Neslihan CENAN

M.S. Thesis In Chemistry

July 2009

METAL-FREE AND METALLOPORPHYRAZINES WITH EIGHT (P-TOLYLMETHYLTHIO), (O-TOLYLMETHYLTHIO) AND (4-BIPHENYLMETHYLTHIO) UNITS

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in

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APPROVAL PAGE

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

_____
Prof.Dr. Ayhan BOZKURT
Head of Department

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

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METAL-FREE AND METALLOPORPHYRAZINES WITH EIGHT (P-TOLYLMETHYLTHIO), (O-TOLYLMETHYLTHIO) AND (4-BIPHENYLMETHYLTHIO) UNITS

By Neslihan Cenan

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Supervisor: Assist. Prof. Ergün GONCA

ABSTRACT

Peripherally functionalized porphyrazines have the potential to exhibit novel optical, magnetic and electronic properties; also maintain some additional features superior to the values met in related materials. The transition metal ion in the inner core offers new ways to induce, modify and control molecular properties.

In this study, we report novel porphyrazines with eight (*p*-tolylmethylthio), (*o*-tolylmethylthio) and (4-biphenylmethylthio) substituents appending to the peripheral positions. Magnesium porphyrazinates have been synthesized by cyclotetramerization of 1,2-bis(*p*-tolylmethylthio)maleonitrile, 1,2-bis(*o*-tolylmethylthio)maleonitrile and 1,2-bis(4-biphenylmethylthio)maleonitrile in the presence of magnesium butanolate. The conversions of magnesium porphyrazinates into the metal-free derivatives were achieved by the treatment with relatively strong acids (e.g. trifluoroacetic acid). Further reactions of these products with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate have led to the metal porphyrazinates (M= Cu, Zn, Co).

The new compounds were characterized by elemental analysis, together with FT-IR, ^{1}H NMR, UV-Vis and mass spectral data.

Keywords: (*p*-tolylmethylthio), (*o*-tolylmethylthio), (4-biphenylmethylthio), maleonitrile, porphyrazine, magnesium.

SEKİZ ADET (P-TOLİLMETİLTİYO) , (O-TOLİLMETİLTİYO) VE (4- BİFENİLMETİLTİYO) BİRİMLERİ İÇEREN METALLİ VE METALSİZ PORFİRAZİNLER

Neslihan CENAN

Yüksek Lisans Tezi-Kimya Bölümü
Temmuz 2009

Tez Yöneticisi: Yrd. Doç. Dr. Ergün GONCA

ÖZ

Periferal konumlarında fonksiyonel gruplar taşıyan porfirazinler yeni optik, manyetik ve elektronik özellikleri sergileyecek potansiyele sahiptir; aynı zamanda porfirazinlerin türevlendirilmesindeki bazı kolaylıklar, söz konusu maddelere olan ilginin artışını teyit etmiştir. İç kürede yer alan geçiş metal iyonu, moleküler özellikleri kontrol ve modifiye etme imkânlarını ortaya çıkarır.

Bu çalışmada periferal konumdaki sekiz adet (*p*-tolilmetiltiyo) ,(*o*-tolilmetiltiyo) ve (4-bifenilmetiltiyo) sübstitüentleri içeren porfirazinleri sentezledik. Magnezyum butanolat içerisinde 1,2-bis(*p*-tolilmetiltiyo)maleonitril, 1,2-bis(*o*-tolilmetiltiyo) maleonitril, 1,2-bis(4-bifenilmetiltiyo)maleonitril'in siklotetramerizasyon yöntemiyle reaksiyonu sonucunda magnezyum porfirazinler sentezlendi. Trifloroasetik asit gibi kuvvetli bir asitle muamele edilerek metalsiz türevine geçildi ve bu ürünün bakır(II) asetat, çinko(II) asetat ve kobalt(II) asetat ile reaksiyona sokulmasıyla metalli porfirazinler elde edildi (M^{+2}= Cu^{+2}, Zn^{+2}, Co^{+2}).

Bu ürünlerin karakterizasyonu ^{1}H NMR, FT-IR, UV-Vis, kütle ve elementel analiz gibi çeşitli spektral verilerle gerçekleştirilmiştir.

Anahtar Kelimeler: *p*-tolilmetiltiyo, *o*-tolilmetiltiyo, 4-bifenilmetiltiyo, maleonitril, porfirazin, magnezyum.

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LIST OF ABBREVIATIONS

M	Metal
H_2AP	Azaporphyrine
H_2P	Porphyrine
H_2Pz	Metal free Porphyrazine
H_2TAP	Tetraazaporphyrine
Pc	Phthalocyanine
H_2MATBP	Monoazatetrabenzoporphyrine
H_2OEP	Octaethylporphyrine
H_2MAP	Monoazaporphyrine
H_2TATBP	Triazatetrabenzoporphyrine
H_2TBP	Tetrabenzoporphyrine
H_2TPP	Meso-tetraphenylporphyrine
H_2TPrP	Meso-tetra (n-propyl) porphyrine
MAP	Metalloazaporphyrine
MP	Metalloporphyrine
MTAP	Metallotetraazaporphyrine
MO	Molecular Orbital
DCM	Dichloromethane
DMF	N,N-dimethylformamide
TFFA	Triflouroacetic acid
NMR	Nuclear Magnetic Resonance
IR	Infrared
UV / VIS	Ultraviolet / Visible Spectrum
Å	Angstrom
Pyr	Pyrrole
LUMO	Lowest Unoccupied Molecular Orbital
HOMO	Highest Occupied Molecular Orbital
L	Ligand

CHAPTER 1

INTRODUCTION

1.1 GENERAL INFORMATION ABOUT TETRAPYRROLE DERIVATIVES

Tetrapyrrole derivatives have been a subject of great interest due to various high synthetic possibilities, numerous technological applications, and biological importance in coordination chemistry. The physical properties of these square planar porphyrine-like molecules depend strongly on their chemical and geometric structure, providing an enormous opportunity for molecular design and control of properties by ligand substitution and ring symmetry modification. Porphyrin, phthalocyanine and porphyrazine molecules have also been a theme of considerable theoretical interest due to their high symmetry, planar molecular arrangements, and electronic delocalization. A large number of theoretical works have been devoted to the understanding of the atomic scale structure of these molecules, their building blocks and the mechanisms of charge transport and optical properties [1, 2].

A 16 - membered electron rich conjugated planar macrocyclic core is common in all these structures. When this main core is composed of four pyrrol units bound to one another through methine (-CH=) bridges, it is called porphyrine (Figure 1.1.a). Four-benzo condensation on each of the pyrrole groups result with tetrabenzoporphyrine (Figure 1.1.b). Changing methine bridges with aza functions (=N-) in porphyrines result with porphyrazines (or tetraazaporphyrines) (Figure 1.1.c). The benzo-condensed porphyrazines are the well-known phthalocyanines (Figure 1.1.d).

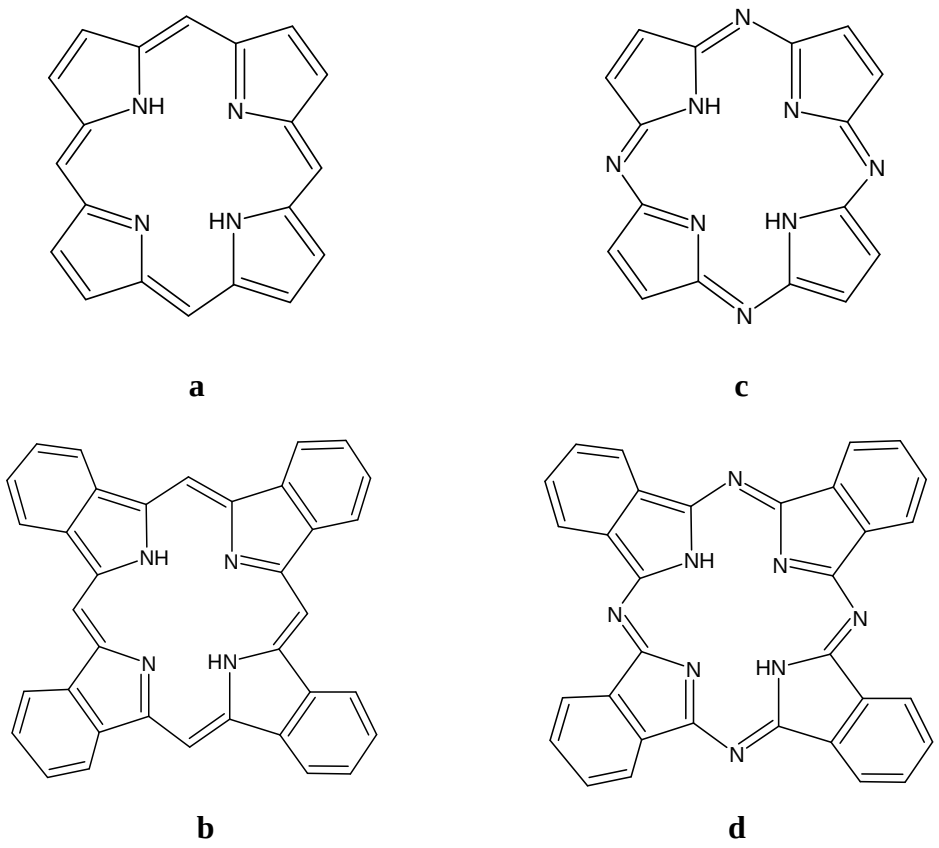


Figure 1.1 (**a**) Porphyrin, (**b**) Tetrabenzoporphyrin, (**c**) Porphyrazine, (**d**) Phthalocyanine .

All porphyrins, porphyrazine-type macrocycles share a common substructure which consists of four pyrrolic subunits. Like porphyrins, porphyrazines also contain a 22-π electron system, and this feature gains porphyrazines wide range of extraordinary properties such as the ability to absorb visible light, to mediate the conversion of absorbed light to other forms of chemical and physical energy, and to enhance thermodynamic and kinetic stability. These conjugated systems assume many resonance forms and can accept substituents at a number of positions.

The chemical versatility of the porphyrazine macrocycle offers the opportunity of varying the electronic structure through ligand and metal modifications; this includes substitution, elaboration, and truncation of the macrocycle. Substitutions in a very controlled manner with certain electron-withdrawing or electron-donating groups to the macrocycle were found to change the electronic properties [3, 4].

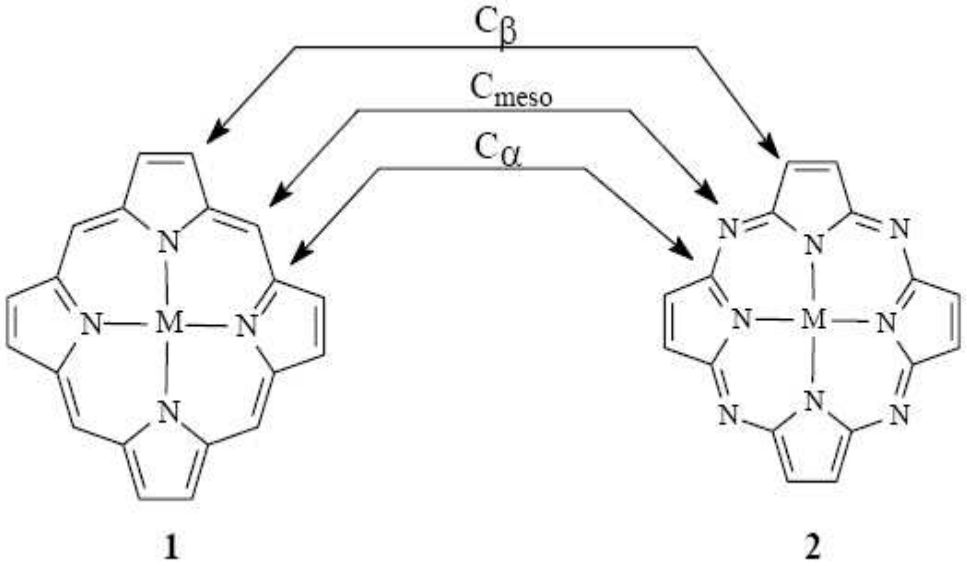


Figure 1.2 Tetrapyrrole-macrocycles (M=Metal or H_2) [3] ,
Porphyrin (**1**),Porphyrazine (**2**).

One of the most important properties of tetrapyrrole ligands is their ability to coordinate to metal ions, yielding stable inter complex salts. Stable complexes of porphyrins, porphyrazines (Fig.1.1, Fig.1.2) and phthalocyanines result from formation of four equivalent σ bonds (N → M) that is filling of vacant s, p_x, p_y and (n - 1) d_{x2-y2} or n d_{x2-y2} orbitals of the cation with σ electrons of the central nitrogen atoms which are called as coordinating N atoms. The chemical versatility of the porphyrazine macrocycle offers the opportunity of varying the electronic structure through ligand and metal modifications; this includes substitution, elaboration, and truncation of the macrocycle. Substitutions in a very controlled manner with certain electron-withdrawing or electron-donating groups to the macrocycle were found to change the electronic properties. The resulting σ bonds are strong that in the case of metals Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} that in solid complexes practically no replacement of the metal ions takes place at H_2SO_4 concentrations ranging from 2 to 7 M. In the case of coordination of triply or quadruply charged ions the formation of a complex involves, in addition to d, s, and p^2 orbitals, p_z and d_{z2} orbitals that participate in the attachment of the extra ligand along the z-axis perpendicular to the plane of the molecule.

The formation of σ bonds (N →M) in porphyrin and porphyrazine complexes leads to four electron pairs of the coordinating nitrogen atoms being excluded from the conjugation. The antibonding π orbitals (π*) of the macroring are filled with the

heteroatomic n orbitals. The attendant decrease in the energy of these antibonding π orbitals favors conjugation of the heteroatomic n electrons which have not taken any part in the coordination to the metal. As a result the remaining n electrons acquire a π rather than a σ character and are not easily protonated with acids. In many cases where the metal ion has filled d orbitals of π symmetry (d_{xy}, d_{xz}, d_{yz}) it forms backward dative π bonds with the macrocyclic tetrapyrrol ligand. The metal serves as a donor of π electrons and the ligand as their acceptor. These bonds are opposite in direction to σ bonds, that is M → N, and are called backbonding. The d-π electrons of the metal fill the antibonding π orbitals of porphyrazine. The filling of antibonding π orbitals increases their energy, which prevents the n electrons of the meso-N atoms from entering into a π conjugation as well as enhancing their σ character and capacity for acid protonation [5].

In addition to electronic and charge effects of coordination complexes with cyclic π ligands such as porphyrins, phthalocyanines, porphyrazines and other macroheterocyclic compounds, may in some cases display steric effects of coordination. If coordination distorts the planar structure of a conjugated cyclic system, the conjugation of n electrons of the nitrogen atoms with the macroring π system weakens. As a result the basicity of the molecules increases. If coordination to a metal creates a more coplanar π system than the ligand, the opposite is true.

The porphyrazine is isoelectronic with the porphyrin, but because of its nitrogen atoms at the meso positions chemically much closer to the technologically important phthalocyanines. To investigate the electronic properties of the phthalocyanines it is, therefore, necessary to address the influence of those nitrogens on the electronic structure.

In the visible absorption spectra of porphyrins, the highly conjugated aromatic macrocycle shows an intense absorption in the region of about 400 nm which is referred to as the Soret Band (Fig.1.3). Visible spectra of porphyrins also show four weaker bands, the Q bands, at longer wavelengths from about 450-700 nm giving rise to reddish purple color of porphyrins [5].

The effects of meso-tetraaza substitution on the UV-Visible absorption bands of porphyrins are to date well documented [3,9]. Porphyrazine complexes exhibit for

instance a significant red shift and an intensification of the lowest energy π → π* Q band, and a more complicated Soret band region due to additional π → π* transitions introduced by azamethine groups [6,7].

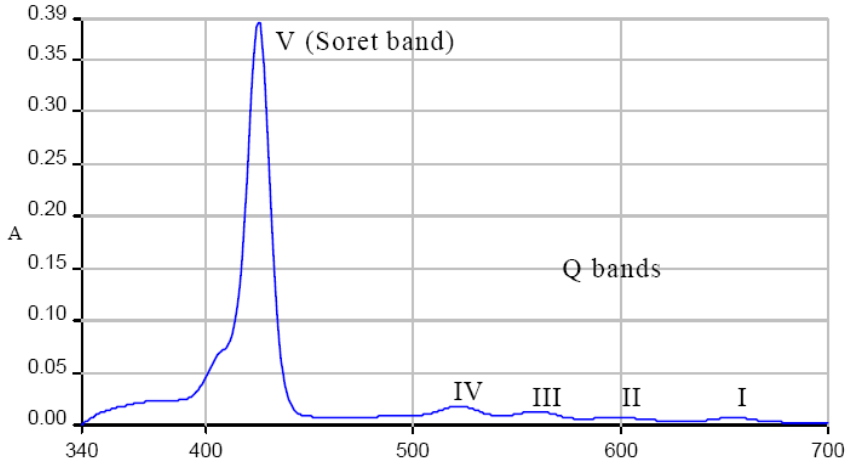


Figure 1.3 UV-Visible spectrum of a porphyrin [3,5].

