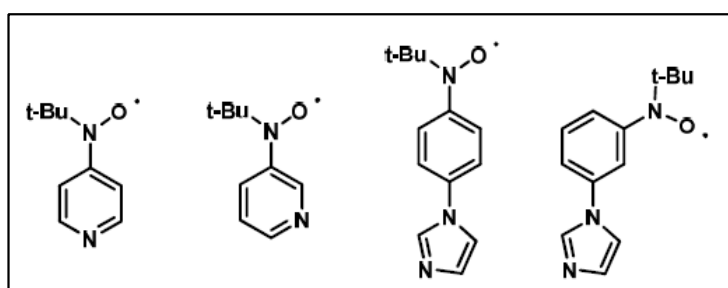


Figure 2. 13: Some tert-butyl nitroxide radicals.

### 2.2.3. Nitronyl Nitroxide

The first report of a nitronyl nitroxide appeared in 1968 and most of these free radicals have been described by Ullman and co-workers[62]. The fundamental aspects of their electronic structure are well-established [22]. These radicals incorporate the necessary features for stability (e.g., no  $\alpha$ -hydrogens) typical for nitroxides, and can thus be made with a wide variety of R groups. The stability of nitronyl nitroxides generally rivals the most stable examples of nitroxides. The spin distribution is symmetrically disposed about the two NO groups and is only slightly affected by the substituent R. In rich nitronyl nitroxide chemistry history, the versatility of these radicals was further enhanced by Rey has developed the synthesis of pyrimidinyl nitronyl nitroxides [63], [64] whose electronic structures are generally quite similar to those of the more familiar imidazolinebased nitronyl nitroxides. Another example is Benzannelated analogues[65], which have not yet received much attention, though recent experimental and computational studies indicate that there is at least partial delocalization of spin from the ONCNO moiety onto the annelated ring[66].

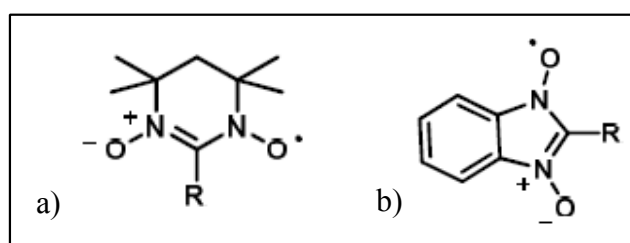


Figure 2. 14: a)Pyrimidinyl nitronyl, b)benzannelated nitroxide.

The nitronyl nitroxides are obtained by condensation of 2,3-bis(hydroxylamino)-2,3-dimethylbutane with an aldehyde, followed by oxidation as depicted in Figure 2.15. Aliphatic aldehydes react rapidly whereas the formation of intermediate molecules requires more time with aromatic aldehydes. This intermediate molecule can be isolated as a white diamagnetic solid. Oxidation by lead dioxide or sodium metaperiodate leads to desired nitronyl nitroxide radical. The corresponding nitroxides are intensely colored blue when the substituent is aromatic and red when it is aliphatic.

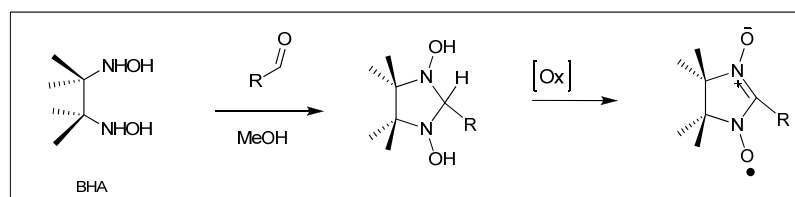


Figure 2. 15: Synthesis of nitronyl nitroxide.

The reaction yield vary widely depending on the susbtituent R. In addition, the preparation of bulk quantities of nitroxides is limited by the avability of the starting bis(hydroxylamino) compound. Although this chemical is commercially available as the sulfate, it very often contains inorganic salts and it is expensive. The bis(hydroxylamino) derivative BHA is prepared by reduction of 2,3-dimethyl-2,3-dinitrobutane; it is surprisingly volatile and removal of the solvents causes loss of most of the product. Better yields can be obtained by using the free base, the synthetic pathway is reported by different scientist with different optimization of the reaction [67], [68].

The nitronyl nitroxides must be kept in the dark and at low temperature with this way they are stable for months. The stability of the nitroxides has been accounted for by the presence of inactive groups attached to the nitrogen atom. Thus the Tempo and Proxyl radicals bear methyl groups on the  $\alpha$ -carbon atoms; the presence of a hydrogen atom would lead to disproportionation to the corresponding hydroxylamine and nitrone. In the case of the nitronyl nitroxide radicals, the nitronyl group confers the required inactivity. It is also likely that the conjugation of the two NO groups contributes to observed stability of these free radicals.

In coordination chemistry the most importance part of these radicals is having two equivalent donor sites on radical. Their powerful characterization by EPR spectra exhibit identical hyperfine couplings for two equivalent nitrogen atoms. Nitronyl nitroxide and imino nitroxide they both bear several oxyl groups and unsaturated structures allowing correlation of the unpaired spin density over the different coordination sites.

Since magnetism is a bulk property spin carrying ligands, such as nitronyl- (NIT) and imino- (IMI) nitroxides, are particularly attractive[69], [70], Luneau has described a set of ligands based on functionalization of imidazole and benzimidazole[71]-[74] (Figure 2. 16).

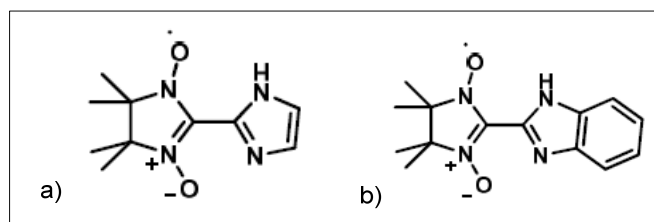


Figure 2. 16: Structure of a)imidazole, b)benzimidazol nitroxide.

These compounds have been successfully employed as bridging ligands in either one- or two-dimensional complexes with  $\text{Mn}(\text{hfac})_2$ . Spin-spin interactions between the metal and ligand are typically moderately strong and antiferromagnetic in nature. The two-dimensional structures based on benzimidazole exhibited evidence for bulk magnetization at 40 K, which far outpaced the similar complex with imidazole derivative, where magnetization was observed only at 1.4 K.

As chemical structure point of view, in the nitronyl nitroxides the sites of coordination are less hindered than in nitroxides. Furthermore, modification of coordination ability can be diversified by crowding.

From the magnetic point of view, due to their bridging properties and well-established antiferromagnetic coupling, most nitronyl nitroxide–metal complexes exhibit ferromagnetic-alternating chains[71],[75]-[77] the discrete  $[\text{Mn}(\text{II})(\text{hfac})_2\text{NITPh}]_6$  ring shown in Figure 2.17[78] a good example for discrete high spin molecules as ferrimagnetic rings. Note that free radicals, thanks to direct coordination of spin density rich donor atoms to metal ions, are well suited for giving large exchange interactions and very robust high-spin ground states. Despite the large  $S$  value, the compound behaves as a paramagnet throughout the temperature range.

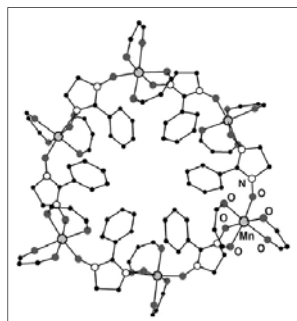


Figure 2.17: Molecular structure of the cyclic  $[\text{Mn}(\text{hfac})_2\text{NNPh}]_6$  complex.

#### 2.2.4. Imino Nitroxides

Imino nitroxides are similar with nitronyl nitroxides since both have one unpaired electron delocalized on two coordination sites but their coordination properties are different. Generally they have higher stability compared to the corresponding nitronyls [79].

EPR spectroscopy, neutron diffraction, and computational studies indicate that spin on the nitroxide nitrogen is substantially larger than on the imino nitrogen, though the latter nitrogen does possess substantial spin density [80], [81]. Coordination through the oxyl fragment leads antiferromagnetic interactions like for nitronyl nitroxides but some rare-earth ions and axial coordination to Cu(II) results ferromagnetic coupling with selected metal ions (Cu, Ni and Co) [69], [82]. The first high-spin molecule ( $S = 5/2$ ) including imino nitroxides is a copper complex[69] (Figure 2.18). It was reported that for the first time that copper–imino nitroxide interactions were ferromagnetic and large. Coupling of the two terminal metal ions through the imino nitrogen of the free radical is large ( $J > +200 \text{ cm}^{-1}$ ) and the central ion is also ferromagnetically coupled weakly ( $J = +10 \text{ cm}^{-1}$ ). It was a good example for to show that imino nitroxides can be used for designing high-spin species.

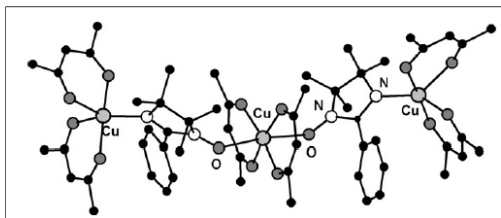


Figure 2. 18: Molecular structure of first high spin molecule involving Cu(II) and imino nitroxides ferromagnetically coupled.

As conclusion we can say that nitronyl and imino nitroxides are the cornerstones of the metal–radical approach toward molecular magnets[34], [49].

## 2.3 Essential of Magnetism

### 2.3.1. Magnetism

Magnets play a crucial role in a modern life; as we know, a vast number of devices are employed in the electromagnetic industry. In ancient times human beings experienced magnetic phenomena by utilizing natural iron minerals, especially magnetite. It was not until modern times that magnetic phenomena were appreciated from the standpoint of electromagnetics, to which many physicists such as Oersted and Faraday made a great contribution. In particular, Ampère explained magnetic materials in 1822, based on a small circular electric current. This was the first explanation of a molecular magnet. Furthermore, Ampère's circuital law introduced the concept of a magnetic moment or magnetic dipoles, similar to electric dipoles. Macroscopic electromagnetic phenomena are depicted in Figure 2. 19, in which a bar magnet and a circuital current in a wire are physically equivalent.

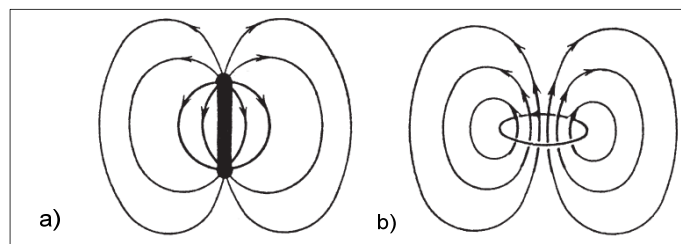


Figure 2.19: Magnetic fields due to a) bar magnet, b) circuital current.

The true understanding of the origin of magnetism, however, has come with quantum mechanics, newly born in the twentieth century. Before the birth of quantum mechanics vast amounts of data concerning the magnetic properties of materials were accumulated, and a thoroughly logical classification was achieved by observing the response of every material to a magnetic field. These experiments were undertaken using magnetic balances invented by Gouy and Faraday. The principle of magnetic measurement is depicted in Figure 2.19, in which the balance measures the force exerted on the materials in a magnetic field. In general, all materials are classified into two categories, diamagnetic and paramagnetic substances, depending on the directions of the force. The former tend to exclude the magnetic field from their interior, thus being expelled effect in the experiments of Figure 2.19. On the

other hand, some materials are attracted by the magnetic field. This difference between diamagnetic and paramagnetic substances is caused by the absence or presence of the magnetic moments that some materials possess in atoms, ions, or molecules. Curie made a notable contribution to experiments, and was honored with Curie's law (1895). Our understanding of magnetism was further extended by Weiss, leading to antiferromagnetism and ferromagnetism, which imply different magnetic interactions of magnetic moments with antiparallel and parallel configurations. These characteristics are involved in the Curie – Weiss law.

There are five main magnetic states of matter [83]. In a *diamagnetic* material all of the electron spins are paired and so the overall net spin is zero. This results in a weak repulsion to an applied magnetic field. All atomic and molecular compounds exhibit diamagnetic behavior to some extent. A *paramagnetic* material has an attraction to an applied magnetic field due to interaction of the external field with one or more unpaired electrons within the material. The interaction between paramagnetic atoms or molecules with their surrounding neighbors gives rise to the bulk magnetic properties of the material (Figure 2.20). In the case of *paramagnetism* each unpaired electron has no effect on any other electrons in its neighbors and so the spins are in random directions. The spins can be easily changed to a uniform direction by application of an external magnetic field. *Ferromagnetism* occurs when adjacent spins are aligned parallel and in the same direction, which results in a large net magnetic moment, even with no applied field. *Antiferromagnetism* occurs when the spins are parallel but face in opposite directions, which leads to a cancelling of the spins and hence a zero magnetic moment. A special case of antiferromagnetic behavior results in the last main class, *ferrimagnetism*. Here the spins are still aligned in an antiparallel arrangement, but the spins in each direction are of different magnitudes and so the substance has an overall magnetic moment.

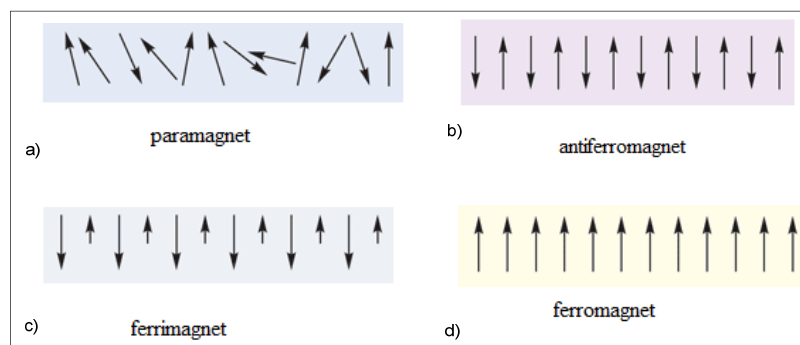


Figure 2.20: The arrangement of spins for a) paramagnet, b) antiferromagnet, c) ferrimagnet, d) ferromagnet.

Magnetism is frequently measured by the material's response (attraction and repulsion) to a magnet. It is a consequence of the spin associated with an unpaired electron and how nearby unpaired electrons interact with each other. Molecules are typically sufficiently large and far apart that their spin-spin exchange coupling energy  $J$  is smaller compared to the coupling breaking thermal energy. Their spins do not couple, but instead form a very weak *paramagnet*. When the spins are closer,  $J$  can be sufficiently large to enable an efficient parallel (or antiparallel) alignment, this increases (or decreases) the measured susceptibility  $\chi$ . The susceptibility is defined as the ratio of the induced magnetic moment per unit volume to the applied magnetic field:

$$\chi = M / H \quad (2.1)$$

Where  $M$  is the magnetization (magnetic moment per unit volume) and  $H$  is the magnetic field strength.  $\chi$  is dimensionless. The molar susceptibility  $[\chi M]$  of a paramagnetic substance is proportional to the thermodynamic temperature  $[T]$ , i.e.

$$\chi M = C/T \quad (2.2)$$

where  $C$  is the Curie constant, which is given by,

$$C = N_A \beta^2 g^2 S(S+1) / 3KB \text{ or } C = 0.125 g^2 S(S+1) \text{ cm}^3 \text{ K} / \text{mol}^{-1} \quad (2.3)$$

where  $N_A$  is Avogadro's number,  $KB$  is Boltzmann constant,  $\beta$  is a constant unit called the Bohr magneton (BM). The Curie constant provides the convenient check of the spin concentration of the sample ( $C = 0.375 \text{ emu K/mol}$  for  $S = 1/2$ ). A

modification of the Curie law, which takes into account the interactions among the individual magnetic moments, is the Curie-Weiss law. It states that,

$$\chi M = C / (T - \theta) \quad (2.4)$$

where  $\theta$  is the Weiss constant in temperature units, a characteristic of the material. It relates the total dipole-dipole exchange interactions  $[J]$  of magnetically active centers with all its magnetic neighbors  $z$  (nearest, next nearest, etc.).

$$\theta = [2S(S+1) / 3KB] \sum z_i J_i \quad (2.5)$$

When the spins coupled in a parallel manner  $\chi$  is enhanced i.e.  $\theta > 0$  [ferromagnetic], and when the spins are coupled in antiparallel manner  $\chi$  is suppressed i.e.  $\theta < 0$  [antiferromagnetic].

$$\chi M = N A \beta^2 g^2 S(S+1) / 3KB (T - \theta) \quad (2.6)$$

In substances with interacting magnetic moments and where the orbital contribution to the magnetic moment is significant, the molar susceptibility is given by,

$$\chi M = N A \beta^2 g^2 J(J+1) / 3KB (T - \theta) \quad (2.7)$$

Here the resultant total angular momentum  $[J]$  is given by,

$$J(J+1) = L(L+1) + S(S+1) \quad (2.7)$$

A typical plot of the effective magnetic moment  $[\mu_{\text{eff}}]$  as a function of temperature  $[T]$  is shown for an ideal paramagnet, ferromagnet, ferrimagnet, and antiferromagnet in Figure 2.20. For the substance that shows bulk ferromagnetism, a transition occurs at a temperature known as Curie temperature  $[T_c]$ , leading to a phase in which there is long range parallel ordering of spins. Below this temperature  $\chi M$  rises abruptly to a very high value.

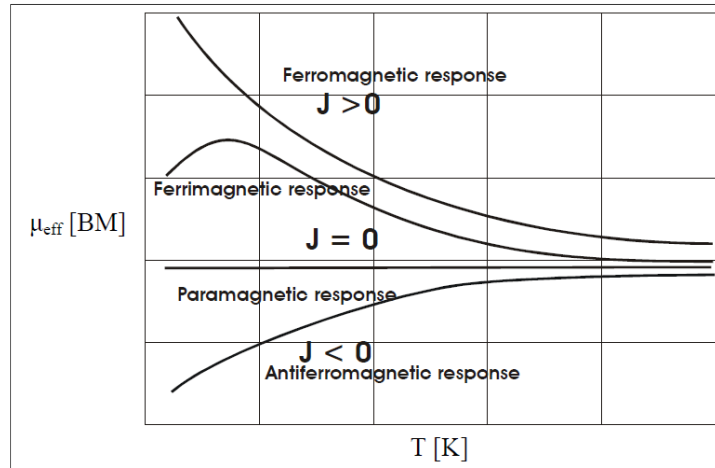


Figure 2.21: Temperature dependence of the effective magnetic moment ( $\mu_{\text{eff}}$ ) in magnetic materials.

If the substance is diamagnetic containing only spin-paired electrons the magnetic response opposes the applied field and  $\chi$  is small and negative. In a paramagnetic substance, i.e. one that contains unpaired electrons the normally randomized spin moments aligns with the external magnetic field. Here the density of the magnetic lines of force within the sample is intensified giving small but positive  $\chi$ , independent of the magnetic field intensity, and  $\chi$  decreases with increase in temperature. In a ferromagnetic substance, the spins are spontaneously parallel to one another in microscopic domains leading to a permanent magnetization. The application of a magnetic field causes the domains to point along the field even when the field is removed. The  $\chi$  is large and positive, dependent on the magnetic field, temperature, and the history of the sample. The related phenomenon, antiferromagnetism occurs when neighboring, equal spin moments couple in an anti-parallel fashion, leading to a lowering of the magnetization, while ferrimagnetism occurs when unequal spin moments couple in a way to leave a net magnetization.

Ferro-, antiferro-, and ferrimagnetic materials often show a hysteresis, which is an irreversibility of the magnetic behavior as the applied magnetic field is changed (see Figure 2.22).

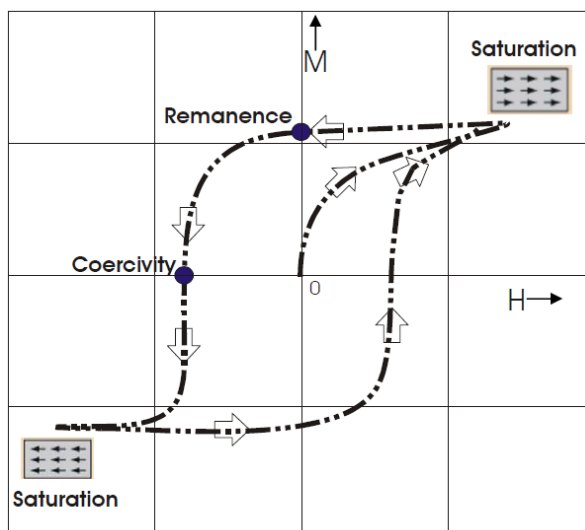


Figure 2.22: Hysteresis curve of a ferromagnetically ordered material with memory.

Although ferromagnets, below  $T_c$  exhibit long-range ordering of spins, a sample may still not behave like a magnet, unless this ordering occurs within “domains”. The domain themselves are randomly oriented and cancel each other out, however application of magnetic field will magnetize the sample. When the field is turned off, the magnetization curve shows hysteresis and the sample retains some magnetization. The amount of magnetization the sample retains at zero driving field is called remanence. It must be driven back to zero by a field in the opposite direction; the amount of reverse driving field required to demagnetize it is called coercivity. If an alternating magnetic field is applied to the material, its magnetization will trace out a loop called hysteresis loop. The area of the hysteresis loop is related to the amount of energy dissipation upon reversal of the field. It is important to emphasize that highly magnetic behavior is not a property of an isolated molecule. It is a cooperative solid-state (bulk) property. This can be achieved through strong intermolecular interactions in 3-D space. The magnetic susceptibility  $\chi$  can be measured using Faraday-type balance or Super conducting quantum interference device - SQUID susceptometer down to liquid helium temperature.

Today the greatest challenge in the field of magnetic materials research remains in the design and synthesis of ferromagnets. Many strategies have currently been followed towards molecular magnets, 1) the pure organic approach with spin carrying molecules, 2) the organic-inorganic hybrid approach and 3) the single molecular magnets (SMMs).

### 2.3.2. Organic Magnets

Atoms in organic molecules are held together with covalent bonds consisting of electron pairs with anti-parallel electron spins. Typical organic materials are diamagnetic for this reason. There are, however, exceptional species, so-called free radicals, which carry an unpaired electron. Most radicals are very reactive and mainly play a role as intermediates in chemical transformation. Fortunately, stable radicals do exist, and these species enable the investigation of possible electron spin-spin interactions in organic magnetic materials. In the area of molecular magnetism, purely organic materials based on radicals are still under active investigation. Therefore, magnets with multiple properties can be synthesized (*i.e. plastic magnets*). These molecular compounds will have no presence of metal ions, but rather rely solely on electron spins residing only in the s and p orbitals. They must also maintain long range order of spins in at least two dimensions to produce ferromagnetic behavior. Many spin carrying units are in active use toward building organic based magnets. Examples are, Nitronylnitroxides (NIT), Iminonitroxides (IMI), *t*Butyl-Nitroxides (NO), Verdazyl radicals (VZ), Carbenes, Nitrenes, Phenoxides (ArO), Ketyl radicals, Triphenylmethyl radical (TPM) (Figure 2.23).

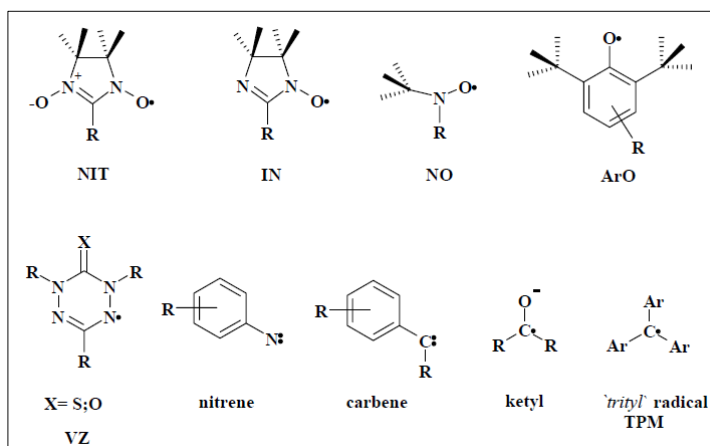


Figure 2.23: Some common organic radical units.

Stable nitronylnitroxide radicals were synthesized by Ullman et al. [44], [62] upon reacting 2,3-dimethyl-2,3-bis(hydroxylamino)-butane I with aliphatic aldehydes to give anhydro adduct II as white solid, which upon oxidation with  $\text{NaIO}_4$  or  $\text{PbO}_2$  give nitronylnitroxide IV. If oxidation of II with lead oxide was not carried

out to completion, a highly reactive intermediate III could be isolated. The color of the nitronylnitroxides varies depending upon the R group (Figure 2.24). Aliphatic radicals are red in color and aromatic compounds are blue or violet, depending on whether the solvent is polar or nonpolar [44], [62].

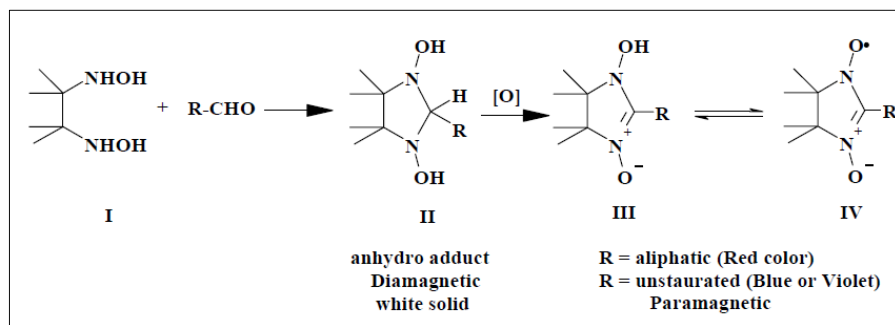


Figure 2.24: Ullman's reaction.

The unpaired electron is delocalized mainly between nitrogen and oxygen and between both N-O groups, it is stabilized by protecting the radical center with geminal dimethyl groups. These methyl groups also prevent NIT from becoming dinitrone [44], [62]. Nitroxide radicals have an inherently stable electronic configuration and can be further stabilized by conjugation with  $\pi$  electrons of aromatic systems and/or by shielding with bulky substituents. The SOMOs of the mononitroxides (NO) are localized mainly on the N-O moiety and the unpaired electron mainly resides there. The general strategy for designing nitroxide containing magnetic materials has been to prepare molecules with large intermolecular spin polarizations, and to minimize the intermolecular overlap integrals between the SOMOs of adjacent radical centers, and the vacant or doubly occupied molecular orbital of neighboring molecules. Each radical unit has its merits and demerits. Amongst the radicals units mentioned above NIT, IN, NO, VZ are stable spin carrying units at ambient conditions. Many molecules have been synthesized based on NIT, IN, NO radicals due to their synthesis, purification and characterization advantages in presence of oxygen [44], [62].

The first pure organic based magnet was reported in 1991 by Kinoshita and coworkers<sup>84</sup> (i.e. the  $\beta$ -Phase of *p*-nitrophenyl nitronylnitroxide (PNN) with  $T_c = 0.65$  K, exhibiting low magnetic anisotropy and small coercive forces. This discovery evoked the successive rapid development and discovery of other ferromagnets. Most of them are based on nitroxide radicals. After PNN an elegant

example was provided by Rassat and his coworkers<sup>3</sup> in 1993, namely 1,3,5,7-tetramethyl-2,6-diazaadamantane- *N,N'*-dioxyl with  $T_c = 1.48$  K. This compound was expected to possess intermolecular ferromagnetic interactions from the orthogonality of the two N-O groups of the biradical, and owing to the favorable 3-D network of NO chains for an intermolecular ferromagnetic interactions. Later in 1995, thiaverdazyl based organic magnet was reported with  $T_c = 0.67$  K<sup>4</sup>. The dithiadiazolyl radical has also displayed properties smaller than expected for a ferromagnet, but has one of the highest  $T_c = 36$  K so far reported [85]. (Figure 2.25).

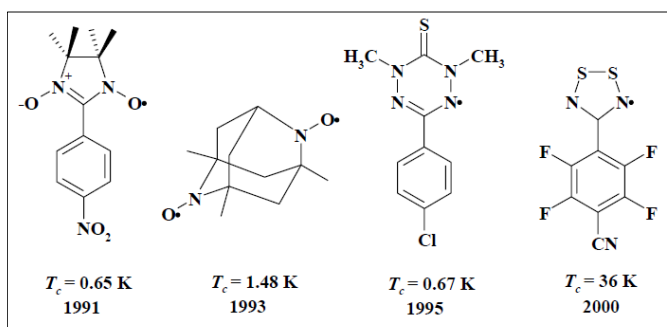


Figure 2.25: Pure organic based magnets obtained from NIT, NO, VZ and dithiadiazolyl radicals.

### 2.3.3. Single Molecule Magnets

A Single Molecule Magnet (SMM) consists of a central large spin metal-oxo core, which is surrounded by organic ligands to form a discrete molecular species. It has the characteristic property that the molecule retains its spin orientation even in the absence of an external magnetic field. If the molecule possesses a large spin ground state ( $S$ ) as well as an Ising type magnetic anisotropy ( $D < 0$ ) then this gives rise to an energy barrier that lies between the ‘spin-up’ and ‘spin down’ configurations as shown in Figure 2.26 [86]. This is the result of Zero Field Splitting (ZFS) of the ground state caused by spin-orbit coupling of the ground and excited states, which splits the  $M_s$  levels in the absence of an applied field [87].

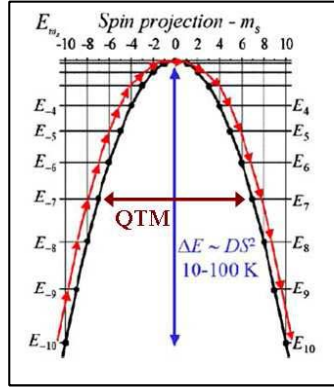


Figure 2.26: The ZFS of the  $M_s$  levels for an  $S = 10$  system with energy barrier  $-E$  between the  $m_s = -10$  and  $m_s = +10$  states. The dark red arrow shows a shortcut through the barrier via Quantum Tunneling of the Magnetisation.

The size of the energy barrier ( $-E$ ) varies with the spin ( $S$ ) and axial zero-field splitting parameter ( $D$ ) via the equations

$$-E = S^2|D| \text{ (for integer spin)} \quad (2.8)$$

$$-E = (S^2 - \frac{1}{4})|D| \text{ (for half-integer spin)} \quad (2.9)$$

This energy barrier will therefore oppose the re-orientation of the magnetization, and so if the height of the barrier is large in comparison to the available thermal energy, the resulting relaxation of the magnetization will be slow [86], [88]. The relaxation rate can be investigated by ac magnetic susceptibility measurements. Ac measurements are used to examine the dynamic susceptibility (*Equation 1*) of a sample by applying an oscillating magnetic field. The dynamic susceptibility is a complex quantity with real (dispersion) and imaginary (absorption) components that are dependent on the angular frequency ( $\omega = 2\pi\nu$ ) of the ac field.

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) \quad (2.10)$$

The relaxation process follows an Arrhenius law for a thermal activation process to overcome the energy barrier with

$$\exp(-\frac{E_a}{kT}) \quad (2.11)$$

where  $t = (w)-1$ . So from an Arrhenius plot of  $\ln(\tau)$  versus  $(1/T)$  the energy barrier ( $E$ ) can be determined from the gradient of the line. As the ac magnetic field frequency becomes close to the relaxation rate of the molecules the observed in-phase susceptibility ( $\chi'$ ) reduces. Therefore the out-ofphase component ( $\chi''$ ) will increase. For measurements where there is only one relaxation process operating, a graph of  $\chi''$  against temperature will show a peak at the temperature where  $w = (t)-1$ . If the switching frequency of the applied field is increased, the peak should be shifted to a higher temperature[89]. This effect is demonstrated in the data obtained for the first SMM  $[\text{Mn}_{12}\text{O}_{12}(\text{MeCO}_2)_{16}(\text{H}_2\text{O})_4] \cdot 2\text{MeCO}_2\text{H} \cdot 4\text{H}_2\text{O}$ , which is shown in Figure 2.27.

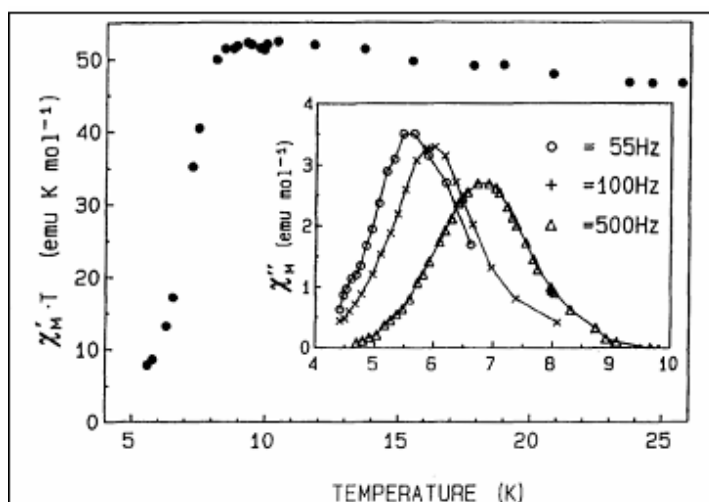


Figure 2.27: The frequency dependent  $\chi''$  peaks seen in the ac susceptibility measurements for the SMM  $[\text{Mn}_{12}\text{O}_{12}(\text{MeCO}_2)_{16}(\text{H}_2\text{O})_4] \cdot 2\text{MeCO}_2\text{H} \cdot 4\text{H}_2\text{O}$ .

A single molecule magnet will also display magnetisation versus field hysteresis loops as shown in Figure 2.27. These often have characteristic steps in the loop due to Quantum Tunnelling of the Magnetisation (QTM) through the energy barrier (see Figure 2.28)[91] QTM is the result of transverse anisotropy which gives a superposition of states of both sides of the barrier with a tunnel splitting. The axial anisotropy (described by the  $D$  term of the spin Hamiltonian) splits the  $ms$  levels, while the transverse anisotropy ( $E$  term) mixes the  $ms$  states (as do the higher terms of the spin Hamiltonian). The application of a magnetic field will alter the relative energies of the  $ms$  states. QTM is only possible when the energy levels on both sides of the barrier are aligned and can therefore only occur at certain points as the field is swept, thus creating steps in the hysteresis loop. SMM hysteresis is temperature and

sweep rate dependent, and the loops broaden on decreasing the temperature or on increasing the sweep rate of the magnetic field.

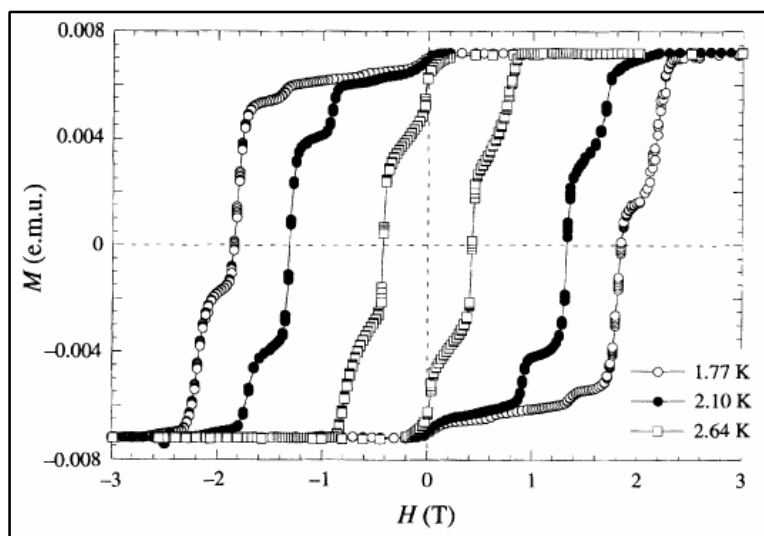


Figure 2. 28: Magnetisation versus field hysteresis loops observed for the SMM  $[\text{Mn}_{12}\text{O}_{12}(\text{MeCO}_2)_{16}(\text{H}_2\text{O})_4] \cdot 2\text{MeCO}_2\text{H} \cdot 4\text{H}_2\text{O}$ .

The steps in the loops are due to quantum tunnelling of the magnetisation[91]. The initial proposal for the application of SMMs was for high density data storage with each molecule representing one bit, however this now appears less likely due to the technological limitations for addressing individual molecules and in obtaining functionality at non-cryogenic temperatures. More promising future applications of SMMs include quantum computing, MRI contrast agents and magnetic refrigeration [88], [89].

## 2.4. Aspects of EPR spectroscopy

### 2.4.1. Introduction

Electron Paramagnetic Resonance (EPR) also call Electron Spin Resonance (ESR) results from microwave-induced transitions between the magnetic energy levels of atoms or molecule, with unpaired electron, in an applied magnetic field.

The magnetic properties are determined by the electron magnetic moment. Nucleus magnetic moment is significantly smaller than the electron magnetic moment; therefore the latter basically defines the magnetic properties of the matter.

Electron magnetic properties in atoms appear due to their motion around the nucleus (orbital magnetic momentum) and intrinsic orbital angular momentum of the electron, or spin.[92]-[96]. Atoms and molecules possess different magnetic properties, depending on their electronic structure. As we have seen earlier (section 2.2.4) materials consisting of molecules with nonzero magnetic moments are called paramagnetic. Examples of paramagnetic materials are some gases (O<sub>2</sub>, NO), alkali metals, various salts of the rare-earth metals, etc.

In the majority of biological and chemical systems the orbital magnetic momentum of paramagnetic particles is negligible. Therefore, the paramagnetic properties of a sample could be attributed to the total spin  $S$  of the molecule. In a magnetic field  $[H]$ , the corresponding  $2S + 1$  degenerated  $M_s$  energy sub-levels are splitted, corresponding to the different projections of the total spin  $S$  in direction of the vector of the applied magnetic field:

$$E(M_s) = g \beta M_s H \quad (2.12)$$

According to the selection rule[92]-[99] two values of  $M_s$  are allowed for a system consisting of one unpaired electron  $S = 1/2$ :  $M_s$  can take the values  $+1/2$  and  $-1/2$ , which will be separated in a magnetic field by an energy interval ( $\Delta E$ ) of  $g\beta H$ . In EPR the resonance absorption is the microwave energy that causes a transition from the lower energy  $M_s = -1/2$  to the higher energy state  $M_s = +1/2$ . The micro-wave frequency required for this transition is commonly in the range of 9-19 GHz(X-band).

The splitting of the energy levels in an applied field is called the Zeeman effect. Because the electron has a magnetic moment  $\mu$ , it acts like a compass in a magnetic field  $H$ . It will have a state of lowest energy where the electron moment  $\mu$  is aligned along the local magnetic field ( $M_s = -1/2$ ) and a state with highest energy where  $\mu$  is aligned against magnetic field ( $M_s = +1/2$ ). From quantum mechanics the derived basic equation for ESR is as follows

$$E = M_s g_e \beta_e H = \pm 1/2 g_e \beta_e H \quad (2.13)$$

$$\Delta E = h\nu = g \beta H \quad (2.14)$$

where  $g$  is the  $g$ -factor (unit less),  $\beta_e$  is the electron magnetic moment or Bohr magneton ( $eh/4\pi me = 9.2740 \times 10^{-24}$  J/T), and  $M_s$  is the magnetic quantum number. The free electron  $g_e$  value is 2.002319304386, for most of the organic radicals generally  $g$  value is  $\leq 2.01$ , but varies depending on the electron configuration especially for transition metal ions.

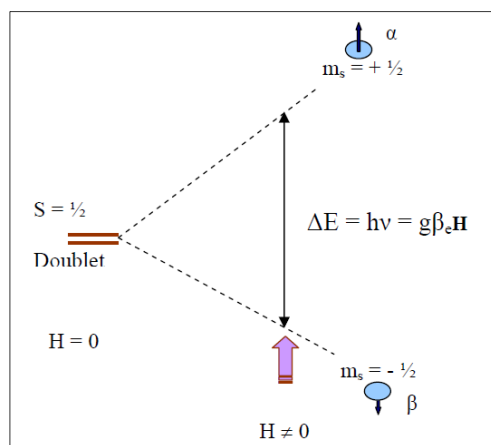


Figure 2.29: Splitting of Zeeman levels in a magnetic field for a system with one unpaired electron.