The UV-visible spectra in porphyrazines are influenced by substituents and the presence or absence of a metal at the centre. Peripheral substitution influences the UV-visible spectra with *cis*- and *trans*- isomers showing different split in LUMOs. *Trans*-isomers show large splitting compared to *cis*-peripherally substituted porphyrazines. In non-metalated porphyrazines with reduced symmetry, reduction in symmetry removes degeneracy of e_g LUMO and gives a split Q-band (Fig.1.4) [8]. In cases where a lone pair of electrons in peripheral ligating atoms (N) becomes bonded to metal ions, the Q-band is split into two sharp bands (Fig.1.4) because their interaction with the porphyrazine ring is suppressed [8].

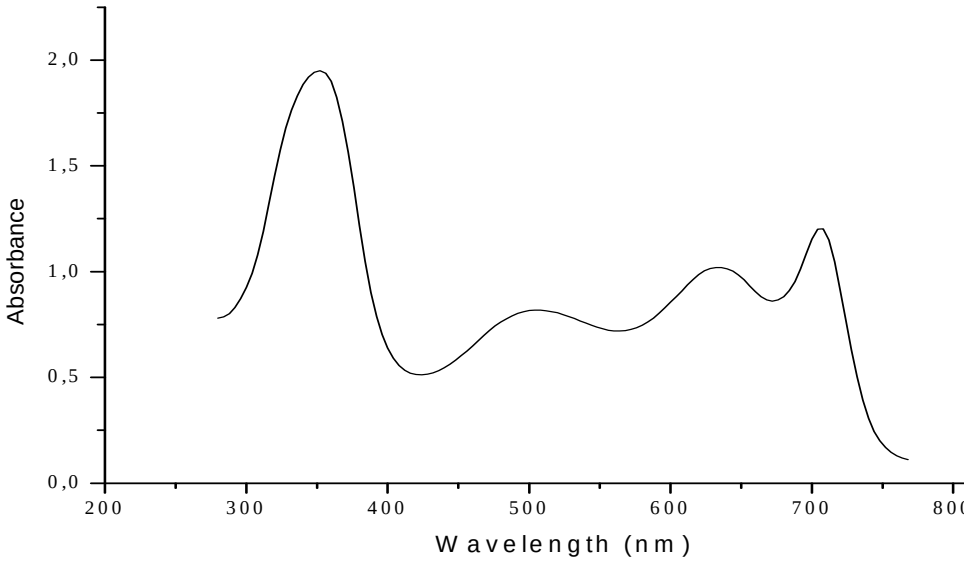


Figure 1.4 Electronic absorption spectrum of H_2Pz.

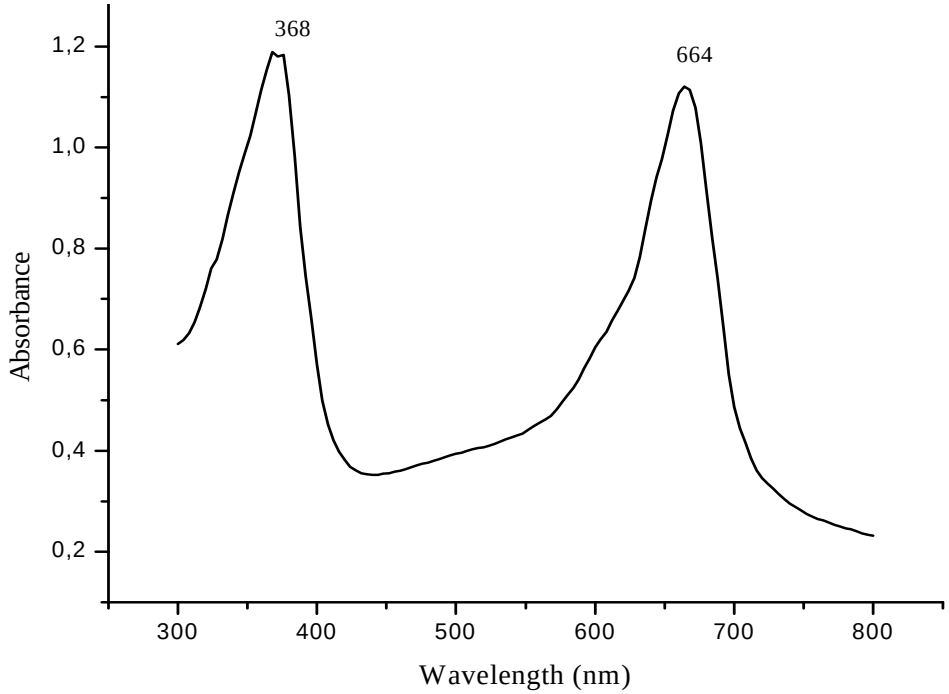


Figure 1.5 Electronic absorption spectrum of MgPz.

For nonmetalated (metal-free) porphyrazines (D_{2h} symmetry) (Fig.1.4), the UV-visible spectra show two lower energy split Q-bands at 550-700 nm and a higher energy Soret (B) band at 300-400 nm, which are assigned to $a_u \rightarrow b_{2g}$ (Qx), $a_u \rightarrow b_{3g}$ (Qy) and $b_{1u} \rightarrow b_{2g}$ (Qx), $b_{1u} \rightarrow b_{3g}$ (B_y) transitions (Fig.1.6). These transition bands are assigned to excitations from the two highest-occupied molecular orbitals (HOMO) (a_{1u} and a_{2u})

into lowest unoccupied molecular orbitals (LUMO, e_g) [8,9]. The lower energy peak which could be found at 400-500 nm is assigned to n-π* transitions from the lone-pair electrons in external meso-nitrogen atoms into a π* ring system.

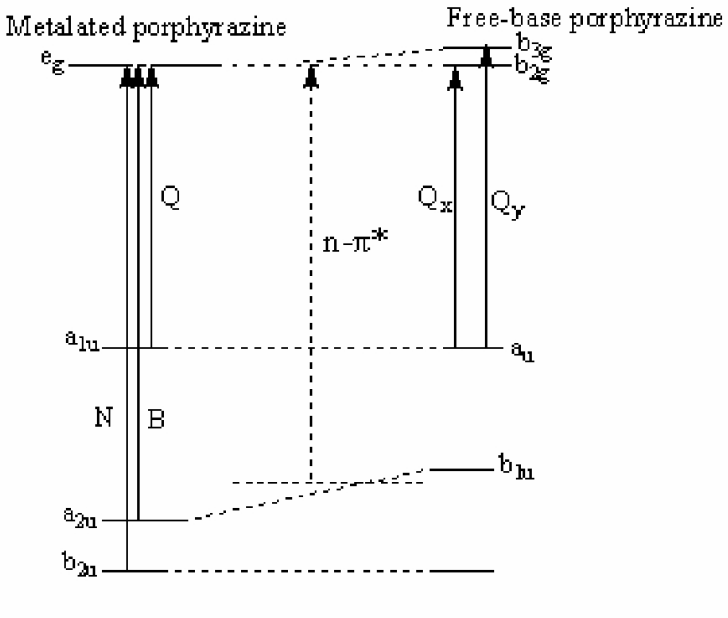


Figure 1.6 Electronic transitions in the visible and close UV regions of metalated and non-metalated porphyrazines [3].

Metalated porphyrazines exhibit two intense π → π* absorbances, a low energy Q band that is accompanied by a slight higher energy shoulder and a higher energy B band. For metalated porphyrazines, the symmetry of the chromophore is D_{4h} with the two LUMOs b_{2g} and b_{3g} giving rise to a two-fold degenerate e_g level resulting to an unsplit Q and B absorptions associated with transitions $a_{1u} \rightarrow e_g$ and $a_{2u} \rightarrow e_g$ [10,11].

Porphyrazine, tetraazaporphyrine or, according to the IUPAC nomenclature, 2,7,12,17,21,22,23,24octaazapentacyclo[16,2,1,13,6,18,11,12,26]tetracosaundecaene), in its structure, occupies an intermediate position between other well studied tetrapyrrole macrocyclic systems, porphyrine and Pc. The conjugation system of the H_2Pzs molecule is multicontour, and its internal chromophore n-electrons (8 double bonds and 2 π-electrons of internal nitrogen atoms) [12].

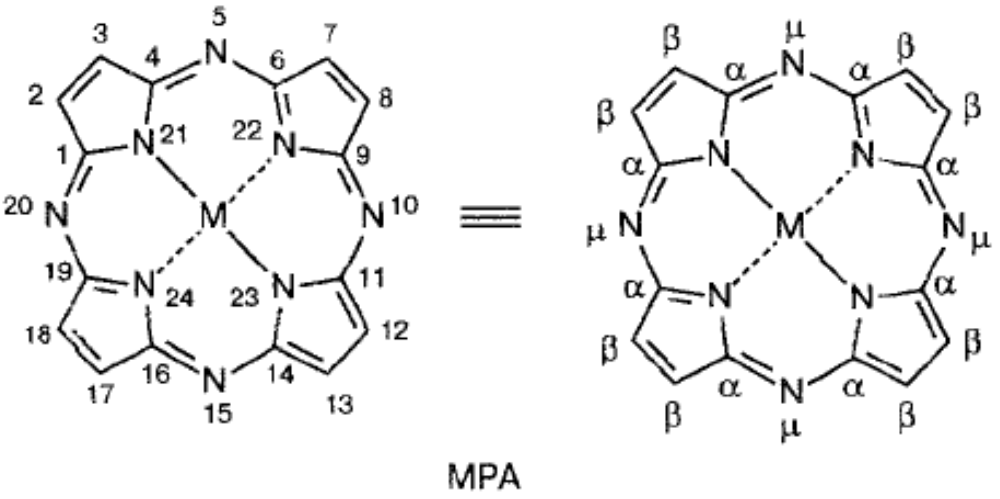


Figure 1.7 General structure of porphyrazine molecules [12].

The skeleton of common porphyrin ligands can be considered as almost planar since the deviations of the C and N atoms from the mean plane do not exceed 0.006 nm. The symmetry of the skeleton is in most cases D_{2h}. A D_{4h} skeletal symmetry was found for monoclinic H_2P and tetragonal H_2TPP. D_{2h} distortion of the porphyrin ligands is connected above all with the inequivalent of the five-membered rings composing the macrocycle. In two trans-located pyrrole type-rings (A) the bonds C_α-C_β are about 0.002-0.003 nm shorter, C_β-C_β bonds are about 0.002 nm longer and the inner angle formed by the nitrogen atom is 2.5-4^o larger compared with a pair of the neighboring pyrrolenine-type rings. At the same time the bond lengths between C_α atoms and the inner nitrogen atoms vary only slightly in these two ring types and are 0.002-0.003 nm shorter than the bonds of C_α atom with C_{meso} atom (Fig.1.8). The symmetric alkyl or aryl substitution in the meso or β positions has little influence the changes in the bond lengths and values of the angles do not exceed 0.002 nm and 2^o. The dimensions of the central coordination cavity (measured as a distance between the intracyclic N atoms N_{pyr} and macrocycle center C_t) vary slightly in the range 0.204-0.206 nm (Table 1.1). One can expect that the direct substitution of the carbon atom in the conjugated π system of the porphyrin with a heteroatom, namely aza-substitution in the meso positions, should produce significantly greater changes in the geometry of the reaction center and that is the case in fact [13].

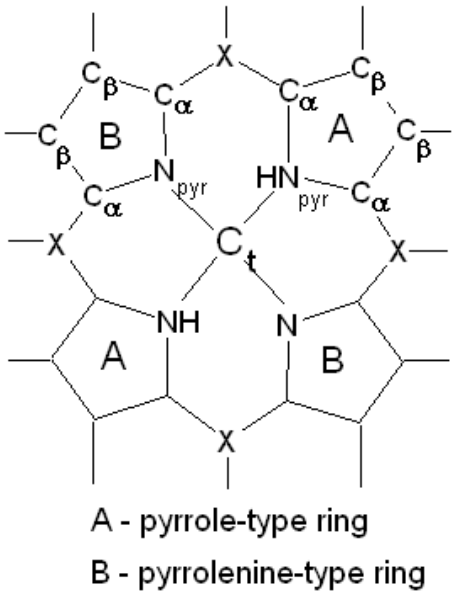


Figure 1.8 Pyrrole-type and Pyrrolenine-type Rings [13].

Table 1.1 Average geometrical parameters for the CN skeleton of porphyrin and azaporphyrin ligands [13].

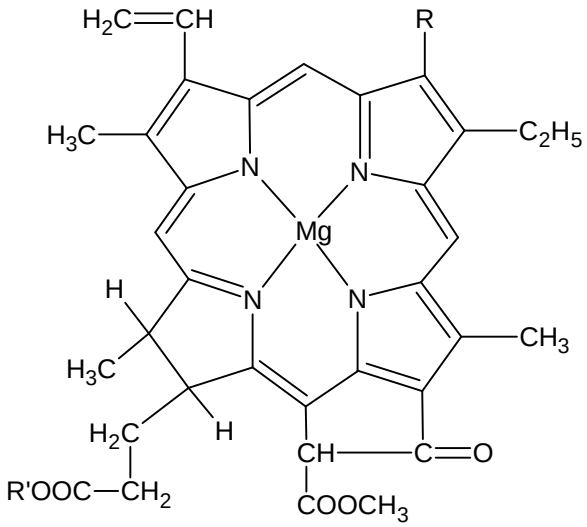
Geometric parameter	H_2P[a]	H_2OEP[a]	H_2TPP[a]	H_2MATBP	H_2Pc	H_2Pc	H_2TAP
C_α-X (nm)	0.1376 0.1387	0.1390	0.1400	0.125 (N) 0.139 (C)	0.1335	0.132	0.133
C_α-N_{pyr} (nm)	0.1377 0.1380	0.1364 0.1367	0.1364 0.1374	0.145	0.1340	0.137	0.136
C_α-C_β (nm)	0.1452 0.1431	0.1462 0.1438	0.1455 0.1428	0.147	0.1490	0.147	0.144
C_β-C_β (nm)	0.1345 0.1365	0.1353 0.1373	0.1347 0.1355	0.152	0.1390	0.140	0.134
N_{pyr}- C_t (nm)	0.2051	0.2062	0.2060		0.1913		0.194
C_α-X-C_α (^{0})	126.9	127.7	125.6	111 (N) 143 (C)	115 119	122 125	122
C_α-N_{pyr}-C_α (^{0})	106.1 108.5	105.7 109.6	106.2 109.2	109	109	109	108
X-C_α-N_{pyr} (^{0})	125.1	125.0	126.2	132 (N) 123 (C)	131	127 130	128

CHAPTER 2

PROPERTIES OF PORPHYRIN AND PHTHALOCYANINE COMPLEXES

2.1 General Concepts of Porphyrin and Phthalocyanine Complexes

Metalloporphyrins, which include, such important natural complexes as chlorophyll (Fig.2.1), haem of the blood (Fig.2.2), and others, represent a vast and unique group of intercomplex compounds [14].



1a: R' $C_{20}H_{39}$; R = CH_3, 1b: R' = $C_{20}H_{39}$; R = CHO

Figure 2.1 Chlorophyll[13].

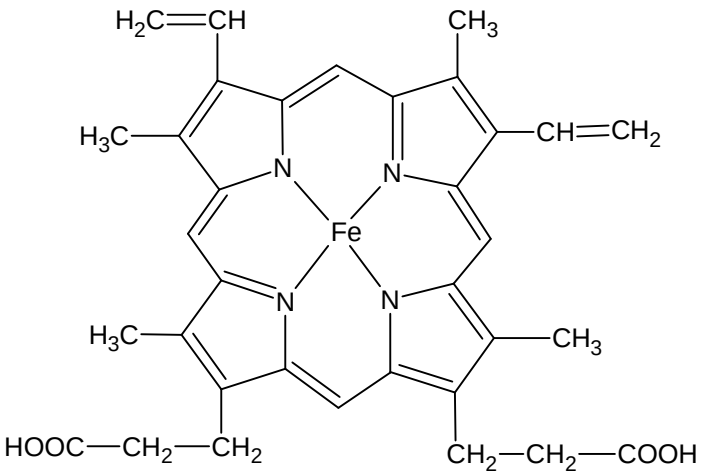


Figure 2.2 Haem of the blood.

The central metal atom displaces two hydrogen ions from the porphyrin ligand and practically finds itself in a symmetrical electrostatic field of four nitrogen atoms with which it may form four equivalent, or almost equivalent, coordinate, donor-acceptor bonds. If the interaction between the metal and the porphyrin anion is primarily electrostatic, labile ion complexes are formed. These include complexes of Na^{+}, K^{+}, Rb^{+}, Cs^{+}, Be^{2+}, Sr^{2+}, Ba^{2+}, Ca^{2+}, and some other ions. But if the electrostatic interaction involves filling of the vacant orbitals of the central atom by the electrons of the donor N atoms of the ligand, stable porphyrin complexes of the covalent or predominantly covalent type are formed. In this case most of the complexes of Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mn^{3+}, Cr^{3+}, Al^{3+}, Ga^{3+}, Si^{4+}, Ge^{4+}, Sc^{3+}, Ti^{4+}, VO^{2+}, Pt^{4+}, Os^{4+} are formed by biometals [14]. As will be seen from what follows, complexes of porphyrins with Mg^{2+}, that is chlorophyll and its structural analogues, do not belong either to purely ionic complexes or to the stable group of predominantly covalent complexes. This peculiarity of chlorophyll, stemming from its intermediate position in the complex stability series, is to some extent responsible for its unique role in nature.

In contrast to chlorophyll, the complex of protoporphyrin with Fe^{2+} (Fe^{3+}) is one of the most stable metalloporphyrins of the covalent type. This property is fully consistent with both the biological composition of the medium in which haem acts in a complex with protein and with its biological functions

The specific features of metalloporphyrins as intercomplex compounds are due not only to the polydentate (tetradentate) nature of the ligand but also to its rigidity. The latter is determined by the planar structure of the large ring of the porphyrin molecule, by the unique conjugation in it which is due to the strong π-electron interaction over the entire large ring (so-called macroring), and by the particularly favorable structure of the coordination center, consisting of four nitrogen atoms, on account of which most metal ions easily enter this space, coming into close contact with the nitrogen atoms. Because of its high rigidity the porphyrin ligand imposes specific requirements on the geometric parameters of the metal ion, whereby they form two clearly defined groups of stable or labile complexes.

Characteristically, the metal ion that has entered into coordination with a porphyrin is in fact a partner of the conjugated porphyrin system and may either stabilize or destabilize it. Owing to this direct contact with the atoms of the conjugated system, it influences all, even the most remote parts, of the large molecule and alters the oxidation-reduction, acid-base, electron-optical, and all other properties of the porphyrin. In this connection it is of particular interest for a coordination chemist to use metalloporphyrins in examining the effect of the nature of the metal involved, the type of chemical bonding, and its strength on the major properties of porphyrins.

A specific feature of metalloporphyrins is their insolubility in water and solubility in organic solvents in cases where no significant solvation centers are present among the functional substituents of the ligand. This is the reason why most studies of porphyrins and metalloporphyrins have been conducted in non-aqueous media.

Another salient feature of porphyrins is their structural diversity, which can be seen in Figure 1.1.a.

Porphyrins differ in the nature of the bridging groups occupying meso positions in the porphyrin molecule. The bridging groups may only be -CH=, -(X)C=, -N=, or their combinations. The structural diversity of porphyrins is further enhanced by the presence of various pyrrole substituents (R_1-R_8) which may be H, CH_3, C_2H_5, $CH=CH_2$, $CH(OH)CH_3$, C(O)H, COOH, CH_2COOH, and CH_2CH_2COOH. If it is also taken into consideration that one or more pyrrole double bonds may be hydrogenated and that adjacent substituents R_1-R_8 and R_α-R_δ may form closed cycles, then the diversity of

molecular structures of porphyrins azaporphyrins, phthalocyanines, and so on becomes more evident. It should be emphasized that a porphyrin molecule ceases to exist as soon as at least one double bond in the macroring is hydrogenated.

The specific features and great diversity of porphyrins particularly metalloporphyrins, are the factors responsible for their importance and wide distribution in nature, their extensive use in various physical, physicochemical, quantum-chemical and biological studies as well as in the production of dyes, semiconductors, and catalysts. The structural diversity of porphyrins and metalloporphyrins opens up enormous possibilities for studying the effect of functional substituents and central atoms on the properties of porphyrins. Such studies will make it possible in the future to provide an answer to the question why Nature has chosen, as the basic component of the photosynthetic and respiratory molecular system, porphyrins with a particular combination of functional such as can be found in chlorophyllic acids and protoporphyrin.

An important characteristic of porphyrin complexes is their extremely high stability to dissociation. This is one of the reasons why nobody has been able so far to measure quantitatively the equilibria of their formation in a direct manner and to characterize this stability in terms of a definite constant. The kinetic method has been widely used in investigating the stability of porphyrin and phthalocyanine complexes.

The capacity of complexes for additional coordination is to some or other degree their common property. However one can hardly find another instance where, the coordination of additional ligands is as manifest as in the case of planarly coordinated metalloporphyrins. It is referred to as extra coordination for the ligands are attached along the z axis passing through the metal atom at a right angle to the plane of the porphyrin molecule. Extra coordination is an important property of such metalloporphyrins as chlorophyll, haem of the blood, catalyses, and others for it results in attachment of the active metal complex to the molecule of the carrier protein and is essentially a transport reaction as far as oxygen, hydrogen peroxide, and the electron are concerned.

Finally, an important and unique feature of porphyrins and their metal derivatives is their electronic absorption and emission spectra. The diversity of the

latter, corresponding to the great variety of porphyrins, the typical arrangement of spectral bands, the sensitivity to certain effects on the molecule, and their complexity, make them not only a most reliable means for identifying porphyrins but also a rich source of information on the structure of porphyrins, the type of their coordinations, the interaction between substituents and ionizing media, and the intramolecular energies.

Porphyrin molecules perform their biological and catalytic functions only within metalloporphyrins. These functions are determined by the coordination (donor acceptor, complexing) properties of the porphyrin molecule and metal. Since they are bound in the metalloporphyrin molecule by a very strong chemical interaction which ensures the integrity of the entire molecule, we may speak of coordination properties of metalloporphyrins, meaning their capacity for further coordination to extra ligands and for staying together that is coexisting in proton-donor media.

Thus the coordination properties of porphyrins determine the conditions for and rates of formation of metalloporphyrins and their ability to survive in various media (including proton-donor, oxidation-reduction, and photoexciting ones) without undergoing protolytic dissociation and oxidative or photo-oxidative degradation. They also determine the capacity of porphyrins for acting as photosynthetic, respiratory pigments and enzyme (catalytic) systems.

Investigations of coordination phenomena involving porphyrin molecules are, thus, of paramount importance in the chemistry of porphyrins. Work in this field has been under way over the past two or three decades and is rapidly progressing with studies being conducted in many countries [15]. However, the total volume of research into coordination phenomena involving metalloporphyrins is still far from being adequate to the scientific magnitude of the problem. This lag of the coordination chemistry of porphyrins is primarily due to the complexity and unavailability of most porphyrin ligands and to the long established concept of poor stability and ephemeral nature of porphyrin molecules isolated from natural sources under conditions normally prevalent in complex formation studies. This is probably why in many physicochemical studies use is made of stable synthetic porphyrins such as tetramethyltetraethylporphyrin (etioporphyrin), α, β, γ, δ-tetraphenylporphyrin and α, β, γ, δ-tetrapyridylporphyrin.

Naturally, of greatest practical interest are the coordination properties of two most important natural porphyrins-chlorophyllic acid (phaeophytine) and protoporphyrin as well as their complexes. In this work they are given primary attention. At the same time, it should be borne in mind that no solution to problems concerning the effect of functional substituents and the structure of a porphyrin molecule as a whole on its activity in biological and other processes can be found without investigating as many porphyrins of different structure as possible, including synthetic ones. This aspect of the problem is also treated at length in the present monograph.

The question as to the role of the central metal atom in molecules of biologically active metalloporphyrins is yet to be answered. Magnesium is present in chlorophyll, while the haem of haemoglobine, cytochromes, and catalase contains an iron atom. To answer the question why these two and no other metals are involved in biological evolution one must examine the effect of the species of the metal atom on all physicochemical phenomena occurring with the participation of porphyrins in photosynthesis, oxygen transport, intracellular oxidation, and other processes. The most interesting in this respect are the electron-optical, oxidation-reduction, and coordination properties. Systematic studies into the kinetic stability of metal analogues of chlorophyll and haemin have given insight into the specific role the magnesium atom plays in the chlorophyll molecule from the standpoint of coordination properties of metalloporphyrins.

As far as the iron atom is concerned, the picture is much clearer. Its particular role stems from the abundance of iron in the Earth’s crust rather than from the specific features of its electronic structure since the function of reversible addition and oxygen transport can be performed by other metals as well, for example, cobalt, which may form complexes with porphyrins, possessing a sufficiently high thermodynamic stability and capable of withstanding oxidative degradation in the presence of active haemoglobine [16].

2.2. Acid Base Properties of Porphyrins

Quite valuable information on the structure of porphyrazines and their analogs can be obtained while studying their behavior in the proton donor media [17,18]. In addition, the possibility of practical application of porphyrazine metal complexes and

their analogs significantly depends on their stability in solutions. In this connection, the study of the acid-base interactions of porphyrazines and their complexes is of interest in both theoretical and practical aspects.

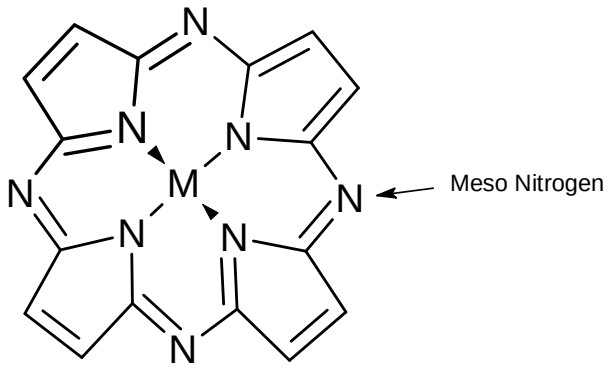


Figure 2.3 Porphyrazine metal complex [22].

Porphyrazines are weak multicenter conjugated bases. The number of porphyrazine donor centers involved in the acid–base interaction with acids, the character of the interaction, and the stability of the acidic forms obtained depend on the porphyrazine structure and the properties of the proton donor medium. The π orbitals of endocyclic N atoms in metal complexes of porphyrazines participate in formation of bonds with a central metal atom. Therefore, only the exocyclic meso-nitrogen atoms are involved in the acid–base interaction (Fig.2.11). The long-wavelength region of the electronic absorption spectra of porphyrazine complexes in a neutral solvent contain intense Q-band due to the $\pi \rightarrow \pi^*$ electronic transitions $a_{1u} \rightarrow e_g^*$ of a macrocyclic ligand. The interaction of porphyrazines with acids is attended by the spectral changes in a visible region corresponding to the formation of different acidic-basic forms. In the case of porphyrazine complexes, the acid-base inter-actions occur in two stages, which are attended by bathochromic shift of the Q-band [19-21].

$$MPz + H^+ <=> MPzH^+ \quad (2.1)$$

$$MPzH^+ + H^+ <=> MPzH_2^{2+} \quad (2.2)$$

The transfer of a proton from acid HA to base B: proceeds through the stages of formation of the acid associate, H-associate, ion–ion associate and fully ionized protonated form:

$$B: + HA <=> B^{\cdot}....HA <=> B^{\cdot} ....H....A <=> BH^{+}.... A^{-} <=> BH^{+} + A^{-} \quad (2.3)$$

Acid associate H-assosiate Ion-ion associate Protonated form

The acidic forms thus obtained differ from one another in a degree of a proton transfer from the acid molecule to the donor center. In media with a low ionizing capability, the electron-donor centers of porphyrazine participate in a weak acid–base interaction and form H-associates and ion–ion associates. The complete transfer of a proton can be observed in strongly ionizing medium only [22].

2.3 Application Field

The diversity of useful properties and structures of metalloporphyrins provides favorable conditions for varying the electronic states of the central metal atom which determines the coordination and catalytic properties, as well as searching for new effective catalytic systems that may be compatible with natural biocatalysts and even surpass them. We are speaking of synthesis, on the basis of porphyrin systems, of new effective catalysts, blood substituents, thermo- and photostabilizers, medicinal substances, organic semiconductors, pigments and dyes, solar cells, and inhibitors of homolytic degradation of protein molecules in living organisms exposed to X and gamma rays.

At present, natural porphyrins and their synthetic analogues are finding a host of industrial uses. Phthalocyanine which is a structural synthetic analogue of porphyrins, and its numerous intercomplex salts and functional derivatives are especially well known pigments.

Their extremely high thermal stability, fastness to light, inertness to acids and alkalis, insolubility in most solvents, high dyeing power, purity, and color intensity have ensured their reputation and wide application in the painting, printing, textile, and paper industries, as well as in chemical fiber and plastic dyeing processes, as superior quality blue, blue-green, and green pigments. Also used as pigments are high-chlorine

derivatives of phthalocyanine and its complexes (e.g. “phthalocyanine green”, which contains up to 15 chlorine atoms in the copper-phthalocyanine nucleus). Sulpho derivatives of copper phthalocyanine are employed as valuable direct dyes for cotton, known as “Sirius turquoise” and “direct light-fast turquoise”. In addition to the most widely used copper complex, complexes of phthalocyanine with Co, Ni, Al, and other metals are also used industrially.

The introduction of various functional substituents into the benzene nuclei of phthalocyanine, whereby it acquires solubility, new chromophore properties, and the ability to be fixed on fibers from solution, permits numerous dyes of different classes to be obtained on its basis.

A popular process in the textile industry is phthalogenic dyeing of fabrics, based on synthesis of phthalocyanines from intermediate products (so called phthalogens) directly on fibers.

Broad possibilities for using porphyrin complexes are being opened up in the technology of semiconductors and lasers, as well as in quantum-electronics research, because of their exhibition of semiconductor and other valuable properties.

Another promising area of their application as oxidation-reduction catalysts includes industrial synthesis, enzyme catalysis, and electrochemical processes involved in the catalytic reduction of oxygen in fuel cells. Other uses of phthalocyanines include, for example, processes for producing heavy isotopes of some elements and oxidation-reduction indicators.

CHAPTER 3

SYNTHESIS METHODS OF PORPHYRAZINE AND PHTHALOCYANINE COMPLEXES

3.1 General Synthesis Methods

Complex compounds of chlorophyllic acid, protoporphyrin and most of their structural analogues are synthesized from available ligand molecules of porphyrins and metal salts. Therefore the problem of synthesis of complexes is determined entirely by the availability of respective porphyrins. Only in the case of phthalocyanine or its polymers are complexes easier to synthesize in sizable amounts from semi-products that is from structural units making up a phthalocyanine ligand, in the presence of a metal.

The majority of TAP structures prepared from 1937 to 1990 have been collected by Luk'yanets and Kobayashi [23]. Since porphyrazines are analogs of phthalocyanines with the only differences of the absence of the fused benzene ring on the pyrrole units, the synthetic methods applied to phthalocyanines can be used to synthesize porphyrazines.

Porphyrazine can be synthesized from functionalized nitriles such as maleonitriles, fumaronitriles and phthalonitriles. Like benzoporphyrazines (phthalocyanines), the synthesis of porphyrazines is limited to Linstead macrocyclisation in which the dinitrile **1** or **2** undergoes a macrocyclisation reaction under reflux in the presence of a magnesium alkoxide in the corresponding alcohol (typically 1-butanol or 1-pentanol) or dimethylaminoethanol to yield **3** (Fig.3.1). Magnesium porphyrazines such as **3** are easily demetallated under acidic conditions to form the free-base porphyrazine such as **4** [24,25].

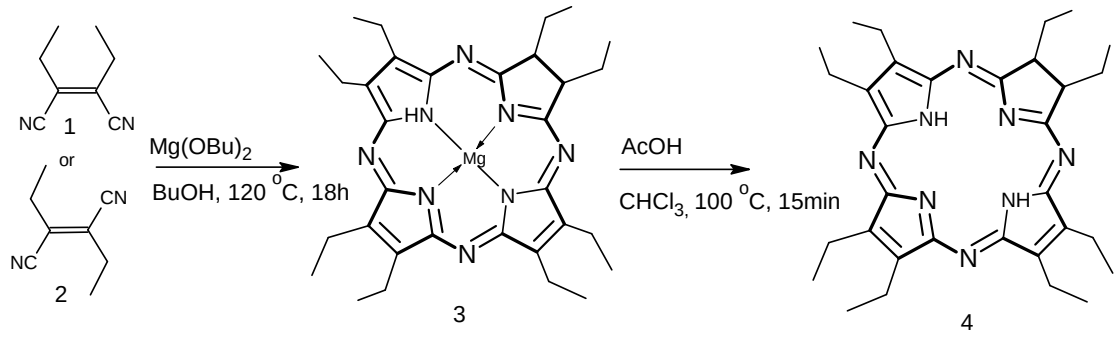


Figure 3.1 An example of porphyrazine synthesis[24].

Removal of magnesium can be achieved by treating a solution of magnesium octaethyltetraazaporphyrin (**3**) in chloroform and acetic acid for 15 minutes, to give free-base porphyrazine (**4**). The above synthetic method is known as Linstead magnesium template macrocyclisation. The same synthetic method is also applicable if two different precursors are macrocyclised to form different porphyrazine hybrids (Fig.3.2) [26].