The position of a line in the EPR spectra is characterized by the magnitude of  $g$  factor:  $g = h\nu / (\beta H)$ , where  $H$  is the magnetic field, at which the resonance condition is met. For a free electron  $g = 2.00232$ . Most of organic radicals, among which nitroxide radicals, show similar values of  $g$  (2.003 - 2.007). In solution the  $g$  factor is isotropic, while in solid state it is anisotropic and becomes orientation dependent:

$$g^2 = g_{xx}^2 I_x^2 + g_{yy}^2 I_y^2 + g_{zz}^2 I_z^2 \quad (2.15)$$

where  $I_x, I_y, I_z$  are the direction cosine between the direction  $H$  and the principle  $g$ -axes. Among the other factors, which cause anisotropy of the  $g$  factor and lead to serious deviations from the spin value of 2.00232, is the influence of anisotropic electric fields, surrounding the atoms, splitting of Zeeman levels in zero magnetic field, etc. Typically significant differences of the magnitude of the  $g$ -factor from a free electron value are observed in the presence of strong spin-orbital interactions (as in the case of transition metals). For paramagnetic species in dilute liquid solution of low viscosity the system is apparently isotropic, due to the free molecular rotation. In such systems all the  $g$  axes  $g_x = g_y = g_z$  are equal to the applied magnetic field  $H$ .

Consequently,  $g$  factor is independent from the field direction and to be regarded as an effective value averaged over all orientations:

$$g_{\text{iso}} = (g_{xx} + g_{yy} + g_{zz})/3 \quad (2.16)$$

In solid-state powder or frozen solution due to anisotropic nature of the paramagnetic site three main components can be seen for a (rhombic case) or in axial case, two anisotropic  $g$  values, ( $g^{\parallel}$  and  $g^{\perp}$ ) are required to describe the ESR spectrum. Since the paramagnetic crystallites have more  $g^{\perp}$  ( $g_x$  and  $g_y$ ) aligned than  $g^{\parallel}$  ( $g_z$ ), the most intense absorption will correspond to  $g^{\perp}$  (see Figure 2.28). In reality, often one finds that due to the overlapping features it is generally difficult to obtain the  $g^{\parallel}$  and  $g^{\perp}$  values. For rhombic systems due to the lower symmetry of the crystallite the observed  $g$  values in different directions ( $x$ ,  $y$ , and  $z$ ) are no longer equal,  $g_{xx} \neq g_{yy} \neq g_{zz}$ . For an axial systems the solid-state anisotropic  $g$  values are [ $g_z = g^{\parallel}$  and  $g_x = g_y = g^{\perp}$ ].

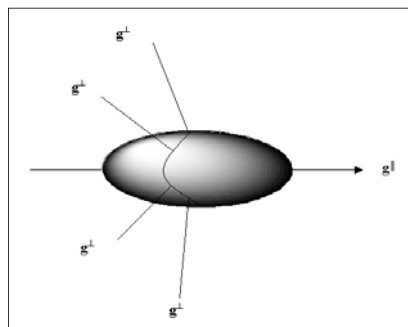


Figure 2. 30: The  $g^{\parallel}$  and some  $g^{\perp}$  axes in a crystallite with three fold and higher axis.

#### 2.4.2. Hyperfine Coupling (hfc)

In addition to the interaction of an electron with the magnetic field (Zeeman effect), it should be taken into account its interaction with the neighboring atoms that have an intrinsic nuclear spin. The magnetic interaction between an unpaired electron magnetic moment (spin) and nuclear magnetic moment (nuclei with non-zero nuclear spin,  $I \neq 0$ ) is called *hyperfine coupling*. This gives spectrum with multiline that is called the hyperfine structure. If there was the Zeeman effect only then all spectra would consist of a single line and this would be of little interest to chemists.

However, the most useful chemical information that can be derived from EPR spectra comes from the hyperfine structure.

The number of the lines depends on the magnetic nucleus number.

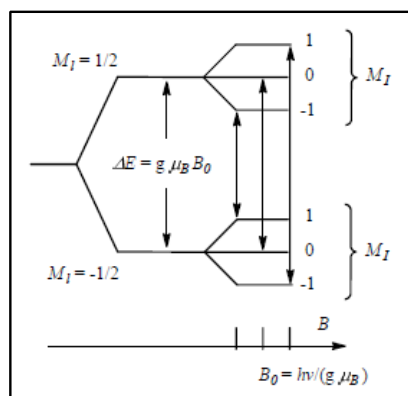


Figure 2.31: Energy-level scheme illustrating origins of hfc in EPR spectra of NO paramagnetic molecule.

Examples of the nucleus with non-zero nuclear spin are:  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{15}\text{N}$ .

Tablo 2. 2: Nuclear spin values for some common element.

| Nuclei          | Spin (I) | Nuclei           | Spin (I) |
|-----------------|----------|------------------|----------|
| $^1\text{H}$    | 1/2      | $^{16}\text{O}$  | 0        |
| $^{12}\text{C}$ | 0        | $^{35}\text{Cl}$ | 3/2      |
| $^{13}\text{C}$ | 1/2      | $^{79}\text{Br}$ | 3/2      |
| $^{14}\text{N}$ | 1        | $^{127}\text{I}$ | 5/2      |
| $^{15}\text{N}$ | 1/2      | $^{31}\text{P}$  | 1/2      |

As an example, let us consider the hyperfine interaction with the nitrogen nuclei of the NO paramagnetic molecule.  $^{14}\text{N}$  nucleus has a spin  $I = 1$ , therefore, three projections of spin are allowed: along the direction, perpendicular and against the applied magnetic field  $H$ . The corresponding values of the magnetic quantum number are:  $I_z = +1, 0, -1$ . It follows, that due to the interactions of a free electron with a nitrogen nuclei each Zeeman level splits in three sub-levels. According to the quantum mechanical selection rules  $\Delta S_z = +1, -1$  (orientation of the electron spin changes) and  $\Delta I_z = 0$  (orientation of the nuclei spin does not change). Thereby, the

The number of hyperfine lines grows multiplicatively with the number  $n$  of magnetic nuclei, because each additional nucleus splits every line into equidistant  $2I+1$  lines of the same intensity. The  $n$  equivalent nucleus thus gives rise to  $(2I+1)^n$  lines. However, when  $n$  nuclei are equivalent, some of the lines coincide and their number is reduced to  $2nI+1$ . The hyperfine pattern then exhibits a characteristic distribution of intensities for  $I = 1/2$  with  $n = 1-6$ , which are given (Pascal's triangle) below,

Figure 2.32: Pascal's triangle.

$$\mathcal{H} = (\beta \hat{\mathbf{S}} \cdot \mathbf{g} \cdot \hat{\mathbf{H}}) + \hat{\mathbf{S}} \cdot \mathbf{A} \cdot \hat{\mathbf{I}} \quad (2.17)$$
$$\mathbf{A} = \mathbf{a}_{\text{iso}} + \mathbf{A}_{\text{dip}} \quad (2.18)$$
$$a_{\text{iso}} = 8\pi \text{ gegeben } \rho(0) \quad (2.19)$$

Where  $\rho(0) = |\psi(0)|^2$  is the unpaired electron density at the nucleus,  $g_n$  the nuclear g-factor,  $\beta_n$  is the nuclear magneton ( $5.0507866 \times 10^{-27} \text{ J T}^{-1}$ ). Equation 2.20 measures the magnetic interaction energy (in joules) between the electron and nucleus. The A term arises due to the interaction between the electron and nuclear dipoles, and is time-averaged to zero in liquid solution due to the random molecular motions. The observed isotropic hyperfine value in liquid solution is exclusively due to the Fermi contact term, EFC.

$$a_{\text{iso}} = [A_{xx} + A_{yy} + A_{zz}] / 3 \quad (2.20)$$

In solid or frozen rigid systems, it is precisely the dipole-dipole interaction between the electron and nuclear dipoles that gives anisotropic component of hyperfine coupling. The magnitude of the A component, like the g component, is dependent of orientation. The Hamiltonian describing the anisotropic interaction takes the following form,

$$\mathcal{H} = (\beta \hat{S} \cdot g \cdot \hat{H}) + (\hat{S}_z \cdot A_{zz} \cdot \hat{I}_z + \hat{S}_x \cdot A_{xx} \cdot \hat{I}_x + \hat{S}_y \cdot A_{yy} \cdot \hat{I}_y) \quad (2.21)$$

Thus we can obtain the principle hyperfine values  $A_{xx}$ ,  $A_{yy}$ , and  $A_{zz}$  for each directional cosines for all three directions or the  $A_{zz} = A^{\parallel}$  and  $A_{xx} = A_{yy} = A^{\perp}$  in case of axial symmetry. Most often g axis and the A axis are collinear.

### 2.4.3. EPR Spectra of Nitronyl and Imino Nitroxide

Nitronyl nitroxide and imino nitroxide monoradicals exhibit very distinct EPR hyperfine structure. In the case of nitronyl nitroxide, the spectrum recorded in dilute ( $\leq 10^{-4} \text{ M}$ ) and oxygen free DMSO solution at room temperature exhibits a clear isotropic five line pattern with  $g_{\text{iso}} = 2.0065(8)$ . The five lines spectra originate from the interaction of the unpaired electron with the two equivalent nitrogen nuclei of the imidazolyl moiety. The relative intensity of each line follows the typical 1:2:3:2:1 ratio, as shown in Figure 2.33 [97]-[100]. The best fitting of the EPR curve was obtained assuming Lorentzian/Gaussian linewidth ratio = 0.66.

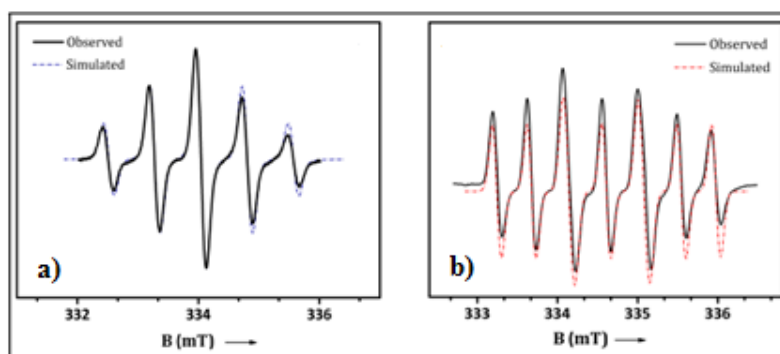


Figure 2. 33: EPR spectra of mono a) nitronyl, b)imino nitroxide free radical.

In the case of imino nitroxide monoradical, the resulting EPR spectrum represents a seven line pattern, as demonstrated in Figure 2.33 (2). Such feature arises from the interaction of the unpaired electron with the two non-equivalent nitrogen nuclei. The seven line pattern follows the intensities ratio of 1:1:2:1:2:1:1 and has  $g_{iso} = 2.0058(3)$ .

#### 2.4.4. Exchange Interactions (J)

The simulated isotropic solution state EPR spectrum of a mono- ( $^{14}\text{N} = 2$ ), bi- ( $^{14}\text{N} = 4$ ) and tri nitronylnitroxide ( $^{14}\text{N} = 6$ ) radicals are given in Figure 2.34. For a mono nitronyl nitroxide radical (NIT), we have to consider the interaction of electron spin with only two equivalent nitrogen nuclei  $^{14}\text{N}$  [ $I = 1$ ], and as seen above this yields, in solution, five lines pattern with intensity distribution 1:2:3:2:1 which contains only information about the nitrogen hyperfine constant  $A_N$  (I). A more resolved spectrum that shows additionally the hyperfine interaction with neighboring hydrogen ( $A_H$ ) can be obtained by using argon bubbled solution of concentration  $c \leq 10^{-4}$  M and low modulation frequency (II). This kind of spectrum gives rich information about the structural environment of the unpaired electron as well the spin density of the different carbons attached to hydrogens, in other words spin polarization pathways. For a bi-nitronyl nitroxide radical, when the intramolecular exchange interaction ( $J$ ) between the two radical units exceeds the hyperfine constant ( $A_N$ ), we have to consider the interaction of one unpaired electron with four equivalent nitrogen nuclei  $^{14}\text{N}$  ( $I = 1$ ). This gives in solution nine lines with intensity ratios close to 1:4:10:16:19:16:10:4:1.(III). The integrated intensity of the signal is 2.66 times that of a monoradical, which provides information about the spin

concentration. For a tri-nitronyl nitroxide radical, which  $J \gg A_N$ , the interaction of the electron spin with now six equivalent nitrogens  $^{14}\text{N}$  ( $I = 1$ ) affords a thirteen line pattern (IV) with the intensity ratio close to 1:6:21:56:96:132:141:132:96:56:21:6:1.

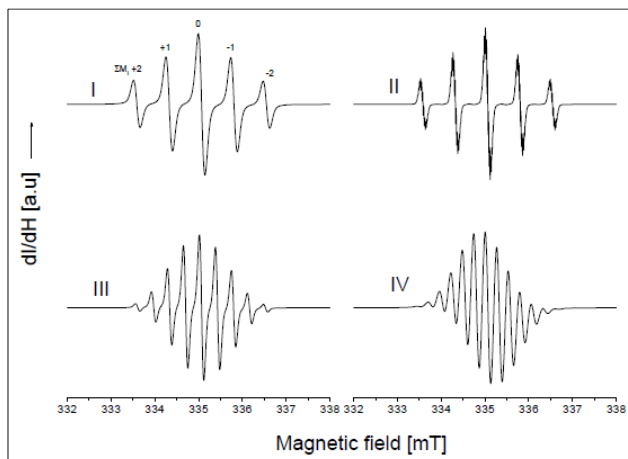


Figure 2.34: Simulated solution state ESR spectrum of the  $\Delta m_s = \pm 1$  transition of I) monoNITradical - poorly resolved [ $A_N = 7.4$  G;  $\Delta BPP = 1.5$  G;  $L/G = 0.33$ ], II) monoNITradical - well resolved [ $A_N = 7.4$  G;  $12\text{ H} = 0.21\text{ G}$ ;  $2\text{ H} = 0.51$  G;  $\Delta BPP = 0.18$  G;  $L/G = 0.33$ ] in the limit of  $J \gg A_N$ , III, IV) diNITradicals.

The number of lines for a polyradical depends of the ratio between the intramolecular exchange interaction ( $J$ ) and the hyperfine constant ( $A_N$ ). This is illustrated in Figure 2.35 for a binitroxide radical  $(\text{NO})_2$  with two equivalent nitrogens [ $I = 1$ ]. For a two-spin system ( $S_1, S_2$ ) the total spin Hamiltonian is given by,

$$H = g\beta H (S_{1z} + S_{2z}) + A(\hat{S}_1\hat{I}_1 + \hat{S}_2\hat{I}_2) - 2J \hat{S}_1 \cdot \hat{S}_2 \quad (2.22)$$

When the exchange interaction between the two spins is zero ( $J = 0$ ), the radical are independent and the spectrum looks like a mononitroxide showing three lines with hyperfine constant ( $A_N$ ) of equal intensity but with double intensity compare to the monoradical. When the exchange interaction is much larger than the hyperfine interaction it shows five lines with intensity close to 1:2:3:2:1 ratio. Importantly the spectral width is the same as for the monoradical but the spacing between the five lines is half those between the three lines of the corresponding monoradical ( $A_N/2$ ). Intermediate cases like  $J < A_N$  or  $J = 2A_N$  changes the total spectral width higher than for the respective monoradical, with a number of

additional lines with different intensities. When the exchange interaction between the two radicals is large the  $J$  value increases, in other words the energy gap between the singlet and triplet state increases. However, when the exchange is weak the singlet and the triplet states are almost degenerate. There also exists an electronspin-electronspin contact interaction analogous to the Fermi contact interaction that is the mechanism of isotropic hyperfine interaction. However, the magnitude of this term is very small. To the extent it is present, it contributes to  $J$ .

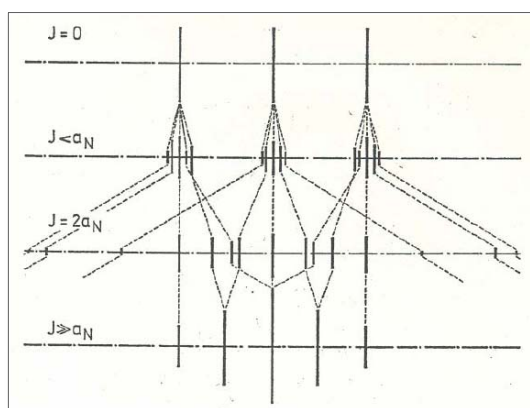


Figure 2.35: Hyperfine coupling of a two spin system having coupling with nuclear spin ( $I=1$ ) with different  $J$  values.

#### 2.4.5. Ground State Spin Multiplicity

For fast electron exchange (i.e., strong coupling) the ground state of the biradical will be either a singlet or a triplet. The ground state of a biradical can be explored by plotting the double integrated signal intensities of the  $\Delta m_s = \pm 1$  transitions or the  $\Delta m_s = \pm 2$  transitions (forbidden transition - the selection rule  $\Delta m_s = \pm 1$  is no longer valid at lower fields; this signal appears exactly at half field of the  $\Delta m_s = \pm 1$  transition, also called half field transition) versus inverse temperatures (down to liquid helium temperature). In order to establish the pure intramolecular spin ground state, it is necessary to use lower concentrated solutions [ $c \geq 10^{-3}$  M] to avoid intermolecular contacts between the molecules. Usually, peak-to-peak signal intensities or better double integrated  $\Delta m_s = \pm 2$  transition signal intensities ( $\chi_{\text{ESR}}$ ) are plotted as a function of inverse temperature. The saturation of the signal can be easily avoided by using lower microwave power. It can be monitored by plotting the observed signal intensities with respect to the square root of the microwave power.

For a species having triplet ground state or triplet-singlet nearly degenerate states the signal intensity follows Curie law [ $\chi_{\text{ESR}} = C/T$ ]. The difference between the singlet-triplet ( $\Delta E_{\text{S-T}}$ ) energy levels is equal to  $2J$  and its magnitude and sign can be estimated by fitting the curve of the product of  $\Delta m_s = \pm 2$  signal intensity and the temperature ( $\chi_{\text{ESR}} \times T$ ) versus temperature using the Bleaney-Bower equation [101].

$$\chi = [2N_A g^2 \beta^2 / 3k_B T] [1 + (1/3) \exp(-2J/K_B T)]^{-1} \quad (2.23)$$

## 3. RESULTS and DISCUSSION

### 3.1. Introduction

The main goal of the thesis was the construction of novel bricks for molecular magnets. All our efforts were dedicated to synthesize, characterize and study the magnetic properties of porphyrin macrocycles including different kind of spin carriers covalently attached to its backbone; preferentially N-*tert*-butyl-N-oxyamino, nitronyl and imino and nitroxide free radicals. One of the most challenging aspects of our work was to design a multi-step synthesis pathway that lead, from desirable starting material to the targeted compounds.

Porphyrin macrocycles were chosen because of their highly polarizable  $\pi$ -conjugated system that should favor the spin delocalization all over the molecule skeleton. Free-radicals were introduced on the *meso* position of tetraphenylporphyrins (**TPP**), one of the most common simple symmetric porphyrin derivatives. Thus, no isomer will be present which will promote crystallization of such a structure and its characterization by X-ray diffraction.

As a spin carrier N-*tert*-butyl-N-oxyamino (**tBuNO**), nitronyl (**NIT**) and imino (IMI) nitroxide free radicals were preferred because they are well-known as among the most stable class of radicals with respect to air, water, dimerization and other radical-involving reactions. They are generally well soluble in most organic solvents but moreover they can be quite easily incorporated on many molecules without affecting the radical site.

Considering all these parameters, three targeted molecules based on *tetrakis* phenylporphyrin macrocycle decorated by four radicals have been designed: one with N-*tert*-butyl-N-oxyamino radicals (1), a second with nitronyl nitroxide radicals (2) and the third one with imino nitroxide radicals (3) as represented in the Figure 3.1 below.

In the following text, the abbreviation mono-, di-, tri- or tetra- radical will be use indicating of the number of radicals present in the macrocycle.

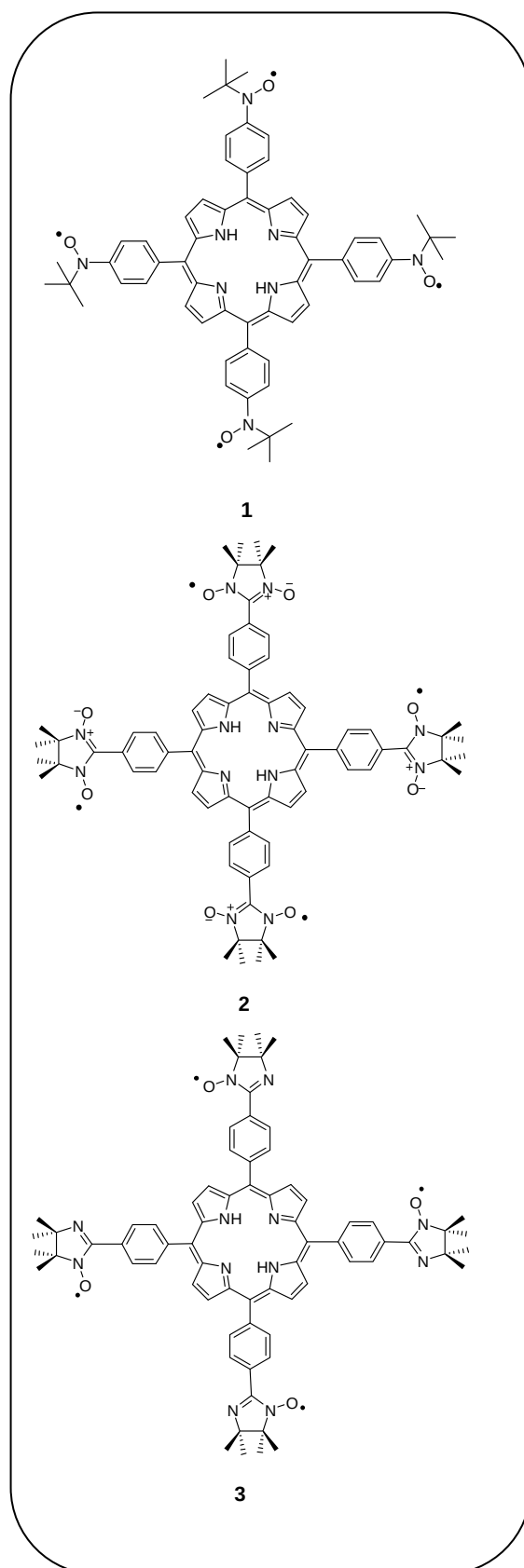


Figure 3.1: Targeted radical porphyrins.

For the three targeted molecules the synthetic pathways envisaged are represented in Figure 3.2.

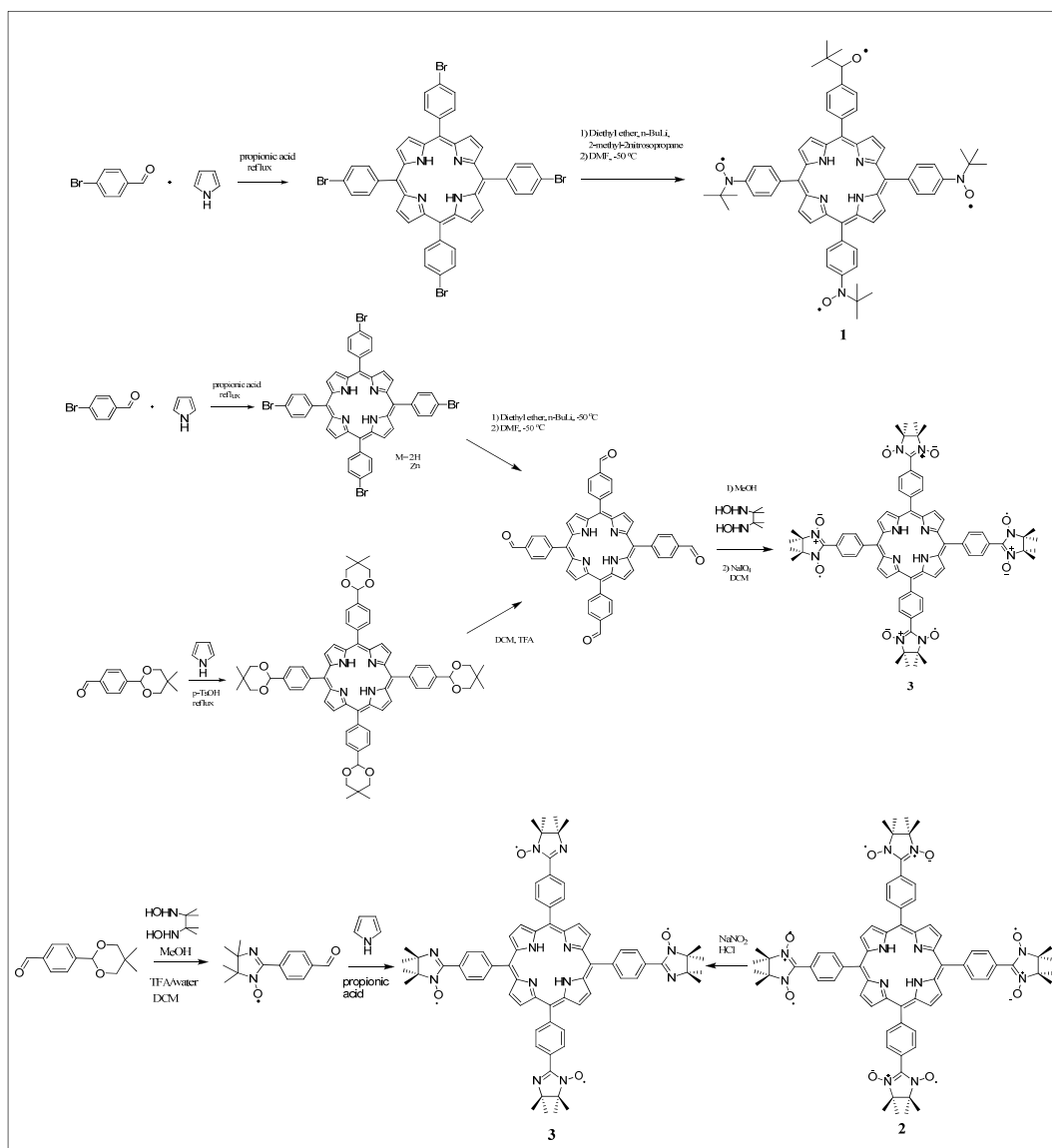


Figure 3. 2: General synthetic pathways for tBuNO tetra radical **1**, NITP tetra radical **2** and IMIP tetra radical **3** porphyrins.

- Looking in depth the reactions
  - tBuNO radical

According to literature, the insertion of a tBuNO radical into a molecule is based on a halogen-lithium exchange reaction. Consequently, to obtain tBuNO porphyrin (**1**) we used the already well-known *meso*-tetrakis(4-bromophenyl)porphyrin (TBrPP) as starting materials as described in Figure 3.3

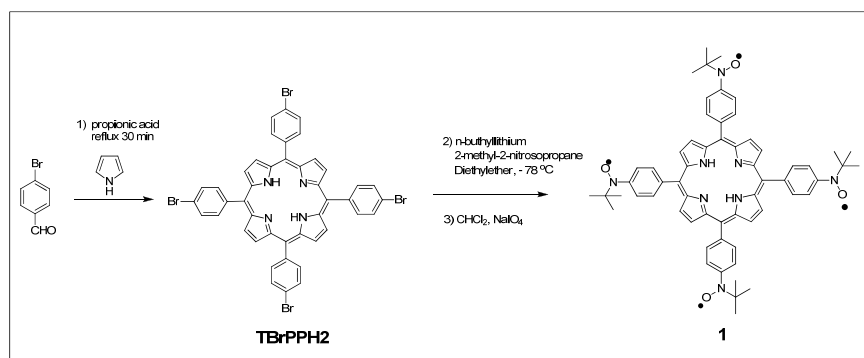


Figure 3. 3: Synthetic pathway for molecule **1**.

To achieve the molecule **1**, some difficulties have to be envisaged:

i) Control of the low temperature is important to prevent the easy decomposition of n-Buthyllithium reagent.

ii) n-Buthyllithium is a very active reagent therefore the protection of the inner nitrogens by Zn metal may be necessary.

iii) Control of multi-site reaction is always a challenge. On TBrPP that contain four brome atoms, the halogen-lithium exchanges followed by the nucleophilic attack by 2-methy-2-nitrosopropane have to be done in four position at the same time. It could be difficult to avoid the formation of mono, di or tri tBuNO porphyrin derivatives.

-nitronyl and imino nitroxide radical

The synthesis of nitronyl and imino nitroxide result on the condensation of 2,3-bis(hydroxylamino)-2,3-dimethylbutane with an aldehyde followed by oxidation of the condensation product with NaIO<sub>4</sub> or PbO<sub>2</sub>.

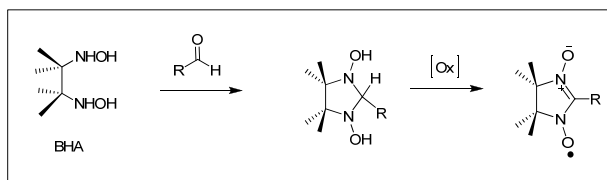


Figure 3.4: Synthesis of nitronyl nitroxide.

Following this pathway, formyl group have to be introduce on tetraphenylporphyrin to obtain *meso*-tetrakis(4-formylphenyl)porphyrin (**ATPP**).

Popularly, the formyl group may be introduced on the para position of the phenyl substituent by regioselective bromine-lithium exchange mechanism starting from the bromo-containing tetraphenylporphyrin. However, to the best of our knowledge, along this method only the mono- and the di- (4-formyl)-tetraphenylporphyrin are known; [102], [103]. Nonetheless, no synthesis and characterization of *meso*-tetrakis(4-formylphenyl)porphyrin has been reported to date which may be ascribe to the difficulty to have a stoichiometric control of the introduction of formyl group in a multi-site reactivity reaction (Figure 3.5).

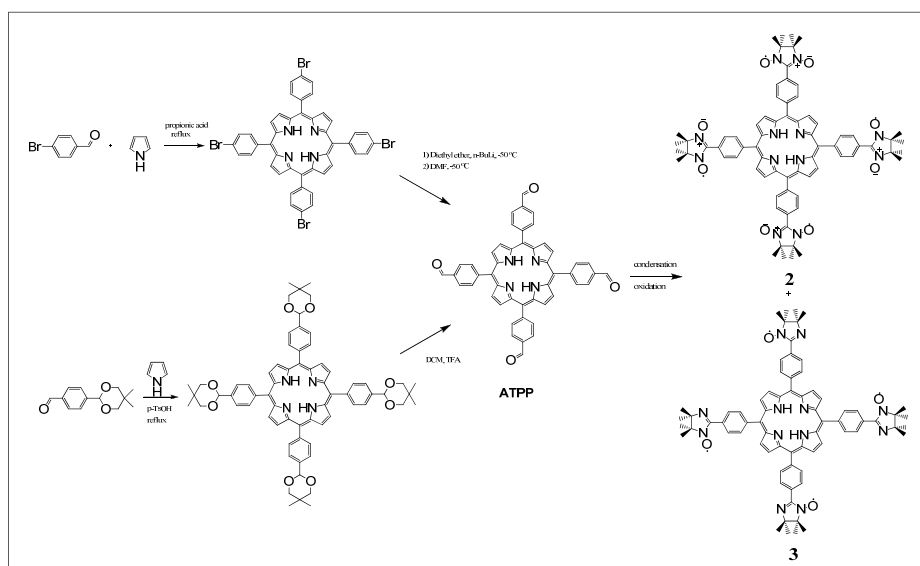


Figure3. 5: Synthetic pathways for **ATPP**, NITP porphyrin **2** and IMIP porphyrin **3**.

Regarding the synthetic pathway of **1** and **ATPP**, both of them have the same starting molecule **TBrTPP**. The use of the same synthon, described in good yield in literature, is a real advantage. Considering that the control of the the halogen-lithium exchange multi-site reaction may be difficult, a protecting route -call acetal route- was also envisaged to by-pass this step. But the synthesis of the *meso*-tetrakis(4-(4,4-Dimethyl-2,6-dioxan-1-yl)phenyl)porphyrin was never described previously, so it has been necessary to find some good conditions of synthesis to obtain this molecules with good yield. Another reaction pathway that we envisaged was first to synthetized the imino nitroxide susbtituted benzaldehyde then IMIP radical (**3**) porphyrin by condensation with pyrrol; by this way the the porphyrin macrocycle would be the last step and the four imino nitroxide incorporated on one poprhyrin simultnously.

Considering that obtaining multi radical substituted porphyrin is a "complicate-not easy" task, we also synthesized porphyrin macrocycle bearing only one radical moiety. The synthetic pathway of mono tBuNO(**4**), mono NIT(**5**) and mono IMI(**6**) nitroxide is described in Figure 3.6. Apart from the simplification of the synthesis these molecules are interesting because they allow comparing the effect of radicals on porphyrin macrocycles.

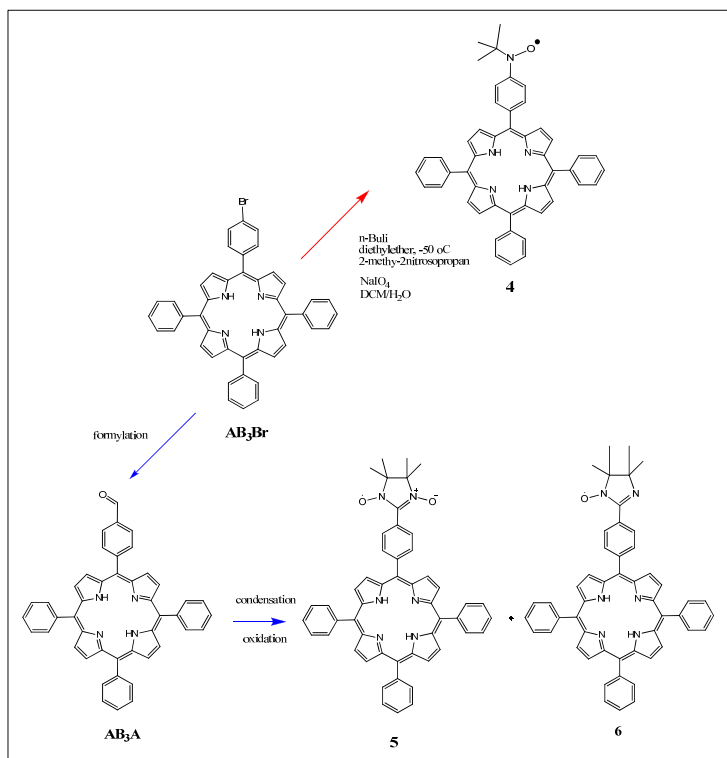


Figure 3. 6: Mono tBuNO(**4**), mono NIT(**5**) and mono IMI(**6**) nitroxide substituted porphyrins synthetic strategies.

In this manuscript, the presentation of our results will be articulated around three parts:

3.2. The synthesis of paramagnetic porphyrins will be described. The advantages and disadvantages of all synthetic pathways will be discussed. The characterization of molecules obtained throughout the thesis was done by the usual technique tools (NMR, IR, UV, MASS spectroscopy).

3.3. EPR spectroscopy investigations were achieved for the paramagnetic compounds to determine the radical group type (tBuNO, NIT/IMI) but also to determine the number of spin present on the molecule. Radical-Radical interactions will be explored. metallation of porphyrins by paramagnetic transition metals as

M=Cu(II) and Mn(II) will be discussed. Like this, the resulting spin number of the molecules will increase.

3.4. In the last part, the results will be summarised by conclusion section.

## 3.2. Synthesis of Radical Substituted Porphyrins

### 3.2.1. TBrPP

#### 3.2.1.1. Synthesis of TBrPP

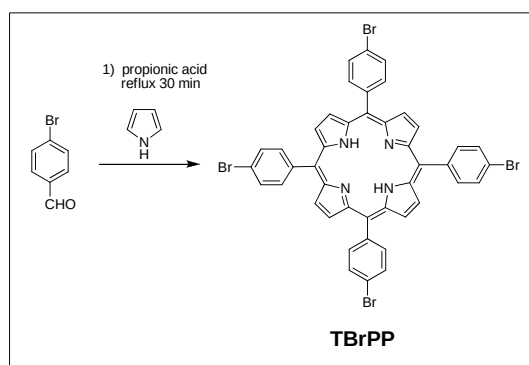


Figure 3.7: Synthesis of TBrPP.

Following Adler method [104], [105], *meso*-tetrakis(4-bromophenyl)porphyrin was obtained from condensation of 4-bromobenzaldehyde with pyrrole in reflux propionic acid. The reaction was completed in a short time; 30 min. The compound was obtained in the form of purple crystals after cooling the reaction mixture slowly down to room temperature. After purification on silica gel column with DCM: Hexane (1:1) as eluent, TBrPP was obtained as a purple compound in 25% yield.

### 3.2.1.2. Characterization of TBrPP

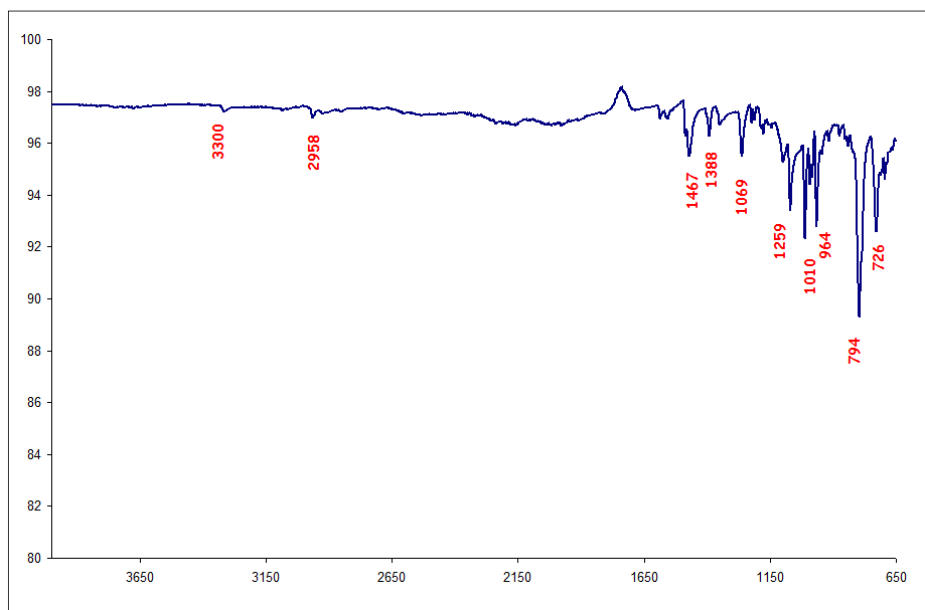


Figure 3. 8: FT-IR spectrum of **TBrPP**.

The FT-IR spectrum of TBrPP shows the characteristic intense peaks of porphyrin macrocycle [106], [107]. The C-H vibration at 2958 cm<sup>-1</sup> corresponds to the aromatic protons. The peak at 964 cm<sup>-1</sup> belongs to porphyrin ring vibration. The vibration at 794 cm<sup>-1</sup> is characteristic of pyrrole ring bending whereas the one at 726 cm<sup>-1</sup> of pyrrole vibration. The NH vibration of the porphyrin free base was observed at 3300 cm<sup>-1</sup> peak and also at 730 cm<sup>-1</sup> is for NH bending. Especially for porphyrin macrocycle, peaks at 1472 cm<sup>-1</sup> and 1382 cm<sup>-1</sup> are characteristics and correspond to C=N and =C-N vibration respectively.

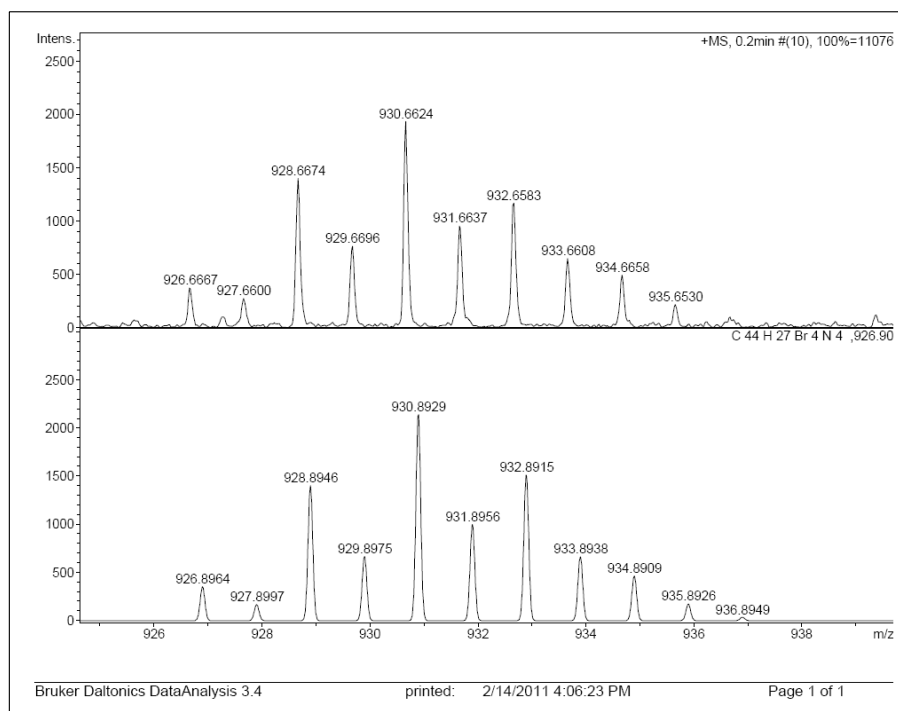


Figure 3.9: MALDI mass spectrum of **TBrPP**.