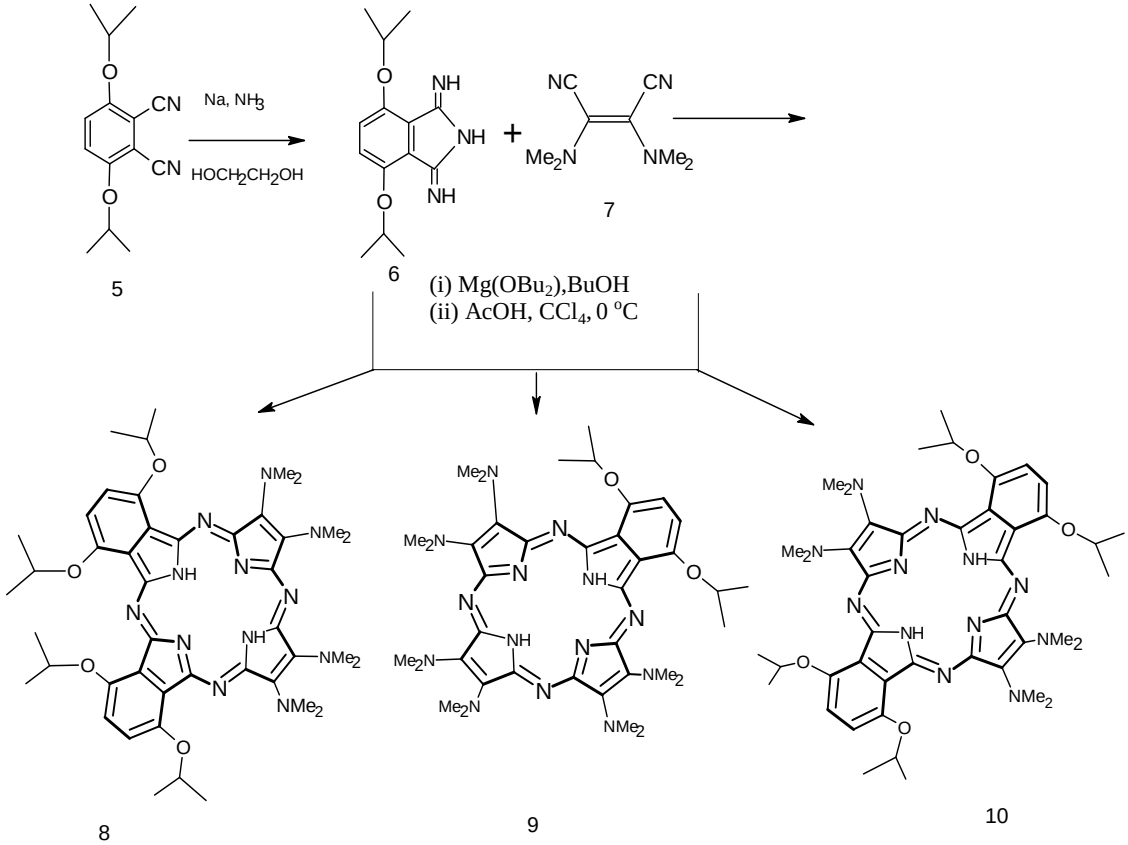


Figure 3.2 Synthesis of porphyrazine molecules from two different precursors [26].

Since phthalonitrile (**5**) is unreactive in the synthesis of either the phthalocyanine or porphyrazine, it is first converted into its corresponding 1,3-diiminoisoindoline **6** to increase its reactivity. A suspension of phthalonitrile **5** in 1,2-ethanediol is bubbled with ammonia gas in the presence of sodium metal. The 1,3-diiminoisoindoline **6** derived from hydroquinone isopropyl ether **5** is then reacted with dimethyl aminomaleonitrile **7** to give porphyrazine hybrids **8**, **9**, **10** (Fig.3.2) [26].

Some metal free porphyrazines can be prepared directly from succinoimidines by heating in high boiling solvents such as chlorobenzene and nitrobenzene (Fig.3.3) [23].

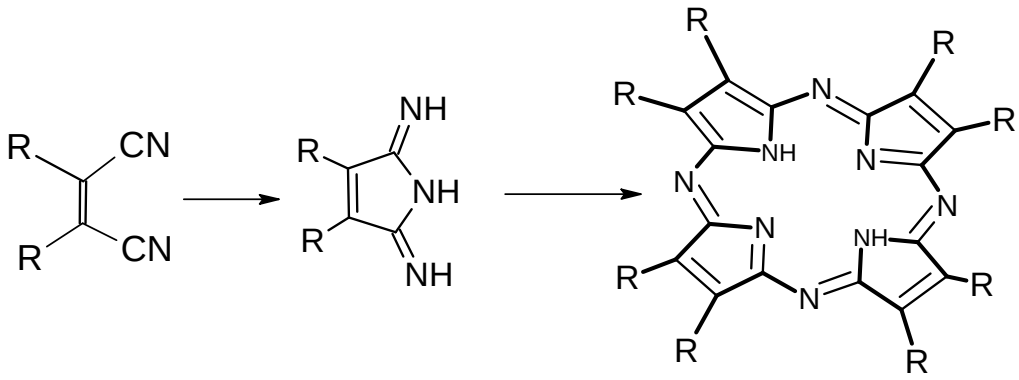


Figure 3.3 Synthesis of metal free porphyrazine directly from succinoimidine [23].

Nowadays metal-free porphyrazines are obtained by demetallation of corresponding magnesium porphyrazine with acid such as TFAA or HCl (Fig.3.4).

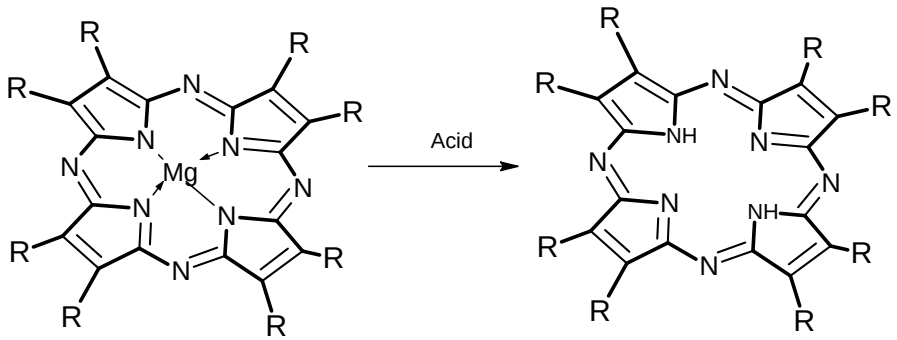


Figure 3.4 Synthesis of metal free porphyrazine by acid treatment [23].

Various substituents provide porphyrazines with substantial organic solubility compared to their porphyrin and phthalocyanine counterparts. Peripheral substitution among porphyrazines is becoming an increasingly popular strategy for the design of

functional dyes and molecular devices. Porphyrazines with peripheral substitution of the form M[Pz-(A_n:B_{4-n})], where A and B are functional groups fused to the β-position of the pyrroles, have the potential to exhibit magnetic and electronic properties [9,27,28]. Due to peripheral substitution, these porphyrazines show unusual UV-Visible spectra, redox chemistry and electrochemistry. In addition, they exhibit interesting coordination chemistry for binding of metal ions within the macrocyclic cavity and by peripheral ligating groups (N, S, O) [29]. Substituted amphiphilic and hydrophilic porphyrazines bearing both hydrophilic and hydrophobic moieties can be more potent as photosensitisers in photodynamic therapy [30-32]. With acetylinic units as peripheral substituents, the π-systems of the chromophores are enlarged and bathochromic shifts in the electron absorption and emission spectra are induced. Alkyl groups also serve as covalent linkers for the assembly of delocalized multichromophore chains or two dimensional polymer networks [33].

The second method involves the macrocyclisation of substituted precursors, which may lead to a cleaner product of known substitution pattern. Peripheral substitution in porphyrazines is achieved by reacting with substituted phthalonitrile (**11**) and a maleonitrile (**12**), or reacting two maleonitriles. However, as shown in Figure 3.5, this method also leads to the formation of isomers due to the symmetry involved in macrocyclisation. While macrocyclisation of substituted precursors has its drawbacks, it is still the method of choice for the synthesis of substituted porphyrazines with improved properties.

Trans-substituted porphyrazines (**13**) can be synthesized by using a phthalonitriles with bulky groups. In this case, the bulky group appears once or twice due to steric hindrance in which the steric groups cannot be adjacent and co-planar (i.e. bulky groups are prevented from being adjacent to each other) as shown in Figure 3.5 [34].

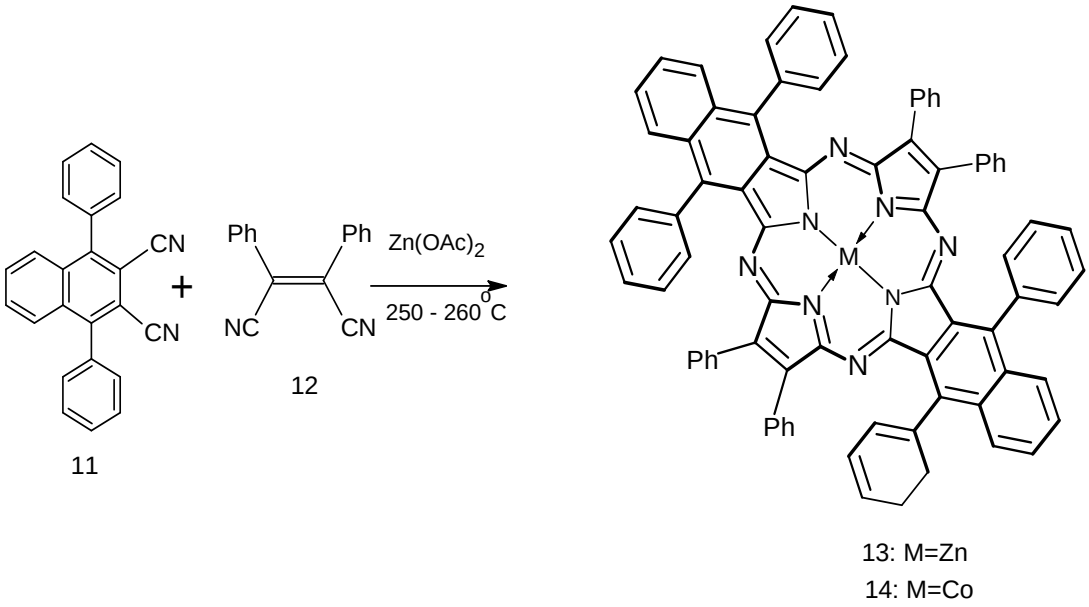


Figure 3.5 Synthesis of *trans*-substituted porphyrazine [34].

The most successful pathway of synthesizing unsymmetrical substituted porphyrazines (**16-21**) is to a use statistical condensation of two substituted precursors A and B (**15**) in which the desired product can be isolated by column chromatography. Although the method also gives a mixture of six compounds, required compound can be isolated as a major product. If, for example, the reaction is done with the precursors A: B at a ratio of 1:8 or above, the major product is that in which A:B is incorporated into the pigment in the ratio of 1:3 (Fig.3.6) [34].

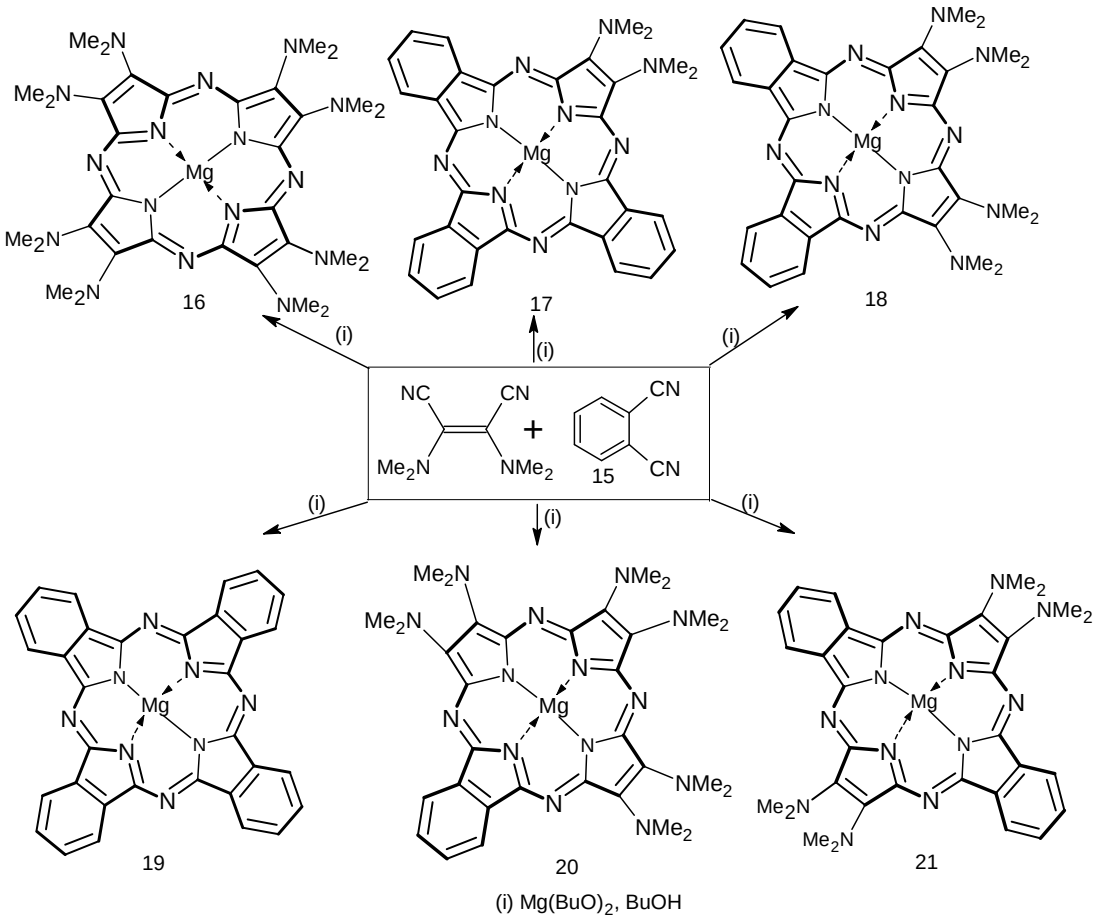


Figure 3.6 Synthesis of unsymmetrical porphyrazine [24].

3.2 Transition Metal Complexes of Porphyrazines

The porphyrazine macrocycle is a good ligand to most metals even though only few porphyrazine metal complexes have been reported compared to their phthalocyanine and porphyrin counterparts, where most research in this area has been centered. This is because porphyrazines still represent a new field of research, with much research based on the selective incorporation of substituents. Even though metallations can be effected as an integral part of their synthesis, such as in cases in which the macrocyclisation in the presence of a templating transition metal salt or Li or Mg alkoxides, the best method that gives a product of high purity is the metallation reaction of a free-base ligand [35,36].

It has been already determined that a metal in the centre, or metal complexes to peripheral ligating groups can alter the physical and chemical properties of a porphyrin, phthalocyanine or porphyrazine [36,37]. When the central metal is iron or cobalt,

phthalocyanines make good electrocatalysts for the reduction of oxygen at a fuel cell cathode [38]. It has also been shown that iron (II) porphyrins decompose oxygen through a mechanism involving two porphyrins acting on oxygen molecule. Metal porphyrins have been also shown to catalyze carbene-type transformations with diazo reagents such as cyclopropanation of alkanes and C-H insertion of alkanes. Recently, it has been reported that iron (II) porphyrin complexes can catalyse the olefination of a selection of aldehydes with diazoacetate in the presence of triphenylphosphine [39]. With porphyrins, phthalocyanines and porphyrazines as photodynamic therapy agents, a metal in the centre may improve their photosensitivity, especially in the instances of the diamagnetic metals like zinc [40].

The normal charge of a porphyrin, porphyrazine or phthalocyanine is (-2). Therefore, the metal ion to be accepted in order to form a stable complex is the one with a (+2) charge. Metal ions with a charge of (+1), requires an additional ion with (+1) charge (Fig.3.7) [38].

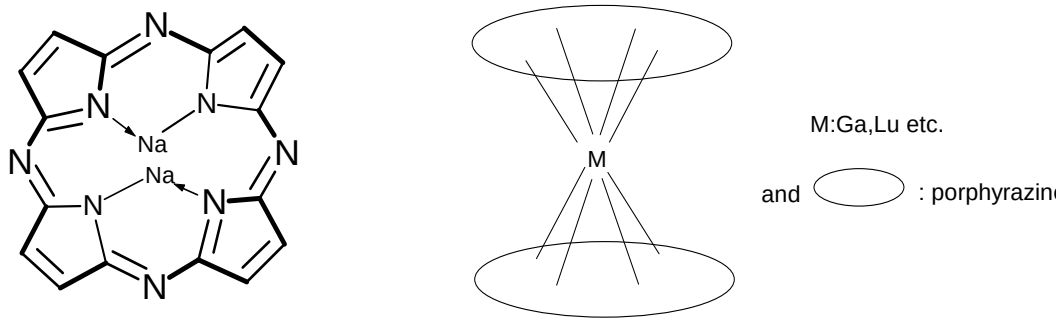


Figure 3.7 Metal complex formation of porphyrazine [38].

Metal ions with a charge of (+3) or higher require additional “axial” ligands. In the case of larger ions, the phthalocyanine or porphyrazine or porphyrin cannot fully accommodate these ions within the core cavity and in this case the metal becomes surrounded by two phthalocyanines, porphyrins or porphyrazines, making a “sandwich” complex (Fig.3.7) [38].

Metalation in phthalocyanine and porphyrazine compounds can be incorporated into the synthesis as shown in Figure 3.8 [39,40]. In a metal-free porphyrazine (**1**), central metallation is mostly done by heating from 50 ºC to reflux the metal-salt [$Ni(OAc_2)$, $MnCl_2$, etc.] in a mixture of chlorobenzene and DMF or in neat DMF.

Peripheral metallation can be effected by heating the porphyrazine in a suitable solvent mixture (mostly using acetonitrile-trichloromethane) [39,42].