ESI-MS exhibit a molecular ion peak at  $m/z = 930.6624$  (calculated for  $C_{44}H_{26}Br_4N_4$   $m/z = 930.8929$ ).

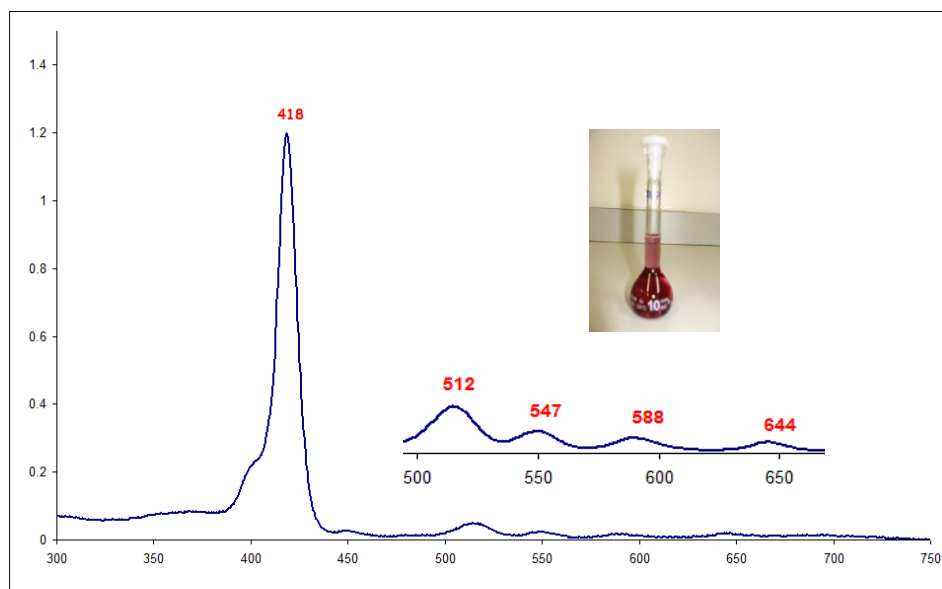


Figure 3.10: Uv-Vis spectrum of **TBrPP** in  $CHCl_3$ .

The electronic absorption spectrum of TBrPP is dominated by a very strong Soret peak at 418 nm which is characteristic of porphyrin macrocycles. Four weak Q

bands are observed in the visible region between 512 to 644 nm, characteristic of the  $D_{2h}$  symmetry of the free base porphyrins[108].

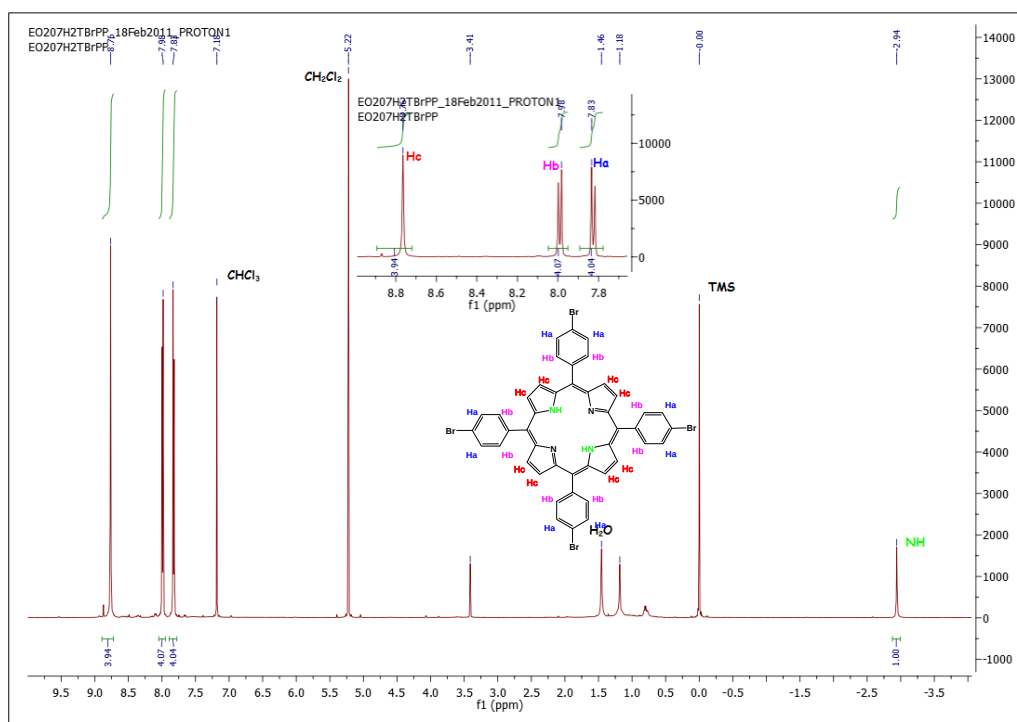


Figure 3.11:  $^1\text{H}$  NMR spectrum of **TBrPP** in  $\text{CDCl}_3$ .

The  $^1\text{H}$  NMR spectrum of **TBrPP** in  $\text{CDCl}_3$  exhibits a singlet at -2.94 ppm assigned to the 2 NH inner protons of the porphyrin. The aromatic region presents two doublets and a singlet due to the *meso*-phenyl proton and the  $\beta$ -pyrrolic protons respectively. The doublet at 7.83 ppm is attributed to the 8 *ortho*- $\text{CH}_{\text{Ar}}$  protons of *meso*-phenyl group whereas the doublet at 7.98 ppm is attributed to the 8 *meta*- $\text{CH}_{\text{Ar}}$  protons. Meanwhile, the  $\beta$ -pyrrolic protons appears at 8.76 ppm.

### 3.2.2. Molecule 1

#### 3.2.2.1. Synthesis Work on Molecule 1

Porphyrins substituted by *N*-*tert*-butyl-*N*-oxyamino (**tBuNO**) radical were previously reported exclusively by Shultz and al with the aim to include them in coordination polymers. One[109] or two[110] tBuNO radical were introduced in the *meso* position of the porphyrins as shown on Figure 3.12.

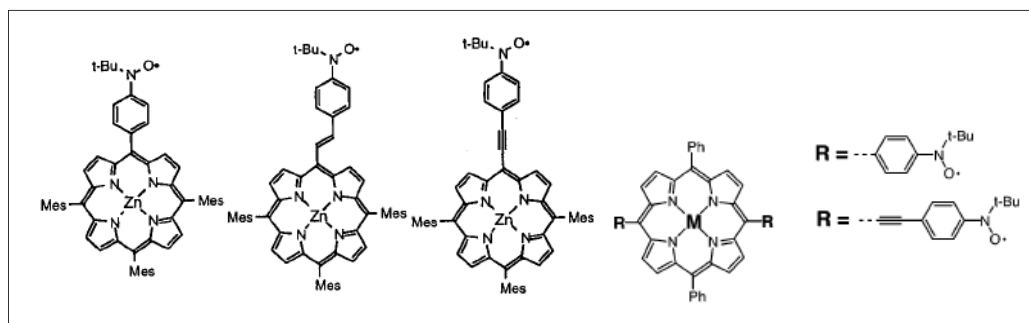


Figure 3.12: Mono and di tBuNO radical substituted porphyrins reported by Shultz.

The synthesis involved four steps of difficult reaction which are based on a Pd-catalyzed coupling reaction of iodo or bromoporphyrin with the appropriate TBS-protected phenylnitroxide, alkene, or alkyne boronate and followed by a Fluoride-promoted TBS deprotection and  $\text{PbO}_2$  oxidation. In Figure 3.13 we present as an example the Zn(II)-porphyrin substituted by a single tBuNO. To the best of our knowledge, there is no other work on *meso*-porphyrin substituted by the *N-tert*-butyl-*N*-oxyamino radical. From which we can concluded that direct covalent attachment of stable nitroxide radical on the *meso*-position of the porphyrin is a challenging task.

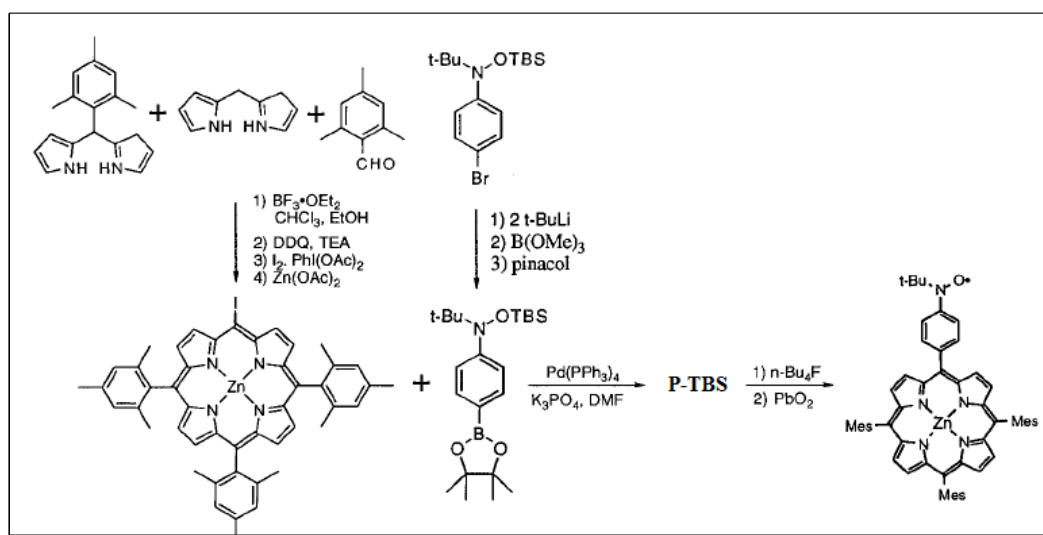


Figure 3.13: Synthesis of mono tBuNO substituted porphyrin.

Along our work, *N-tert*-butyl-*N*-oxyamino (tBuNO) radical were incorporated on porphyrins starting from *meso*-tetrakis(4-bromophenyl)porphyrin TBrPP in a two step reaction. We choose a bromo-lithium exchange reaction followed by the addition of 2-methyl-2-nitrosopropane to form the targeted *meso*-tetrakis(*N-tert*-

butyl-*N*-hydroxyamino)porphyrin. Further oxidation by NaIO<sub>4</sub> in biphasic solution (NaHCO<sub>3</sub> sat/CH<sub>2</sub>Cl<sub>2</sub>) should give the tetraradical.

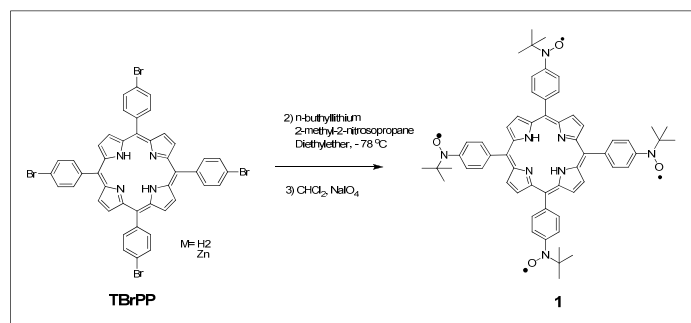


Figure 3.14: Synthesis work on tetra-tBuNO radical porphyrin.

As we want to obtain a porphyrin decorated by radicals on the four para position of the *meso*-phenyl, the conditions of the reaction need to be optimized to avoid the formation of mono, di- and three- substituted derivatives. In this regards, the choice of the solvent and the number of n-buLi equivalent to be added play a crucial role. As the bromo-lithium exchange reaction require to work at low temperature (-78 °C) diethyl ether and THF were tested because of their very low melting point (THF mp -108.4, Diethyl ether -116.3 °C. In diethyl ether the solubility of TBrPP decreases drastically upon cooling resulting in a dispersed suspension at low temperature. THF seem a better solvent without any solubility problem. Unfortunately at the end of the reaction a green product was handling as a side product which was ascribed to chorin macrocycle [111]. EPR spectroscopy was used to check whether or not the porphyrin was substituted by radicals and how many (Table 2). It resulted that in THF no radical were fixed on porphyrin macrocycle while in diethylether up to two radical were introduced. Therefore THF was discarded and diethylether privileged despite low solubility. For THF as well as for diethylether we found the results were not dependent of the concentration (Table 3.2).

Table 3. 1: Solvent studies for solubility problem of porphyrin.

| entry | Solvent (mL)         | Radical number |
|-------|----------------------|----------------|
| 1     | Diethyl ether, 25 mL | -mono and -di  |
| 2     | Diethyl ether, 50 mL | -mono and -di  |
| 3     | THF, 25 mL           | -no radical    |

Low temperature is crucial to avoid decomposition of n-Buthyllithium reagent as well as to control the number of nBu-Li equivalent to be introduced (see Table 3.2). For bromo-lithium exchange it is habitual to work at -78 °C. Due to solubility problem in diethylether, higher temperatures were tested to carry out the reaction. However, the best results were obtained at -78 °C and with 10 equiv of n-BuLi for synthesis of tBuNO radical porphyrin.

Tablo 3. 2: Temperature studies for synthesis of in Diethyl ether.

| entry | Temp. (°C) | Radical number |
|-------|------------|----------------|
| 1     | -78        | -mono and -di  |
| 2     | -50        | -mono and -di  |
| 3     | -25        | -mono and -di  |
| 4     | 0          | -no radical    |

Tablo 3. 3: Different equivalent studies of n-BuLi for synthesis of tBuNOP in Diethyl ether.

| Entry | n-BuLi (mol/ eqv) | Radical number |
|-------|-------------------|----------------|
| 1     | 6.25 eqv.         | -mono and -di  |
| 2     | 10 eqv.           | -mono and -di  |
| 3     | 150 eqv.          | -mono and -di  |

Zn(II) metallated **TBrPP** was also try as starting material. Zn could be indeed a good protecting group of the the two core nitrogens of the porphyrin against the very reactive n-Buthyllithium. However, as the reaction is quenched by 5% HCl<sub>sol</sub> this leads to the partial demetallation of the porphyrin due to the acidic condition. As a result; it gives a mixture of metallated and free base tBuNO porphyrin derivatives that result in lower yield of the reaction. Keeping the porphyrin in acidic condition for more than 10 min, to try to achieve the complete demetallation of all porphyrin derivatives and get higher yield, was not successful as it results in the decomposition of many products.

### 3.2.2.2. Characterization Work

Upon chromatography on silica gel, we evidenced many fractions (more than 8), not totally separated. All fractions correspond to compounds that contain porphyrin macrocycles as may be concluded from their UV-vis spectra that show the characteristic Soret peak ( $\sim 420$  nm) as seen above for **TBrPP**. However, among the all fractions there were only two (**A** and **B**) that could be identified by EPR spectroscopy as bearing radicals. Accordingly, fractions **A** contain mono tBuNO radical and fraction **B** contains di tBuNO radical (See Figure 56 in the section 3.3.)

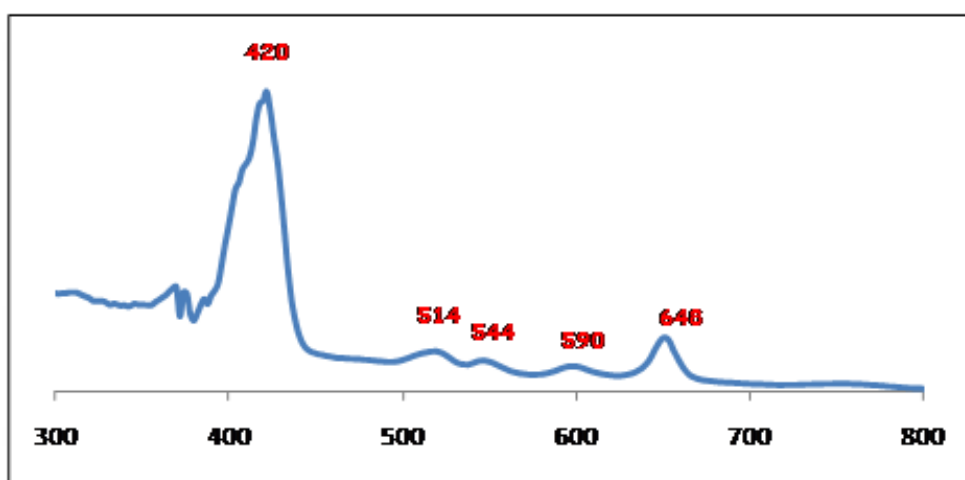


Figure 3.15: The UV-Vis spectrum of fraction **A** mono tBuNO substituted free porphyrin  $1.10^{-6}$  M in  $\text{CHCl}_3$ .

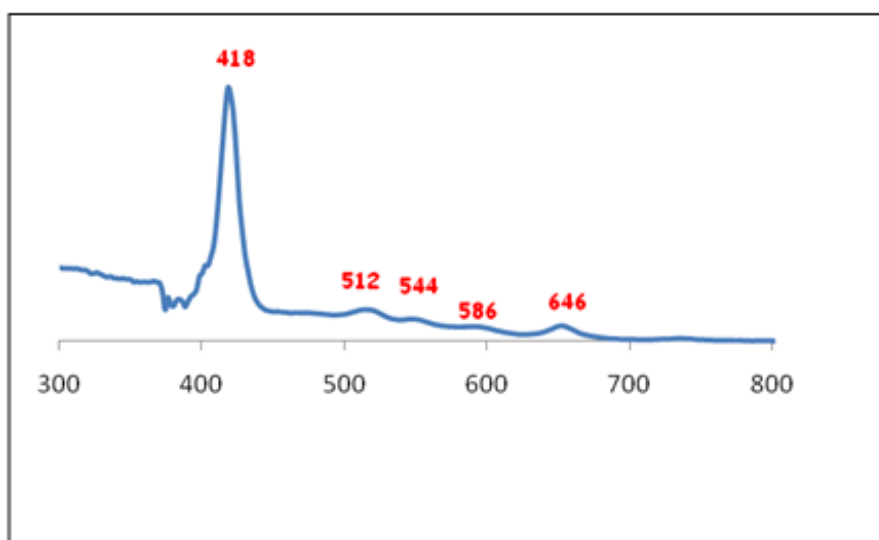


Figure 3.16: The UV-Vis spectrum of fraction **B** di tBuNO substituted free porphyrin  $1.10^{-6}$  M in  $\text{CHCl}_3$ .

It is clearly seen from Table 3.5, that there is no significant shifted of the absorption band due to the incorporated radical moieties. But it is noticeable that there is a change of the intensity of the Q bands. The bands at 648 nm or 646 nm for mono- tBuNO and di-tBuNO (see Figure 32, 33) increase dramatically.

Tablo 3. 4: Uv-Vis spectra data of **TBrPP** and tBuNO substituted porphyrins fraction A and B in CHCl<sub>3</sub>.

| Compound           | Q band $\lambda_{\max}$ | Soret(B) bands $\lambda_{\max}$ |
|--------------------|-------------------------|---------------------------------|
| <b>TBrPP</b>       | 418                     | 512, 547, 588, 644              |
| <b>fraction -A</b> | 420                     | 514, 544, 590, 648              |
| <b>fraction-B</b>  | 418                     | 512, 544, 586, 646              |

### 3.2.2.3. Mass spectroscopy

Mass spectroscopy is one of the usefull and popular tool for the characterization of molecular structure and of quite an easy acces. Depending of the mass spectroscopy experiment conditions (ionisation, presence of matrix) molecular ion peak of tetra tBuNO could be observed. The best result was obtained without matrix, radicals were detected as the  $M^+$  specie. In the presence of DHB as matrix a  $m/z= 88$  fragment corresponding to the addition of the tBuNHO was observed. The Mass spectra exhibit molecular ion peak of di tBuNO porphyrin with the BHA matrix and tetra tBuNO porphyrin molecular ion peak without matrix (See Figure 3.17 and 3.18 bellow).

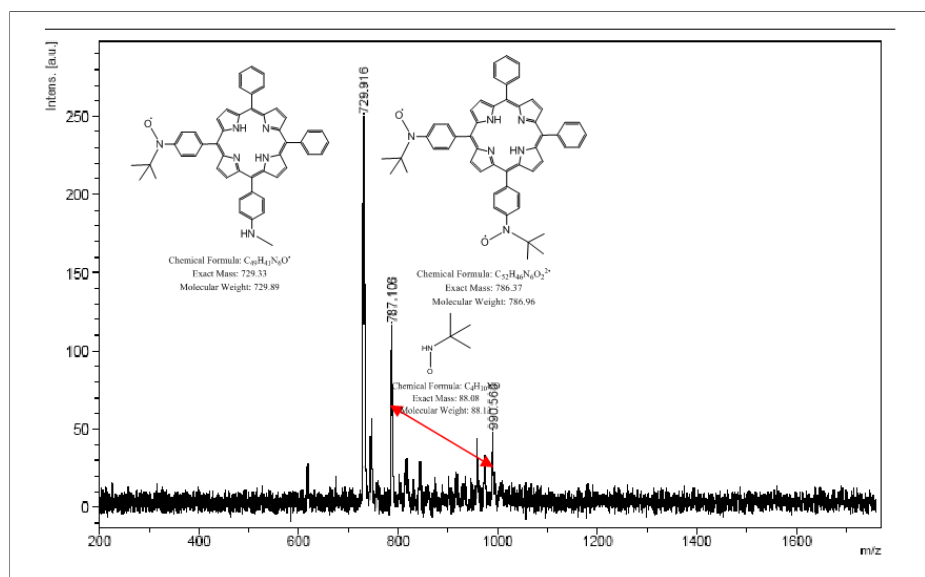


Figure 3.17: MALDI-MS spectrum of tBuNO porphyrin experiment with DHB matrix.

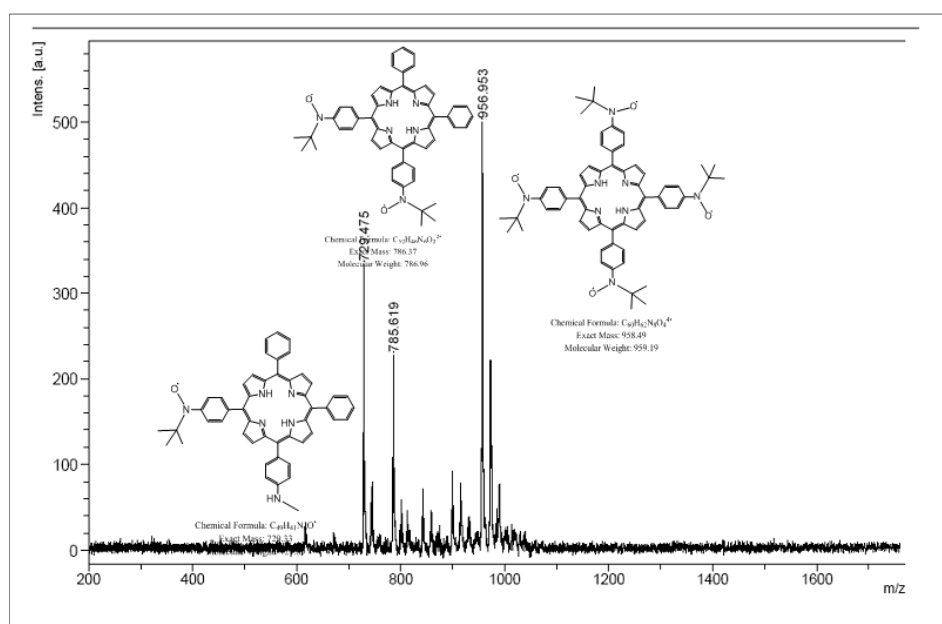


Figure 3.18: MALDI-MS spectrum of tBuNO porphyrin experiment without DHB matrix.

### 3.2.2.4. Concluding remarks

The radical moieties on porphyrin could be proven by EPR spectroscopy(see section 2.4.3). But for these porphyrins although working on different mass spectroscopy method like MALDI spectroscopy using different matrix DHB,

ANTRA or without matrix and ESI mass spectroscopy, we could not obtaine their molecular ion peak on spectra.

On the other hand, even there is no EPR signals of some fractions, according to the mass spectroscopy results they contain porphyrin bearing radical(see Figure 3.17, 3.18). We are optimistic to isolate our targeting molecule tetra tBuNO porphyrin and works in this direction are on going.

Except the two reports by Shultz et al. there is no literature on *N-tert*-butyl-*N*-oxyamino radical covalently link to porphyrin. When we consider these two reports, it is clear that the reaction conditions are not easy, giving radical in small amount. The oxidation step was done in a glovebox in 0.2 mM toluene directly in EPR quartz tube containing an excess of PdO<sub>2</sub>. All the EPR studies have been carried out with this limited quartz tube amount.

In conclusion, according to EPR result we can synthesize and characterized mono- and di- *N-tert*-butyl-*N*-oxyamino substituted free base porphyrin (tBuNO porphyrin).

### 3.2.3. Molecule 2

#### 3.2.3.1. Synthesis Work on Molecule 2

The general synthesis of nitronyl nitroxyde free radicals is based on condensation of 2,3-bis(hydroxyamino)-2,3-dimethylbutane (**BHA**) with an aldehyde and followed by oxidation step with NaIO<sub>4</sub> or PbO<sub>2</sub>.

In our work to obtain porphyrins substituted by nitronyl nitroxide (2 and 5) we used *meso*-tetrakis(4-formylphenyl)porphyrin (**ATPP**) as the aldehyde for condensation with **BHA**.

#### 3.2.3.2. 2,3-bis(hydroxyamino)-2,3-dimethylbutane (BHA)

The main precursor of Ullman's route[62] 2,3-bis(hydroxyamino)-2,3-dimethylbutane (**BHA**) has difficult reproducibility and questionable purity with low yield. Dr. Hirel[67] reported new route for the free base **BHA** in a very pure form and up to 60% yield. It is based on using the classical reduction process with zinc in ammonium chloride buffered solution of the dinitro analogue and fallowed by

purification of Zn contant with continuous extraction with chloroform from sodium carbonate and sodium chloride solution in water.

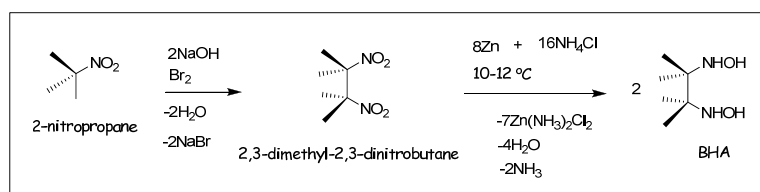


Figure 3.19: Hirel route for **BHA** synthesis.

Chandru [112] started from 2,3-dimethyl-2,3-bis(hydroxylamino)-butane sulphate salt which is commercially available and purification of insoluble **BHA** sulphate salt was done in THF by drop-by-drop addition of cooled aqua NaOH solution at room temperature with 70 % yield.

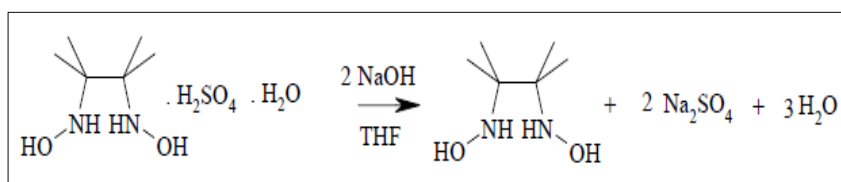


Figure 3.20: Chandru's purification method.

Rajca[113], [68] used Aluminum foil shreds /  $\text{HgCl}_2$  solution for the reduction in THF/ water at  $-7\text{ }^\circ\text{C}$ . The purification was based on washing with ether and the yield was % 79 maximum.

The purity of the free base is important for the success and the yield of the condensation reaction. This is especially acute in the case of our porphyrin substituted with aldehydes for which the yield is low and the condensation a difficult step. This can takes long time with reflux during more than 1 day. In our study we used Hirel's and Rajca's methods explained above and pure free base **BHA** was obtained with % 40 yield maximum.

### 3.2.3.3. *meso*-tetrakis(4-formylphenyl)porphyrin (ATPP)

The synthetic sequence towards porphyrin substituted with four nitronyl nitroxide (**NITP**, **2**) is based on *meso*-tetrakis(4-formylphenyl)porphyrin (**ATPP**) as

the key building block (Figure 3.20) As for the synthesis of tBuNO substituted porphyrin we choose also here a bromo-lithium exchange reaction followed this time by reaction with with N,N'-dimethylformamide (DMF). This has long been known in organic syntheses as a desirable method for the preparation of aldehydes [114]. The target **NITP** tetra radical **2** was prepared by subsequent condensation reaction of **BHA** with **ATPP** by reflux for one day in DCM/ MeOH solvents to afford condensed molecule TPPNOH. The oxidation reaction of TPPNOH was performed in phase transfer solution (CHCl<sub>3</sub> / H<sub>2</sub>O) with NaIO<sub>4</sub> solution as oxidant to give radical as dark purple powder.

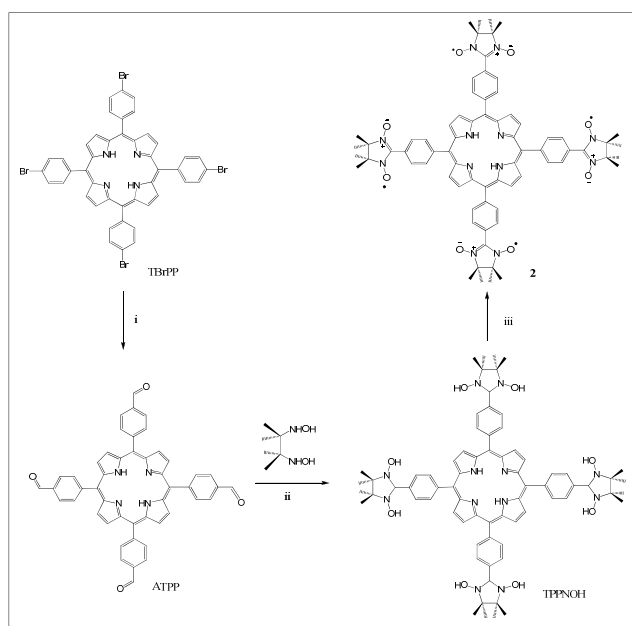


Figure 3.21: Synthesis of NITP tetra radical **2** and the key building block **ATPP**.  
Reagents and conditions: i) n-Bulithium / diethyl ether / DMF / -78 °C, ii) 2,3-Dimethyl-2,3-bis (hydroxylamino) butane (BHA) / MeOH / DCM / reflux, Overnight, iii) NaIO<sub>4</sub> / CHCl<sub>3</sub> / H<sub>2</sub>O.

The synthesis of the tetra formyl substituted porphyrin has been a challenging step. As we underlined with molecule **1** it is a difficult task to substitute each of the four *meso* position of porphyrin macrocycle. There are generally mixture of mono-, di-, tri- and tetra substitution . Therefore it is necessary to optimize the best condition for the formylation reaction to achieve the final product. The most well known methods for *meso*-formyl porphyrins are stated below. Four synthetic methods could be inventoried.

–Bromo-lithium exchange reaction

According to literature, only limited examples were described as shown below. In 1989 Olof Wennerström et al. [102] obtained *meso*-5-(4-formylphenyl)-10,15,20-triphenylporphyrin (*meso*-mono formyl porphyrin) from the corresponding *meso*-5-(4-bromophenyl)-10,15,20-triphenylporphyrin by bromo-lithium exchange reaction (Figure 3.22.a). The *meso*-mono formyl porphyrin was obtained with 15% yield after a treatment with six equiv. of butyllithium in ether at 0°C for 3h, addition of DMF followed by hydrolysis with dilute HCl to finish the reaction.

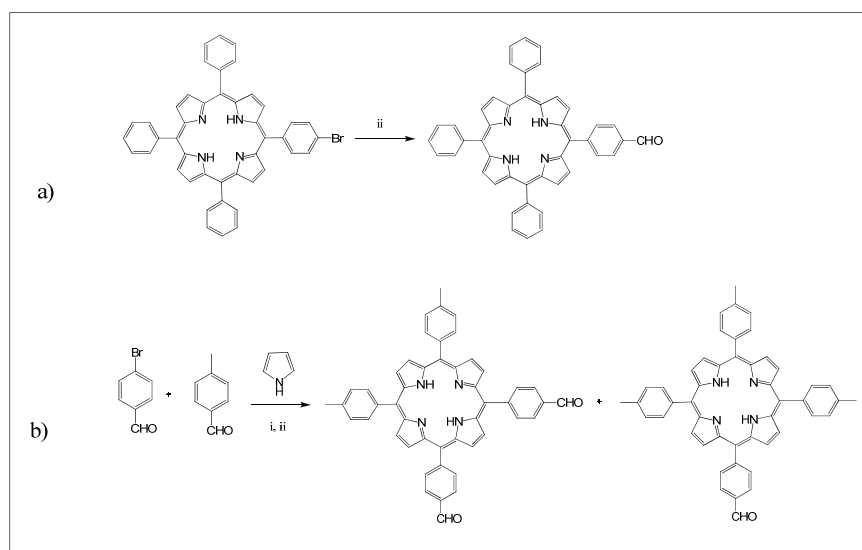


Figure 3.22: Synthesis of a) *meso*- di formyl porphyrin b) *meso*- mono formyl porphyrin. Reagents and conditions: i) pyrrole/propionic acid/reflux, ii) n-Bulithium /diethyl ether / DMF / -78 °C.

Another work was done by Attila J. Mozer et al [115]. They used the same bromo-lithium exchange reaction method (Figure 3.22.b) and could obtain Porphyrin dialdehyde in two steps; in the first step, a mixture of different aldehydes and pyrrole were refluxed in propionic acid for 45 minutes, resulting in an inseparable statistical mixture of mono-, di- and tribromo porphyrins. The mixture was treated with butyllithium and DMF to give a mixture of aldehydes.

Same group tried to control of the formyl position (ABAB formyl) on the porphyrin macrocycle and they worked on condensation of Tollydipyrromethane with aldehyde in hot DMSO to give mainly the ABAB porphyrin with 20% of AABB isomer. After butyllithium/DMF formylation, ABAB formyl porphyrin was obtained (Figure 3.23).

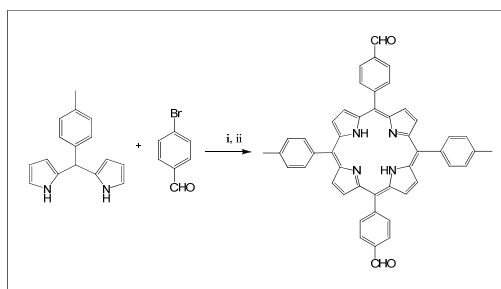


Figure 3.23: Synthesis of ABAB formyl porphyrin. Reagent and conditions: i) Tollyldipyrromethane/4-bromobenzaldehyde/DMSO/90°C/NH<sub>4</sub>Cl/9h., ii) diethyl ether/-15 °C/n-butyllithium, 2,5 eqv./2h./DMF, 15 eqv., 30 min/ diluted HCl.

–The use of acetal protecting group method

Lindsey et al [116] reported new route for free base porphyrins bearing one or two (*cis* or *trans*) *meso*-formyl substituents which entails the use of a dipyrromethane bearing an acetal group at the 5-position and a bicarbinol or 1-acyldipyrromethane or 1,9-diacyldipyrromethane. Reduction of acyldipyrromethane with NaBH<sub>4</sub> and self-condensation of the resulting dipyrromethane-monocarbinol in presence of InCl<sub>3</sub> followed by oxidation with DDQ. Hydrolysis of the acetal groups in porphyrins with CH<sub>2</sub>Cl<sub>2</sub>/TFA/H<sub>2</sub>O (10:1:1) gave mono or diformylporphyrins 90-95% yield (Figure 3.24).

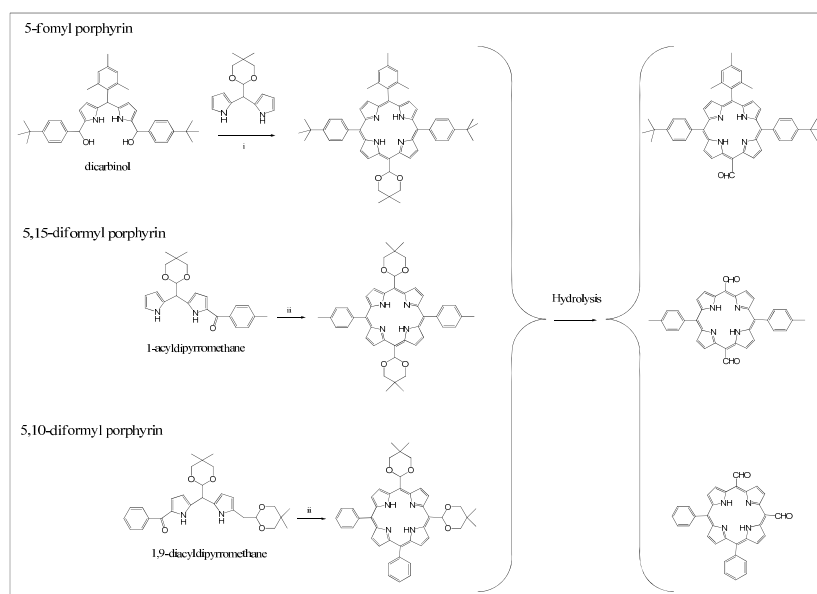


Figure 3.24: Synthesis of 5-formyl, 5,15-diformyl and 5,10-diformyl porphyrin. Reagent and conditions: i) CH<sub>2</sub>Cl<sub>2</sub> / InCl<sub>3</sub>/ DDQ, 1.50 eqv./MeOH and TEA., ii) THF/methanol (3:1)/NaBH<sub>4</sub>(excess)/CH<sub>2</sub>Cl<sub>2</sub> /InCl<sub>3</sub> /DDQ/TEA. Hydrolysis: CH<sub>2</sub>Cl<sub>2</sub> /TFA/water (10:1:1), room temp. stirring 2.5 h.

The acetal group protection was also used by Maxence Urbani and his group [117] to obtain Formyl-Fullereno porphyrin compounds. They first prepared a protected benzaldehyde molecule, that is involved in the condensation with pyrrole to give a porphyrin substituted by a protected formyl group. Deprotection step was done in a biphasic solution with TFA/H<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub> yielding 93 % of the desired formyl porphyrin.

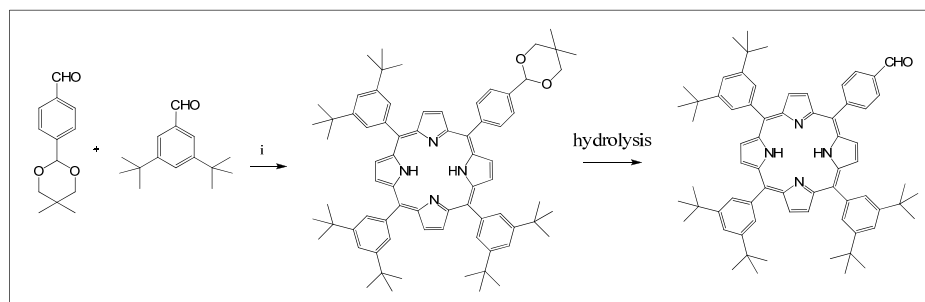


Figure 3.25: Synthesis of 5-formylphenyl porphyrin. Reagent and conditions: i) Pyrrole, BF<sub>3</sub>·Et<sub>2</sub>O, CHCl<sub>3</sub> (containing 0.75% EtOH), room temp. then *p*-chloranil, reflux. Hydrolysis: CH<sub>2</sub>Cl<sub>2</sub> /TFA/water (10:1:1), room temp.

#### –The use of organosulfur reagent

Katja Dahms et al [118] choose to work on a pre-formed porphyrin. 1,3-dithian-2-yl group was introduced by reaction of *n*-butyllithium with 1,3-dithiane at –30 °C in THF under an atmosphere of argon to give an adequate precursor to introduce a formyl group.

The respective formylporphyrins were obtained in varying yields ranging from 39–94% (Figure 3.25).

In conclusion of this study, only the porphyrins containing one or two dithian-2-yl residues in a 5,15 orientation were stable, the tri- and tetra substituted porphyrins were increasingly unstable especially towards traces of acid. The latter had to be stored under an atmosphere of argon at –20 °C. The instability of these compounds result from the increased steric strain in such systems [119] and the reactivity of the dithian-2-yl residues.

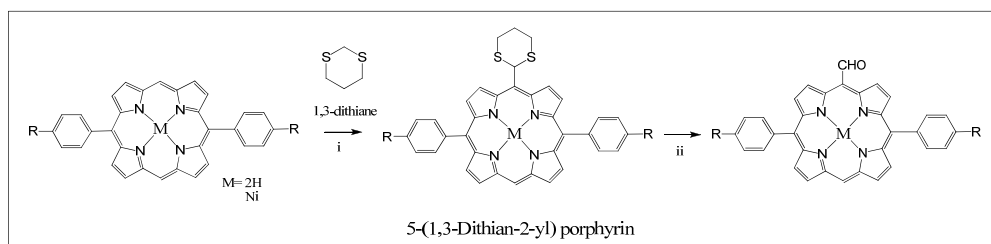


Figure 3. 26: Synthesis of 5-formyl porphyrin with organosulfur reagent method. Reagent and conditions: i) 1,3-dithiane/n-buLi/TMEDA(*N,N,N,N*-tetramethylethylenediamine) then H<sub>2</sub>O/DDQ, ii)DDQ/BF<sub>3</sub>. Et<sub>2</sub>O.

#### –Vilsmeier Formylation Method

The same group worked on direct *meso*-formylation on porphyrin macrocycle by Vilsmeier formylation method (Figure 3.27.a). The detailed mechanism is given in the Figure 3.27.b. The reaction starts by forming an electrophilic iminium cation of DMF-POCl<sub>3</sub> complex at low temperature (0-2°C) under argon atmosphere follow by electrophilic aromatic substitution to obtained to corresponding formyl porphyrin [120]. Once again the limitation of the method is that only mono or di formyl groups could be introduced in porphyrin macrocycle.

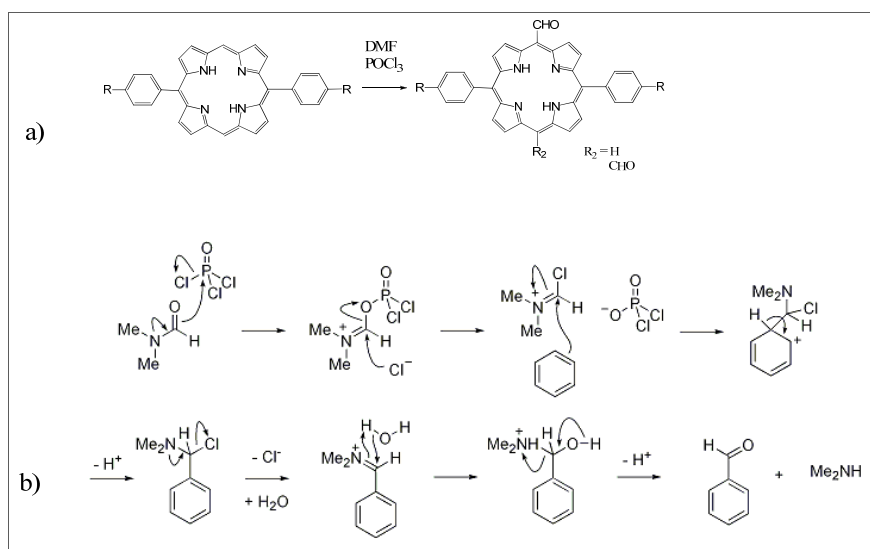


Figure 3.27: a) Synthesis of mono or diformyl porphyrin by Vilsmeier Formylation Method, b) Mechanism of Vilsmeier Formylation reaction.

Considering the literature work on *meso*-formylation methods, the major limitations of the described methods are that only mono or di-aldehyde were

obtained. And in some case the instability of tri- and tetra- intermediate syntons was mentioned limiting the synthetic possibilities.

Up to date, there is not a good description of synthesis of *meso*-tetrakis(4-formylphenyl)porphyrin (**ATPP**) in literature. We choose to prepare it via the Bouveault reaction, a regioselective bromine-lithium exchange mechanism quench by N,N'-dimethylformamide (DMF) to introduce the formyl groups, a well-known organic syntheses for the preparation of aldehydes [114] When we look over the reaction conditions and reagents based on organometallic synthesis, one has to be very careful with the parameters of the reactions; low temperature should be kept during the reaction because organometallic reagents can be easily decomposed when the temperature rise up. As organometallic compound are highly reactive, contaminants such as water, alcohols and oxygen must be avoided. Consequently, all the solvents have to be very dry and pure. Also, the reaction has to be worked under absolute dry nitrogen atmosphere. All the reaction vessels were dried in oven during 24h before the usage. All the solvents and liquid reagent bottles were purchase with molecular sieve.

*meso*-tetrakis(4-formylphenyl)porphyrin **ATPP** was prepared from *meso*-tetrakis(4-bromophenyl)porphyrin (**TBrPP**) derivative in diethylether by using n-buthyllithium and dry DMF at low temperature. For hydrolysis a %5 HCl solution was used.

- As pointed above, controlling the low temperature was crucial due to the easy decomposition of n-Buthyllithium reagent. However, the decrease of the temperature lowers the solubility of the porphyrin in diethylether solution. That is why we used more dilute solution for better solubility.

- To increase the yield of **ATPP** and to avoid the formation of mono and di formyl derivative, different equivalent of n-Buthyllithium in 2.5M solution in Hexane, from 6.25 equiv to 32 equiv, were tested. The excess of equiv of n-buLi did not change anything to the reaction.

The different conditions are summarized in table 3.5 the optimized conditions were -50 °C and 6,25 equiv per mol of *meso*-tetrakis(4-bromophenyl)porphyrin (**TBrPP**). Like this, n-BuLi was stable during the reaction time and **TBrPP** was well soluble. Utilizing this optimized conditions, only tri- and tetra- formyl porphyrin were obtained in 40% and 30% yield respectively.

Tablo 3. 5: different reaction conditions for **ATPP**.

| Solvent (mL)         | Temp. (°C) | n-BuLi (mol/<br>equiv) |
|----------------------|------------|------------------------|
| Diethyl ether, 25 mL | -78        | 6.25 eqv.              |
| Diethyl ether, 50 mL | -78        | 6.25 eqv.              |
| Diethyl ether, 50 mL | -50        | 6.25 eqv.              |
| Diethyl ether, 50 mL | -50        | 10 eqv.                |
| Diethyl ether, 50 mL | -50        | 25 eqv.                |
| Diethyl ether, 50 mL | -50        | 32 eqv.                |

- The scrambling of the mixture was performed on silica gel by three column chromatography one after the other 1)DCM, 2) Diethyl ether/ DCM 1:9, 3) Diethyl ether/DCM 1:5, 1:3,1:2 .

- According to literature, and especially the article of Shultz Zn(II) was used to protect the porphyrin nitrogens core against the very reactive n-Buthyllithium, but the quenching of the reaction by a 5% HCl solution lead to the demetallation of the obtained porphyrin due to the acidic condition, as a result a mixture of metallated (**ZnATPP**) and free base formyl porphyrin (**ATPP**) derivatives were obtained, lowering the yield of the reaction and increasing the problem of purification by column chromatography due to the raise of products.

According to these parameters we take into account also the possibility to introduce the formyl function not directly on a pre-formed porphyrin macrocycle but on an adequate precursor, like benzaldehyde derivative.

With this intention, we also explored a synthetic method base on acetal protection; 4-bromobenzaldehyde was protected by 2,2-dimethylpropane-1,3-diol in toluene catalyzed by *p*-TsOH to give 1-Bromo-4-(4,4-dimethyl-2,6-dioxan-1-yl)benzene in 90% yield, follow by the formylation of the protected product by halogen-lithium exchange reaction (2 eqv. of n-BuLi, THF, -78 °C) giving 4-(4,4-Dimethyl-2,6-dioxan-1-yl )benzaldehyde **7** with 80% yield. [116], [121], [122] All the spectroscopic results were consistent with literature.

To synthesis the macrocycle porphyrin, the classical Adler method [7], [10] consisting on the cross-condensation of pyrrole and aldehyde **7** in refluxing propionic acid was tested, but this method failed and the *meso*-tetrakis(4-(4,4-

Dimethyl-2,6-dioxan-1-yl-phenylporphyrin **8** was never obtained in these conditions.

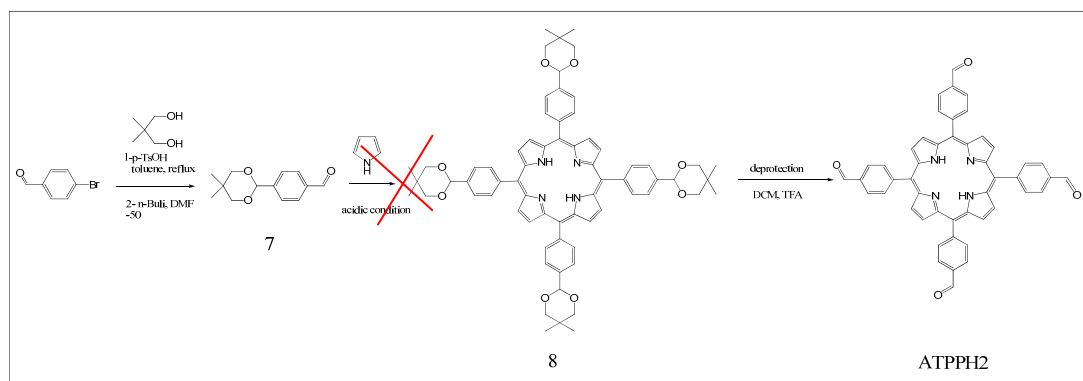


Figure 3.28: Acetal protected formyl group method.

Tablo 3. 6: Acidic conditions for synthesis of **8**.

| Acid                                                            | Solvent                         |
|-----------------------------------------------------------------|---------------------------------|
| Propionic acid                                                  | Propionic acid                  |
| Trifluoroacetic acid (TFA)                                      | CH <sub>2</sub> Cl <sub>2</sub> |
| Boron trifluoride etherate (BF <sub>3</sub> .OEt <sub>2</sub> ) | CNPh                            |

### 3.2.2.4. Characterization Work of ATPP

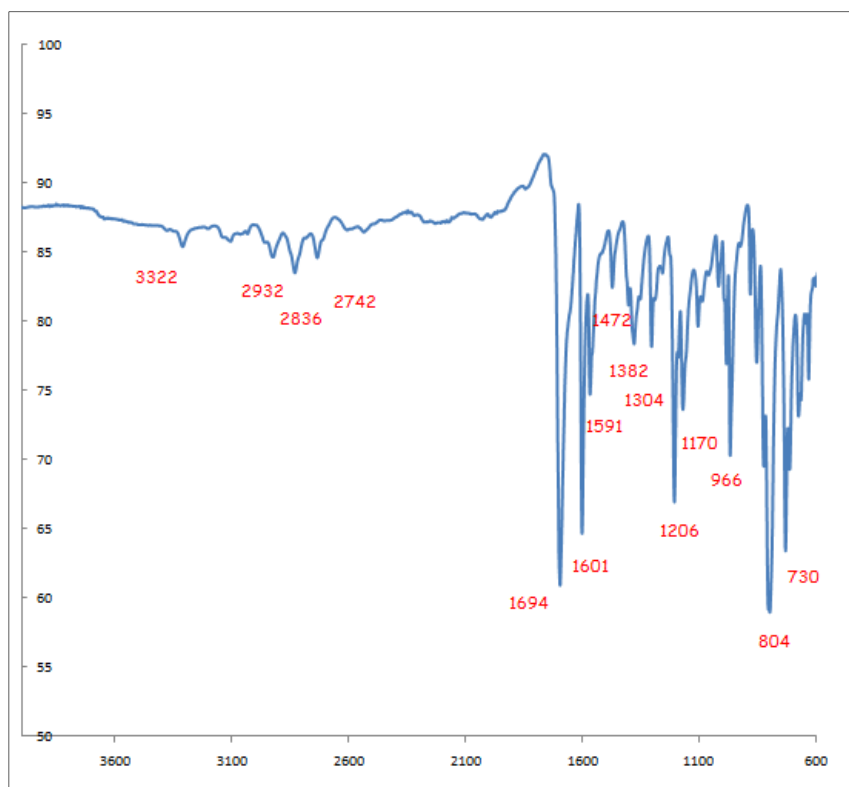


Figure 3.29: FT-IR spectrum of tetra formyl porphyrin **ATPP**.

The FT-IR spectrum of **ATPP** shows the characteristic intense peaks of porphyrin macrocycle [106]. At  $2932\text{ cm}^{-1}$  C-H vibration corresponding to the aromatic protons, at  $1694\text{ cm}^{-1}$  C=O intense peaks correspond to aldehyde vibration. The porphyrin ring vibration was at  $966\text{ cm}^{-1}$ , also the peak at  $804\text{ cm}^{-1}$  is characteristic for pyrrole ring bending and at  $1170\text{ cm}^{-1}$  is for pyrrole ring vibration. NH vibration was observed at  $3322\text{ cm}^{-1}$  and NH bending vibration at  $730\text{ cm}^{-1}$ . Especially for the porphyrin macrocycle, the vibration C=N at  $1472\text{ cm}^{-1}$  and the =C-N vibration at  $1382\text{ cm}^{-1}$  are characteristics.

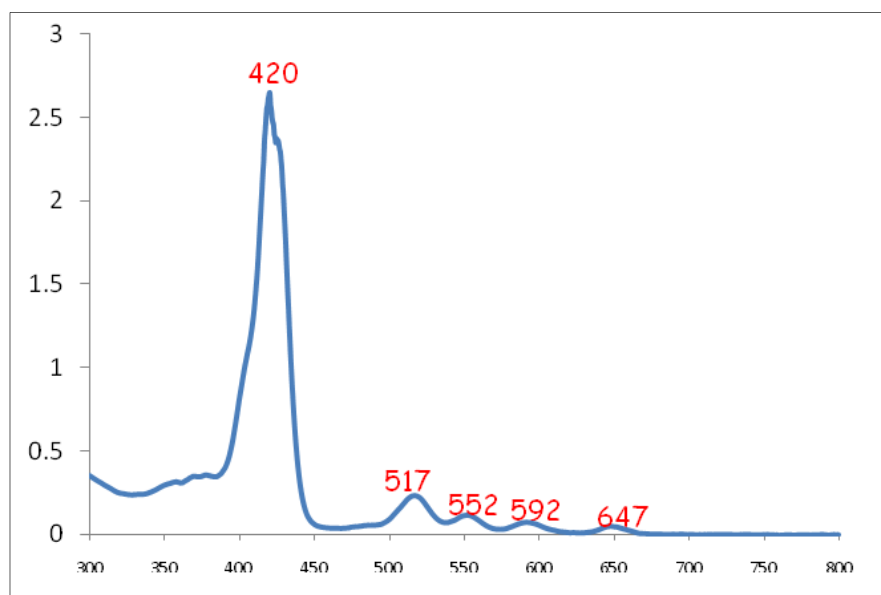


Figure 3.30: The UV-Vis spectrum of tetra formyl porphyrin **ATPP**  $1.10^{-6}$  M in  $\text{CHCl}_3$ .

The electronic absorption spectrum of the **ATPP** is dominated by a very strong Soret band located at 420 nm which is characteristic for porphyrin macrocycles. Four Q bands located in the spectral range of 517- 647 which are typical of free base porphyrins according to the  $D_{2h}$  symmetry[108].

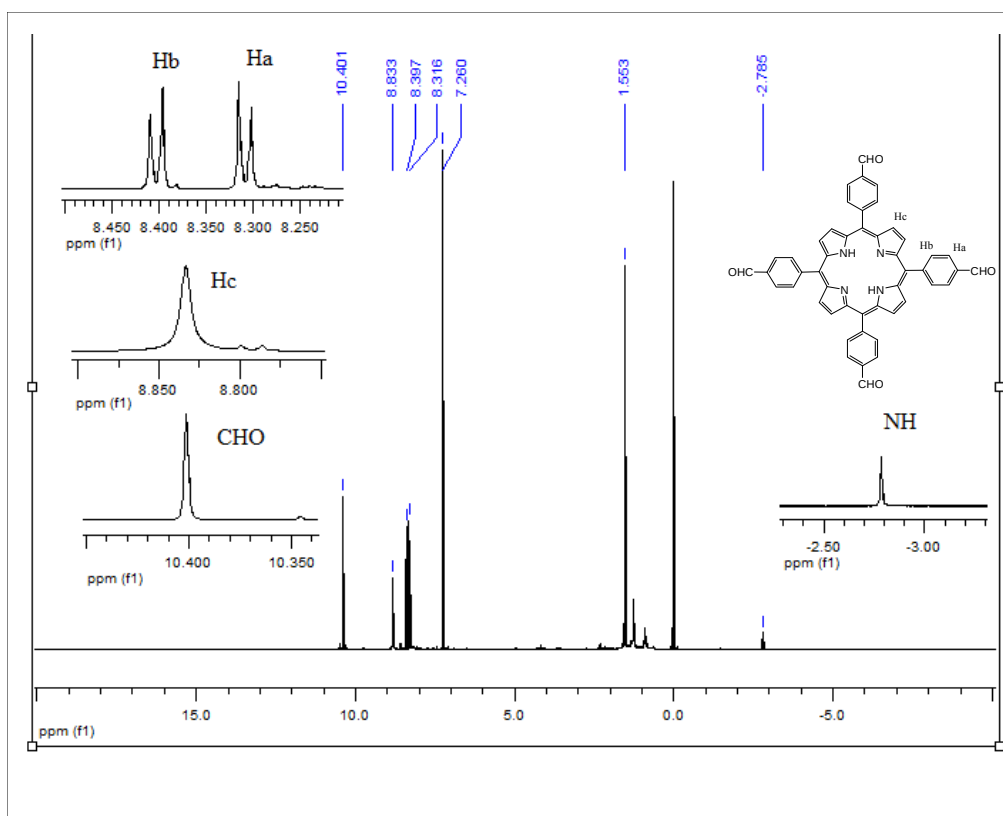


Figure 3.31:  $^1\text{H}$  NMR spectrum of tetra formyl porphyrin **ATPP** in  $\text{CDCl}_3$ .

The  $^1\text{H}$  NMR spectrum of **ATPP** was recorded in  $\text{CDCl}_3$ , the 2NH inner protons inside the porphyrin core are located at -2.85 ppm, 8 *orto*- $\text{CH}_{\text{Ar}}$  protons of *meso*-phenyl group appear at 8.25 ppm, 8 *meta*- $\text{CH}_{\text{Ar}}$  protons of *meso*-phenyl group at 8.32 ppm, 8 pyrrolic CH protons at 8.76 ppm and specifically a singlet peak at 10.33 ppm corresponding to the CHO proton were observed.

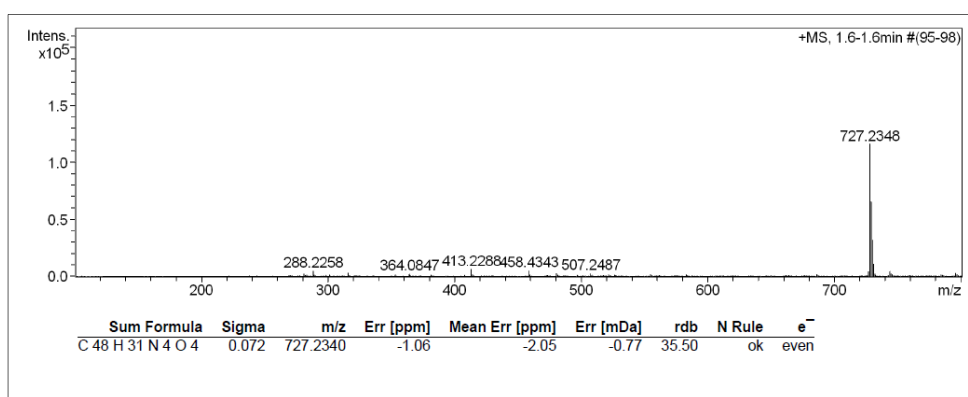


Figure 3.32: HR-ESI Mass spectrum of tetra formyl porphyrin **ATPP**.

High-resolution electrospray ionization mass spectrometry (HR-ESI-MS) displayed a parent molecular peak at  $m/z = 727.415$  (calculated for  $C_{48}H_{30}N_4O_4$   $m/z = 726.23$ ) which correspond to  $[M+H]$ , see Figure 3.16

### 3.2.2.5. Condensation-Oxidation

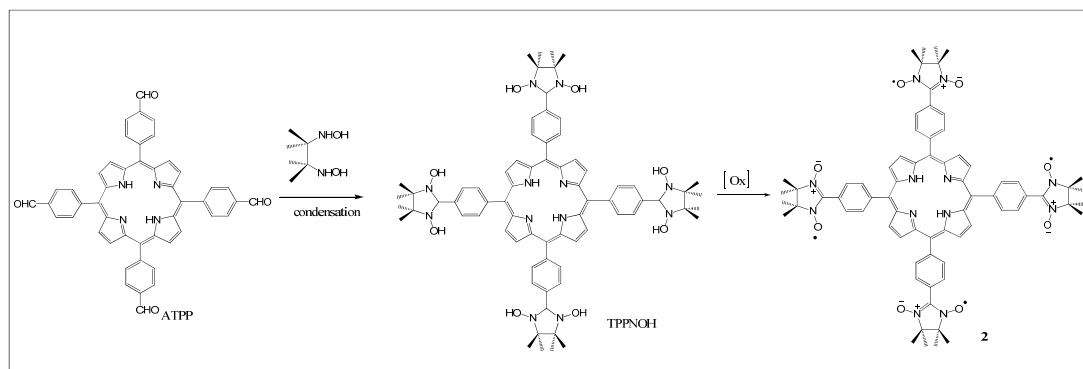


Figure 3.33: Condensation and oxidation reactions.

The condensation reactions of **ATPP** with 2,3-dimethyl-2,3-bis(hydroxylamino)-butane (**BHA**) were performed:

- i) in methanol in a presence of dichloromethane as a co-solvent or
- ii) toluene in presence of p-TsOH as catalyseur

After refluxing for one night the reaction lead to the condensed products, the crude product was used without purification for further reaction. The oxidation reaction was performed in phase transfer solution ( $NaHCO_3$  solution /  $CH_2Cl_2$ ) with  $NaIO_4$  by stirring in an ice-bath for just 15 min and some drops of saturated  $NaHCO_3$  solution was used to prevent the over oxidation of nitronyl nitroxide to the imino nitroxides.

### 3.2.2.6. Characterization Work for NITP

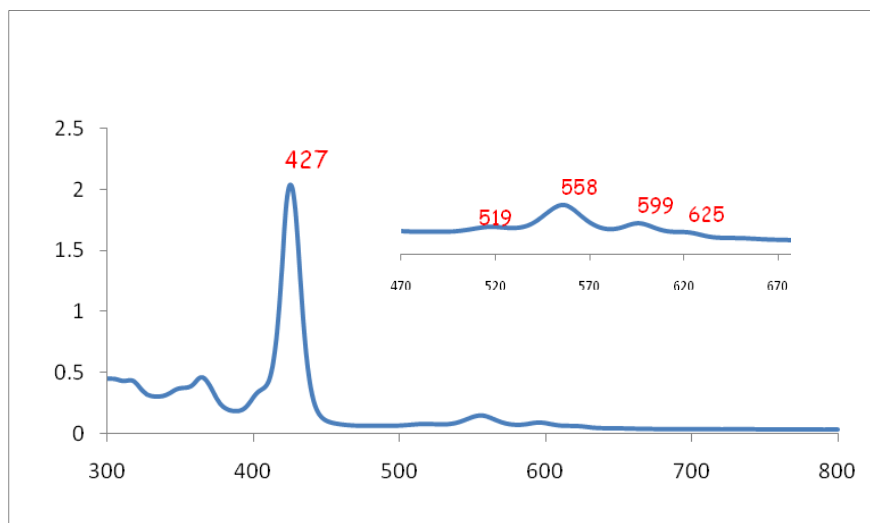


Figure 3.34: The UV-Vis spectrum of Nitronyl nitroxide substituted porphyrin (**2**)  $1.10^{-6}$  M in  $\text{CHCl}_3$ .

Tablo 3. 7: UV-Vis spectrum of **ATPP** and molecule **2**  $1.10^{-6}$  M in  $\text{CHCl}_3$ .

| Compound    | Soret(B) band $\lambda_{\text{max}}$ | Q bands $\lambda_{\text{max}}$ |
|-------------|--------------------------------------|--------------------------------|
| <b>ATPP</b> | 420                                  | 517, 552, 592, 647             |
| <b>2</b>    | 427                                  | 519, 558, 599, 625             |

The electronic absorption spectrum of **2** exhibits one Soret band at 427 nm and four Q bands located in the spectral range of 519-625 nm. The influence of the attachment of the nitroxide moiety to the porphyrin macrocycle result of a 7 nm bathochromic shift of the Q band and of 22 nm band (from 647 nm to 625 nm) hypsochromic shift of the last Q band. Especially the intensities of the Q bands are affected by the presence of the radicals. The first band at 519 nm decreases and the band at 558 nm increases compared to the electronic absorption of **ATPP**.

The EPR results are a first and trustful characterization work for radical substituted porphyrins. The EPR spectroscopy measurements in solution will be discussed in section 3.3.

### 3.2.4. Molecule 3

#### 3.2.4.1. Synthesis work on Molecule 3

For the synthesis of Imino nitroxide substituted porphyrin (**3**), two different methods were used; one is based on the conversion of nitronyl nitroxide to imino derivative by the well known over oxidation reaction with  $\text{NaNO}_2$ . A second method was also tried, based on the cross condensation of 4-(4,4-Dimethyl-2,6-dioxan-1-yl)benzaldehyde (**7**) precursor by the Adler synthetic pathway.

#### 3.2.3.2. Method 1: Conversion of NITP to IMINP

According to Ullman [45] when nitronyl nitroxides are heating in the presence of triphenylphosphine in benzene or treated with nitrous acid, imino nitroxides are obtained in high yields. It is possible to reconvert to the starting nitronyl nitroxides with m-chloroperbenzoic acid.

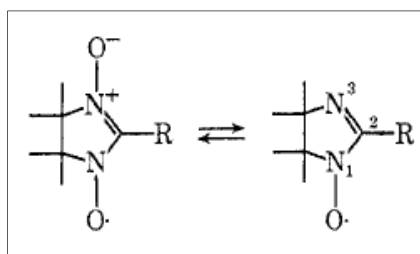


Figure 3.35: Reconversion of imino nitroxide to nitronyl nitroxide.

The over oxidation of **2** by  $\text{NaNO}_2$  in an-ice bath, following the classical method described above, gives **3**.

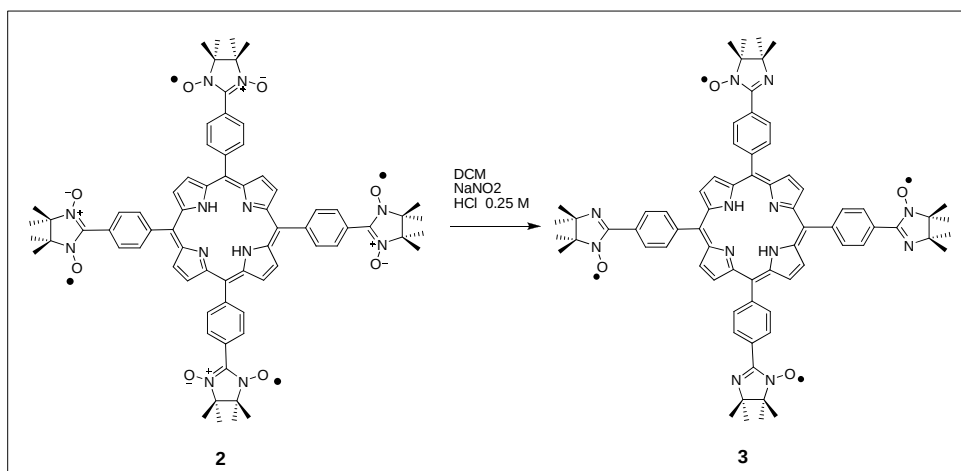


Figure 3.36: Synthesis of imino nitroxide substituted porphyrin **3**.

According to EPR results nitronyl nitroxide moieties were fully converted to imino nitroxide derivative successfully. EPR measurements will be discussed in section 3.3.

### 3.2.3.2. Method 2: Protecting group pathway

Another synthetic way was to introduce the radical on the precursor to get a mixture of predominant nitronyl nitroxide radical 2-[4-(4,4-dimethyl-2,6-dioxan-1-yl)benzene]-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (**9**) with some imino nitroxide derivative 2-(4,4-dimethyl-2,6-dioxan-1-yl)benzene]-4,4,5,5-tetramethylimidazoline-1-oxyl (**10**) as described in Figure 3.37.

The non-protected formyl derivative (**11**) was recovered by reacting the raw mixture of (**9**) and (**10**) by trifluoroacetic acid (TFA). The reaction was carried out on the raw mixture of (**9**) and (**10**) taking into account that acidic conditions change the nitronyl nitroxide in imino nitroxide as mentioned earlier. Accordingly and as expected, only the orange imino derivative was obtained by this way due to treatment by trifluoroacetic acid and further reoxidation by air here in the excellent yield of 98%. It should be notified that although, 2-(4-benzaldehyde)-4,4,5,5-tetramethylimidazoline-3-Oxide-1-oxyl (**11**) has already been mentioned there were no previous details of the synthesis and lack of EPR spectrometry work which is fundamental characterization tool for radicals [123].

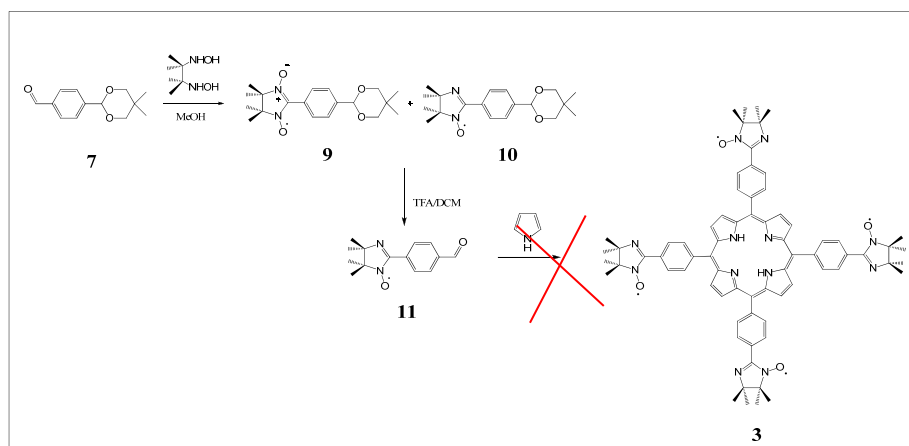


Figure 3.37: Synthetic strategy for imino nitroxide radical substituted porphyrin.

Syntheses of **3** in different acidic condition were attempted but unfortunately we could not succeed up to now.

#### 3.2.4.4. Characterization Work of Precursors

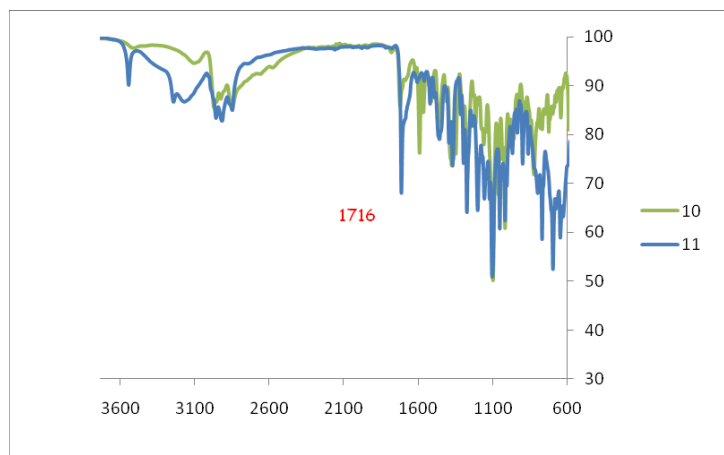


Figure 3.38: 1: FT-IR spectrum of imino nitroxides **10** and **11**.

According to IR spectra, the carbonyl stretch  $\text{C}=\text{O}$  of aromatic aldehyde was obtained at  $1716\text{ cm}^{-1}$  as expected, but is not easy to differ  $\text{H}-\text{C}=\text{O}$  stretch ( $2830\text{--}2695\text{ cm}^{-1}$ ) of aldehyde from aromatic  $\text{C}-\text{H}$  stretch ( $2870\text{--}2960\text{ cm}^{-1}$ ).

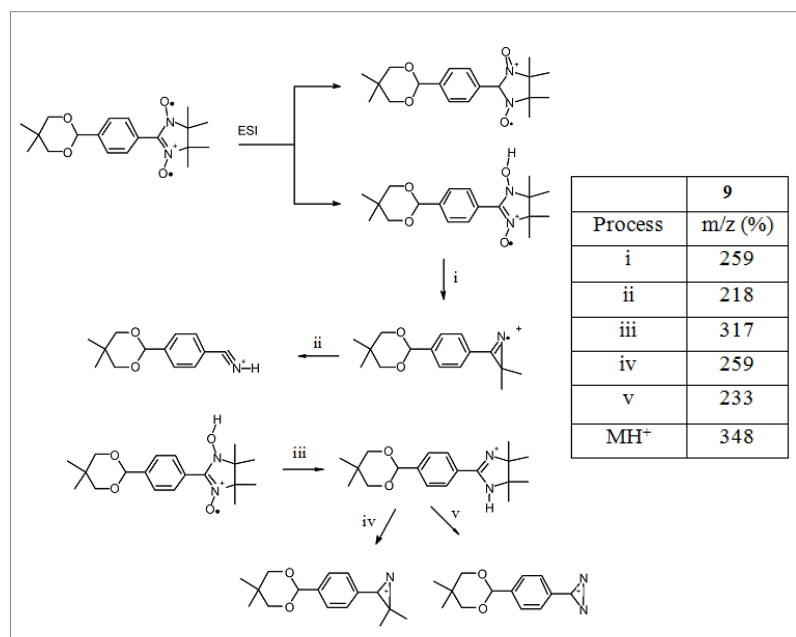


Figure 3. 39: Proposed fragmentation mechanism of nitronyl nitroxide **9**.

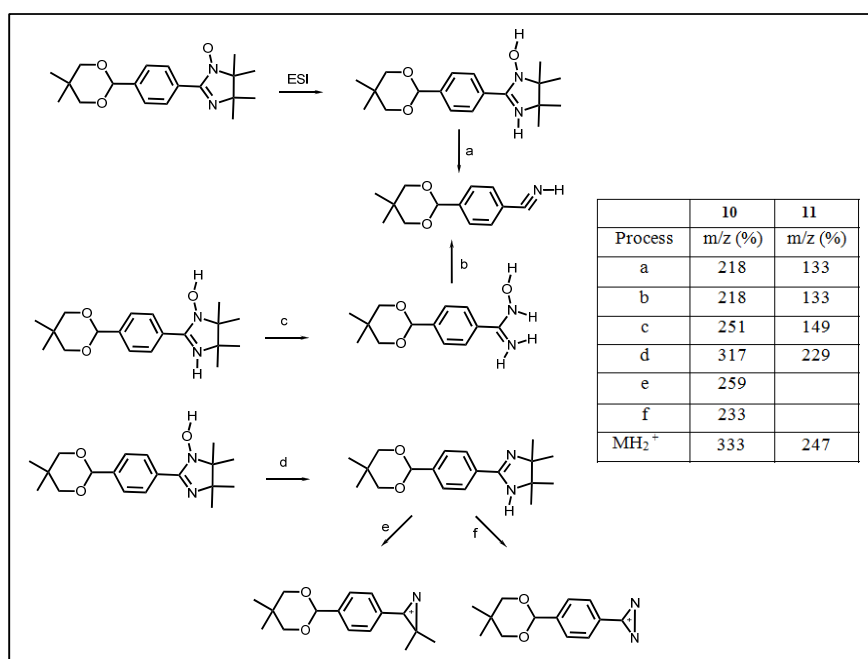


Figure 3. 40: Proposed fragmentation mechanism of imino nitroxide **10**.

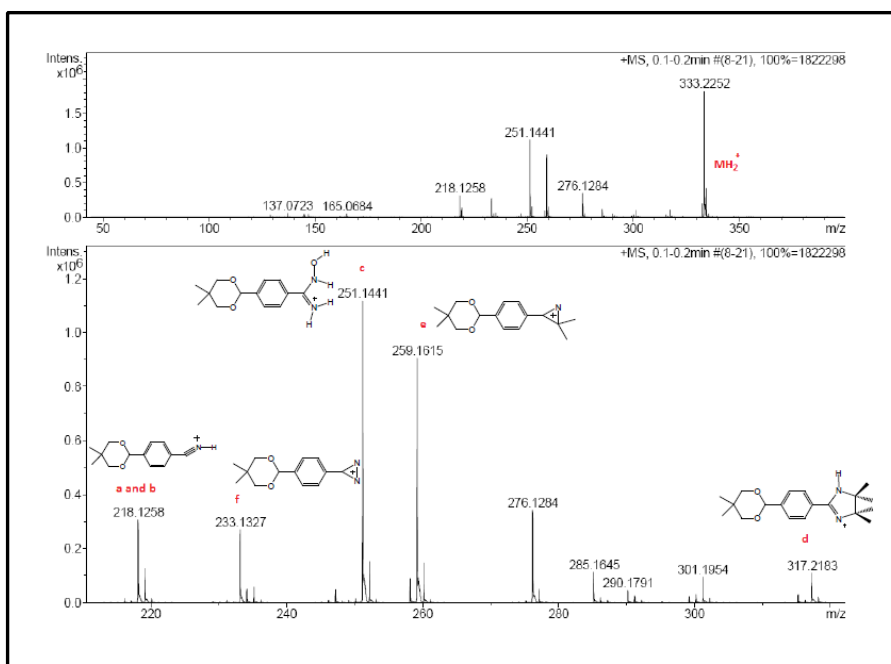


Figure 3. 41: ESI mass spectrum of imino nitroxide **10**.

Electrospray ionization mass spectroscopy (ESI) was used as rapid and useful characterization tool of radical precursors **9**, **10**, **11**. According to nature of the radicals nitronyl nitroxide radical **9** was detected as the  $[MH]^+$  radical cation and imino nitroxide radicals **10** and **11** were detected as the  $[MH_2]^+$  ion. All the radicals exhibit large-scale fragmentation and their mechanisms are summarized in Figure 3.39 and 3.40

#### 3.2.4.5. Characterization work for IMIP

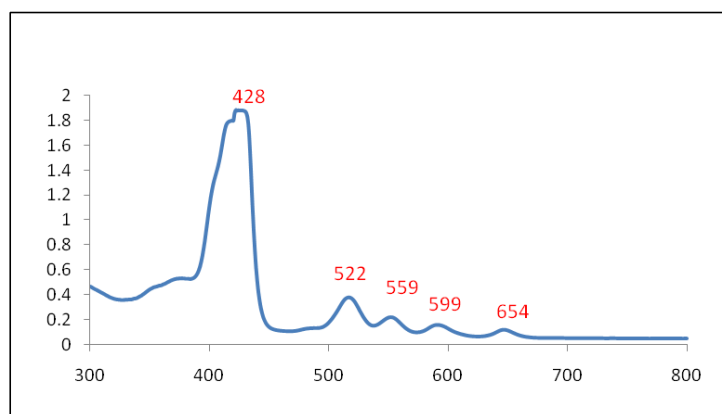


Figure 3. 42: The UV-Vis spectrum of imino nitroxide substituted porphyrin (**IMIP**)  $1.10^{-6}$  M in  $CHCl_3$ .

Tablo 3. 8: Uv-Vis spectra data of **ATPP** and **IMIP** in CHCl<sub>3</sub>.

| Compound    | Q band $\lambda_{\max}$ | Soret(B) bands $\lambda_{\max}$ |
|-------------|-------------------------|---------------------------------|
| <b>ATPP</b> | 420                     | 517, 552, 592, 647              |
| <b>IMIP</b> | 428                     | 522, 559, 599, 654              |

The electronic absorption spectrum of imino nitroxide radical substituted porphyrin **IMIP** shows remarkable spectral change. Characteristic Q band exhibit more red-shifted to 428 nm and B bands also red-shifted to 522,559,599 and 654 nm.

### 3.2.5. Molecule 4

As seen above and as may be expected the incorporation of four nitroxide on the porphyrin is difficult and complicated. In a tentative of simplification and with the objective to test the synthetical approach we decided to work on the porphyrin substituted a single nitroxide radical.