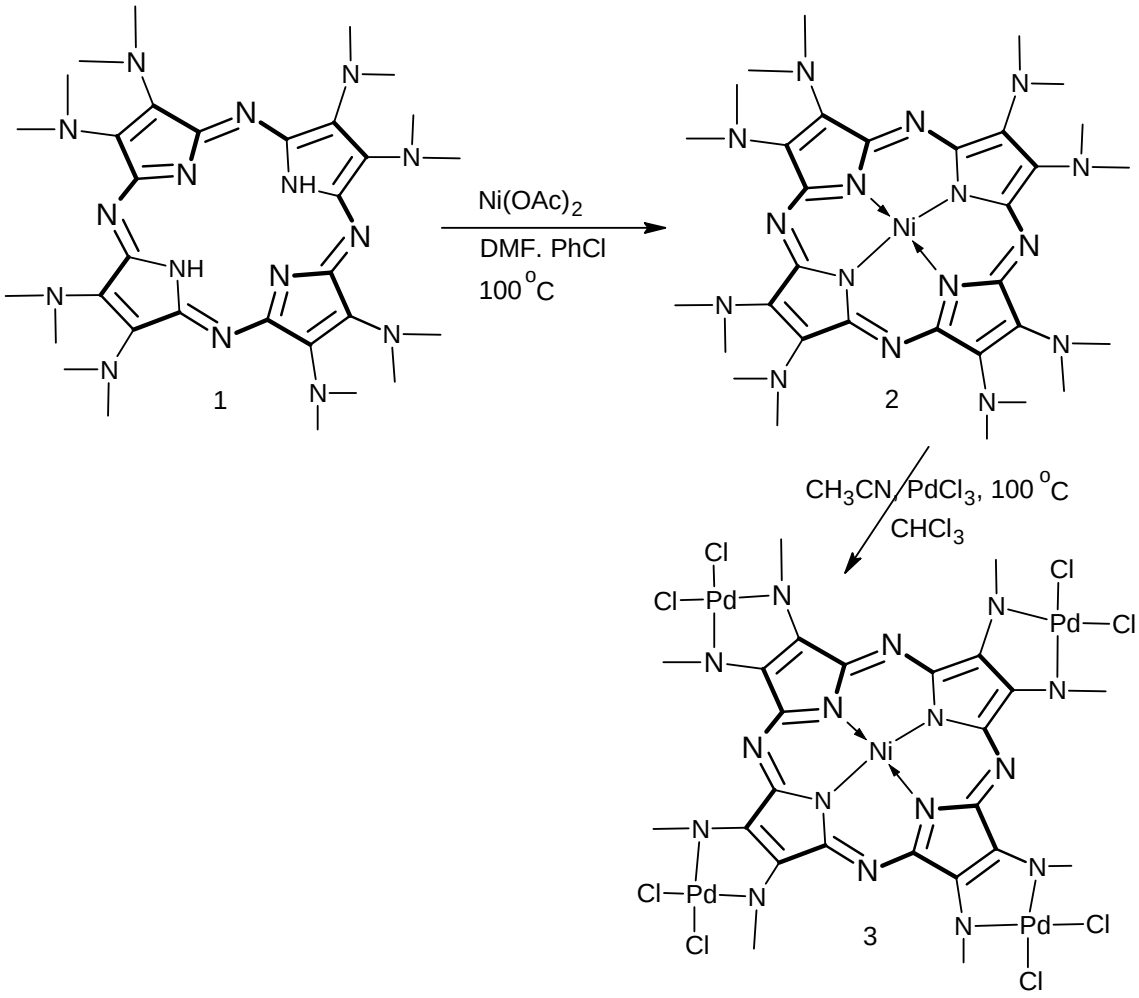


Figure 3.8 The synthesis of metal complex of porphyrazine **2** with Ni (central) and Pd (peripherally) metals **3** [31,42].

If the starting porphyrin contains etherified carboxyl groups, for example H_2MP DME or H_2PP DME, etherification and chromatographic separation on a column are required after complex formation under stringent conditions, in some cases with subsequent recrystallization. Such procedures are described for vanadyl mesoporphyrin synthesized from H_2MP DME and VCl_4 in a scaled glass tube at 165 °C for Mn^{3+} mesoporphyrin synthesized from mesoporphyrin hydrochloride and $MnAc_2$ in glacial HAc with admission of air, and by other investigators.

Many metals form metalloporphyrins with different degrees of oxidation of the central atom. They include Fe^{2+}-Fe^{3+}, Co^{2+}-Co^{3+}, Ag^{+}-Ag^{2+}, Mn^{2+}-Mn^{3+}-Mn^{4+}, Sn^{2+}-

Sn^{4+}, Cr^{2+}-Cr^{3+}. The least stable of all are Fe^{2+}, Mn^{2+}, Ag^{+}, Cr^{2+} and Sn^{2+} porphyrins. Cobalt usually yields complexes in the form of Co^{2+}; special oxidation conditions are required for it to become Co^{3+}. However, some porphyrins promote oxidation in air; for example, protoporphyrin with $MnAc_2$ and $CoAc_2$ in hot glacial HAc forms (HO)MnPP and (HO)CoPP in the presence of HCl and air.

A complex of mesoporphyrin DME with Co^{2+} prepared in methanol turns to (HO)CoMP when kept in air. The metal oxidation process is catalyzed with olefins and acetylenes.

3.3 Recent Progress for Porphyrazine Synthesis

In recent study published by Giribau L. et al, [43] a novel single-step preparation of free-base and metalloporphyrazines from maleonitriles was studied for the first time by treatment with metal salts, hexamethyldisilazane (HMDS) and *p*-toluene sulfonic acid (PTSA) in DMF at 120 °C. This reaction provides a new preparative method under mild conditions for direct synthesis of metalloporphyrazines having a variety of metals and substituted maleonitriles.

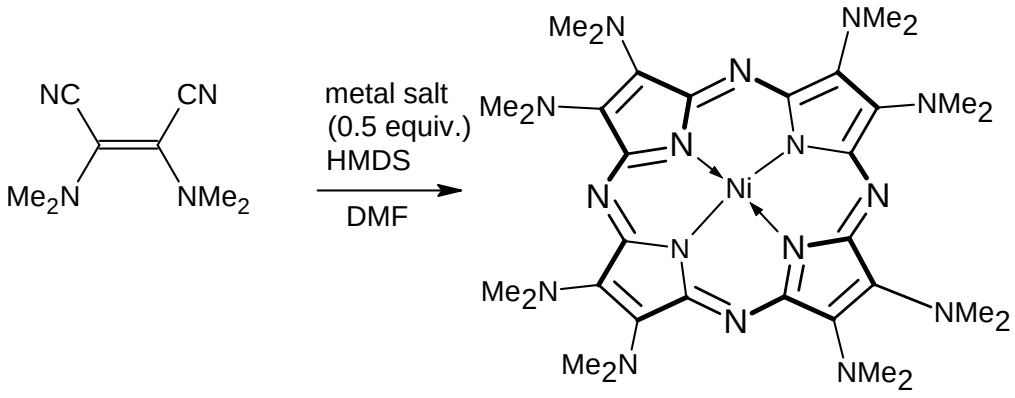


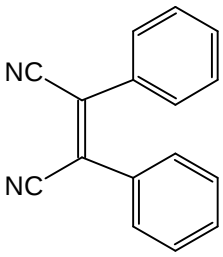
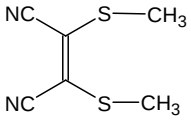
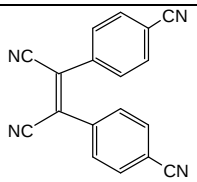
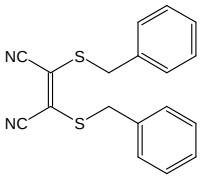
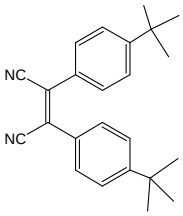
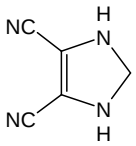
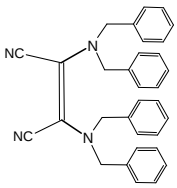
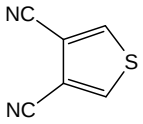
Figure 3.9 Synthesis of metalloporphyrazine with HMDS method [43].

Toru and co-workers have recently reported a simplistic method for the synthesis of metallophthalocyanines by hexamethyldisilazane (HMDS) method under mild conditions. [43]. Giribabu, L. et al. extendend HMDS method to the synthesis of metalloporphyrazines. They reported for the first time a convenient method for the synthesis of porphyrazines on treatment of maleonitriles with metal salts and HMDS under mild conditions. By adopting this method it is possible to synthesize metalloporphyrazines directly. In the Table 3.1, the reaction of maleonitriles with

$Zn(OAc)_2$ in the presecence of HMDS and PTSA were summarized by Giribabu L. et al. Some of the maleonitrile derivatives do not give cyclization reaction with metal salt to prepare porphyrazines. The same maleonitrile precursor were reacted with the different metal salt such as $CuCl_2$, $CoCl_2$, $Mg(OAc)_2$ etc. The results were given in the Table 3.1 and Reference [43].

Toru and co-workers have published synthesis of porphyrazines with HMDS methods in microwave. Microwave-assisted reactions have attracted much interest because of their simplicity in operation and milder reaction conditions. The salient features of the microwave approach are enhanced reaction rates, formation of pure products in high yields and ease of isolation. They extended the microwave technology to synthesize porphyrazines efficiently, in short reaction times, and improved yields using a laboratory microwave oven [45].

Table 3.1 Preparation of substituted porphyrazines by treatment of maleonitrile derivatives with $Zn(OAc)_2$ and HMDS in DMF [43].

Entry	Maleonitrile Derivatives	Yield (%)	Entry	Maleonitrile derivatives	Yield (%)
1		40	5		35
2		31	6		28
3		29	7		-
4		38	8		-

When the microwave-assisted reactions were compared to oil-bath procedure for the synthesis of porphyrazine from the same precursors with HMDS, the microwave-assisted reaction has advantages for the reaction time and higher yield than oil-bath reactions. The time takes with microwave-assisted reaction 10-15 minutes where oil-bath reactions take for hours. The yields are 40-53% in the microwave-assisted and 28-43% for the oil-bath reactions [45].

3.4 Metallo-Porphyrazines That Bearing Different Substituents

Novel metallo-porphyrazines substituted with dimethylaminoethylthio, crown ether, 1-naphthylmethylthio, 4-*tert*-butylphenylthio, 9-anthracenylmethylthio ect. have

been described in this section. These novel compounds have been characterized by elemental analysis, together with FT-IR, ^{1}H NMR, UV-Vis and mass spectral data.

3.4.1 Porphyrazines with Tosylamine Functional Groups

Metal-free and metallo-porphyrazines (M= Mg, Ni and Co) carrying eight functional tosylaminoethylthia- groups on peripheral positions have been synthesized for the first time from cyclotetramerization of 1,2-bis (2-tosylaminoethylthia)maleonitrile in the presence of magnesium propoxide; the metal-free derivative was obtained by treatment of with trifluoroacetic acid and it was further converted into Co(II) and Ni(II) derivatives by using acetate salts of corresponding metal ions. The reactivity of tosylamino-groups was verified by its alkylation to yield octakis[(tosyl)(hexyl)amino-ethylthia]porphyrazinatomagnesium(II) (Fig.3.10) [46].

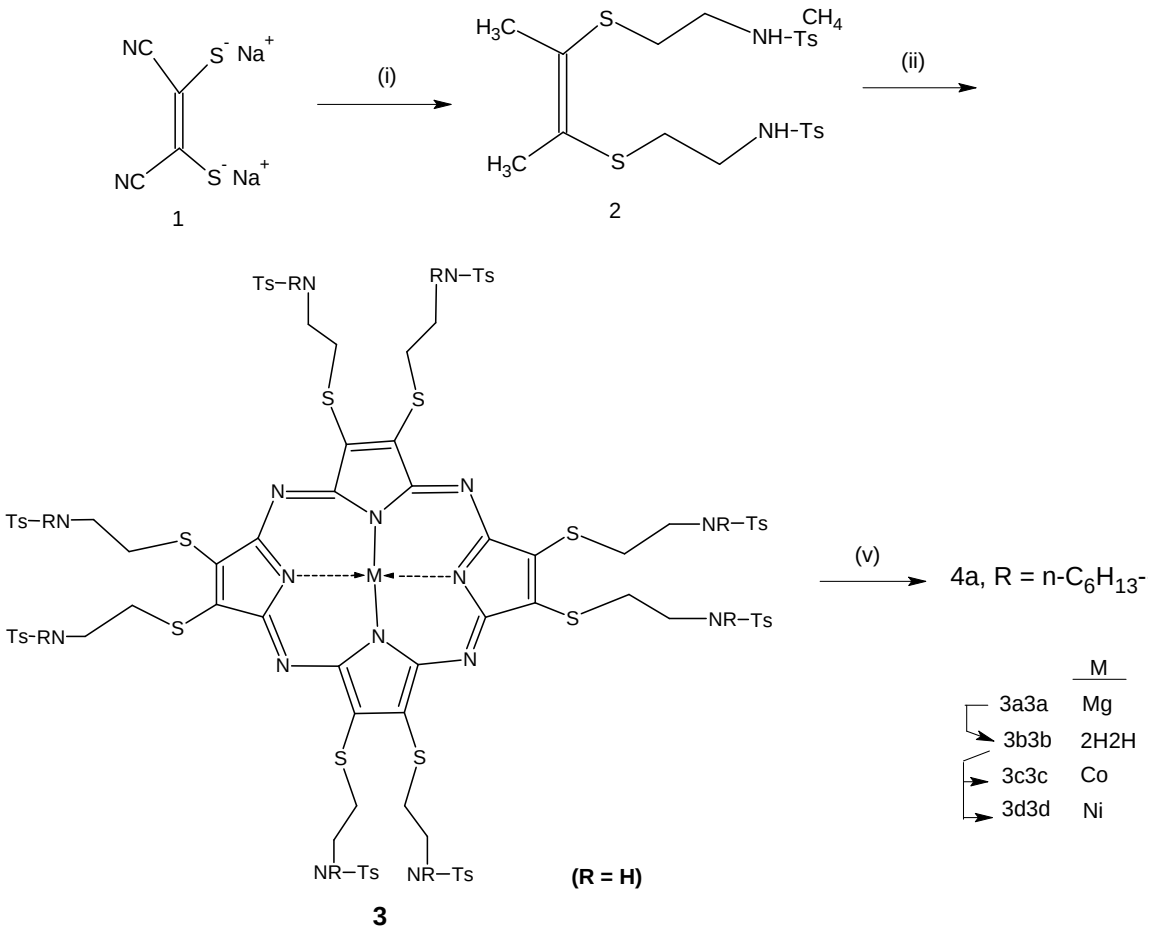


Figure 3.10 Synthesis route to novel porphyrazines. (**i**) di(tosyl)aminoethanol; (**ii**) magnesium, I_2 propanol; (**iii**) trifluoroacetic acid; (**iv**) cobalt(II) acetate or nickel(II) acetate; (**v**) *n*-hexylbromide [46].

The electronic absorption spectra of all the metallo porphyrazines **3a**, **3c**, **3d** and **4a** exhibit a strong absorption between 647–670 nm which is due to a p→p* transition and is commonly referred to as Q band. A second intense and broad p→p* transition in the range 343–374 nm which is called Soret or B band is also a characteristic of these tetrapyrrole derivatives (Fig.3.11). As expected, the metal-free derivative **3b** shows a splitted Q band because of the change in symmetry from D_{4h} in metallo-species to D_{2h} in metal-free ones. Aggregation of symmetrical porphyrazines and phthalocyanines can be efficiently followed from band broadening to a blue shift of the Q bands. However, spectra recorded of 10^{-4} and 10^{-5} M solutions of porphyrazines **3a**, **3b**, **3c**, **3d** and **4a** in chloroform are identical in shape, implying that aggregation is not very effective in the present case. This might be attributed to the bulky nature of the substituents which prevent the interactions between porphyrazine cores at least in these concentrations. Similarly, negligible differences between the spectra obtained in different solvents (chloroform, dichloromethane and acetone) can be also taken as a further confirmation of this proposal.

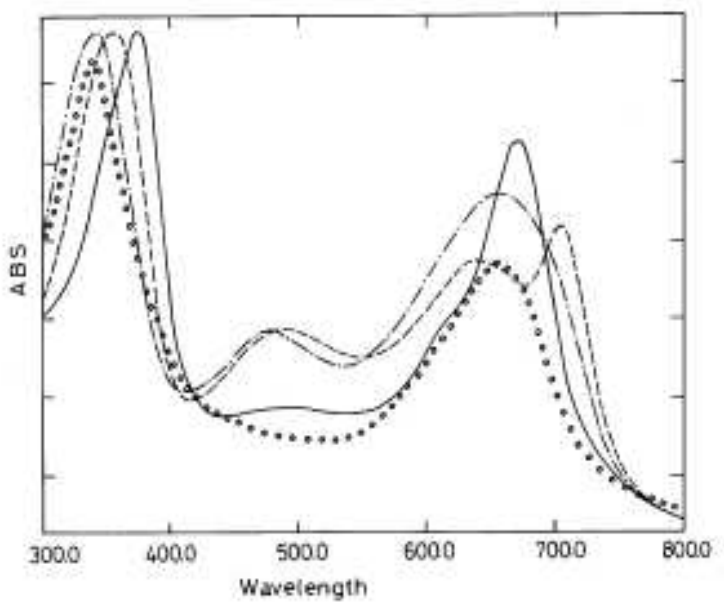


Figure 3.11 Electronic spectra of porphyrazines in chloroform. (—), **3a**; (---), **3b**; (**…**), **3c**; (-·-·-·),**3d**.