#### 3.2.5.1. Synthesis of **AB<sub>3</sub>BrP**

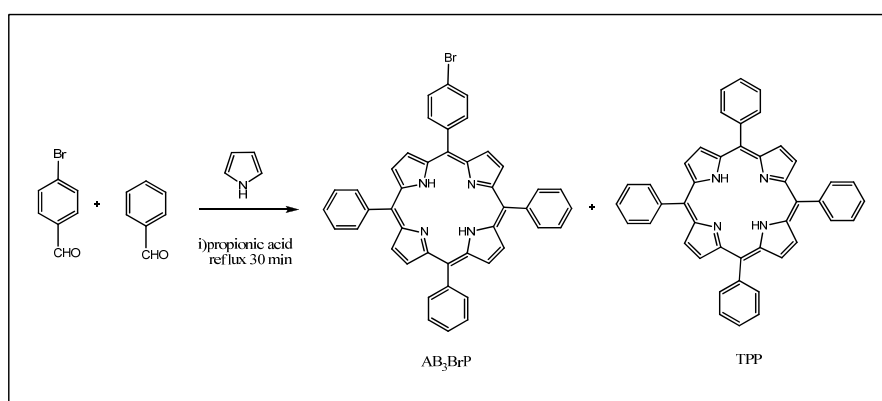


Figure 3.43: Synthesis of **AB<sub>3</sub>BrP**.

The starting precursor of the mono nitroxide substituted porphyrin was the 5-(4-bromophenyl)-10-15-20-tripheylporphyrin (**AB<sub>3</sub>BrP**) which was synthesized by routine Adler method using 1 eqv. of 4-bromobenzaldehyde and 10 eqv. of benzaldehyde to avoid formation of di- and tri-*meso*-4-bromophenyl porphyrin

derivatives. Inseparable **AB<sub>3</sub>BrP** porphyrin and unsubstituted *meso*-tetraphenyl porphyrin **TPP** were used together for further reactions.

### 3.2.5.2. Halogen Lithium Exchange Reaction and Oxidation

Mono *meso*-*N*-*tert*-butyl-*N*-oxyamino substituted porphyrin **4** was prepared from **AB<sub>3</sub>BrP** according to the same method as described for molecule **1** (Figure 3.14) which is based on Lithium-halogen exchange reaction at low temperature.

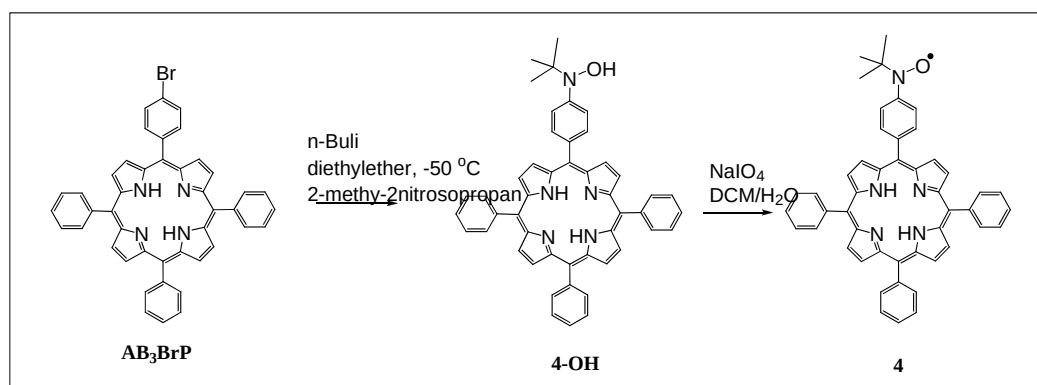


Figure 3.44: Synthesis of molecule **4**.

### 3.2.5.3. Characterization Work

Tablo 3.9: Uv-Vis spectra data of **AB<sub>3</sub>BrP** and Molecule **4** in CHCl<sub>3</sub>.

| Entry                    | B band $\lambda_{\text{max}}$ (nm) | Q bands $\lambda_{\text{max}}$ (nm) |
|--------------------------|------------------------------------|-------------------------------------|
| <b>AB<sub>3</sub>BrP</b> | 418                                | 522, 556, 596, 652                  |
| <b>Molecule 4</b>        | 420                                | 522, 556, 596, 654                  |

According to Table 3.9 there is no significant shift of the absorption band due to introduction of *N*-*tert*-butyl-*N*-oxyamino radical moiety. The results are consistent with the UV-Vis spectroscopic work for molecule **1** explained before in section 3.2.2.

### 3.2.6. Molecule 5 and 6

#### 3.2.6.1. Synthesis of AB<sub>3</sub>AP

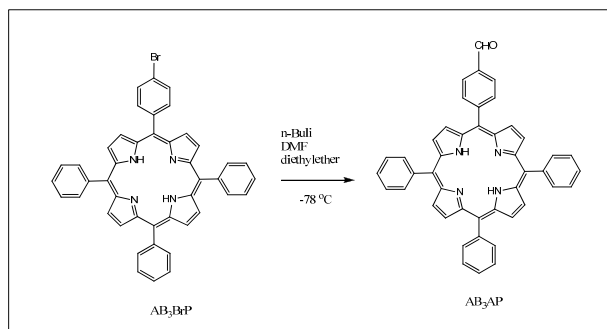


Figure 3.45: Synthesis of AB<sub>3</sub>AP.

5-(4-formylphenyl)-10,15,20 phenylporphyrin was prepared via the reaction of Lithium-halogen exchange reaction as described for ATPP (see section 3.2.2.3) with 60% yield.

#### 3.2.6.2. Characterization Work of AB<sub>3</sub>AP

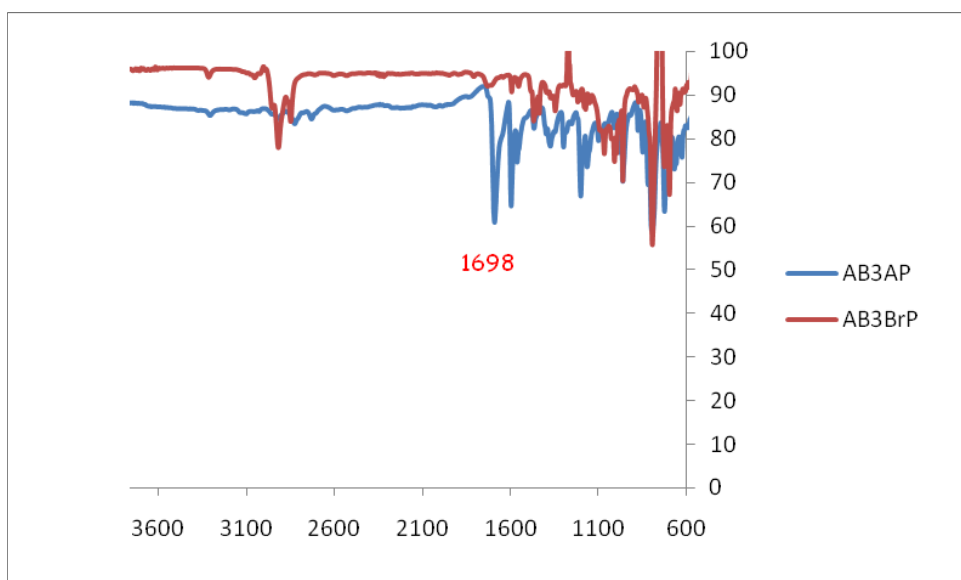


Figure 3.46: IR spectra of AB<sub>3</sub>BrP and AB<sub>3</sub>AP.

From Figure 3.46 it is clear that the carbonyl stretch C=O of aromatic aldehyde was obtained at 1698 cm<sup>-1</sup> as expected.

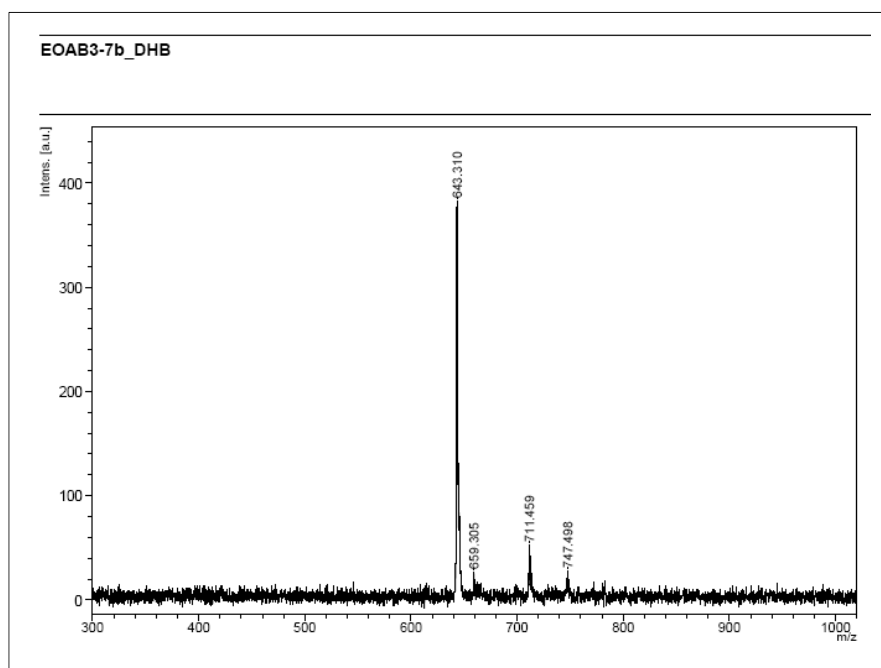


Figure 3.47: MALDI-MS spectrum of **AB<sub>3</sub>AP** porphyrin.

The mass spectrum of **AB<sub>3</sub>AP** was obtained by MALDI-MS in presence of a DHB matrix, displaying a molecular peak at  $m/z=643.31$  (calculated for  $C_{45}H_{30}N_4O$   $m/z=642.24$ ) which correspond to  $[M+H]$ .

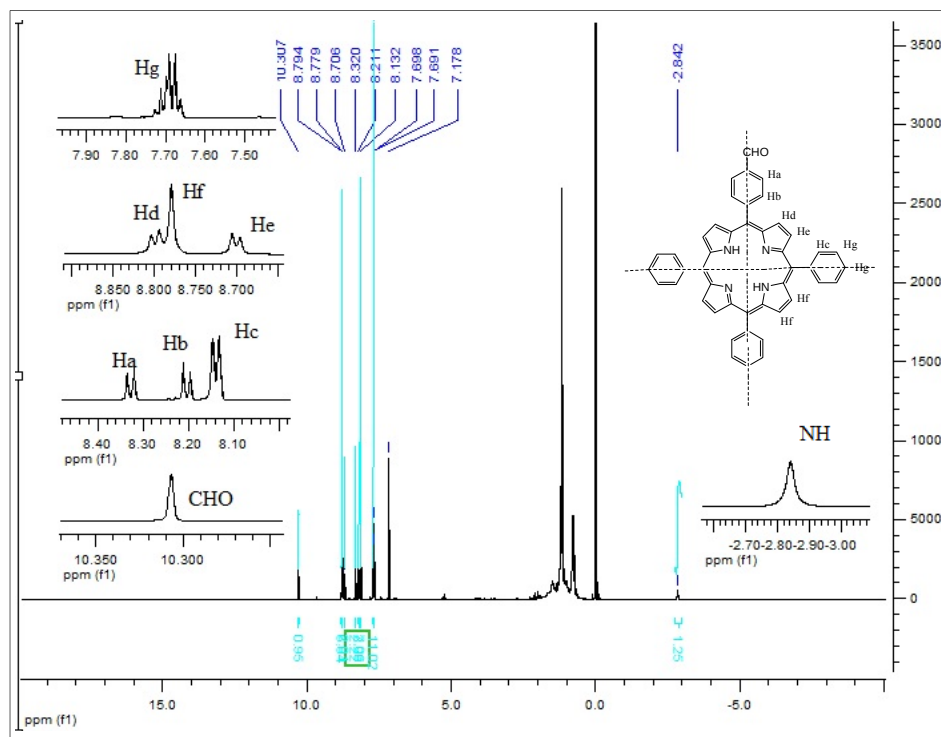


Figure 3.48:  $^1\text{H}$  NMR spectrum of **AB<sub>3</sub>AP** porphyrin obtained in  $\text{CDCl}_3$ .

Considering the  $^1\text{H}$  NMR spectrum of **AB<sub>3</sub>AP** in  $\text{CDCl}_3$ , the 2NH protons inside the porphyrin core are located at -2.84 ppm. The 15 protons of *meso*-phenyl group appear respectively at 7.66 ppm (Hg, m, 9H) and 8.13 ppm (Hc, m, 6H). 2 *o*-CH<sub>Ar</sub> protons of *meso*-phenyl group at 8.21 ppm, 8 pyrrolic CH protons differs from each other because of low symmetry of porphyrin; 2H *m*-CH<sub>Ar</sub> at 8.32 ppm doublet, 2H CH<sub>pyrrole</sub> at 8.71, 4H CH<sub>fpyrrole</sub> at 8.79, 2H CH<sub>pyrrole</sub> at 8.78, and at 10.33 ppm singlet CHO proton corresponds to formyl group on porphyrin macrocycle.

### 3.2.6.3. Condensation-Oxidation

The target 5-(4,4,5,5-tetramethylimidazoline-1-oxyl)-10,15,20-phenyl porphyrin radical **5** was prepared as described before by condensation reaction of **BHA** with **AB<sub>3</sub>AP** by reflux for one day in DCM/ MeOH to afford **AB<sub>3</sub>NOH**. The oxidation reaction of **AB<sub>3</sub>NOH** was performed in phase transfer solution ( $\text{CHCl}_3$  /  $\text{H}_2\text{O}$ ) with  $\text{NaIO}_4$  as oxidant to give the radical as a dark purple powder. Porphyrin **6** was obtained by over oxidation step with  $\text{NaNO}_2$ .

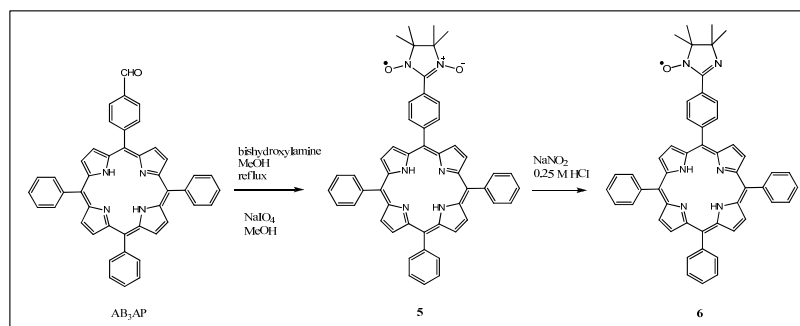


Figure 3.49: Synthesis of molecule **5** and **6**.

### 3.2.6.4. Characterization Work

Tablo 3. 10: The UV-Vis spectra data of **AB<sub>3</sub>A**, Molecule **5** and **6** radical  $1 \cdot 10^{-6}$  M in  $\text{CHCl}_3$ .

| Entry                   | B band $\lambda_{\text{max}}$ (nm) | Q bands $\lambda_{\text{max}}$ (nm) |
|-------------------------|------------------------------------|-------------------------------------|
| <b>AB<sub>3</sub>AP</b> | 419                                | 516, 550, 591, 648                  |
| <b>Molecule 5</b>       | 426                                | 520, 556, 598, 653                  |
| <b>Molecule 6</b>       | 429                                | 521, 557, 598, 654                  |

The electronic absorption spectrum of **5** and **6**, shows striking spectral changes. For molecule **5** and **6** the B and Q bands exhibit a red-shift. These significant red shifts can be referred to the contribution of nitronyl and imino nitroxide moieties on the porphyrin macrocycle.

### 3.2.7. Metal insertion to Porphyrin Macrocycles

To our best knowledge, up to today there were only three reported work<sup>124-126</sup> that mentioned the utilization of **ATPP** but without any experimental and characterization part as well no report for metallo-derivative of **ATPP**.

In this study, after an easy metallation process of **ATPP**, **ATPPCu(II)** and **ATPPMn(III)** were full characterized for the first time as well as **TBrPPCu(II)** and **TBrPPMn(II)**.

According to traditional preparative procedures to generate metalloporphyrins, free base porphyrin is generally reacted with a large excess of metal salt or metal carbonyl in high boiling solvents.

To obtained **ATPPMn(III)** [127], [128] Mn(OAc)<sub>2</sub> was chosen as metal source and CHCl<sub>3</sub>/MeOH as solvent system that present the advantage of being easy removable from reaction media.

**ATPPCu(II)** and **TBrPPCu(II)** were obtained by MW irradiation in short time (30 min) with 70-90 % yield from **ATPP**. Dry DMF was chosen as efficient conducting solvent, its high polarity (6.4) and dielectric constant (37.7) which makes it MW active solvent. Secondly, Cu(OAc)<sub>2</sub>.H<sub>2</sub>O was highly soluble of in DMF.

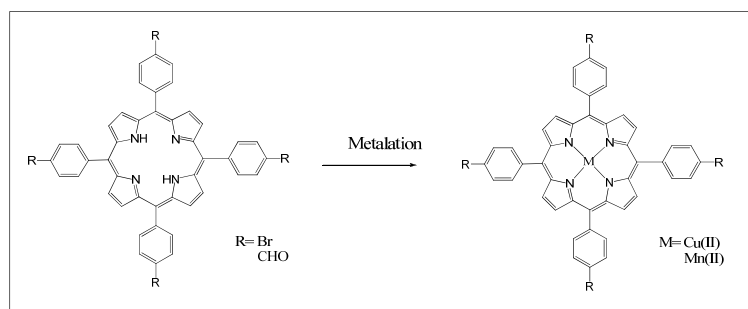


Figure 3.50: Synthesis of metallated porphyrins.

Tablo 3. 11: The UV-Vis spectra data of **TBrPP**, **TBrPPCu(II)**, **TBrPPMn(III)**, **ATPP**, **ATPPCu(II)** and **ATPPMn(III)**  $1.10^{-6}$  M in  $\text{CHCl}_3$ .

| Entry               | B band $\lambda_{\text{max}}$ (nm) | Q bands $\lambda_{\text{max}}$ (nm) |
|---------------------|------------------------------------|-------------------------------------|
| <b>TBrPP</b>        | 413                                | 512, 548, 588, 642                  |
| <b>TBrPPCu(II)</b>  | 416                                | 542, 576                            |
| <b>TBrPPMn(III)</b> | 479                                | 588, 626                            |
| <b>ATPP</b>         | 420                                | 517, 552, 592, 647                  |
| <b>ATPPCu(II)</b>   | 419                                | 540, 588                            |
| <b>ATPPMn(III)</b>  | 479                                | 582, 624                            |

The Q bands collapse into two bands due to the higher  $D_{4h}$  symmetry of the metalloporphyrins, 542 and 576 for **TBrPPCu(II)**, 540 and 588 for **ATPPCu(II)** which are typical in metallo porphyrins.

Mn(II) porphyrins are generally air-sensitive, giving rise to Mn(III)-compounds. According to the electronic absorption spectra of TBrPPMn and **ATPPMn** (see Table 3.12), a strong Soret band (B band) located at 479 nm is present that correspond to Mn(III)- compounds which are described in literature [129]. In case of Mn(II)-complex Q band have to be located at 434-442 nm [130], [131].

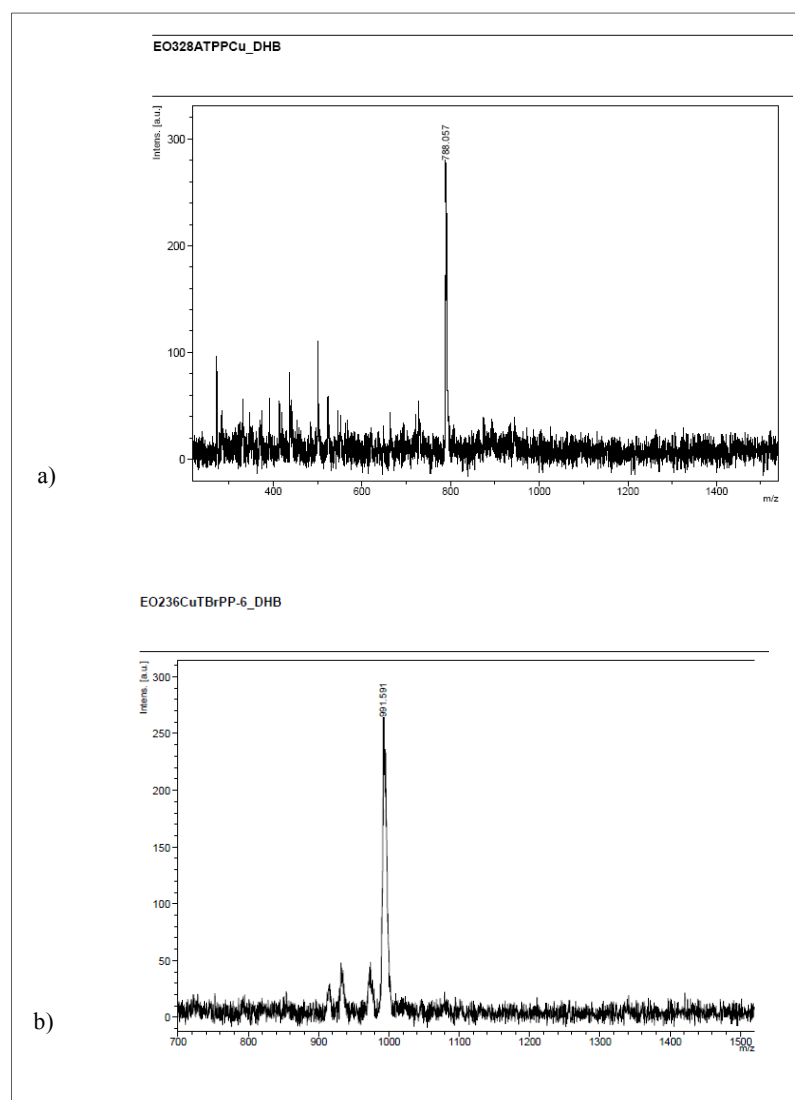


Figure 3.51: MALDI-MS spectra of a) **ATPPCu(II)**, b) **TBrPPCu(II)**.

MALDI mass spectrometry displayed a parent molecular peak at  $m/z = 788.057$  (calculated for  $C_{48}H_{28}CuN_4O_4$   $m/z = 787.14$ ) which correspond to  $[M+H]$  for **ATPPCu(II)** and molecular peak at  $m/z = 991.85$  (calculated for  $C_{48}H_{28}CuN_4Br_4$   $m/z = 991.591$ ) correspond to  $[M]^+$  for **TBrPPCu(II)**.

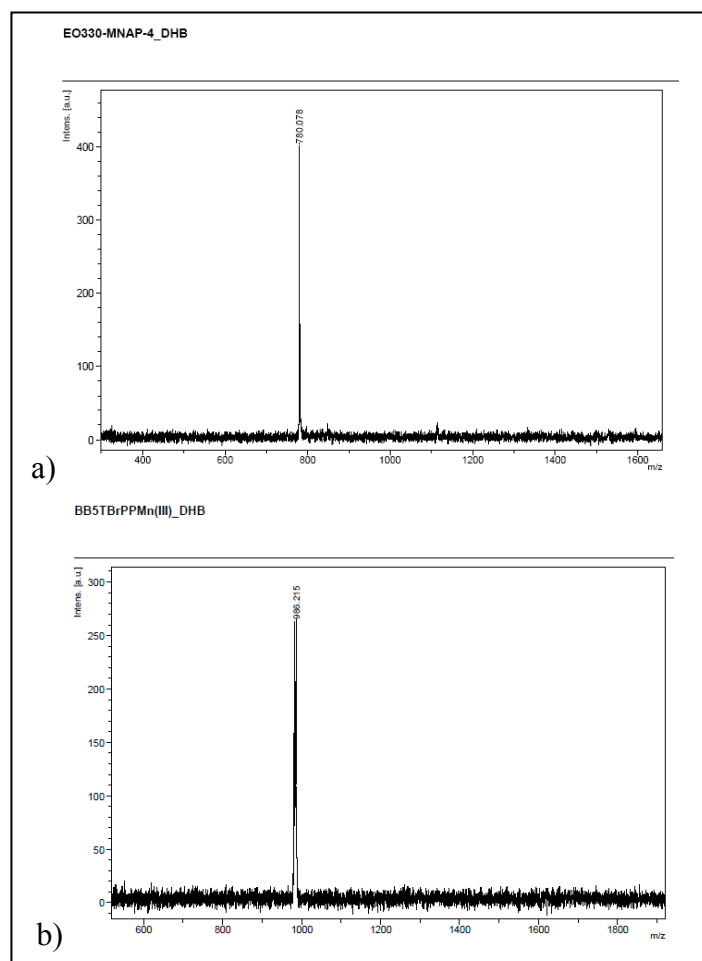


Figure 3.52: MALDI-MS spectra of a) **ATPPMn(III)**, b) **TBrPPMn(III)**.

MALDI mass spectrometry displayed a parent molecular peak at  $m/z = 780.078$  (calculated for  $C_{48}H_{28}MnN_4O_4$   $m/z = 779.70$ ) which correspond to  $[M+H]$  for **ATPPMn(III)** and molecular peak at  $m/z = 986.215$  (calculated for  $C_{48}H_{28}MnN_4Br_4$   $m/z = 983.24$ ) correspond to  $[M+3H]$  for **TBrPPMn(III)**.

From all works were described above, one can conclude that among many *meso*-position formylation methods Butyllithium/DMF formylation is the best way to get tetra formyl porphyrin. Microwave irradiation makes possible metallation of porphyrin macrocycle in short time with perfect yield. In our work we could synthesized **ATPP**, **ATPPCu(II)** and **ATPPMn(III)** and also full characterization work was done for the first time.

### 3.3. EPR Work on Nitroxide Substituted Porphyrins

#### 3.3.1. EPR Spectroscopy of Nitroxides

Nitroxide monoradicals exhibit very distinct EPR resonance envelopes.

For the mono *N-tert*-butyl-*N*-oxyamino (tBuNO) the EPR spectrum exhibits a triplet hyperfine structure with an intensity distribution in the ratio of 1:1:1, due to the interaction of the unpaired electron with the one nitrogen atom ( $^{14}\text{N}$ ,  $I = 1$ ) in isotropic media, characteristic of a tBuNO nitroxide radicals system(see Figure 3.53).

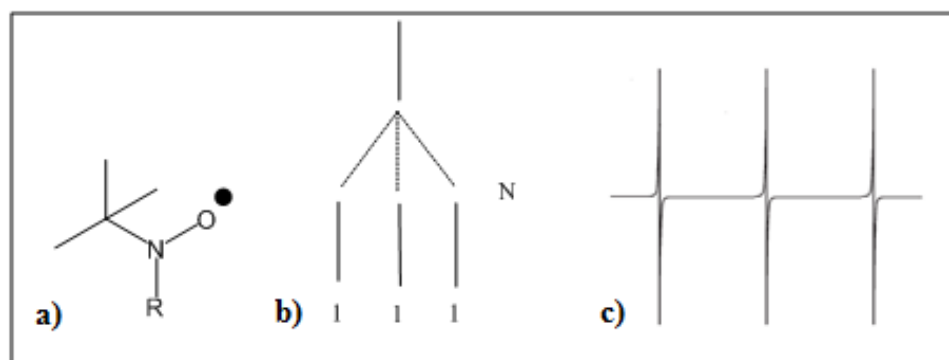


Figure 3.53: a) Molecular structure of nitroxide, b) stick diagram, c) resulting EPR signals of mono tBuNO nitroxide moieties.

The number of hyperfine lines grows multiplicatively with the number  $n$  of magnetic nuclei, because each additional nucleus splits every line into equidistant  $2I+1$  lines of the same intensity. The  $n$  equivalent nucleus thus gives rise to  $2nI+1$  lines.

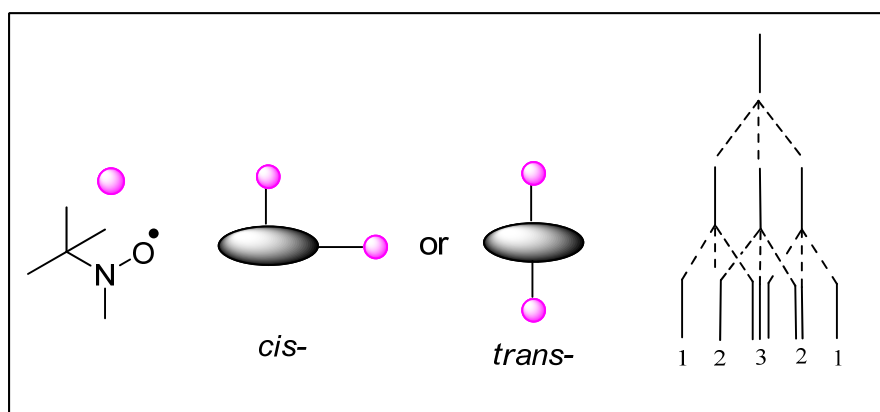


Figure 3.54: General EPR solution spectrum of di-*t*BuNO radicals.

EPR spectrum di-tBuNO radical represents a quintet hyperfine structure ( $2nI+1=5$ ) with an intensity distribution in the ratio of 1:2:3:2:1, due to the interaction of the unpaired electron with the two equivalent nitrogen atoms ( $^{14}\text{N}$ ,  $I = 1$ ) in isotropic media for di-tBuNO radicals.

In the case of mono nitronyl(NIT) the EPR spectrum represents a quintet hyperfine structure with an intensity distribution in the ratio of 1:2:3:2:1, due to the interaction of the unpaired electron with the two equivalent nitrogen atoms ( $^{14}\text{N}$ ,  $I = 1$ ) in isotropic media (see Figure 3.55).

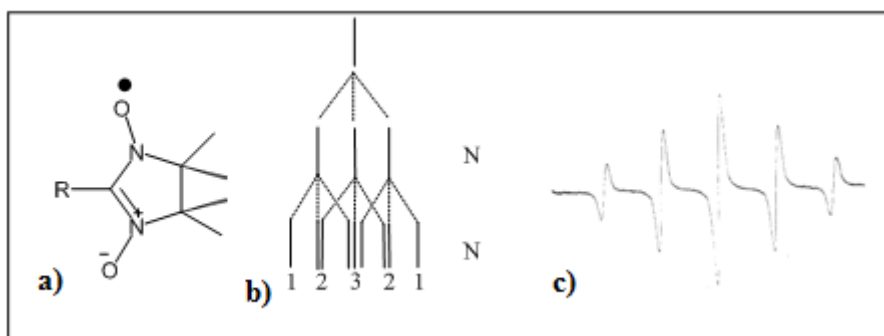


Figure 3.55: a) Molecular structure of nitronyl, b) stick diagram, c) resulting EPR signals of interaction between the unpaired electron and the  $^{14}\text{N}$  nucleus for nitronyl nitroxide moities.

Imino(IMI) nitroxide radicals have the resulting EPR spectrum forming a seven line hyperfine structure with intensities ratio of 1:1:2:1:2:1:1. This kind of hyperfine pattern arises from the interaction of the unpaired electron with the two non equivalent nitrogen nuclei include in imino nitroxide monoradical (see Figure 3.56).

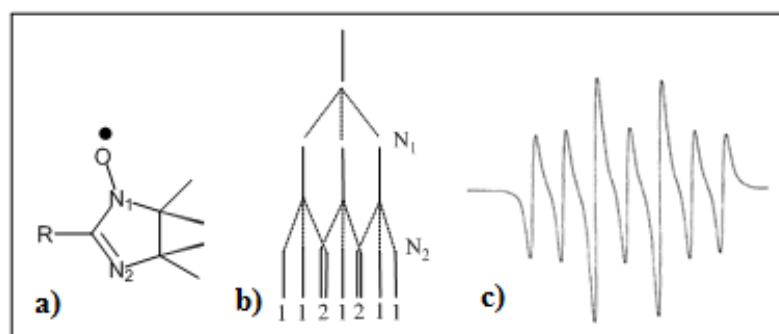


Figure 3.56: a) Molecular structure of nitroxide, b) stick diagram, c) resulting EPR signals of mono imino nitroxide moities.

In our study the X-band measurements of chloroform solution of N-*tert*-butyl-N-oxyamino (**tBuNO**), nitronyl(**NIT**) and imino(**IMI**) nitroxide radicals were carried at ambient temperature in chloroform solution. The spectra were simulated with the values of  $g$ ,  $a_N$  (isotropic hyperfine coupling constant in gauss) and linewidth extracted from the solution spectrum, using Jeol IsoSimu and Winsim computer programs [133].

### 3.3.2. EPR Study for Targeted Molecule 1

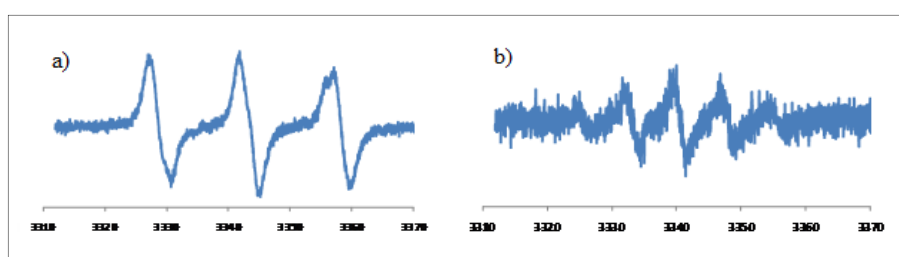


Figure 3.57: EPR solution spectra of a) mono **tBuNOP** (4.028 mW, 60 dB, 1G, 1 scan), b) di **tBuNOP** (4.027 mW, 60 dB, 1G, 1 scan) radical porphyrins at  $c = 1 \times 10^{-6}$  M in  $\text{CHCl}_3$ .

According to our many EPR experiments most hyperfine couplings correspond to mono ( $2nI+1=3$  lines) and di ( $2nI+1=5$  lines) **tBuNOP** porphyrin radical. Nevertheless, three-line profile is typical of isolated nitroxide moieties in solution, therefore low temperature (helium temperature) study should be done to observe the anisotropic coupling between the nitroxides.

### 3.3.3. EPR Study for Targeted Molecule 2

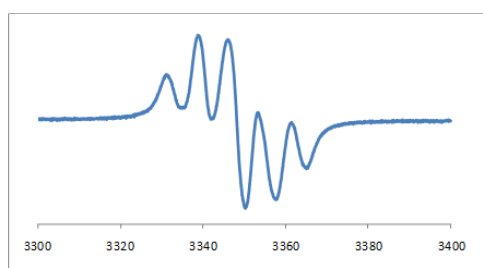


Figure 3.58: EPR solution spectrum of nitroxide substituted radical porphyrin at  $c = 1 \times 10^{-6}$  M in  $\text{CHCl}_3$  (2.03 mW, 60 dB, 1G, 1 scan).

According to the EPR solution spectra of nitronyl nitroxide substituted porphyrins, the hyperfine structure corresponds to the mono ( $2nI+1= 5$  lines) nitroxide radical. As there are not references for this kind of molecules, we can not conclude that the molecule obtained during the synthesis of molecule 3 bears one radical, or four radicals without interactions. Further studies are ongoing in this direction.

### 3.3.4. EPR Study for Targeted Molecule 3

- Precursors for targeted molecule 3

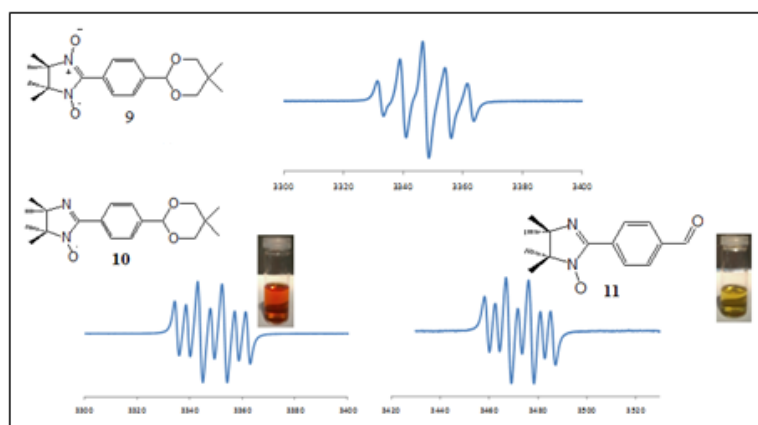


Figure 3.59: EPR spectrum of precursors **9**, **10**, **11** at  $c = 1 \times 10^{-6}$  M in  $\text{CHCl}_3$ .

Following the general EPR behavior description of nitronyl and imino nitroxide above, the hyperfine structures in Figure 3.34 proves the radical structures of original synthons **9**, **10** and **11** a suitable porphyrin precursor candidate.

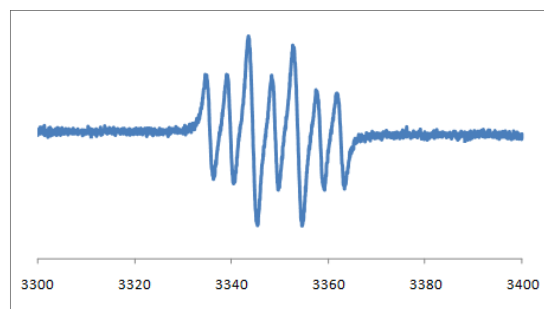


Figure 3.60: EPR solution spectra of imino radical porphyrin at  $c = 1 \times 10^{-6}$  M in  $\text{CHCl}_3$  (6.399 mW, 60 dB, 1G, 1 scan).

Figure 3.30 shows the typical seven lines well-resolved EPR spectrum corresponding to a mono imino nitroxide substituted porphyrin structure. One should consider that a seven-line profile is typical of an isolated imino nitroxide moieties in solution, but to observe the anisotropic coupling of the corresponding different number of imino nitroxides and to investigate the spin-spin interactions in case of the presence of multi radicals, low temperature (helium temperature) study should be done with freeze–pump–thaw cycles to avoid oxygen effect on spin interactions.

### 3.3.5. EPR Study for Targeted Molecule 4, 5, 6

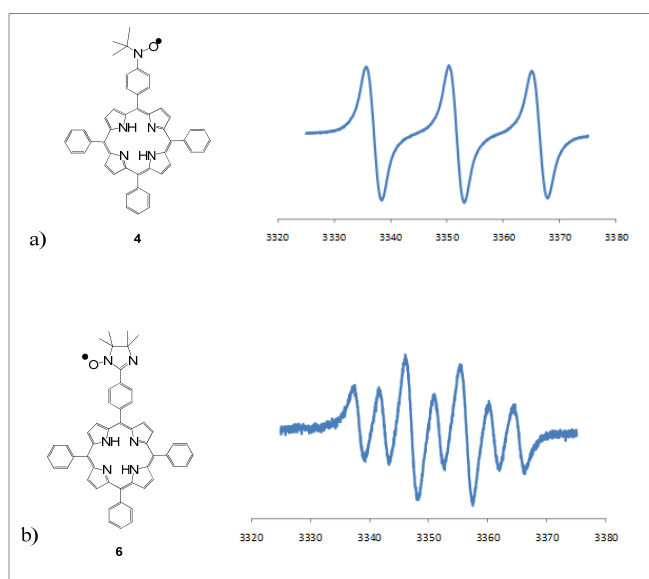


Figure 3.61: EPR solution spectra of a) mono tBuNO substituted porphyrin **4** (6.399 mW, 60 dB, 1G, 1 scan), b) mono imino nitroxide substituted porphyrin **6** (6.399 mW, 60 dB, 1G, 1 scan) at  $c = 1 \times 10^{-6} \text{ M}$  in  $\text{CHCl}_3$ .

Well resolved 3 lines ( $2nI+1=3$ ) and 7 lines for nonequivalent two imino nitroxide nitrogens in EPR spectra (Figure 3.36) resemble of mono radical porphyrins as expected. If it is necessary to remind once again, it is possible to convert nitronyl nitroxide to imino easily with presence of acid or long reaction time in air condition that over oxidation can occur. Thus in our case it was difficult to control nitronyl-imino conversion. In most case we obtained imino derivative.

### 3.4. Conclusion

- Result 1

Mono-**tBuNOP**, mono-**NITP** and mono-**IMIP** were obtained successfully and characterized without any doubt concerning the structure. Although we used the same synthetic pathway to obtain **1** (tetra- tBuNOP), **2** (tetra-NITP) and **3** (tetra-IMIP) the reactions were not so easy. Probably due to the multi-site reaction that complicated the lithium-halogen exchange mechanism, some more studies have to be done to clarify the relationship because of the different spectroscopic characterization and the ESR results.

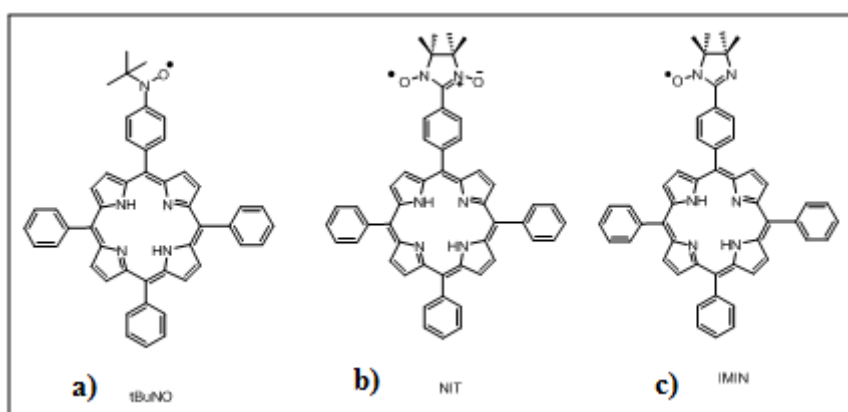


Figure 3.62: a) mono tBuNO, b) nitronyl(NIT), c) imino(IMI) nitroxide radical substituted porphyrins.