In conclusion, new porphyrazine derivatives with reactive tosylamino groups on the periphery was synthesized and demonstrated that this reactive site can be used to prepare diverse macromolecules based on porphyrazines

3.4.2 Porphyrazines with Tertiary or Quaternized Aminoethyl Substituents

Metal-free and metallo porphyrazines (M=Mg or Co) carrying eight dimethylaminoethylthia-groups on peripheral positions have been synthesized from the disodium salt of dithiomaleonitrile and the hydrochloride of dimethyl-aminoethylchloride [47]. The magnesium derivative (MgPza) was converted into quaternized product (MgPzq) (Fig.3.12) by reaction with methyl iodide. The metal-free derivative was obtained by treatment with trifluoroacetic acid and its reaction with cobalt (II) acetate led to the cobalt derivative (CoPza). Aggregation of MgPzq molecules (Fig.3.13) has been observed in aqueous solution by the blue-shift of the Q-band absorption with an accompanying decrease in intensity.

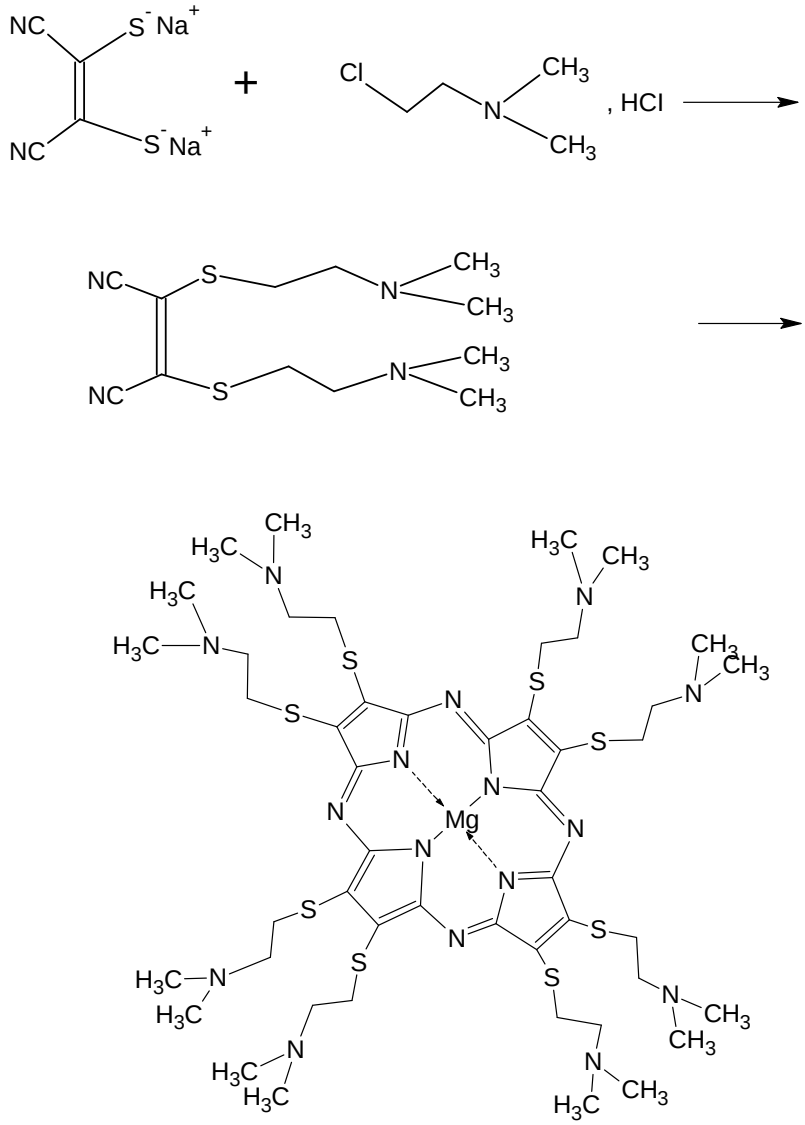


Figure 3.12 Octakis(2-dimethylaminoethylthio)porphyrazinato-magnezyum(MgPza)

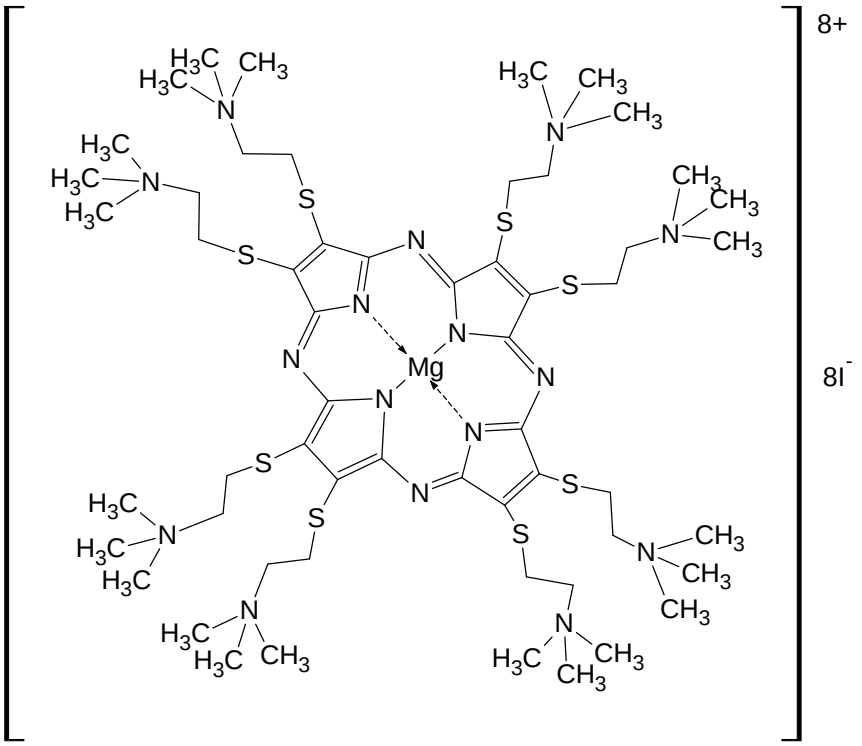


Figure 3.13 [Octakis (2-trimethylammoniumethylthio) porphyrazinato-magnesium] octaiodide (MgPzq) [47].

3.4.3 Magnesium Porphyrazinate with Eight Triphenylphosphonium Moieties Attached Through (2-Sulfanyl-Ethoxycarbonyl-2-Propyl) Bridges

A new magnesium porphyrazinate with eight [triphenyl-(2-sulfanyl-ethoxycarbonyl-2 propyl)phosphonium]bromide groups has been prepared from octakis (2-hydroxyethylthio)porphyrazinatomagnesium and (2-carboxy-1-methylethyl) triphenylphosphonium bromide {[$(Ph)_3PCH_2CH(Me)CO_2H$]Br}(Fig.3.14) [48].

The aim of this work has been to synthesize a novel porphyrazine structure carrying phosphorous containing groups on the periphery. The phosphoniumyl porphyrazine has eight positive charges in the periphery of the p-plane of the tetrapyrrole core. The cationic sites are separated from one another by the porphyrazine unit together with the ester bridges. Thus, these octa-cationic structures are totally different from the cationic porphyrazine derivatives whose cationic centers can influence the electron density by inductive effect.

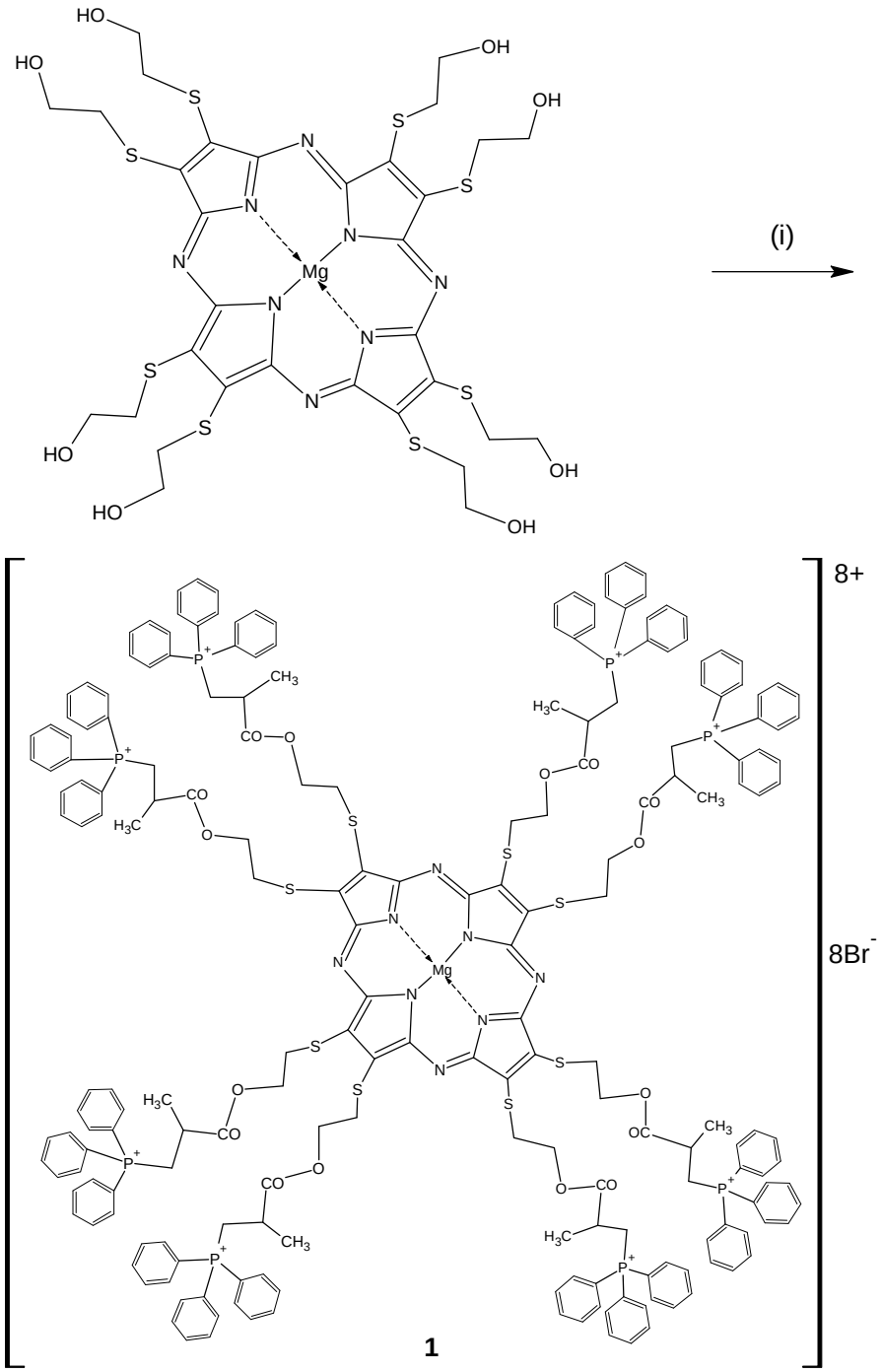


Figure 3.14 (**i**) $[(Ph)_3PCH_2CH(Me)CO_2H]Br$, DCCI, toluene-*p*-sulfonic acid and dry pyridine.
{octakis[triphenyl-(2-sulfanyl-ethoxycarbonyl-2-propyl)phosphonium]yl-porphyrazinatomagnesium}octabromide (**1**) [48].

UV–Vis spectra of complex in solvents of different polarity (dichloromethane, ethanol, chloroform and pyridine) are given in (Fig. 3.15). There is almost no difference with respect to the changes in the nature of the solvent. As expected for a porphyrazine

core, there are two intense absorptions: one of them in the UV-range around 366 nm and another at the lower energy side of visible region (670 nm). In most tetrapyrrole derivatives, Q band absorption is more intense than B band absorption although both of them correspond to p→p* transition [49,50,51]. When we compare the absorbance values in these two peaks, the one in the UV-range is higher. The reason for this controversy is the combination of p→p* transitions of phenyl groups in triphenylphosphonium units with the B band of the porphyrazine core.

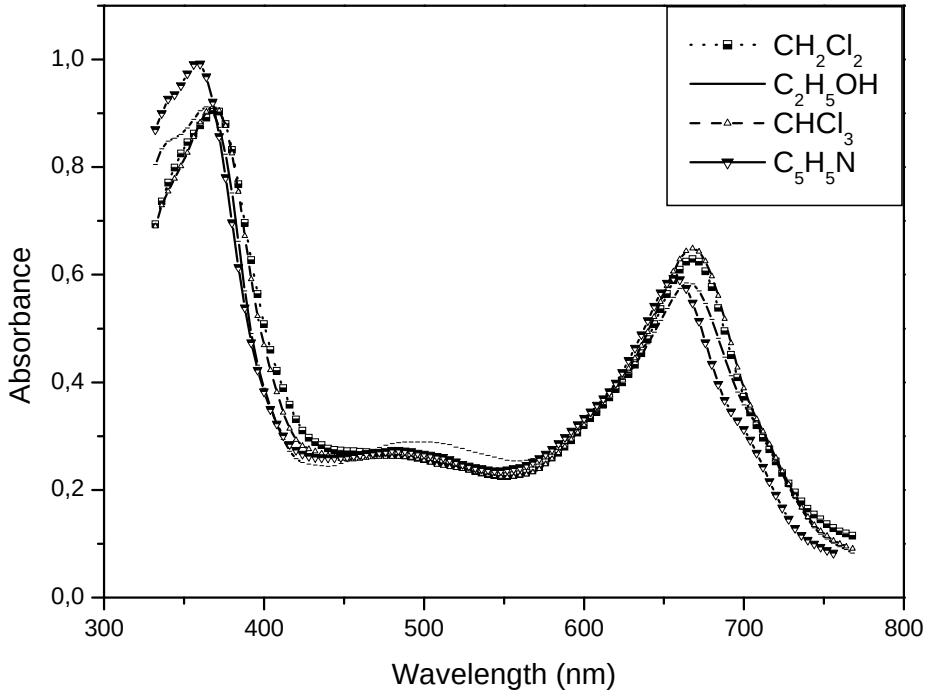


Figure 3.15 UV–Vis spectra of **1** in various solvents.

3.4.4 Octakis (9-anthracenylmethylthio) Iron Porphyrazine Derivatives

Chloro[octakis(9-anthracenylmethylthio)porphyrazinato]iron(III), [FePzCl] (Fig.3.16), was prepared by the reaction of metalfree porphyrazine with iron(II) acetate and further treatment with HCl solution. The monomeric bisaxial complex $[FePz(py)_{2}]$ as well as the bridged complex $[FePz(pyz)]_n$ (Fig.3.17) were formed as stable complexes by reacting [FePzCl] with pyridine or pyrazine, respectively [52].

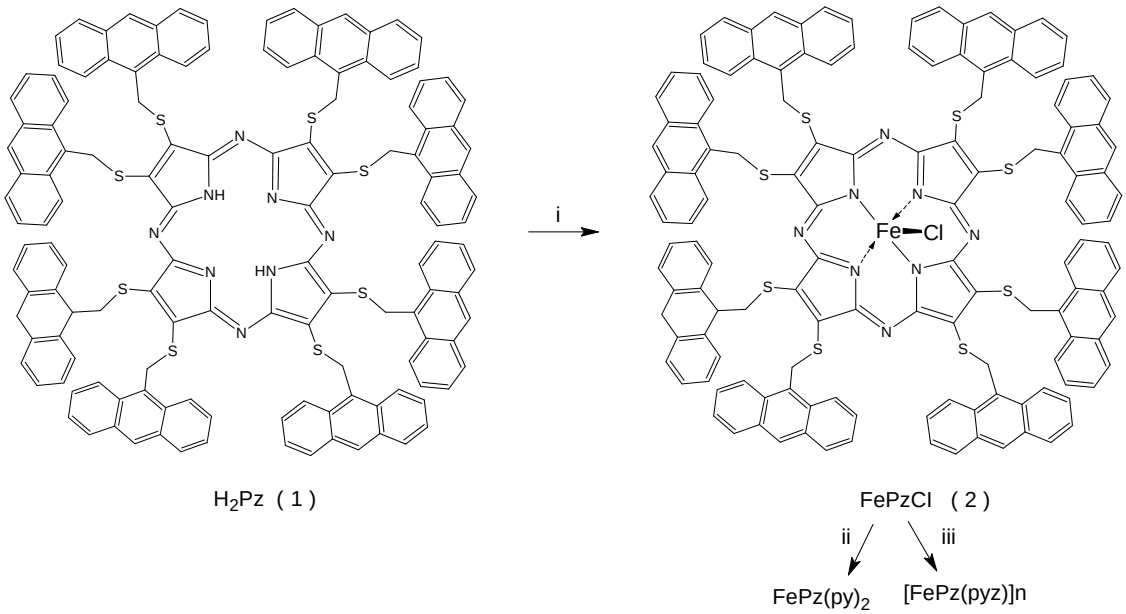


Figure 3.16 Synthesis route to new compounds: (**i**) $Fe(OAc)_2$, acetic acid, HCl; (**ii**) pyridine; (**iii**) pyrazine [52].