- Result 2

Novel nitronyl and imino nitroxide mono radical synthons (**9**, **10**, **11**) were obtained and characterized.

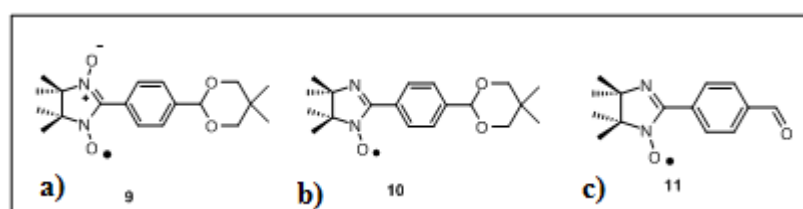


Figure 3.63: a,b) Nitronyl(**9,10**), c) imino(**11**) nitroxide mono radical synthons.

- Result 3

One can conclude that among the *meso*-position formylation methods, the Butyllithium/DMF formylation is the best way to get formyl porphyrin. Formylation reaction conditions were well optimized.

- Result 4

Microwave irradiation makes possible metallation of porphyrin macrocycle in short time with perfect yield.

- Result 5

For the first time, **ATPP** was well described and molecular structure was confirmed by a full characterization work. Metallated derivatives **ATPPCu(II)** and **ATPPMn(III)** were also synthesized for the first time.

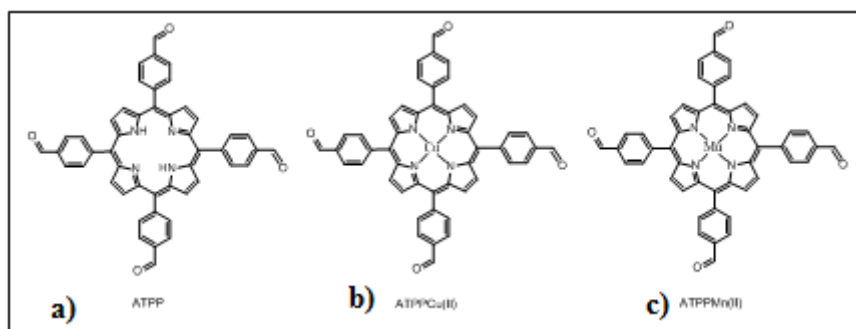


Figure 3.64: Molecular structure of a) **ATPP**, b) **ATPPCu(II)**, c) **ATPPMn(III)**.

- Result 6

Contrary to the reported literature work, we demonstrated it is disadvantageous to use Zn(II) protected porphyrin, and that the inner nitrogens were not involve in the halogen-lithium exchange reaction.

## 4. EXPERIMENTAL SECTION

### •General

Absorption and fluorescence spectra were recorded by using a Shimadzu 2101 UV-Visible spectrophotometer and a Varian Cary Eclipse spectrofluorometer, respectively. IR spectra were recorded between 4000 and 600  $\text{cm}^{-1}$  using a Perkin Elmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian 500 MHz spectrometer (with the deuterated solvents as the lock and tetramethylsilane as the internal reference). Mass spectra were acquired in linear modes with an average of 50 shots on a Bruker Daltonics Microflex mass spectrometer (Bremen, Germany) equipped with a nitrogen UV-Laser operating at 337 nm. MALDI MS spectra were obtained using 2,5-dihydroxybenzoic acid as the MALDI matrix. ESI MS analyzer was a Bruker Daltonics MicrOTOF mass spectrometer equipped with orthogonal electrospray ionization (ESI) source. The instrument was operated in positive or negative ion mode using a range of  $m/z$  50–3000. The instrument was calibrated with caffeine, Met-Arg-Phe-Ala acetate (MRFA), and Ultramark 1621 (all from Aldrich) in the mass range 195-1822 amu. The X-band EPR measurements were carried at ambient temperature on chloroform solution of tBuNO, nitronyl and imino nitroxide radicals. Column chromatographies were carried out on silica gel Merck-60 (43–63 mesh) and TLC on aluminum sheets precoated with silica gel 60F254 (Merck).

### • 2,3-dimethyl-2,3-dinitrobutane

40.8 g(1 mol) NaOH in 170 mL distilled water was put in a 1000 mL flask. The solution was placed in an ice-bath, then 90 mL(1 mol) of 2-nitropropane was added and stirred for 1h vigorously. 28 mL(0.54 mol) of bromine was added drop by drop and stirred for 1h. Then the temperature rose to room temperature. 320 mL of ethanol was added and refluxed for 3 hr. When heating was stopped white precipitate occurred immediately. 250 mL of water and ice was added. After filtration white

precipitate was washed with water. 95 g 2,3-dimethyl-2,3-dinitrobutane was obtained. Yield %54.

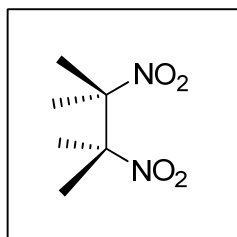


Figure 4.1: Molecular structure of 2,3-dimethyl-2,3-dinitrobutane.

- 2,3-bis(hydroxyamino)-2,3-dimethylbutane (**BHA**)

2,3-dimethyl-2,3-dinitrobutane (17.6 g, 0.1 mol) was dissolved in tetrahydrofuran (THF, 300 mL) and water (50 mL).  $\text{NH}_4\text{Cl}$  (43 g, 0.8 mol) in water (150 mL) was added to this solution drop by drop. The two-phase system was cooled in a ice bath (8 - 12 °C). Then, Zn powder (27 g) was added while the temperature was kept below 12°C. Stirring was continued for 90 min, and the flask was placed in a refrigerator (4 - 6 °C) over a night. Then, the mixture was filtered, the precipitate carefully washed with THF and the solution concentrated under vacuum until THF ceased to distill off. Then the solution was protected from air, and sodium carbonate (50 g) and sodium chloride (30 g) were added with cooling. Continuous extraction with chloroform (400 mL) was performed over night. A white powder was obtained and was stored in freezer. Yield 45%.

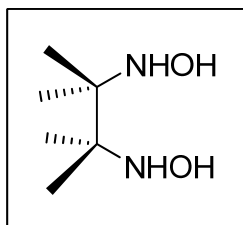


Figure 4.2: Molecular structure of **BHA**.

- 1-Bromo-4-(4,4-dimethyl-2,6-dioxan-1-yl)benzene

A solution of *p*-bromobenzaldehyde (5 g, 27 mmol), 2,2-dimethylpropane-1,3-diol

(5.6 g, 54 mmol), and p-TsOH( 16,6 mg) in Toluene (40 mL) was refluxed for 24 h using a Dean-Stark trap. After cooling, addition of NaHCO<sub>3</sub> (0.2 g) and stirring for 5 min. After filtration the solution was evaporated to dryness and recrystallisation with EtOH. Yield 90%. Mass (ESI-MS, m/z) : 271.0 [M+H]<sup>+</sup>, (C<sub>12</sub>H<sub>16</sub>BrO). <sup>1</sup>H NMR : δ (ppm), CDCl<sub>3</sub> 0.81 (s, 3H, CH<sub>3</sub>), 1.29 (s, 3H, CH<sub>3</sub>), 3.67 (d, 1H, CH<sub>acetyl</sub>), 3.76 (d, 1H, CH<sub>acetyl</sub>), 5.36(s, 1H, CH<sub>acetyl</sub>), 7.41 (d, 2H, CH<sub>phenyl</sub>), 7.50 (d, 2H, CH<sub>phenyl</sub>).

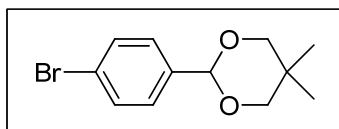


Figure 4.3: Molecular structure of 1-Bromo-4-(4,4-dimethyl-2,6-dioxan-1-yl)benzene.

- 4-(4,4-Dimethyl-2,6-dioxan-1-yl)benzaldehyde (Molecule 7)

A 2.5 M solution of *n*-BuLi in Hexane ( 10,8 mL, 16,2 mmol 2,2 eqv) was slowly added to a degassed solution of 1-Bromo-4-(4,4-dimethyl-2,6-dioxan-1-yl)benzene (2g, 7.38 mmol, 1 eqv) in dry THF (20 mL) at -50°C under nitrogen (g). After 45 min at -50 °C, the solution was allowed to warm to 0 °C over 1h and cooled again to -50 °C. 1.15 mL (2 eqv) of dry DMF was added and the resulting mixture allowed to warm to 0 °C over 1h. An aqueous 1M HCl solution (10 mL) was added and after stirring for 5 min the mixture was concentrated then aqueous layer was extracted with DCM, dried over NaSO<sub>4</sub> and evaporated to dryness. The white product was purified on silica gel with EtOAc/ Hexane 1:5 eluent system. Yield 80%. <sup>1</sup>H NMR : δ (ppm), CDCl<sub>3</sub>. 0.82 (s, 3H, CH<sub>3</sub>), 1.23 (s, 3H, CH<sub>3</sub>), 3.69 (d, 1H, CH<sub>acetyl</sub>), 3.78 (d, 1H, CH<sub>acetyl</sub>), 5.45(s, 1H, CH<sub>acetyl</sub>), 7.70 (d, 2H, CH<sub>phenyl</sub>), 7.91 (d, 2H, CH<sub>phenyl</sub>), 10.03 (s, 1H, COH).

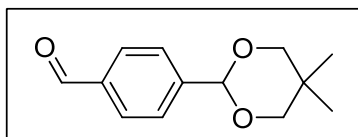


Figure 4.4: Molecular structure of molecule 7.

- 2-[4-(4,4-dimethyl-2,6-dioxan-1-yl) benzene]-4,4,5,5 tetramethylimidazoline 3-oxide 1-oxyl (Molecule **9**)

1,6 g (7.38 mol) 4-(4,4-Dimethyl-2,6-dioxan-1-yl)benzaldehyde and 1,6 g (7.8 mol) 2,3-bis(hydroxyamino)-2,3-dimethylbutane (ZnCl<sub>2</sub> complex) were dissolved in 40 ml MeOH and stirred at room temperature for 2 h. After evaporation of MeOH the crude product was dissolved in 40 mL of DCM and 20 mL of distilled water was added to the mixture. After addition of some drops of NaHCO<sub>3</sub> solution, saturated NaIO<sub>4</sub> solution in 40 mL water was added to the mixture in an ice-bath slowly. The color convert to intense blue. The mixture was extracted with DCM and dried over NaSO<sub>4</sub> then the solution was concentrated and nitronyl nitroxide was purified by column chromatograph with EtOAc/ Hexane (1:2) eluent system. Mass (ESI-MS, m/z) : 948 [M+H]<sup>+</sup>, (C<sub>19</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub>). EPR :  $c = 10^{-6}$ , 298 K,  $\nu = 9.404212$  GHz, 0.6421 mW, CHCl<sub>3</sub>. Five lines,  $g_{iso} = 2.0070$ ,  $a_N = 7.60$  G

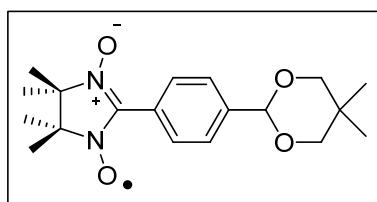


Figure 4.5: Molecular structure of molecule **9**.

- 2-[4-(4,4-dimethyl-2,6-dioxan-1-yl) benzene]-4,4,5,5 tetramethylimidazoline 1-oxyl (Molecule **10**)

0.5 g(1.5 mmol) molecule **9** was dissolved in DCM then 20 mL NaNO<sub>2</sub>(0.02 g) solution was added and the reaction mixture was placed in an ice-bath, stirred for 5 min. Then 10 mL 0.25 M HCl solution was added drop by drop, the color was converted to orange. The reaction mixture was extracted with DCM and washed with water many times. After drying with NaSO<sub>4</sub> the solvent was evaporated to dryness. The orange product was purified on silica gel with n-heptane/EtOAc (2:1) eluent system. Yield % 98. Mass (ESI-MS, m/z) : 333 [M+2H]<sup>+</sup>, (C<sub>19</sub>H<sub>29</sub>N<sub>2</sub>O). EPR :  $c = 10^{-6}$ , 298 K,  $\nu = 9.404158$  GHz, 6.421 mW, CHCl<sub>3</sub>. Seven lines,  $g_{iso} = 2.0064$ ,  $a_{N1} = 9.21$ ,  $a_{N2} = 4.30$ .

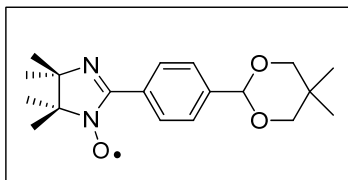


Figure 4.6: Molecular structure of molecule **10**.

- 4-(4,4-Dimethyl-2,6-dioxan-1-yl)benzaldehyde(Molecule **11**)

A solution of [4-(4,4-dimethyl-2,6-dioxan-1-yl)benzene]-4,4,5,5-tetramethylimidazoline-1-oxyl (molecule **10**) ( 0.03 g, 0.09mmol) in 10 mL of DCM was treated with TFA/water (1 mL, 1:1) to give a biphasic solution. After stirring at room temperature for 30 min-2h, DCM was added. The organic layer was washed with saturated aqueous NaHCO<sub>3</sub> and brine solution. Dried with NaSO<sub>4</sub>, concentrated and purified on silica gel with EtOAc to give yellow solid(**11**). Mass (ESI-MS, m/z) : 247 [M+2H]<sup>+</sup>, (C<sub>14</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>). EPR :  $c = 10^{-6}$ , 298 K,  $\nu = 9.404158$  GHz, 6.421 mW, CHCl<sub>3</sub>. Seven lines,  $g_{iso} = 2.0067$   $a_{N1} = 9.11$ ,  $a_{N2} = 4.20$ .

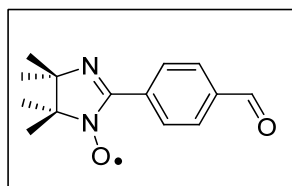


Figure 4.7: Molecular structure of molecule **11**.

- 2-Formyl-5,5-dimethyl-1,3-dioxane (**monoacetal**)

A mixture of glyoxal (2.5 g of 40 wt. % aqueous solution, 0.0175 mol, 1 eqv), 2,2-dimethyl-1,3-propanediol (1.82 g, 0.0175 mol, 1 eqv) and p-TsOH ( 0.065 g, 0.34 mmol) in 40 mL of Toluene was refluxed for 4 h with Dean-Stark trap. Then the reaction mixture was treated with solid NaHCO<sub>3</sub> (0.0625 g, 0.725 mmol) and filtered. The crude product was used for further reaction without purification.

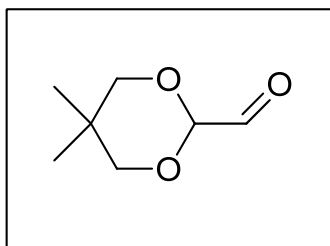


Figure 4.8: Molecular structure of **monoacetal**.

- 5-(5,5-dimethyl-1,3-dioxan-2-yl)dipyrromethane(**AcetDPM**)

The crude 2-Formyl-5,5-dimethyl-1,3-dioxane (**monoacetal**) was treated with pyrrole (55 mL, 0.86 mol 50 eqv) and  $\text{ICl}_3$  (0.190 g 0.86 mmol) was added and the mixture was stirred under nitrogen(g) at room temperature for 2 h. The reaction mixture was worked up by addition of NaOH (1.03 g, 25.75 mmol), after filtration, recovery of excess pyrrole from the filtrate, trituration of the resulting residue with hexane to remove traces of pyrrole. After evaporation of pyrrole chromatography work was done with EtOAc. Yield 23%.

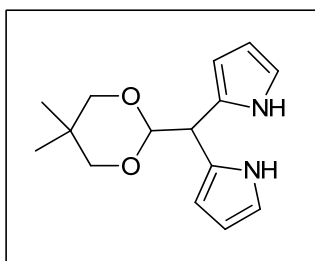


Figure 4.9: Molecular structure of **AcetDPM**.

- 5-(4-bromophenyl)-10,15,20-thiophenylporphyrin (**AB<sub>3</sub>BrP**)

0.92g(0.005 mol, 1 eqv.) 4-bromobenzaldehyde, 4.5 mL(0.045 mol, 9 eqv.) benzaldehyde were added to 200 mL refluxing propionic acid(Merck), then 3.5 mL (0.05 mol, 10 eqv.) pyrrole were added to the reaction mixture. After refluxing at 141 °C for 1h, the reaction mixture was cooled to room temperature. After filtration the filter cake was washed with methanol and hot water. 0.8 g the resulting molecules were purified on silica gel with n-Hexane/DCM 2:1, 1/1 eluent system, but **AB<sub>3</sub>BrP** + **TPP** could not separated because of polarity of two product were so

closed to each other. Yield total %10. Mass (MALDI-MS,  $m/z$ ) : 615.5  $[M+H]^+$  ( $C_{48}H_{30}N_4$ ), 691.1  $[M-H]^+$  ( $C_{44}H_{29}N_4Br$ ).

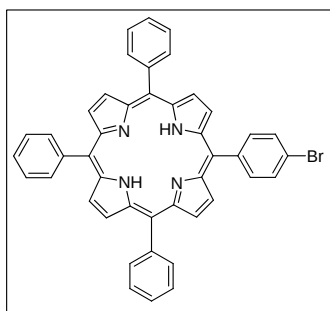


Figure 4.10: Molecular structure of **AB<sub>3</sub>BrP**.

• *meso*-tetrakis(4-bromophenyl)porphyrin (**TBrPP**)

3.5 mL (0.05 mol) pyrrole and 9 g(0.05 mol) 4-bromobenzaldehyde were added to 200 mL refluxing propionic acid(Merck). After refluxing at 141 °C for 1h, the reaction mixture was cooled to room temperature. The reaction was monitored with TLC (DCM), there was only purple target molecule, no impurities. After filtration the filter cake was washed with methanol and hot water. 3 g resulting molecule powder was purified on silica gel with n-Hexane/DCM 2:1, 1/1 eluent system. Yield %25.FT-IR : $\nu$  ( $cm^{-1}$ ). 3300 (NH), 2958 ( $CH_{Ar}$ ), 1467 ( $C=N$ ), 1388 ( $=C-N$ ), 1010 ( $C-H_{pyrrole}$ ), 964 porphyrin ring, 796 pyrrole ring, 726 (NH bending).  $^1H$  NMR :  $\delta$  (ppm),  $CDCl_3$ , -2.94 (s, 2H, NH), 7.88 (d, 8H,  $CH_{Ar-phenyl}$ ), 7.98 (d, 8H,  $CH_{Ar-phenyl}$ ), 8.76 (s, 8H,  $CH_{pyrrole}$ ).  $^{13}C$  NMR:  $\delta$  (ppm),  $CDCl_3$ , 118.08( $C_{meso}$ ), 121.85 ( $CH-C_2$ ), 129.42 ( $CH-C_\beta$ ), 134.80 ( $CH-C_3$ ), 139.07( $C-C_4$ ). UV-visible :  $\lambda$ , nm,  $CHCl_3$ , 418; 512; 547; 588; 644. Mass (ESI-MS,  $m/z$ ) : 930.6624  $[M+H]^+$ , ( $C_{44}H_{27}N_4Br_4$ ).

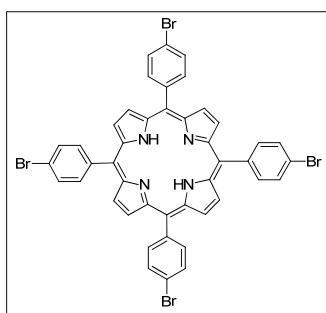


Figure: 4.11. Molecular structure of **TBrPP**.

- *meso*-tetrakis(4-bromophenyl)porphyrinato Zn(II) (**TBrPPZn**)

2.5 g **TBrPP** (2.69 mmol) and 0.6 g (2.69 mmol) Zn(OAc)<sub>2</sub> and 50 ml of DMF were placed in 100 mL of flask. The reaction was done with MW irradiation at 180 °C with 600 W power for 30 min. and monitored by TLC (DCM/n-Hexane 1/1). The reaction mixture was cooled to room temperature then the mixture was poured to the water drop by drop to precipitate the target molecule. After filtration the filter cake was dissolved in DCM and Na<sub>2</sub>SO<sub>4</sub> was added. After second filtration n-heptan was added then DCM n-heptan were removed by evaporation. The target molecule was purified on silica gel with DMC/n-Hexane 2/1, 1/1 eluent system, dried under vacuum over a night. Yield % 96. IR :  $\nu$  (cm<sup>-1</sup>). 2916 (CH<sub>Ar</sub>), 1479 (C=N), 1388 (=C-N), 1066 (C-H<sub>pyrrole</sub>), 997<sub>por. ring</sub>, 793<sub>pyr. ring</sub>. <sup>1</sup>H NMR :  $\delta$  (ppm), CDCl<sub>3</sub>, 7.84 (d, 8H, CH<sub>Ar</sub>-phenyl), 7.99 (d, 8H, CH<sub>Ar</sub>-phenyl), 8.87 (s, 8H, CH<sub>pyrrole</sub>). <sup>13</sup>C NMR:  $\delta$  (ppm), CDCl<sub>3</sub>, 129.81 (CH- C<sub>2</sub>), 131.99 (CH- C <sub>$\beta$</sub> ), 135.77 (CH- C<sub>3</sub>). UV-visible :  $\lambda$ , nm, CHCl<sub>3</sub>, 419; 545. Mass (ESI-MS, m/z) : 994.5598 [M+H]<sup>+</sup>, (C<sub>44</sub>H<sub>25</sub>N<sub>4</sub>Br<sub>4</sub>Zn).

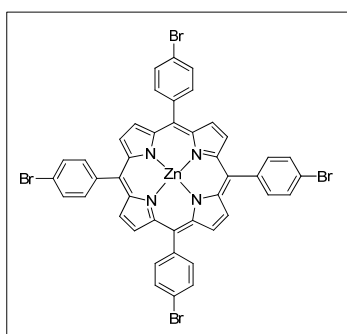


Figure 4.12: Molecular structure of **TBrPPZn**.

- *meso*-tetrakis(4-bromophenyl)porphyrinato Cu(II) (**TBrPPCu**)

0.02 g (0.027 mmol) **TPPBr** and 0.01 g (0.041 mmol, 1.5 eqv.) Cu(OAc)<sub>2</sub>.H<sub>2</sub>O was placed in flask containing 20 mL of dry DMF (Merk, septum bottle). The reaction was occurred with MW irradiation at 150 °C in 40 min. The reaction mixture was cooled to room temperature then the mixture was poured to the water. After filtration the filter cake was dissolved in DCM and Na<sub>2</sub>SO<sub>4</sub> was added. After evaporation of the solvent red-orange **ATPPCu(II)** porphyrin was purified by column chromatography with Hexane/ DCM 4:1, 1:1, DCM eluent system. Yield

% 62. UV-visible :  $\lambda$ , nm, CHCl<sub>3</sub>, 416; 548. Mass (MALDI-MS, m/z) : 993.697 [M+2H]<sup>+</sup>, (C<sub>44</sub>H<sub>26</sub>N<sub>4</sub>Br<sub>4</sub>Cu).

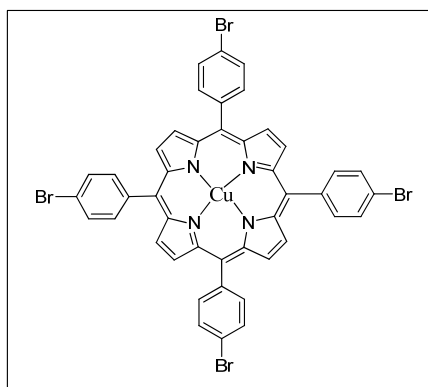


Figure 4.13: Molecular structure of **TBrPPCu**.

- *meso*-tetrakis(4-bromophenyl)porphyrinato Mn(III) (**TBrPPMn**)

0.01 g (0.0013 mmol) **TBrPP** and 0.03 g (0.013 mmol, 10 eqv.) dry Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O were refluxed in 20 mL (1 :1) chloroform/methanol . After 24 h the solvent was completely removed in a rotary evaporator then CH<sub>2</sub>Cl<sub>2</sub> was added. The solution was washed twice with water to remove excess of Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The 0.009 g green product was then purified by column chromatography on silica using DCM/Acetone 9 :1, 8:2, 5 :1, 1 :1 as eluent. Yield % 84. UV-visible :  $\lambda$ , nm, CHCl<sub>3</sub>, 478; 625. Mass (MALDI-MS, m/z) : 986.215[M+2H]<sup>+</sup>, (C<sub>44</sub>H<sub>27</sub>N<sub>4</sub>Br<sub>4</sub>Mn).

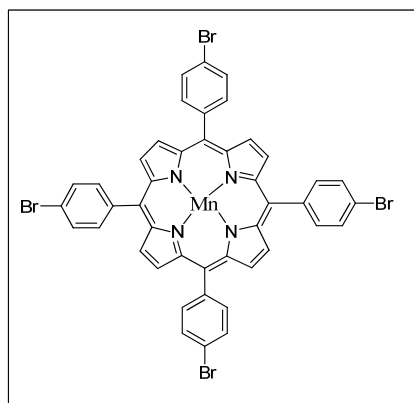


Figure 4.14: Molecular structure of **TBrPPMn**.

- 5-(4-formylphenyl)-10,15,20-triphenylporphyrin (**AB<sub>3</sub>AP**)

0.4 g (0.28 mmol) of **TPP** and **AB<sub>3</sub>BrP** porphyrin mixture was purged nitrogen(g) then vacuum for many times. Then 25 mL of dry diethylether was added by syring under nitrogen(g) at room temperature and continued bubbling with nitrogen(g). Purple color. Then the solution was placed in an acetone-ice bath at -15 °C bath for 10 min. Then 5 mL of n-buthyllithium was added by syring under nitrogen(g). Green resulting mixture was stirred for 3 hr. Then 5 ml of dry DMF was added. The cooling bath was removed and the reaction mixture was stirred for 3 h more, dark blue colour. At room temperature 250 mL of HCl % 5 was added and vigorously stirred for 15 min. The purple colour mixture was neutralised by NH<sub>4</sub>OH. Then the resulting emulsion was extracted with chloroform, dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness at 45 °C. 0.07 g AB<sub>3</sub>A free porphyrin was separated by column chromatography diethyl ether/ DCM 1:9. At the end of the reaction TPP was taken back without reacting. Yield % 35. <sup>1</sup>H NMR : δ (ppm), CDCl<sub>3</sub>, -2.84 (s, 2H, NH), 7.66 (m, 15H, CH<sub>Ar</sub>-phenyl), 7.66 (d, 2H, CH<sub>a</sub>-phenyl), 8.13 (d, 2H, CH<sub>b</sub>-phenyl), 8.21(d, 2H, CH<sub>c</sub>-pyrrole), 8.32(d, 2H, CH<sub>d</sub>-pyrrole), 8.71 (d, 2H, CH<sub>e</sub>-pyrrole), 8.79 (d, 2H, CH<sub>f</sub>-pyrrole), 8.78 (s, 2H, CH<sub>g</sub>-pyrrole), 10.31(s, H, COH). UV-visible : λ, nm, CHCl<sub>3</sub>, 419; 516; 550; 591; 648. Mass (MALDI-MS, m/z) : 643.310 [M+H]<sup>+</sup>, (C<sub>46</sub>H<sub>30</sub>N<sub>4</sub>O).

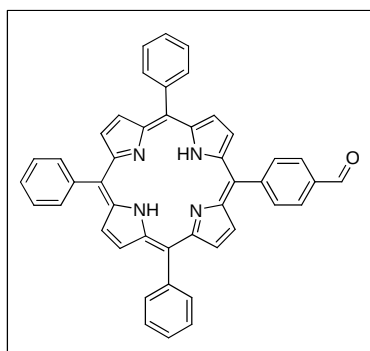


Figure 4.15: Molecular structure of **AB<sub>3</sub>AP**.

- *meso*-tetrakis(4-formlyphenyl)porphyrin (**ATPP**)

400 mg *meso*-tetrakis(4-bromophenyl)porphyrin **TBrPP** (0.4 mmol) was purged nitrogen(g) then vacuum for many times. Then 50 mL of dry diethylether was added

by syring under nitrogen(g) at room temperature and continued bubbling with nitrogen(g), purple color. Then the solution was placed in an liquid nitrogen-ice bath at -50 °C for 10 min. Then 5 mL(6,25 mmol) of n-buthyllithium was added by syring under nitrogen(g). Green resulting mixture was stirred for 3 hr. Then 5 ml(37,5 mmol) of dry DMF (Merck) was added at -50 °C. The cooling bath was removed and the dark blue reaction mixture was stirred for 3 h more. At room temperature 250 mL of HCl % 5 was added and vigorously stirred for 15 min. The mixture was neutralised by NH<sub>4</sub>OH. Then the resulting emulsion was extracted with chloroform, dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness at 45 °C. Tetra formyl (0.2 g) substituted free base poprhyrin was separated by coloumn chromatography diethyl ether/ DCM 1:9 elunet system. Yield 80%. FT-IR : $\nu$  (cm<sup>-1</sup>), 3322 (NH), 2932 (CH<sub>Ar</sub>), 1694(C=O), 1472 (C=N), 1382 (=C-N), 1170(CH<sub>pyrrole</sub>), 966 porphyrin ring , 804 pyrrole ring, 730 (NH bending). <sup>1</sup>H NMR :  $\delta$  (ppm), CDCl<sub>3</sub>, -2.85 (s, 2H, NH), 8.25 (d, 8H, CH<sub>Ar</sub>-phenyl), 8.32 (d, 8H, CH<sub>Ar</sub>-phenyl), 8.76 (s, 8H, CH<sub>pyrrole</sub>), 10.33(s, H, COH). UV-visible :  $\lambda$ , nm, CDCl<sub>3</sub>, 420; 517; 552; 592; 647. Mass (MALDI-MS, m/z) : 727.415 [M+H]<sup>+</sup>, (C<sub>48</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>).

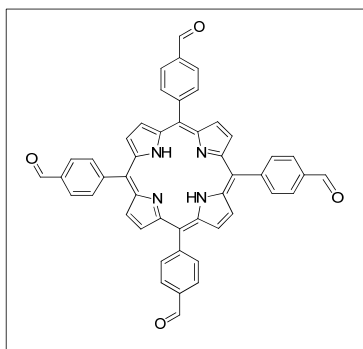


Figure 4.16: Molecular structure of **ATPP**.

• *meso*-tetrakis(4-formylphenyl)porphyrinato Cu(II) (**ATPPCu(II)**)

0.02 g ( 0.027 mmol) **ATPP** and 0.01 g (0.041 mmol, 1.5 eqv.) Cu(OAc)<sub>2</sub>.H<sub>2</sub>O was placed in flask containing 20 mL of dry DMF(Merk, septum bottel). The reaction was occurred with MW irradiation at 150 °C in 40 min. Red-orange **ATPPCu(II)** porphyrin was purified by coloumn chromatography Hexane/ DCM with 4:1, 1:1, DCM eluent system. Yield % 62. UV-visible :  $\lambda$ , nm, CHCl<sub>3</sub>, 419; 540. Mass (MALDI-MS, m/z) : 788.057 [M+H]<sup>+</sup>, (C<sub>48</sub>H<sub>29</sub>N<sub>4</sub>O<sub>4</sub>Cu).

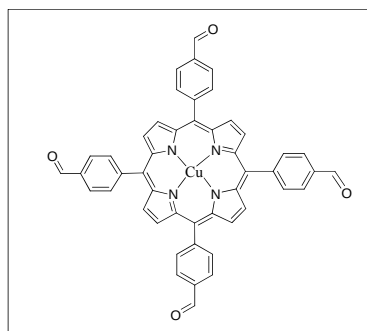


Figure 4.17: Molecular structure of **ATPPCu(II)**.

- *meso*-tetrakis(4-formylphenyl)porphyrinato Mn(III) (**ATPPMn(III)**)

0.01 g (0.0013 mmol) **ATPP** and 0.03 g (0.013 mmol, 10 eqv.) dry  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  were refluxed in 20 mL (1 :1) chloroform/methanol . After 24 h the solvent was completely removed on a rotary evaporator then  $\text{CH}_2\text{Cl}_2$  was added. The solution was washed twice with water to remove excess of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ , and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The 0.009 g green product was then purified by column chromatography on silica using DCM/Acetone 9 :1, 8:2, 5 :1, 1 :1 as eluent. Yield % 84. UV-visible :  $\lambda$ , nm,  $\text{CHCl}_3$ , 417; 618. Mass (MALDI-MS,  $m/z$ ) : 780.078  $[\text{M}+\text{H}]^+$ , ( $\text{C}_{48}\text{H}_{29}\text{N}_4\text{O}_4\text{Mn}$ ).

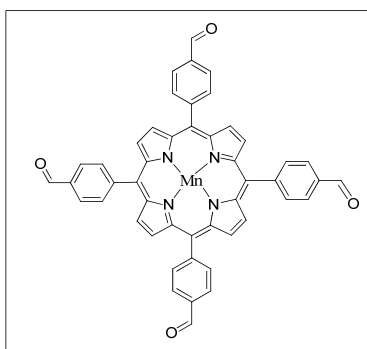


Figure 4.18: Molecular structure of **ATPPMn(III)**.

- *meso*-tetrakis-[4-(*N*-*tert*-buthyl-*N*-oxyamino)phenyl]porphyrin (Molecule **1**)

Step 1: 200 mg (0.2 mmol) *meso*-tetrakis(4-bromophenyl)porphyrin **TBrPP** was purged nitrogen(g) then vacuum for many times. Then 50 mL of dry diethylether was added by syring under nitrogen(g) at room temperature and continued bubbling with

nitrogen(g). Then the purple solution was placed in an acetone-liquid nitrogen bath (-78°C) for 10 min. Then 2.5 mL of n-butyllithium solution was added by syringe under nitrogen(g). The green mixture was warmed slowly at room temperature over 1 h.

Step 2: 0.522 g (3 mmol) of 2-methyl-2-nitrosopropane(dimer) was placed in a 50 mL of Schlenk and 10 mL of dry diethylether was added under nitrogen(g). After two minutes the color of mixture converted to blue which is the color of monomer 2-methyl-2-nitrosopropane. Blue solution was added to the green solution at -78 °C under nitrogen(g). After one hour the color of mixture was converted to red/brown. Then the reaction mixture was allowed to room temperature and stirred over night. The reaction was monitored with TLC system DCM/Hexane 1:1. 20 mL of saturated aqueous ammonium chloride solution was added to the reaction mixture. Then the organic phase extracted with diethyl ether and dried with Na<sub>2</sub>SO<sub>4</sub>, without purification the compound was used for the next Step 3.

Step 3: *meso*-tetrakis[4-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]porphyrin was dissolved in 40 mL of CHCl<sub>3</sub>. 1.5 g NaIO<sub>4</sub> was dissolved in 40 mL of water. Then NaIO<sub>4</sub> solution was added to the first mixture and stirred very strongly for 10 min. The reaction was monitored with TLC then stirred for more 1 hr. The green mixture was extracted with DCM for many times. Organic phase was combined and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and solvent was evaporated. The chromatography work was done with DCM then second chromatography work was done with n-heptane/EtOAc eluent system (9:1, 4:1, 1:1). After evaporation of the solvent, TLC (n-heptane/DCM 2:1) was performed to identify the radicals formed. The spots were identified as mixture of more than 8 radicals and non radical porphyrins. Only mono and di radicals could be identified by EPR studies. UV-visible :  $\lambda$ , nm, CHCl<sub>3</sub>, mono tBuNOP: 420; 519; 555; 594; 659. di tBuNOP: 418; 512, 544, 586, 646. ESR :  $c = 10^{-6}$ , 298 K,  $\nu = 9.404158$  GHz, 6.421 mW, CHCl<sub>3</sub>, mono tBuNOP : 3 lines,  $g_{iso}=2.0062$ ,  $a_N = 7.38$ .  $c = 10^{-6}$ , 298 K,  $\nu = 9.404158$  GHz, 6.421 mW, CHCl<sub>3</sub>, di tBuNOP: 5 lines,  $g_{iso}=2.0063$ ,  $a_N = 7.36$ .

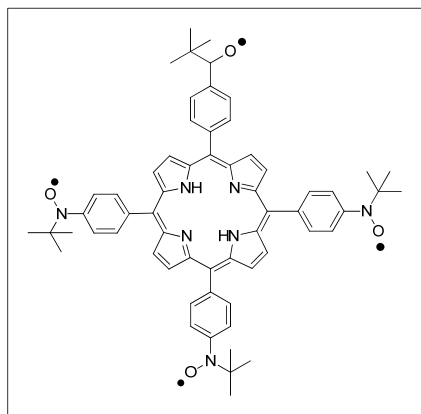


Figure 4.19: Molecular structure of **1**.

• *meso*-tetrakis(4,4,5,5-tetramethyl-1-oxyl-3-oxide-2-phenyl imidazole)porphyrin (Molecule 2)

Step 1: 0,03 g (0,04 mmol) *meso*-tetrakis(4-formylphenyl)porphyrin **ATPP** was dissolved in 40 mL of methanol then 0.06 g(0.016 mmol) 2,3-bis(hydroxylamine)-2,3-dimethylbutane (**BHA**) was added and reaction mixture was refluxed over night and protected from light. Then the reaction mixture was cooled to room temperature, and methanol was evaporated. Because of instability of the molecule, the purple residue was used for last oxidation step without purification and characterization.

Step 2: The purple residue was dissolved in 30 mL of DCM and 15 mL of distilled water was added to the solution. After addition of some drops of concentrated NaHCO<sub>3</sub> solution, the reaction mixture was stirred for 5 min. 30 mL of NaIO<sub>4</sub> solution (0.25 g 1.2 mmol, 4 eqv) was added slowly to the reaction mixture and the color of solution converted to red/purple color immediately. After stirring for 5 min the mixture was extracted with DCM, dried over Na<sub>2</sub>SO<sub>4</sub> and the residue was chromatographed on silica with a mixture (1:2) Ethyl acetate and Hexane. After evaporation of the solvent, TLC (-heptane/DCM 2:1) was performed to identify the radicals formed. The spots were identified as mixture of not only nitronyl and imino radicals but also non radical porphyrins. Only mono nitronyl nitroxide radical could be identified by EPR studies. UV-visible :  $\lambda$ , nm, CHCl<sub>3</sub>: 427; 519; 558; 599; 625. EPR :  $c = 10^{-6}$ , 298 K,  $\nu = 9.408191$  GHz, 6.406 mW, CHCl<sub>3</sub>: 5 lines  $g_{iso}=2.0063$ ,  $a_N = 7.39$

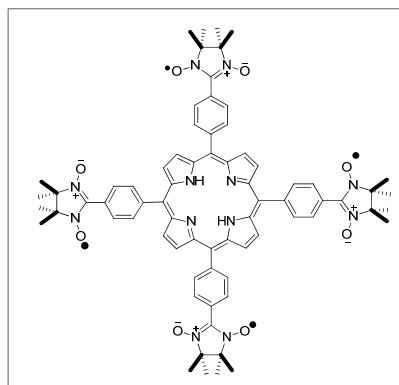


Figure 4.20: Molecular structure of 2.

- *meso*-tetrakis(4,4,5,5-tetramethyl-1-oxyl-2-phenyl imidazole)porphyrin (Molecule 3).

Step 1: 0,064 g (0,08 mmol) *meso*-tetrakis(4-formylphenyl)porphyrin **ATPP** was dissolved in 40 mL of methanol then 0.06 g(0.016 mmol) 2,3-bis(hydroxylamine)-2,3-dimethylbutane **BHA** was added and reaction mixture was refluxed over night and protected from light. Then the reaction mixture was cooled to room temperature and methanol was evaporated.

Step 2: The purple residue was dissolved in 40 mL of DCM and 15 mL of distilled water was added to the solution. After addition of some drops of concentrated NaHCO<sub>3</sub> solution, the reaction mixture was stirred for 5 min. NaIO<sub>4</sub> solution (0.25 g 1.2 mmol, 4 eqv) was added slowly to the reaction mixture and the color of solution converted to red/purple color immediately. After stirring for 5 min the mixture was extracted with DCM, dried over Na<sub>2</sub>SO<sub>4</sub> and solvent was evaporated.

Step 3: The crude product from step 2 was dissolved in 20 mL of DCM then 20 mL NaNO<sub>2</sub> (0.03 g) solution was added and the reaction mixture was placed in ice-bath, stirred for 5 min. Then 10 mL 0,25 M HCl solution was added drop by drop, the color was converted to green. The reaction mixture was extracted with DCM and washed with water many times. The color was converted purple again. After drying with Na<sub>2</sub>SO<sub>4</sub> the solvent was evaporated to dryness. with this method all nitronyl nitroxide radicals were converted to imino nitroxide porphyrins. After evaporation of the solvent, TLC (n-heptane/DCM 2:1) was performed to identify the radicals formed. The spots were identified as mixture of mono imino radical porphyrin which

were characterised by EPR spectroscopy. UV-visible :  $\lambda$ , nm, CHCl<sub>3</sub>: 428; 522; 559; 599; 654. EPR:  $c = 10^{-6}$ , 298 K,  $\nu = 9.408191$  GHz, 6.406 mW, CHCl<sub>3</sub>: 7 lines,  $g_{iso}=2.0067$ ,  $a_{N1} = 9.17$ ,  $a_{N2} = 4.33$ .

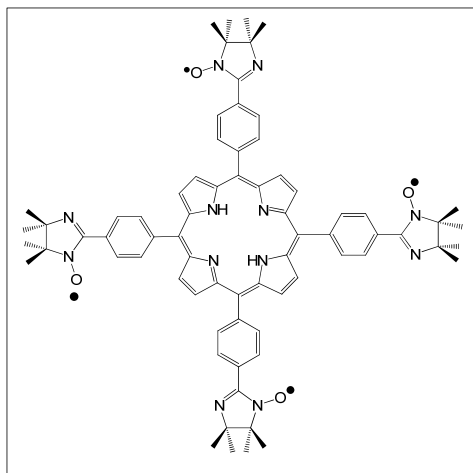


Figure 4.21: Molecular structure of **3**.

- 5-(4-(*N*-*tert*-buthyl-*N*-oxyamino)]-10,15,20-thriphenyl-porphyrin (Molecule **4**)

Step 1: 200 mg (0.2 mmol) 5-(4-bromophenyl)-10,15,20-triphenyl porphyrin **AB<sub>3</sub>BrP** was purged nitrogen(g) then vacuum for many times. Then 50 mL of dry diethylether was added by syreng under nitrogen(g) at room temperature and continued bubling with nitrogen(g). Then the purple solution was placed in an acetone-liquide nitrogen bath(-78°C) for 10 min. Then 2.5 mL of *n*-buthyllithium solution was added by syreng under nitrogen(g). The green mixture was warmed slowly at room temperature over 1 h.

Step 2: 0.522 g (3 mmol) of 2-methy-2-nitrosopropane(dimer) was placed in a 50 mL of schlenk and 10 mL of dry diethylether was added under nitrogen(g). After two minutes the color of mixture converted to blue which is the color of monomer 2-methyl-2-nitrosopropane. Blue solution was added to the green solution at -78 °C under nitrogen(g). After one hour the color of mixture was converted to red/brown. Then the reaction mixture was allowed to room temperature and stirred over night. The reaction was monitored with TLC system DCM/Hexane 1:1. 20 mL of saturated aqua ammonium chloride solution was added to the reaction mixture. Then the organic phase extracted with diethyl ether and dried with Na<sub>2</sub>SO<sub>4</sub>, without purification the compound was used for the next Step 3.

Step 3: 5-[4-(*N-tert*-buthyl-*N*-hydroxyamino)-10,15,20-triphenyl]porphyrin was dissolved in 40 mL of CHCl<sub>3</sub>. 1,5 g NaIO<sub>4</sub> was dissolved in 40 ml of water. Then NaIO<sub>4</sub> solution was added to the first mixture and stirred very strongly for 10 min. The reaction was monitored with TLC then stirred for more 1 hr. The green mixture was extracted with DCM for many times. Organic phase was combined and dried over NaSO<sub>4</sub>, filtered and solvent was evaporated. The chromatography work was done with DCM then second chromatography work was done with n-heptane/EtOAc eluent system (9:1, 4:1, 1:1). After evaporation of the solvent, TLC (n-heptane/DCM 2:1) was performed to identify the radicals formed. The spots were identified as mixture of more than 5 radicals and non radical porphyrins. mono radical was identified by EPR study. UV-visible :  $\lambda$ , nm, CHCl<sub>3</sub>: 420; 522; 556; 596; 654. ESR :  $c = 10^{-6}$ , 298 K,  $\nu = 9.404158$  GHz, 6.421 mW, CHCl<sub>3</sub>: 3 lines,  $g_{iso}=2.0062$ ,  $a_N = 7.38$ .

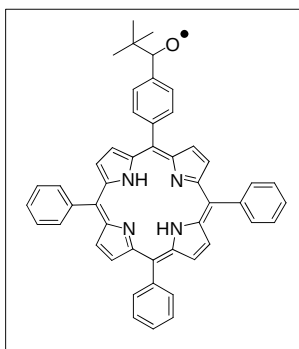


Figure 4.22: Molecular structure of **4**.

- 5-[4 (4,4,5,5-tetramethyl-1-oxyl-2-phenyl imidazole)]-10,15,20-thriphenyl-porphyrin (Molecule **6**)

Step 1: 0.01 g (0.015 mmol) 5-(4-formylphenyl)-10,15,20-triphenylporphyrin (**AB<sub>3</sub>AP**) was dissolved in 20 mL of methanol then 0.01 g (0.016 mmol, 1.5 eqv.) 2,3-bis(hydroxylamine)-2,3-dimethylbutane was added and reaction mixture was refluxed over night and protected from light. Then the reaction mixture was cooled to room temperature and methanol was evaporated.

Step 2: The purple residue was dissolved in 20 mL of DCM and 15 mL of distilled water was added to the solution. After addition of some drops of concentrated NaHCO<sub>3</sub> solution, the reaction mixture was stirred for 5 min. NaIO<sub>4</sub>

solution (0.0125 g 0.6 mmol, 2 eqv) was added slowly to the reaction mixture and the color of solution converted to red/purple color immediately. After stirring for 5 min the mixture was extracted with DCM, dried over NaSO<sub>4</sub> and solvent was evaporated.

Step 3: 0.01 g of crude mixture from step 2 was dissolved in 20 mL of DCM then 20 mL NaNO<sub>2</sub> (0.03 g) solution was added and the reaction mixture was placed in ice-bath, stirred for 5 min. Then 10 mL 0.25 M HCl solution was added drop by drop, the color was converted to green. The reaction mixture was extracted with DCM and washed with water many times. The color was converted purple again. After drying with NaSO<sub>4</sub> the solvent was evaporated to dryness. Imino nitroxide substituted porphyrin were characterised with EPR spectroscopy. UV-visible :  $\lambda$ , nm, CHCl<sub>3</sub>: 420; 522; 556; 596; 654. EPR :  $c = 10^{-6}$ , 0.6mw-20ms, -1G, CHCl<sub>3</sub>: 7 lines,  $g_{iso} = 2.0072$ ,  $a_{N1} = 9.15$ ,  $a_{N2} = 4.3$

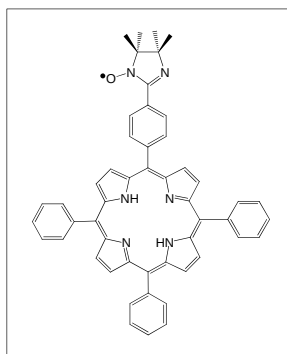


Figure 4.23: Molecular structure of **6**.

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## **BIOGRAPHY**

Emel ÖNAL was born in 1981 in Turgutlu, Turkey. She obtained her B.S. degree in Chemistry from Uludağ University in 2004, she then moved to Gebze Institute of Technology(GIT) to begin her graduate study under the supervision of Asst. Prof. Dr. Catherine HIREL. Then she obtained her master degree in 2009. Her current research interests include design, synthesis, and magnetic properties of porphyrin derivatives.

## APPENDICES

### Appendix A: Published work

Önal E., Yerli Y., Cosut B., Pilet G., Ahsen V., Luneau D., Hirel C.,(2014), “Nitronyl and Imino Nitroxide Free Radicals as Precursors of Magnetic Phthalocyanine and Porphyrin Building Blocks”, New Journal of Chemistry,38, (9),4440-4447.

### Appendix B: Spectra

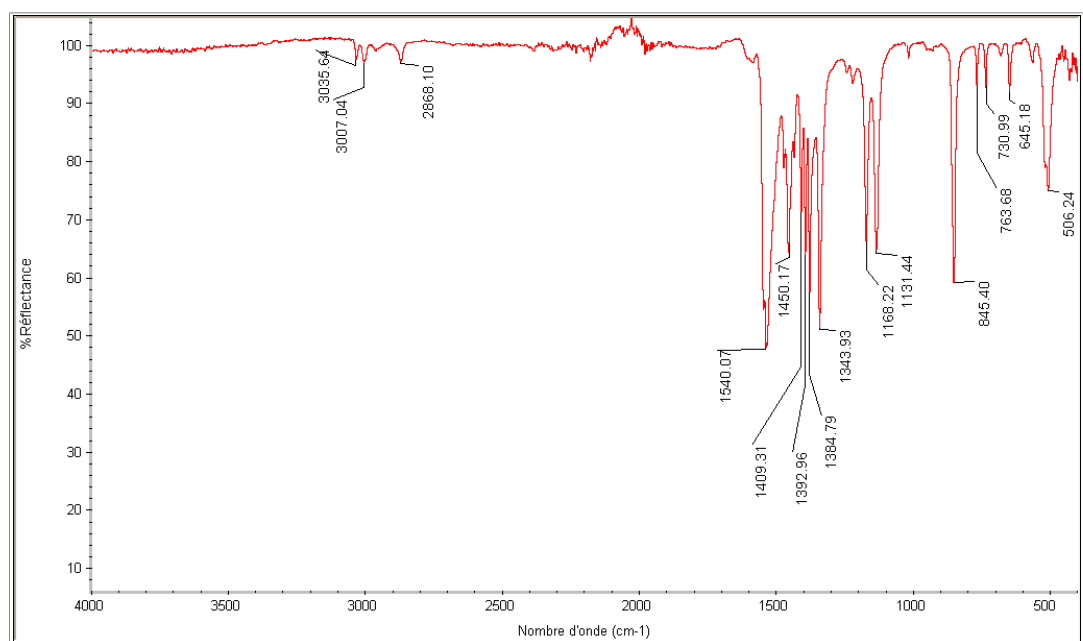


Figure B1.1: IR spectrum of 2,3-dimethyl-2,3-dinitrobutane.

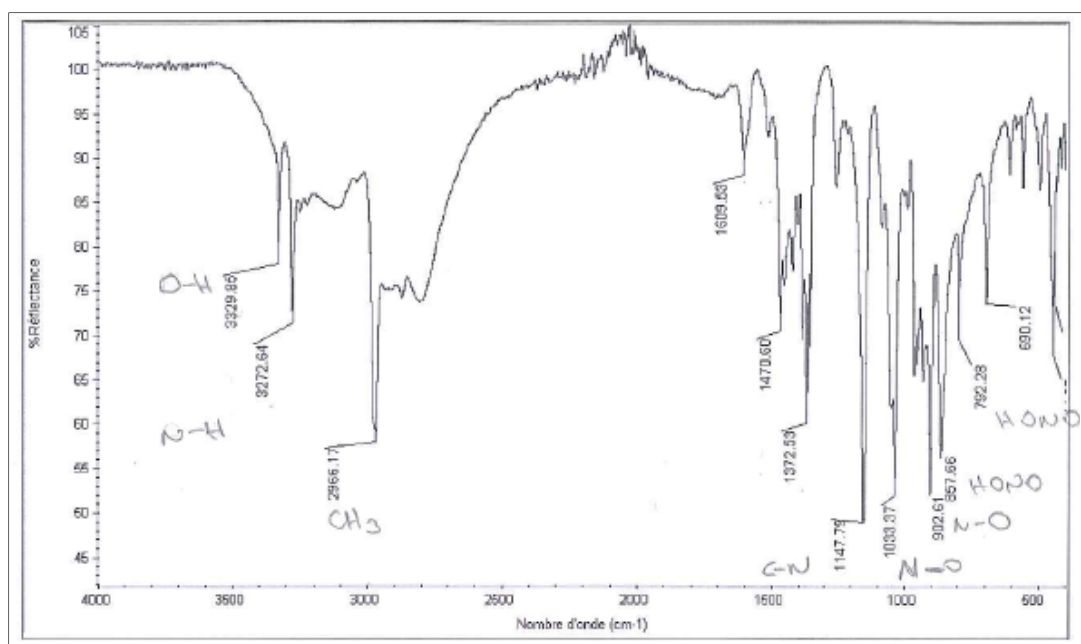


Figure B1.2: IR spectrum of 2,3-bis(hydroxyamino)-2,3-dimethylbutane (BHA).

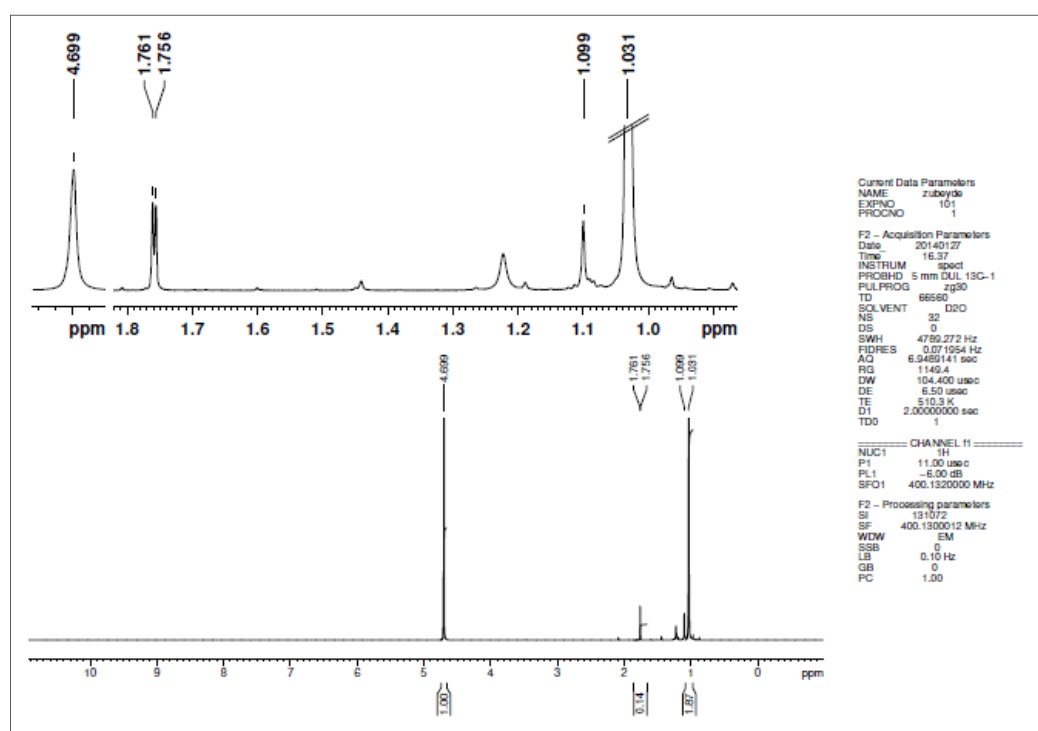


Figure B1.3:  $^1\text{H}$  NMR spectrum of 2,3-bis(hydroxyamino)-2,3-dimethylbutane (BHA) in  $\text{D}_2\text{O}$ .

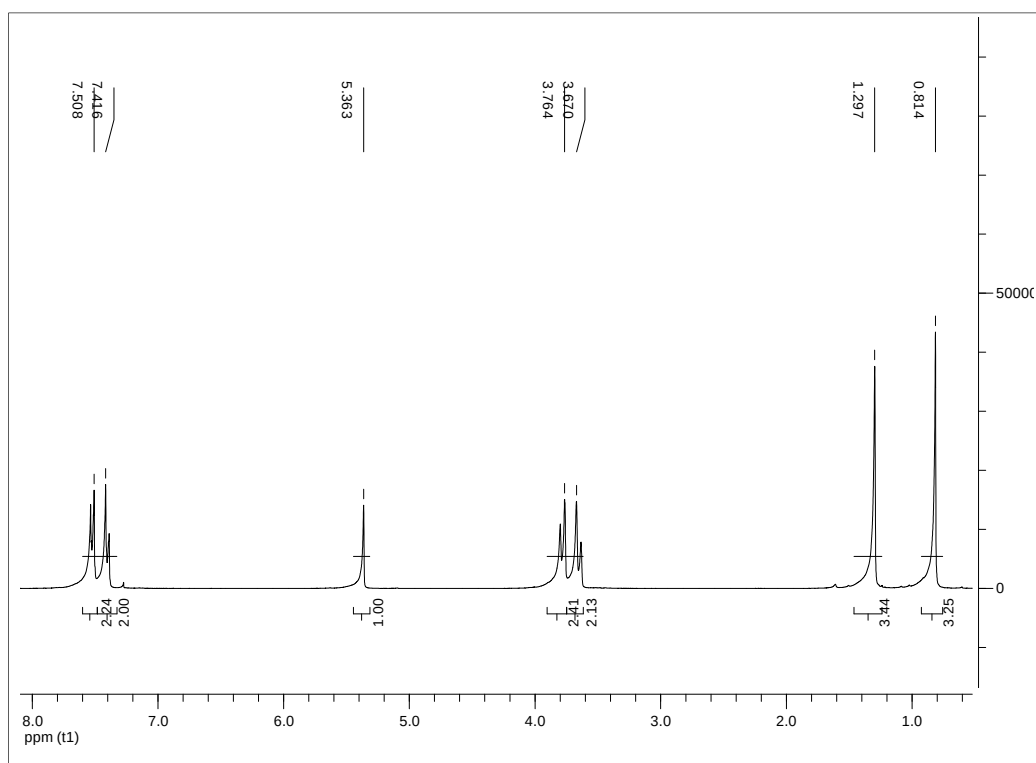


Figure B1.4:  $^1\text{H}$  NMR spectrum of 1-Bromo-4-(4,4-dimethyl-2,6-dioxan-1-yl)benzene in  $\text{CDCl}_3$ .

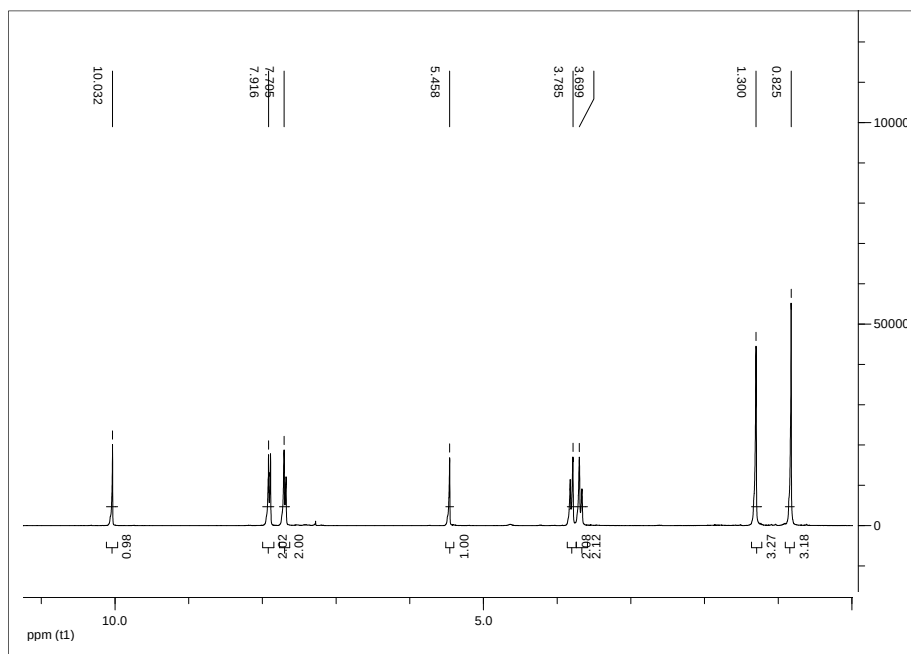


Figure B1.5:  $^1\text{H}$  NMR spectrum of 1-Bromo-4-(4,4-dimethyl-2,6-dioxan-1-yl)benzaldehyde in  $\text{CDCl}_3$ .

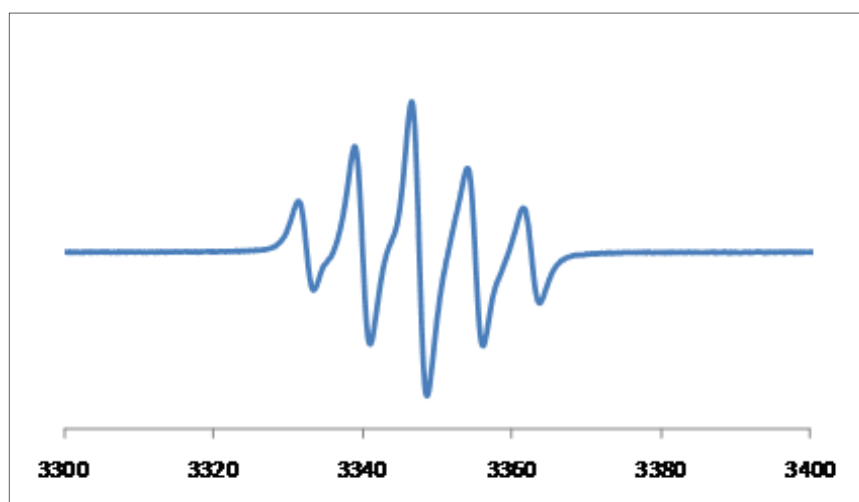


Figure B1.6: EPR spectrum of **9** at  $c = 1 \times 10^{-6}$  M in  $\text{CHCl}_3$  4.028 mW, 60 dB, 1G, 1 scan.

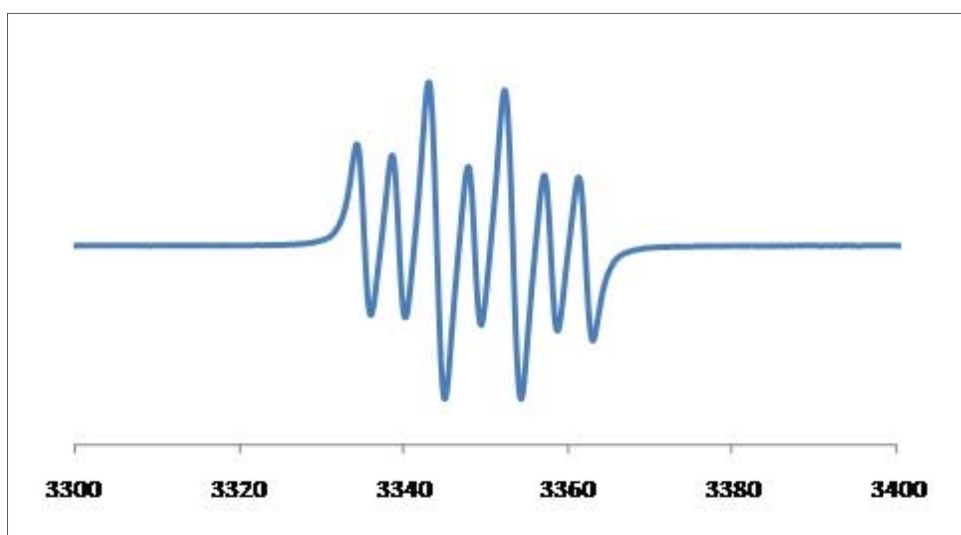


Figure B1.7: EPR spectrum of (Iminacet) at  $c = 1 \times 10^{-6}$  M in  $\text{CHCl}_3$  4.028 mW, 60 dB, 1G, 1 scan.

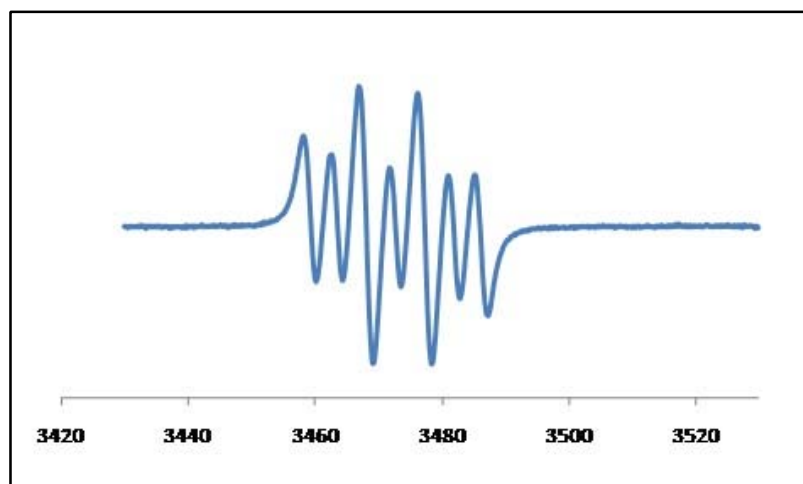


Figure B1.8: EPR spectrum of **11** at  $c = 1 \times 10^{-6}$  M in  $\text{CHCl}_3$  4.028 mW, 60 dB, 1G, 1 scan.

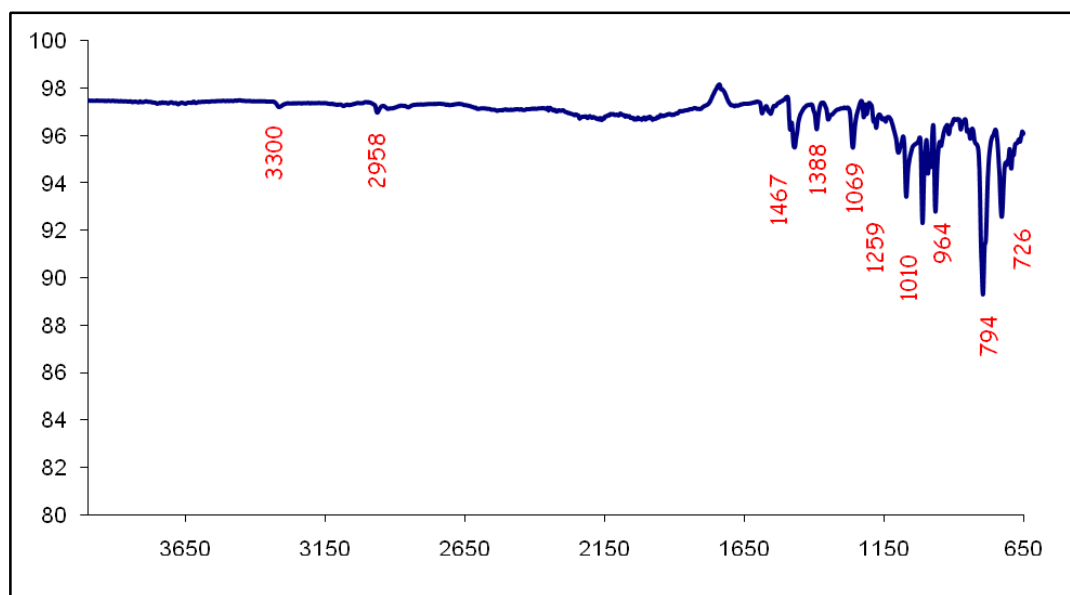


Figure B1.9: IR spectrum of *meso*-tetra(4-bromophenyl)porphyrin (TBrPP).

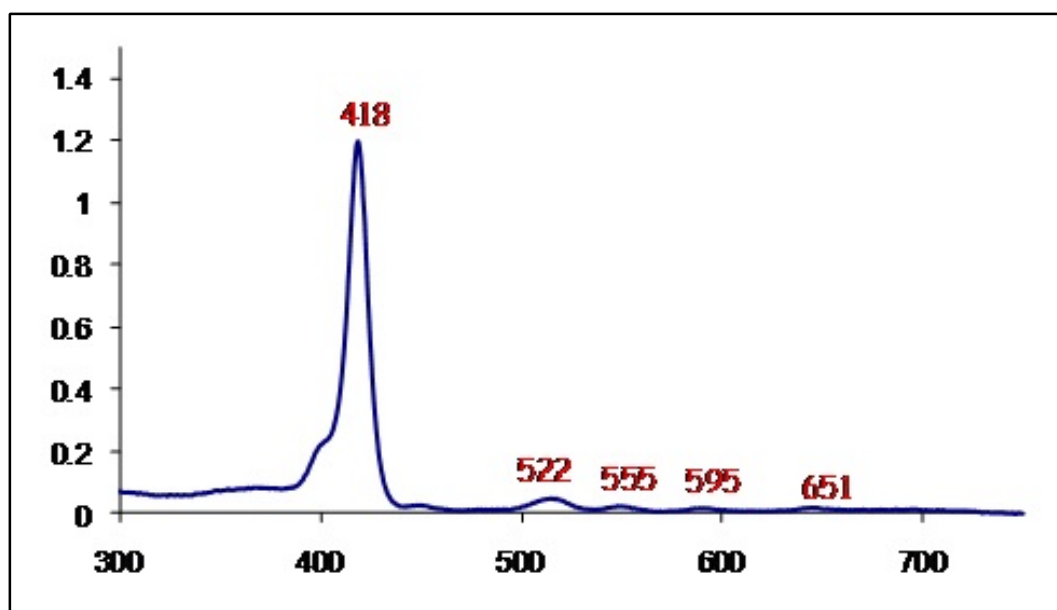


Figure B1.10: UV-Vis spectrum of *meso*-tetra(4-bromophenyl)porphyrin (TBrPP) in  $\text{CHCl}_3$ .

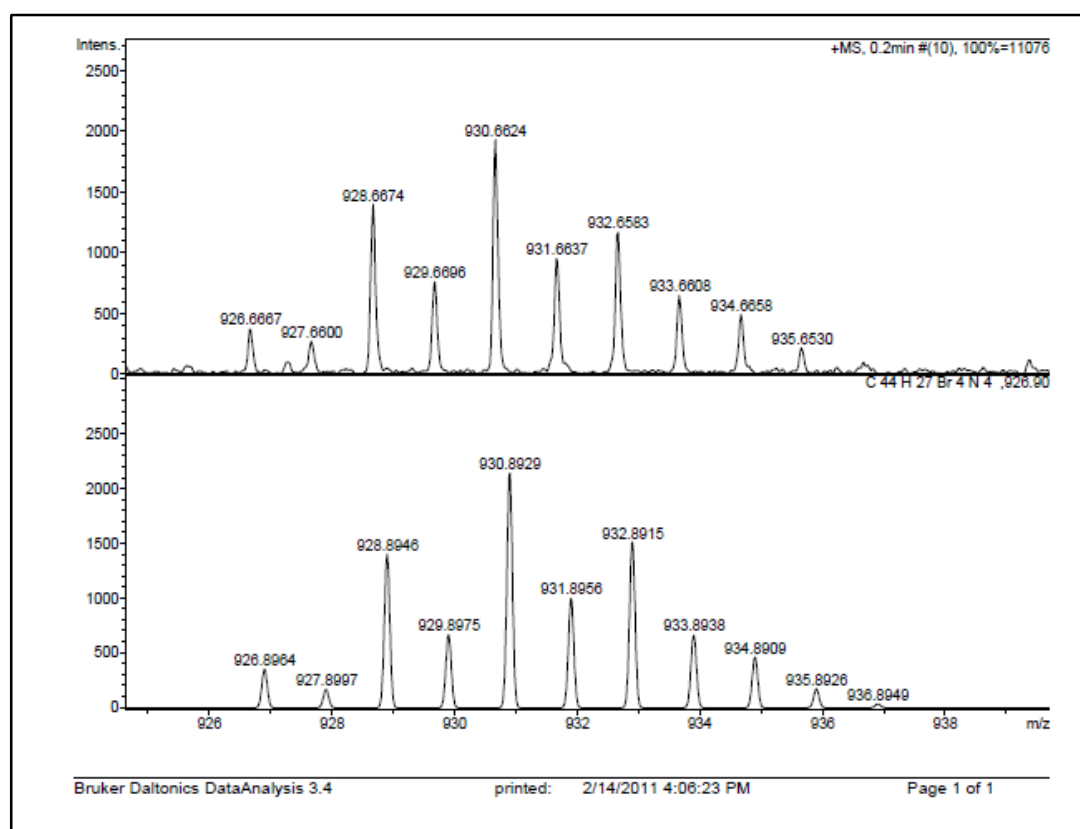


Figure B1.11: ESI-MS spectrum of *meso*-tetra(4-bromophenyl)porphyrin (TBrPP).

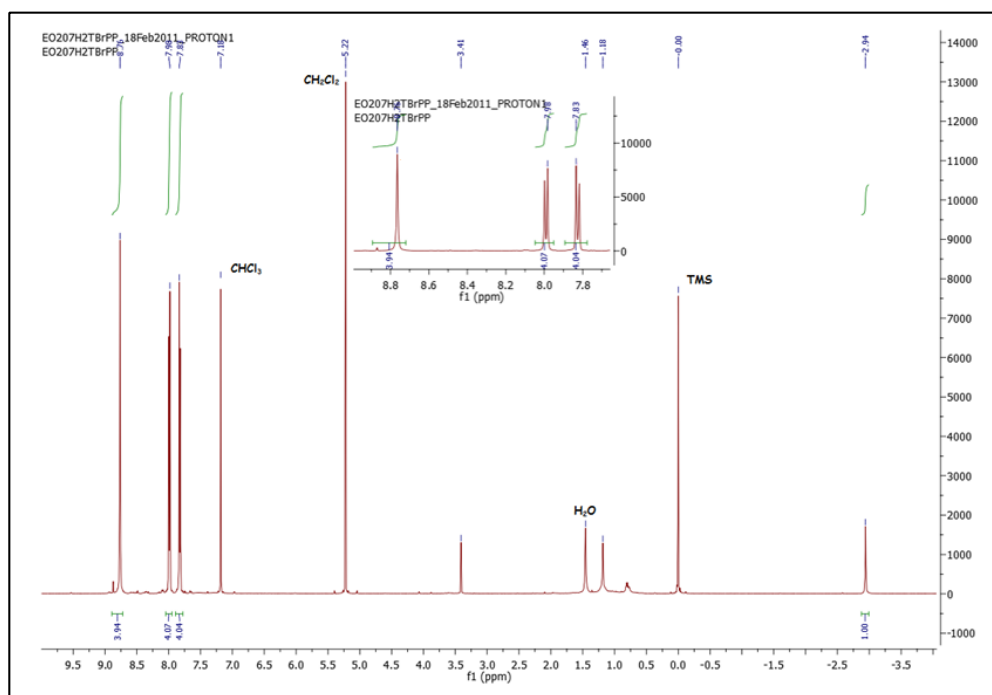


Figure B1.12:  $^1\text{H}$  NMR spectrum of *meso*-tetra(4-bromophenyl)porphyrin (TBrPP) in  $\text{CDCl}_3$ .

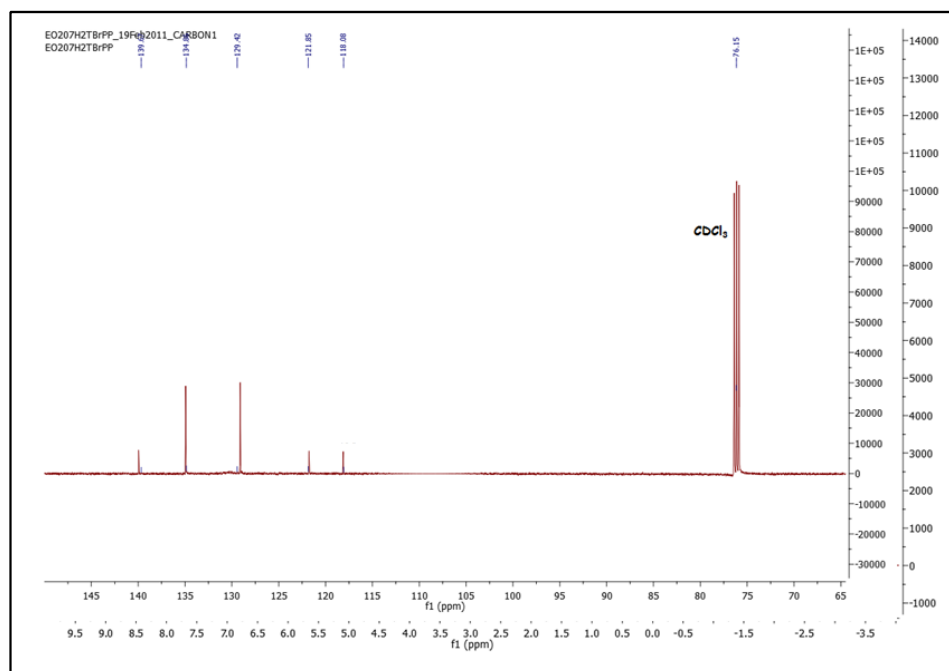


Figure B1.13:  $^{13}\text{C}$  NMR spectrum of *meso*-tetra(4-bromophenyl)porphyrin (TBrPP) in  $\text{CDCl}_3$ .

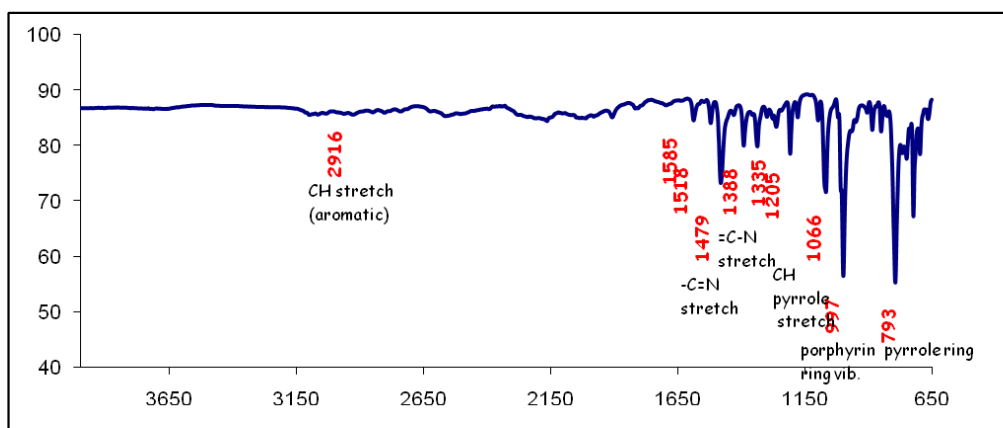


Figure B1.14: IR spectrum of *meso*-tetra(*p*-bromophenyl)porphyrinato Zn(II) (TBrPPZn).

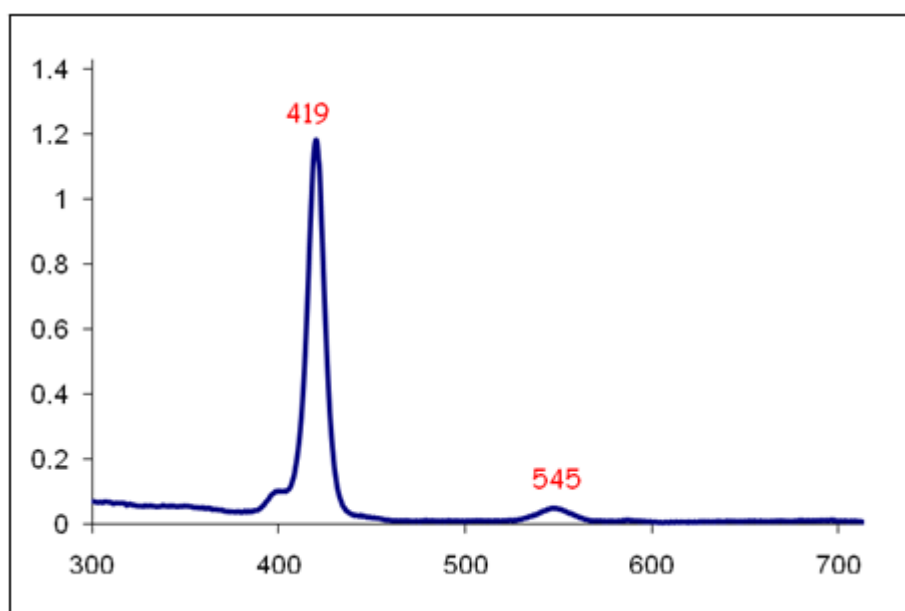


Figure B.1.15: UV-Vis spectrum of *meso*-tetra(*p*-bromophenyl)porphyrinato Zn(II) (TBrPPZn) in CHCl<sub>3</sub>.