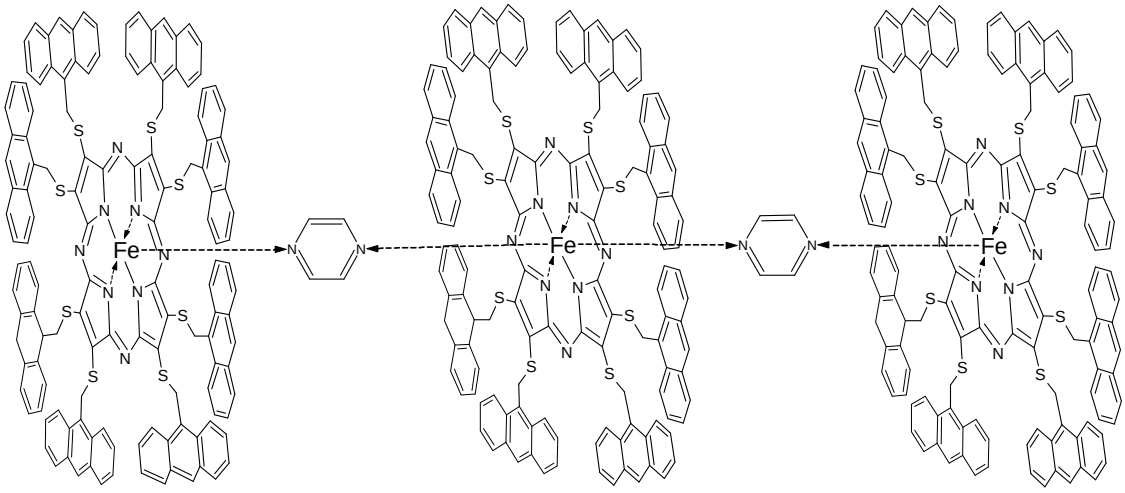


Figure 3.17 μ-Pyrazine[octakis(9-anthracenylmethylthio)porphyrazinato]iron(II) $[FePz(pyz)]_n$ [52].

3.4.5 Phthalocyanine-Porphyrazine Hybrid and its Palladium(II) Complex

A phthalocyanine-porphyrazine hybrid molecule composed of three phthalonitrile units and one maleonitrile moiety was prepared by cyclomerization of the reactants in the presence of magnesium butoxide. Two thioether groups fused to pyrrol positions were complexed with $PdCl_2$ (Fig.3.18) [53].

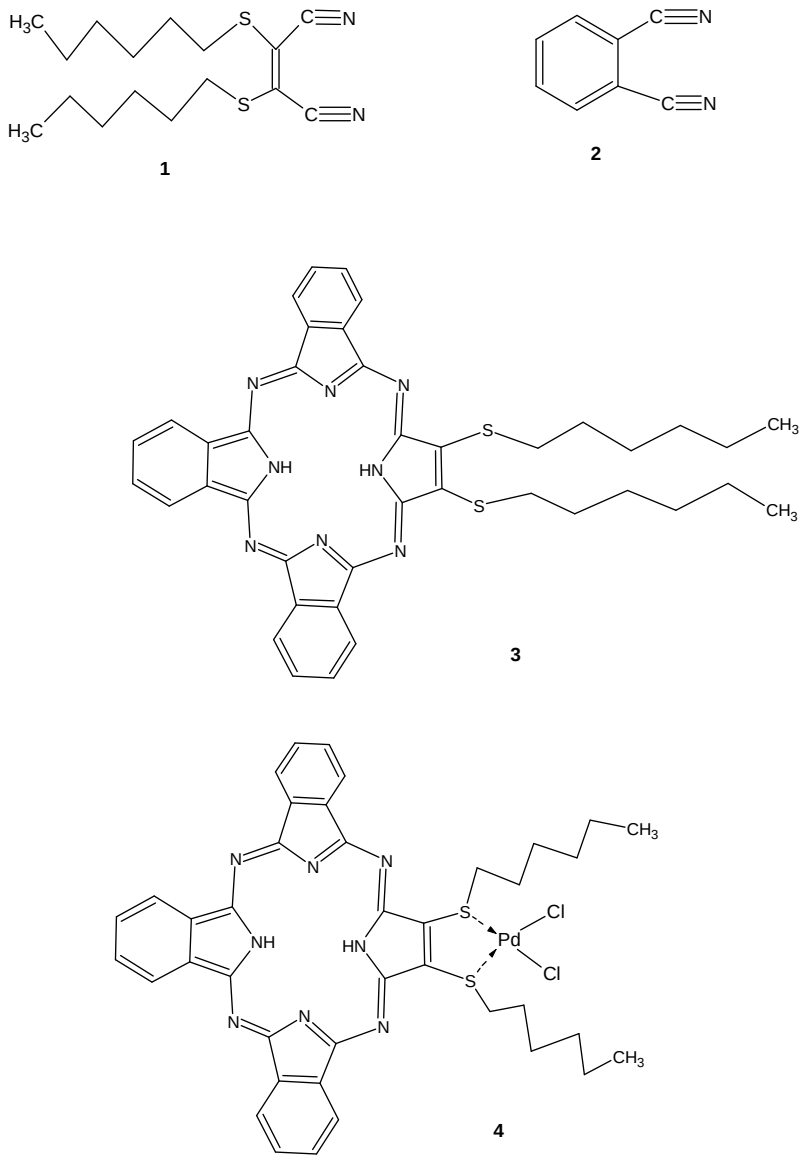
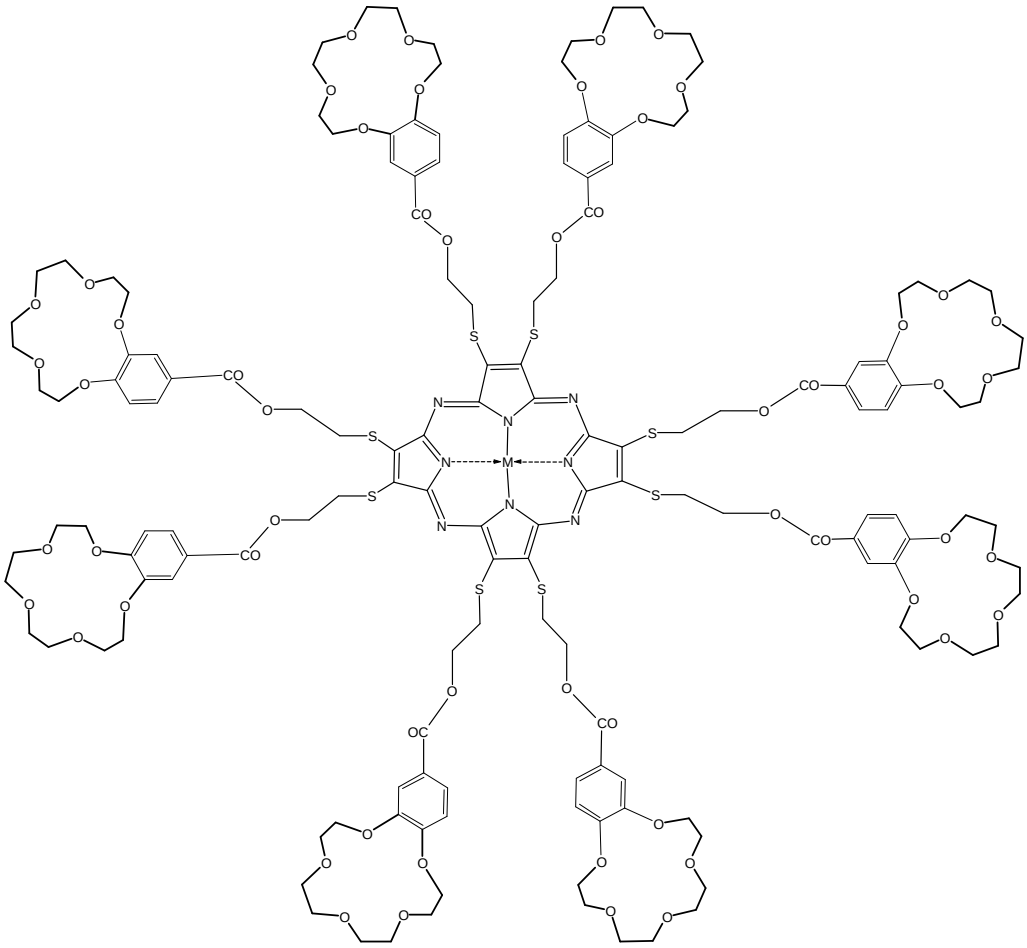


Figure 3.18 Bis-hexylthio-maleonitrile (**1**), phthalonitrile (**2**), phthalocyanine-porphyrazine hybrid (**3**), and the four-coordinate palladium complex (**4**).

3.4.6 Porphyrazines with Appending Eight Crown Ethers

Porphyrazines (M= 2H, Mg, Cu, Co or Zn) with eight crown ether groups appending on the periphery through flexible alkylthio-bridges have been synthesized through esterification of octakis (hydroxyethylthio)-porphyrazinatomagnesium with a carboxylic acid derivative of benzo-15-crown-5 in the presence of dicyclohexyl-carbodiimid (Fig.3.19). Alkali metal interaction of the crown ethers on the magnesium porphyrazinate are shown to form intramolecular sandwich type adducts by the changes

occurring after gradual portion wise addition of these salts into the porphyrazine solutions [54].



M: **Mg** **2H** **Co** **Cu** **Zn**

4 **5** **6** **7** **8**

Figure 3.19 Octakis (crown ether) substituted phthalocyanines [54].

3.4.7 Octakis(1-naphthylmethylthio) Substituted Porphyrazine Derivatives

Magnesium porphyrazinate substituted with eight (1-naphthylmethylthio)groups on the peripheral positions has been synthesized by cyclotetramerization of 1,2-bis(1-naphthylmethylthio)maleonitrile in the presence of magnesium butanolate. The metal-free derivative was obtained by its treatment with trifluoroacetic acid and further reaction of this product with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate led to the metal porphyrazinates (M=Cu, Zn, Co) (Fig.3.20) [55].

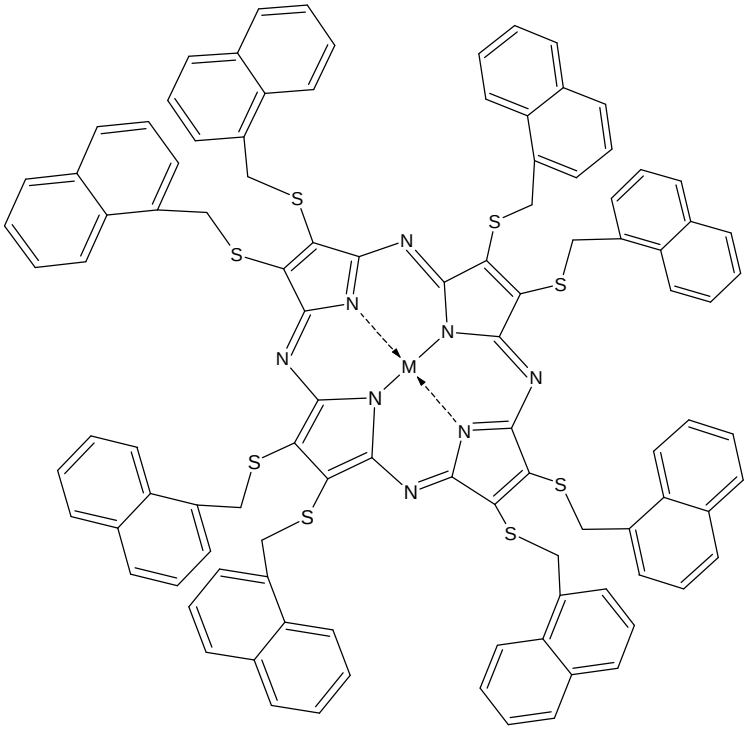


Figure 3.20 Octakis (1-naphthylmethylthio) substituted porphyrazines (M=Mg; 2H; Cu; Zn; Co) [55].

3.4.8 Porphyrazines with Bulky Substituents

Magnesium porphyrazinate substituted with eight 4-tert-butylphenylthio-groups on the peripheral positions has been synthesized by cyclotetramerization of 1,2-bis(4-tert-butylphenylthio)maleonitrile in the presence of magnesium butanolate. The metal-free derivative was obtained by its treatment with trifluoroacetic acid and further reaction of this product with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate led to the metal porphyrazinates (M = Cu, Zn, Co) (Fig.3.21). By using EPR technique, room temperature paramagnetic properties of Cu(II) doped porphyrazine sample as powder and solution forms were measured. The first-derivative EPR signals taken from as powder and solution forms shows that the sample is axially symmetric. The trend $g_{ll} > g_{\perp} > 2$ indicates that the unpaired electron is located mainly in the d_{x2_y2} orbital ($^2B_1$ as ground state) [56].

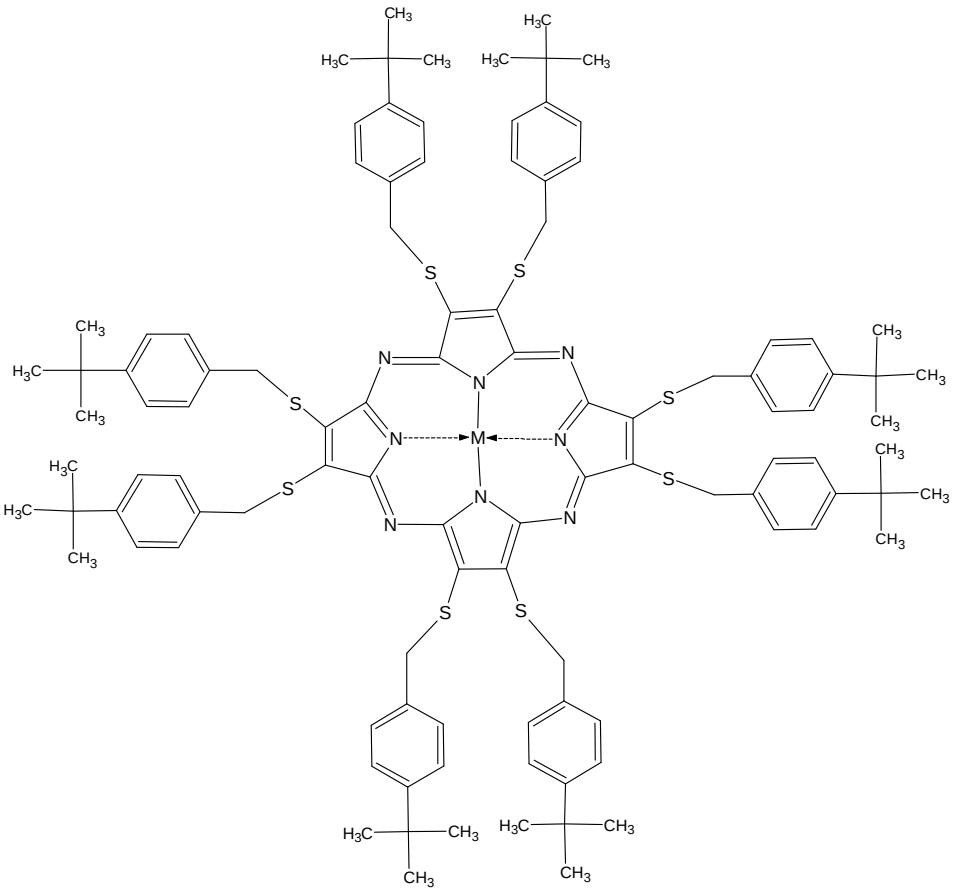


Figure 3.21 Octakis(4-tert-butylbenzylthio) substituted porphyrazines (M =Mg; 2H; Cu; Co; Zn) [56].

3.4.9 Construction of Nonanuclear Supramolecular Structures from Simple Modular Units

A porphyrazine based supramolecule with a nonanuclear structure has been prepared by the ready coordination of pyridine donor sites in octakis(4-pyridoxyethylthio) porphyrazinatomagnesium with vanadyl bis(acetylacetonate) (Fig.3.22) [57].