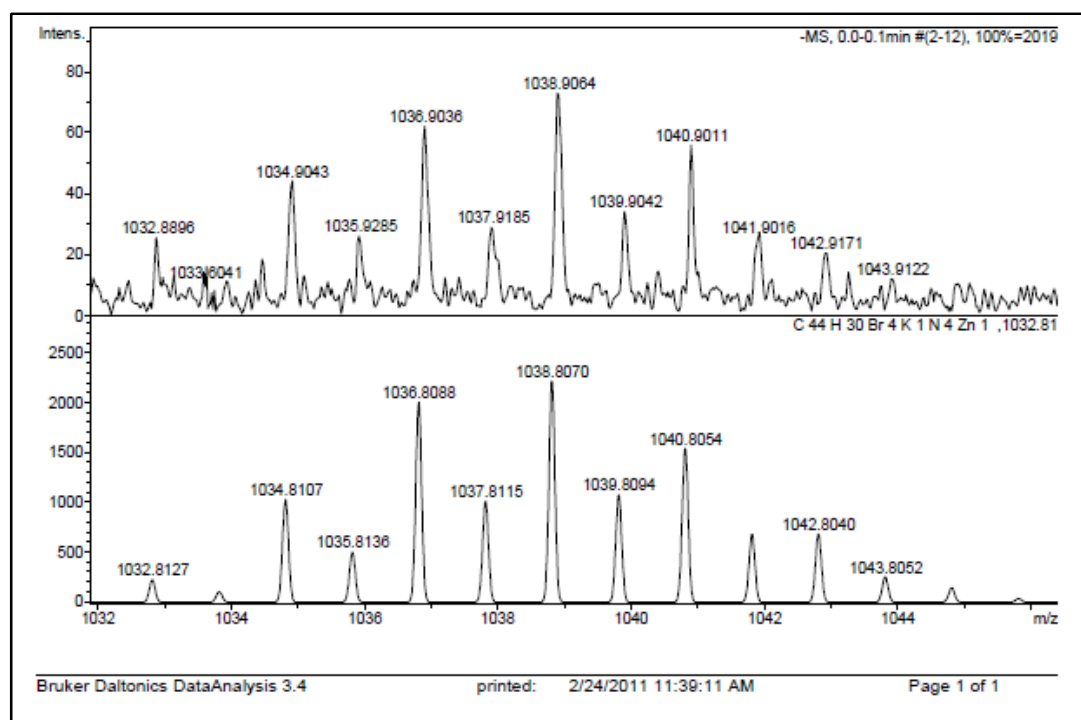


Figure B1.16: ESI-MS spectrum of *meso*-tetra(*p*-bromophenyl)porphyrinato Zn(II) (TBrPPZn).

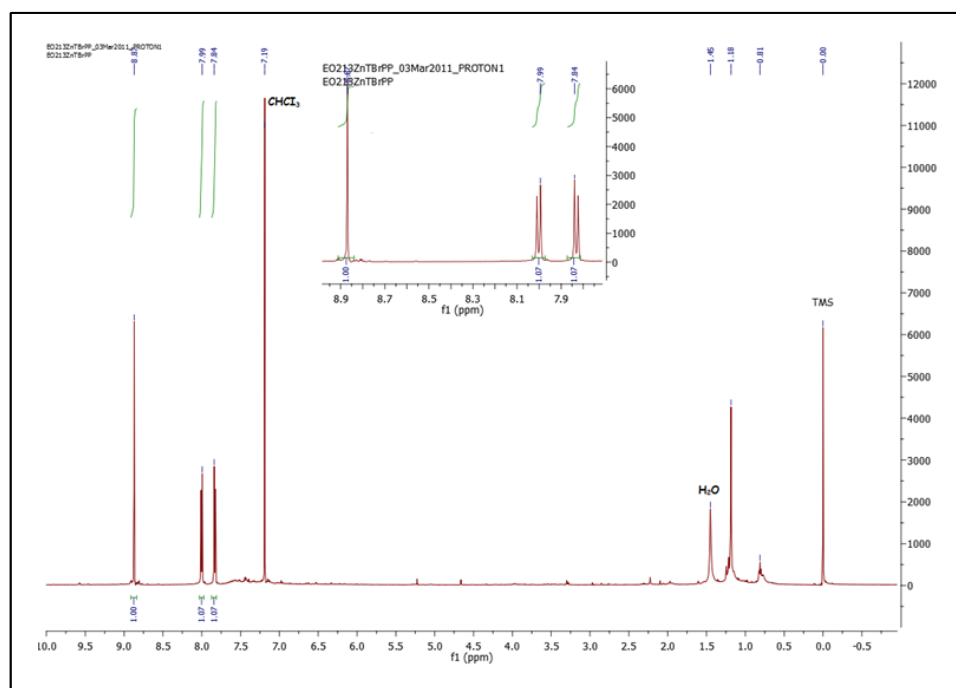


Figure B.1.17:  $^1H$  NMR spectrum of *meso*-tetra(*p*-bromophenyl)porphyrinato Zn(II) (TBrPPZn).

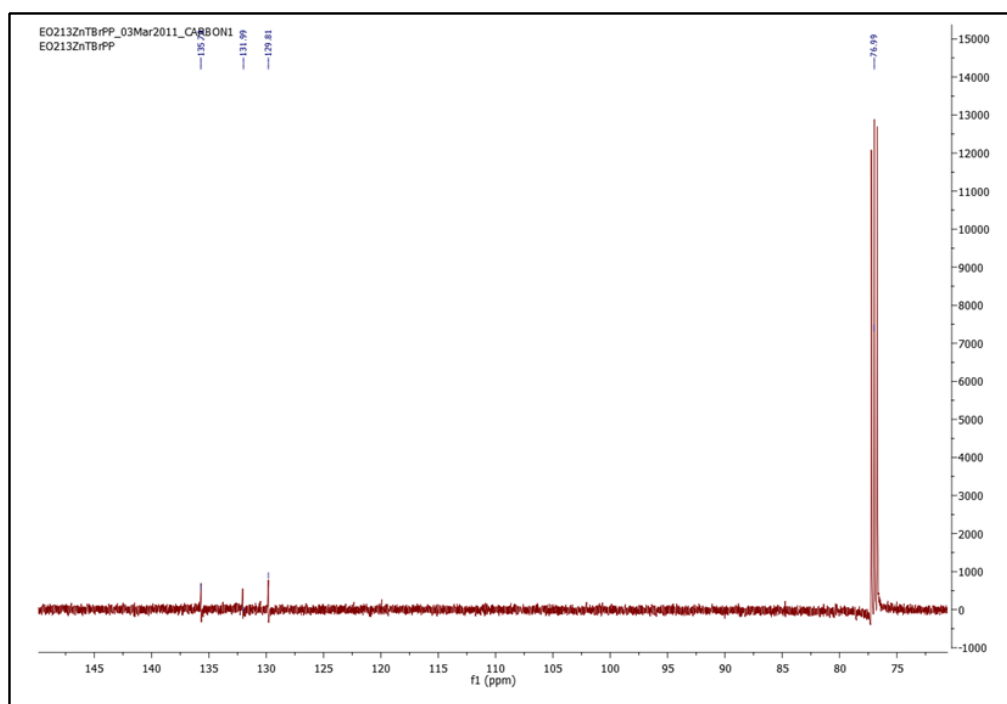


Figure B.1.18:  $^{13}\text{C}$  NMR spectrum of *meso*-tetra(*p*-bromophenyl)porphyrinato Zn(II), (TBrPPZn).

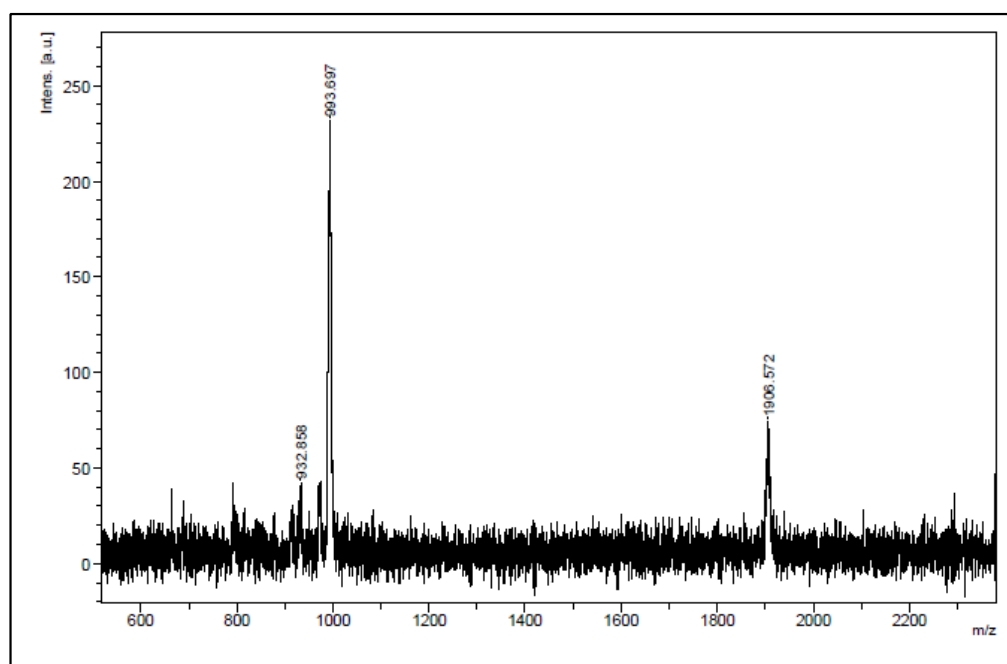


Figure B1.19: MALDI-MS spectrum of *meso*-tetra(*p*-bromophenyl)porphyrinato Cu(II), (TBrPPCu).

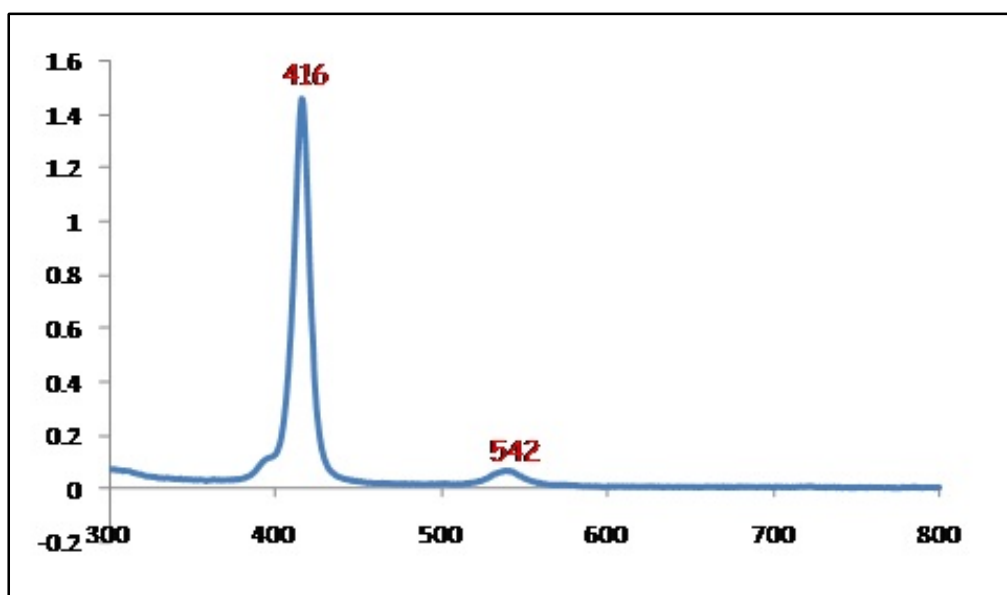


Figure B1.20: UV-Vis spectrum of *meso*-tetra(*p*-bromophenyl)porphyrinato Cu(II) (TBrPPCu) in CHCl<sub>3</sub>.

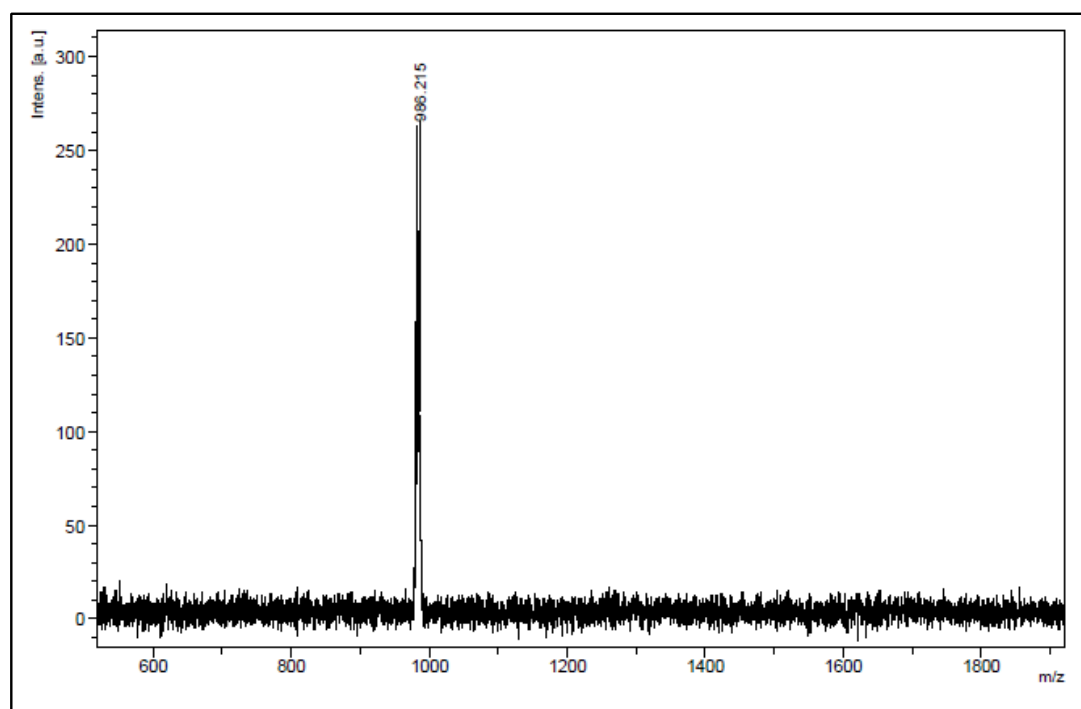


Figure B1.21: MALDI-MS spectrum of *meso*-tetra(*p*-bromophenyl)porphyrinato Mn(III), (TBrPPMn).

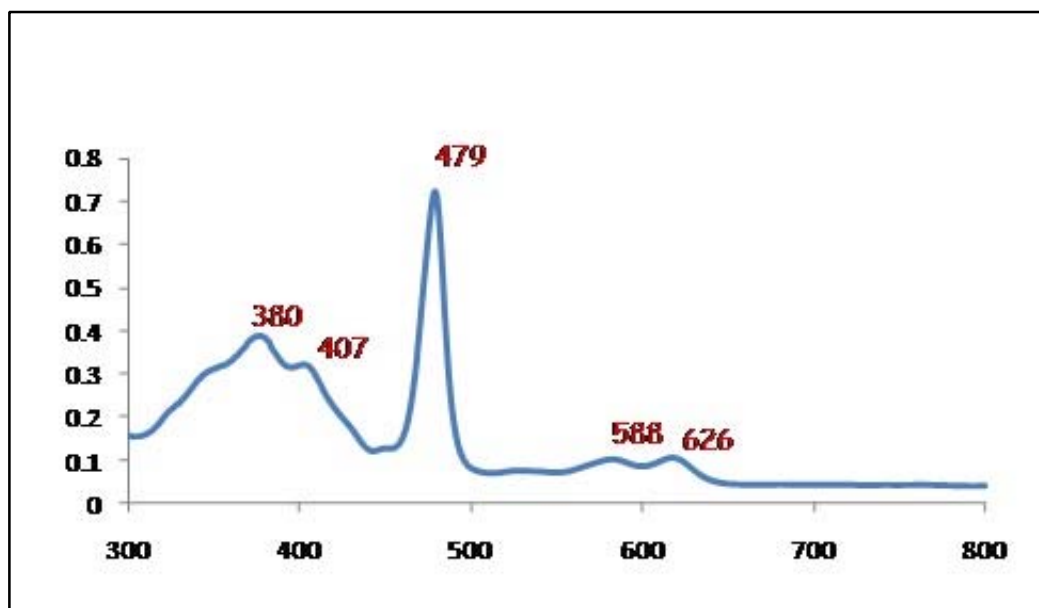


Figure B1.22: UV-Vis spectrum of *meso*-tetra(*p*-bromophenyl)porphyrinato Mn(III), (TBrPPMn).

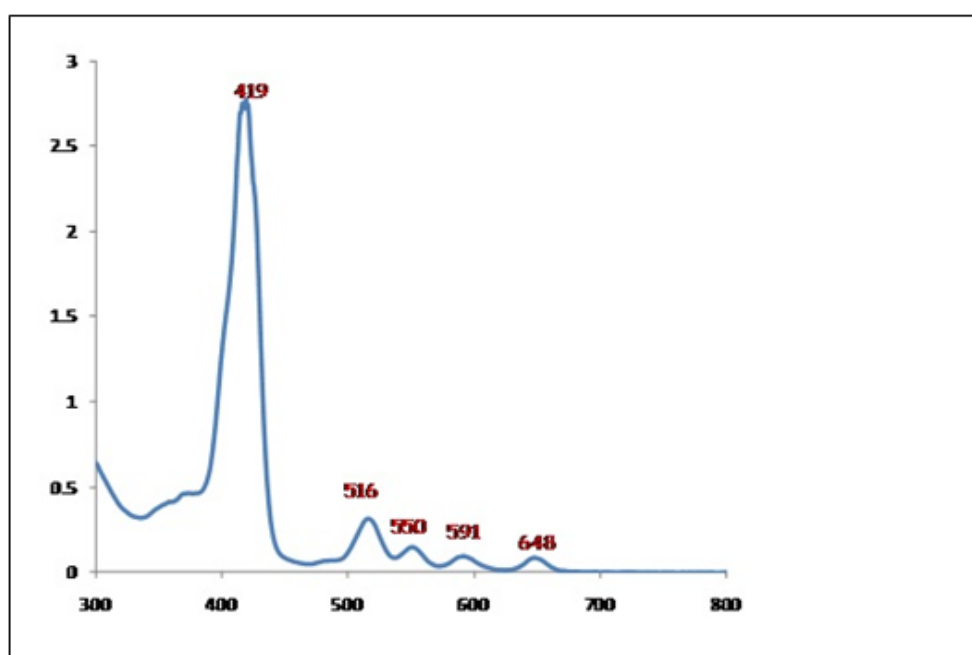


Figure B1.23: UV-Vis spectrum of 5-(4-formylphenyl)-10,15,20-triphenylporphyrin (AB<sub>3</sub>AP) in CHCl<sub>3</sub>.

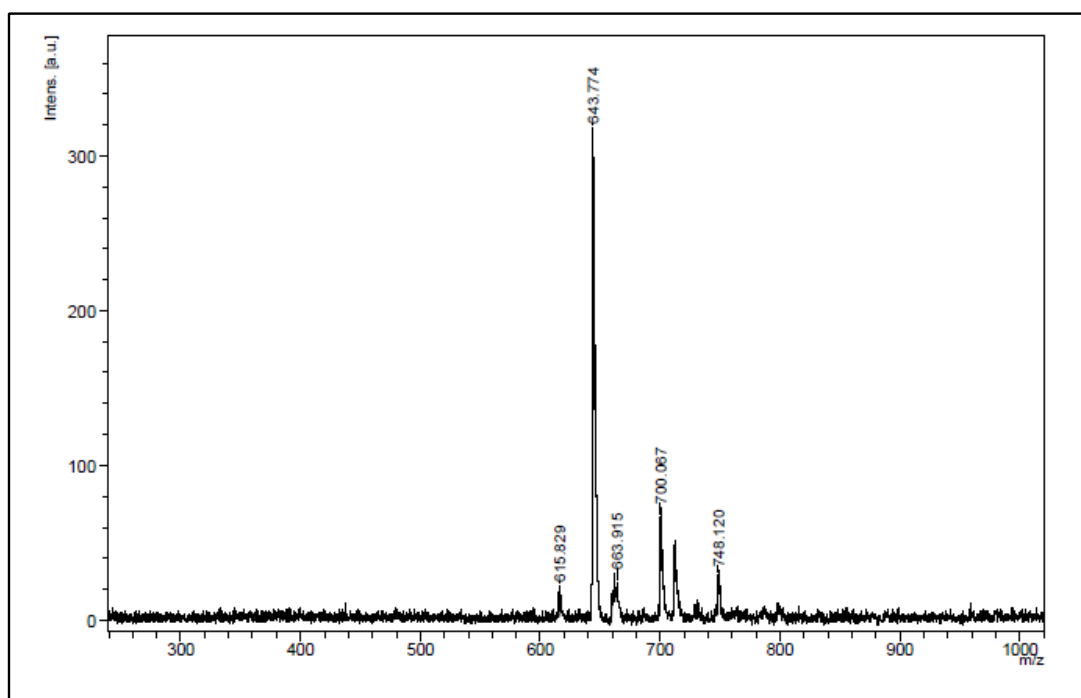


Figure B1.24: MALDI-MS spectrum of 5-(4-formylphenyl)-10,15,20-triphenylporphyrin (AB<sub>3</sub>AP).

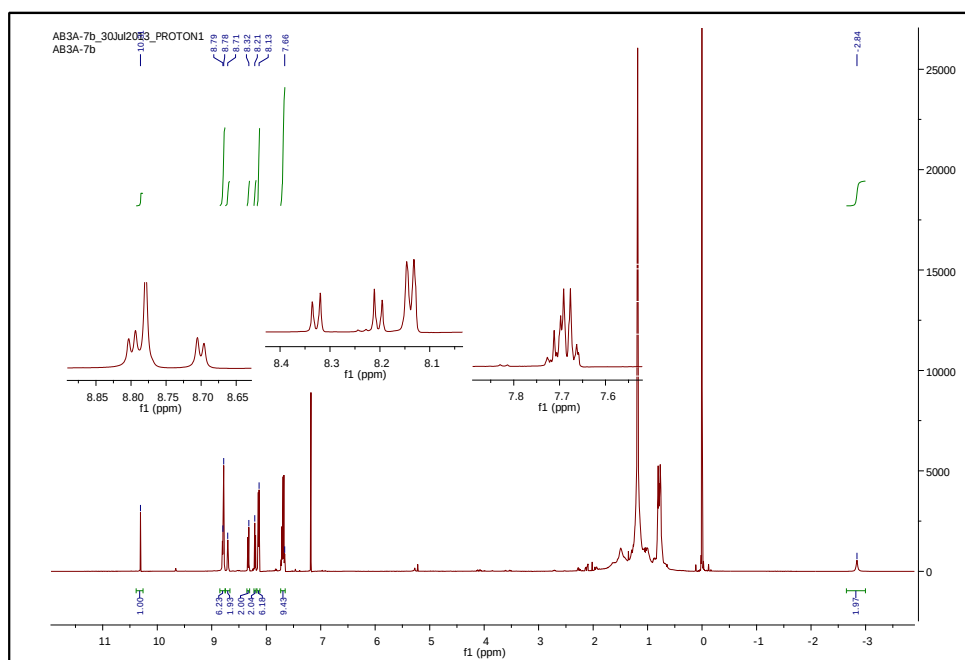


Figure B1.25: <sup>1</sup>H NMR spectrum of 5-(4-formylphenyl)-10,15,20-triphenylporphyrin (AB<sub>3</sub>AP) in CDCl<sub>3</sub>.

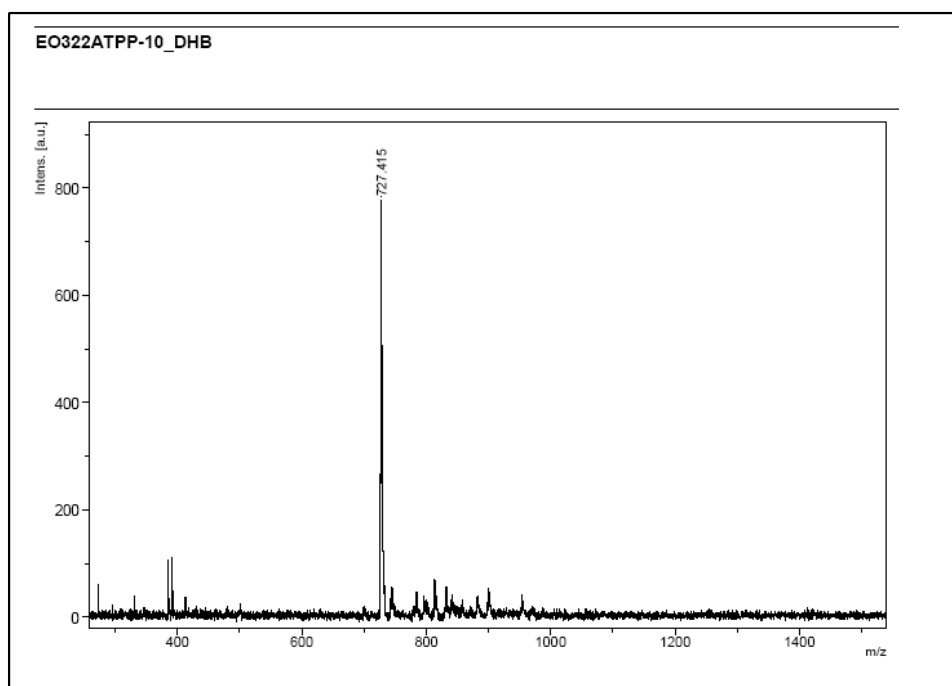


Figure B1.26: MALDI-MS spectrum of *meso*-tetra(4-formlyphenyl)porphyrin (ATPP).

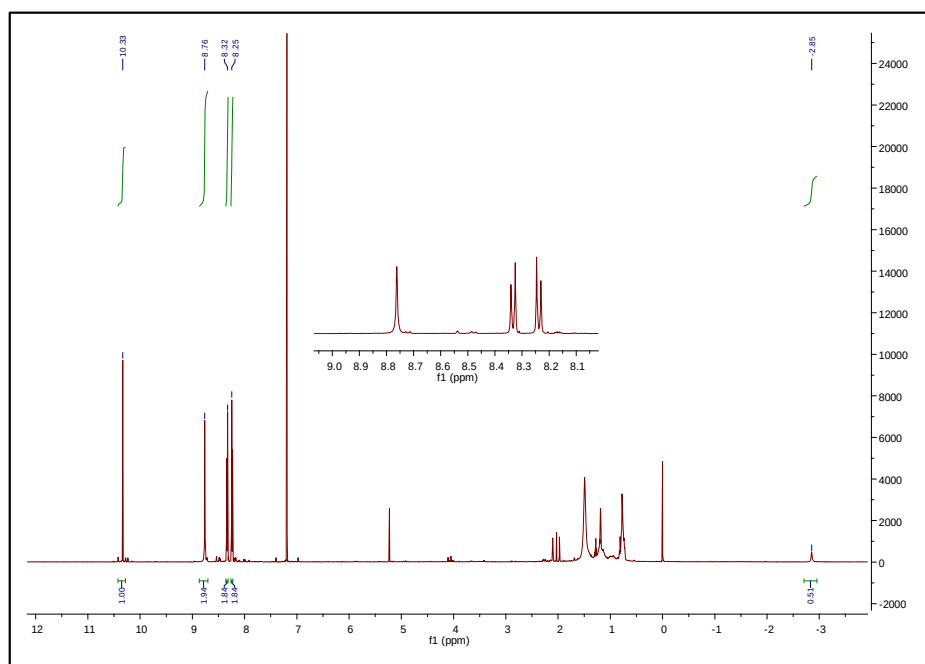


Figure B1.27:  $^1\text{H}$  NMR spectrum of *meso*-tetra(4-formlyphenyl)porphyrin (ATPP) in  $\text{CDCl}_3$ .

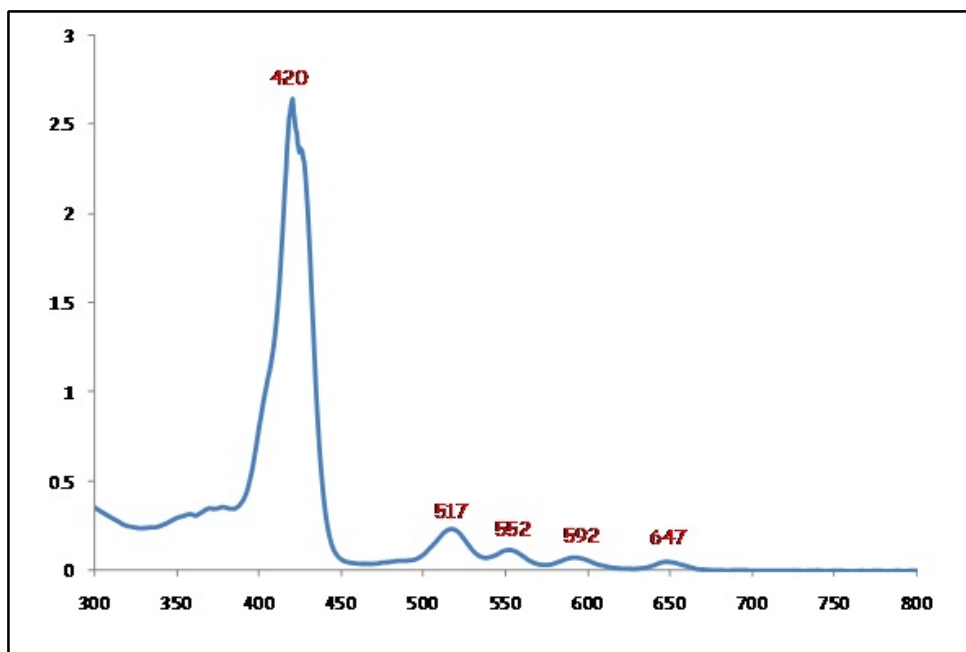


Figure B1.28: UV-Vis spectrum of *meso*-tetra(4-formlyphenyl)porphyrin (ATPP) in  $\text{CHCl}_3$ .

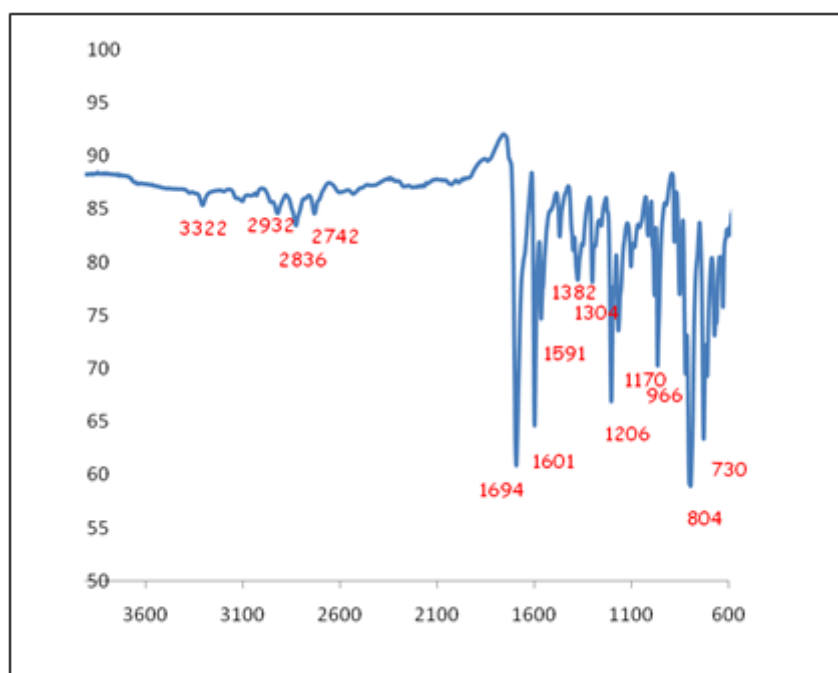


Figure B1.29: IR spectrum of *meso*-tetra(4-formlyphenyl)porphyrin (ATPP).

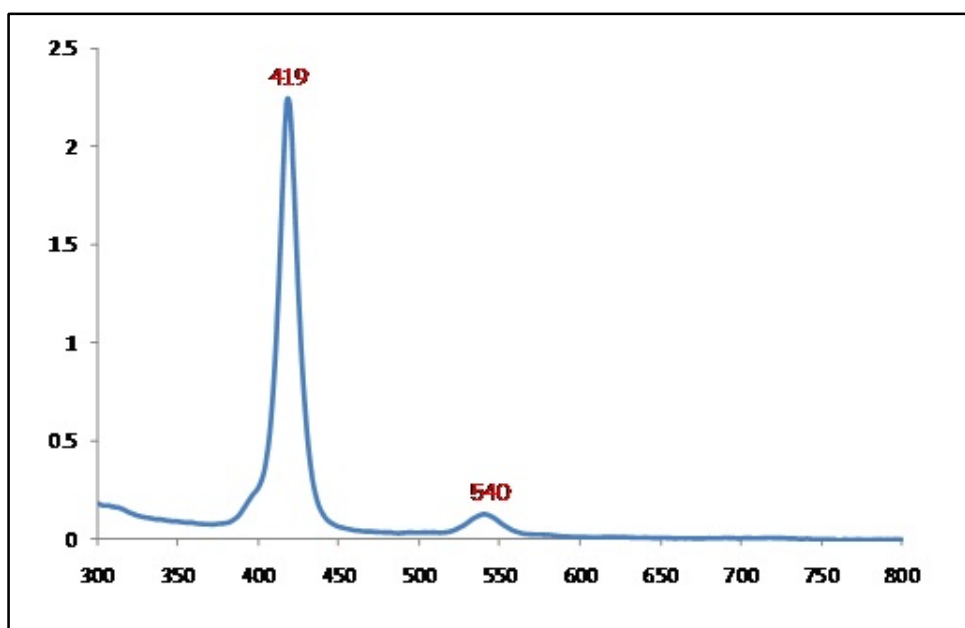


Figure B1.30: UV-Vis spectrum of *meso*-tetra(4-formylphenyl)porphyrinato Cu(II), ATPPCu(II).

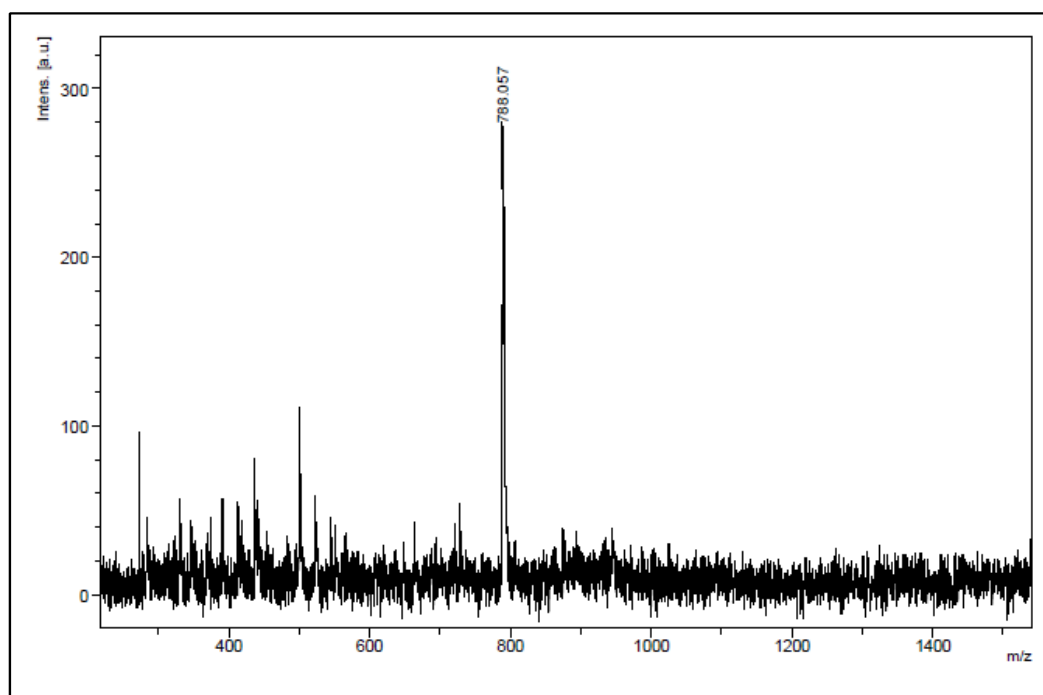


Figure B1.31: MALDI-MS spectrum of *meso*-tetra(4-formylphenyl)porphyrinato Cu(II), ATPPCu(II).

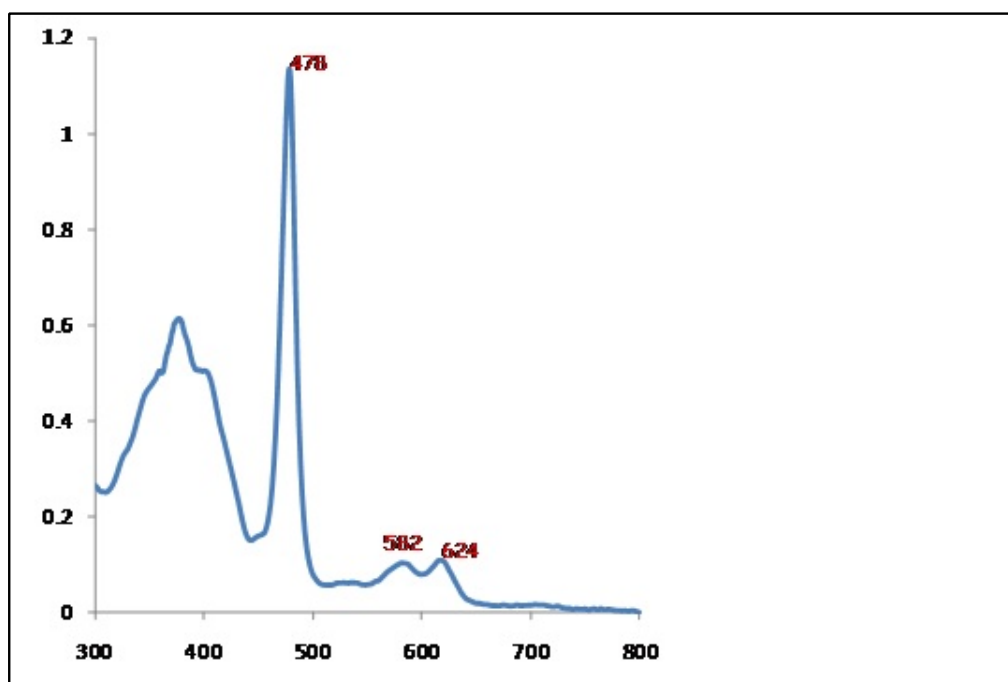


Figure B1.32: UV-Vis spectrum of *meso*-tetra(4-formylphenyl)porphyrinato Mn(III) in  $\text{CHCl}_3$ .

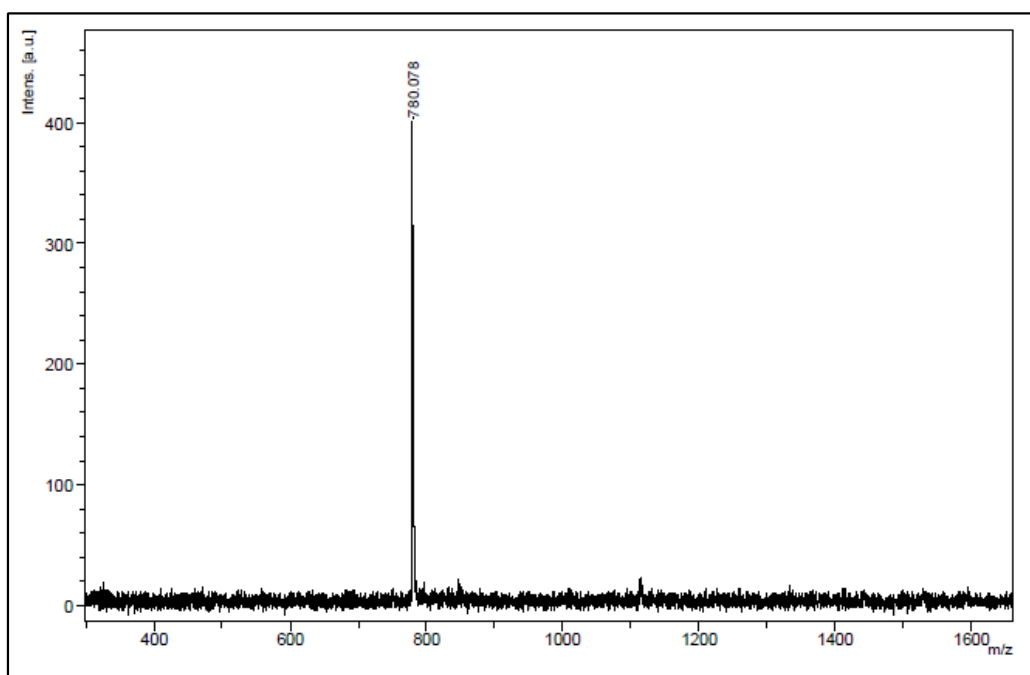


Figure B1.33: UV-Vis spectrum of *meso*-tetra(4-formylphenyl)porphyrinato Mn(III) in  $\text{CHCl}_3$ .