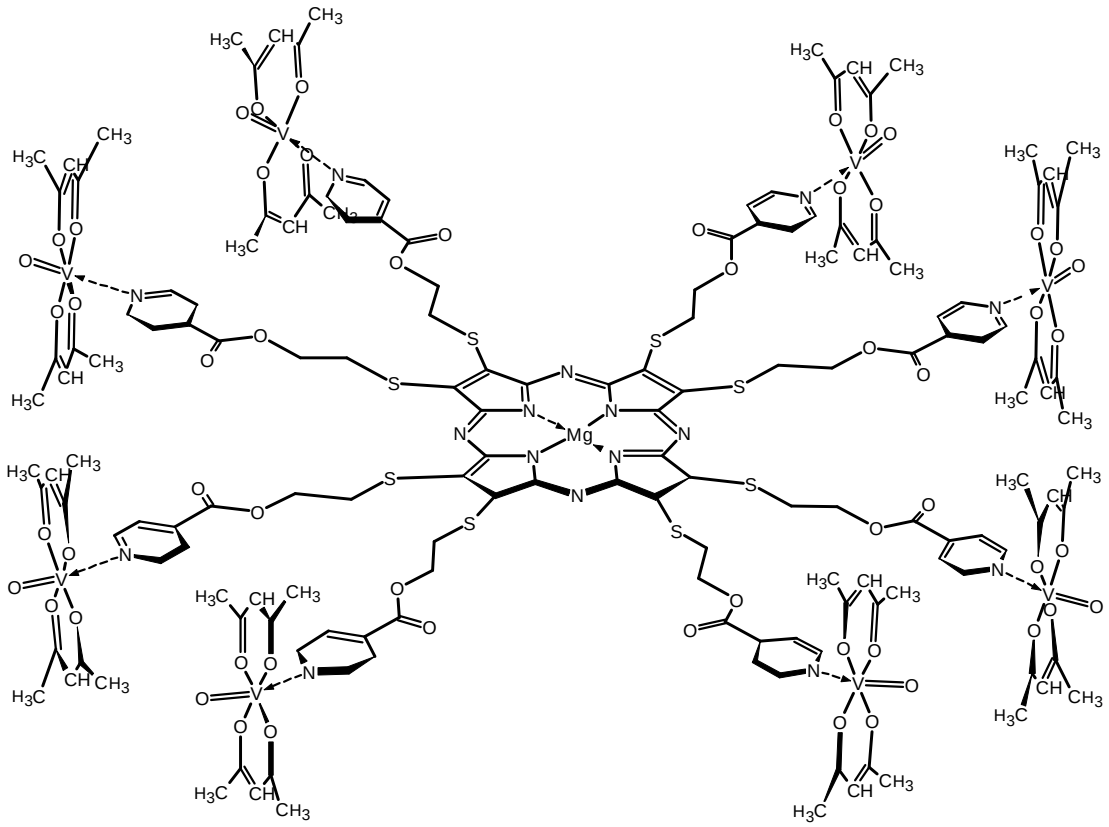
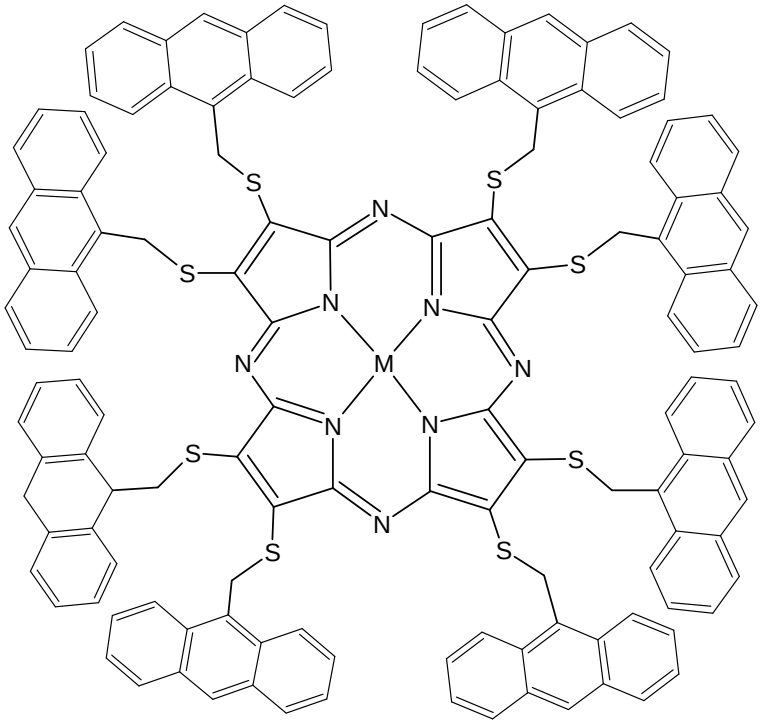


Figure 3.22 Octakis (4-pyridoxyethylthio) porphyrazinatomagnesium with vanadyl bis(acetylacetonate) $[VO(acac)_2(4\text{-}pyCOOCH_2CH_2S)]_8$ MgPz [57].

3.4.10 Octakis-(9-anthracenylmethylthio) Substituted Novel Porphyrazines

A magnesium porphyrazinate carrying eight (9-anthracenyl) units on the periphery through flexible methylthio bridges has been synthesized by cyclotetramerization of 3,4-(9-anthracenylmethylthio) pyrroline-2,5-diimine (Fig.3.23) in the presence of magnesium butanolate. The metal-free derivative was obtained by treatment with trifluoroacetic acid and further reaction of this product with copper(II) acetate, zinc(II) acetate, and cobalt(II) acetate led to the metal porphyrazinates (M = Cu, Zn, Co) [58].



M= Mg (**4a**); 2H (**4b**); Cu (**4c**); Zn (**4d**); Co (**4e**)

Figure 3.23 Octakis(9-anthracenylmethylthio)substituted porphyrazines [58].

UV-Vis spectra of porphyrazine core are dominated by two intense bands, both correlated to $\pi \rightarrow \pi^*$ transitions [59,60]. The presence of an electron donating group on the periphery causes a bathochromic shift on Q bands. UV-Vis spectra of metallo porphyrazines (**4a, 4c-e** in $CHCl_3$) prepared in this present work exhibited intense single Q band absorption of the $\pi \rightarrow \pi^*$ transitions around 648-656 nm and B bands in the UV region around 344-352 nm. For the metal-free derivative (**4b**), the Q band is split into two peaks at 624 and 680 nm as a consequence of the change in the symmetry of porphyrazine core from D_{4h} (in the case of metallo derivatives) to D_{2h} . Here, in the case of porphyrazines with appending (9-anthracenylmethylthio) substituents in addition to these absorptions of the porphyrazine core, an intense absorption due to the $\pi \rightarrow \pi^*$ transition of anthracene groups appeared for all these porphyrazines derivatives (**4a-e**) in the UV region at about 284-288 nm [55,61]. An absorbance vs concentration study indicated that due to the bulky anthracene substituents, no aggregation occurred for (**4a***).*

In conclusion, novel porphyrazines surrounded with eight bulky anthracenylmethylthio units have been described; high electron density on the

substituents resulted in a second absorption in the ultraviolet region of comparable intensity as the intense B band of porphyrazines.

3.4.11 Octakis (ferrocene) Substituted Porphyrazines

Metal-free porphyrazine and metal porphyrazinates (M= Mg, Cu, Co or Zn) substituted with eight ferrocene moieties on the periphery through flexible alkylthio-bridges have been synthesised in a multi-step reaction sequence (Fig.3.24) [62].

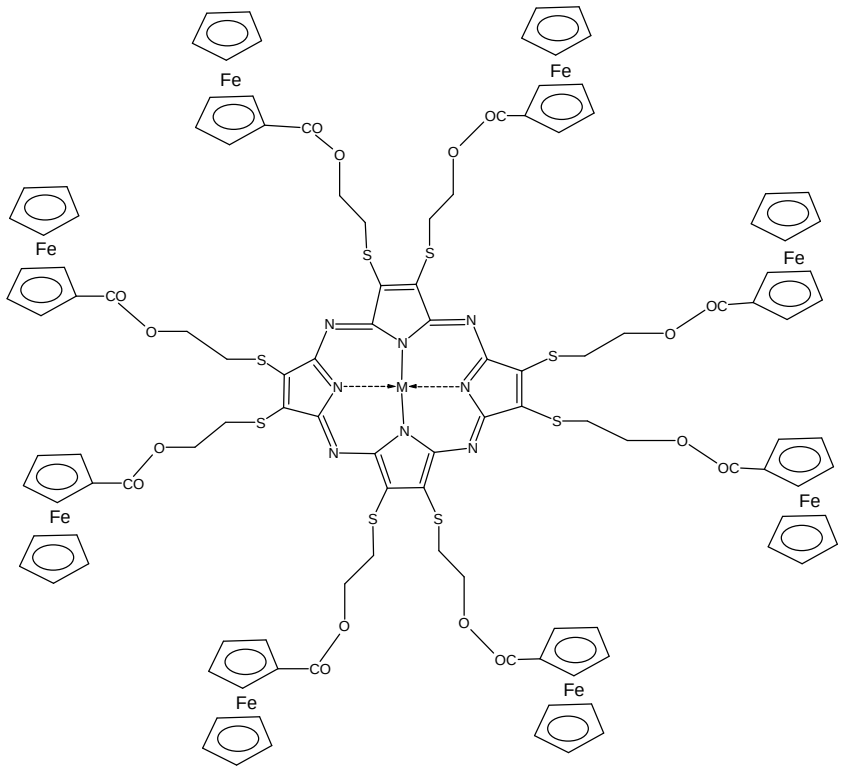
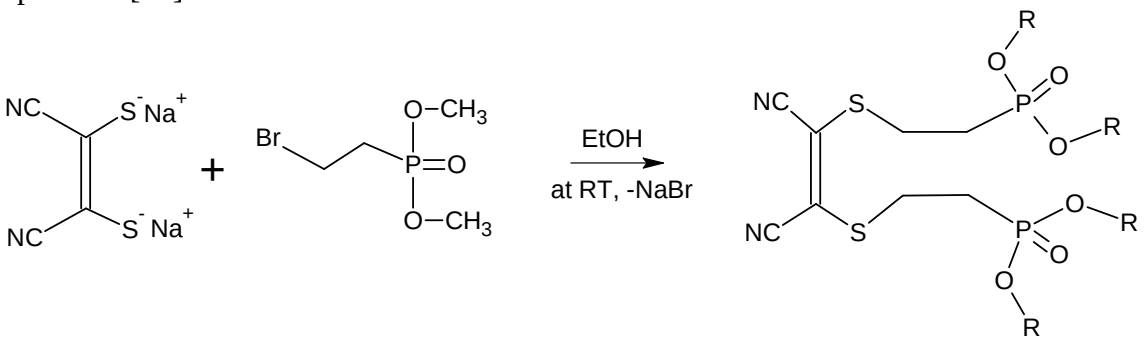


Figure 3.24 Octakis(ferrocene)substituted porphyrazines [62].

3.4.12 Phosphonic Acid-Substituted Porphyrazines

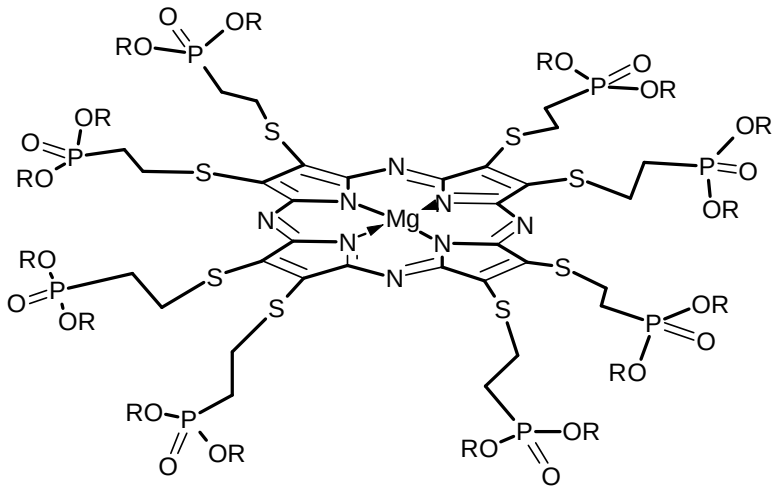
It is synthesized phosphonate-substituted maleonitrile **1** by the reaction of dithiomaleonitrile disodium salt with diethyl(2-bromoethyl)phosphonate in absolute ethanol under nitrogen at ambient temperature for 12 h (Fig.3.25). The phosphonate-substituted porphyrazine molecule **2** has been prepared by the Linstead macrocyclization of 1,2-bis{2-(diethylphosphonate) ethylthio}maleonitrile with freshly prepared $Mg(OPr)_2$ in 1-propanol under reflux for 12 h (Fig.3.26). The proposed structures of maleonitrile **1** and porphyrazine **2** are consistent with their spectral

characterizations; the phosphonate groups were easily identified by FT-IR, ^{31}P and ^{13}C NMR spectroscopy. Because of the macrocyclization, the phosphorous peak of the $P{=}O(OR)_2$ groups of maleonitrile shifts from doublet 26.5 to 29.8 ppm in ^{31}P NMR spectrum [63].



1

Figure 3.25 Synthesis of 1,2-bis{2-(diethyl phosphonate) ethylthio}maleonitrile **1**.



2

R: Ethyl or Propyl

Figure 3.26 The structure of magnesium octakis(2-(diethylphosphonate)ethylthio) porphyrazine [63].

3.4.13 Octakis (3-Methylbutylthio) Substituted Porphyrazines

Porphyrazines, MPz (M = Mg, H, Ni, Zn and Co) with octakis (3-methylbutylthio) substituents have been synthesized starting with the corresponding unsaturated dicarbonitrile derivative [64].

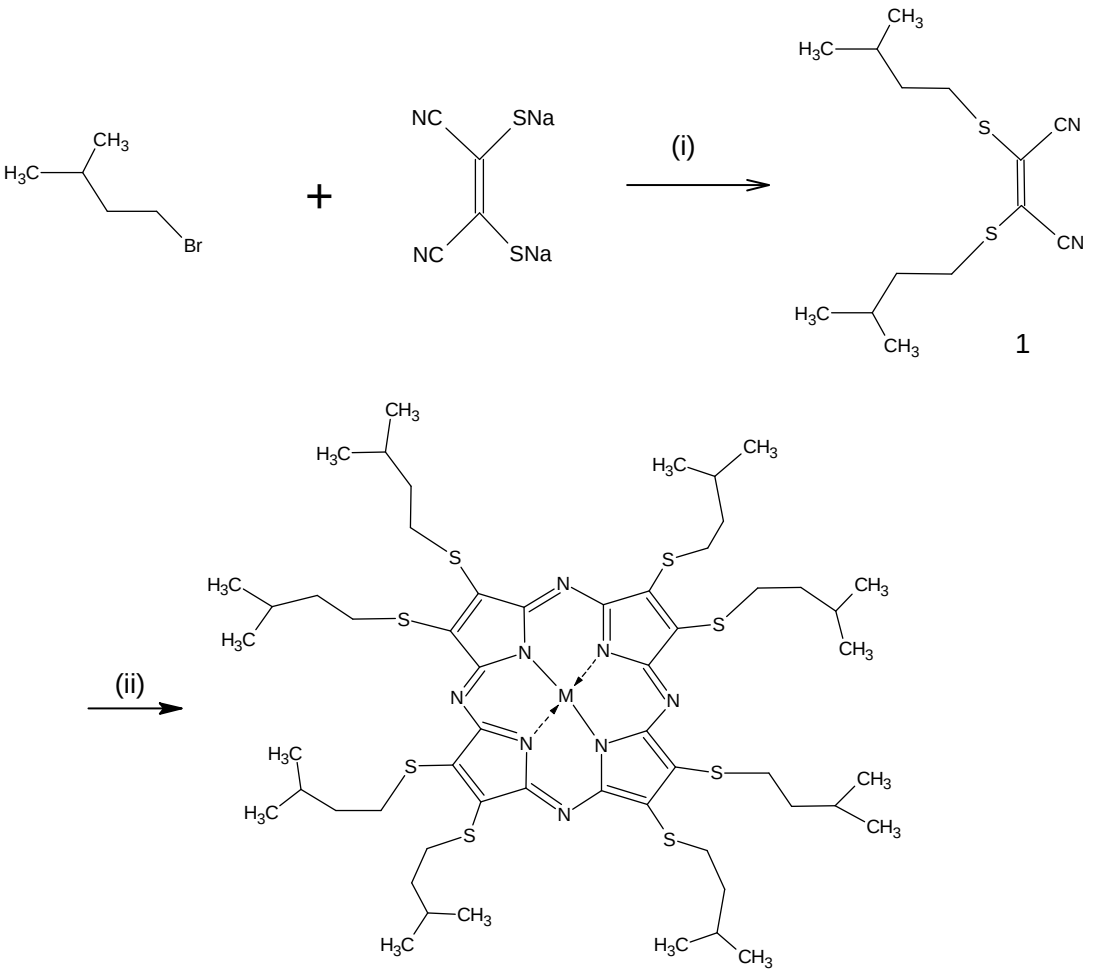


Figure 3.27 (**i**) Acetone, (**ii**) $Mg(BuO)_2$; CF_3COOH; $M(OAc)_2 \cdot 4H_2O$ (M: Ni, Zn,Co). Bis(3-methylbutylthio) maleonitrile (**1**) and the porphyrazines (**2-6**) derived from it [64].

The electronic absorption spectra of the metal-free porphyrazine **3** exhibited a splitted Q band absorption which is due to $\pi \longrightarrow \pi^*$ transitions of these completely conjugated 18 π electron systems. With the insertion of metal into the core of porphyrazines, the characteristic Q band transitions of the metal porphyrazinates were observed as a single band of high intensity. The effect of eight S-substituents on the periphery of the porphyrazine core was a shift in these intense Q bands to longer wavelengths when compared with those of unsubstituted or alkyl substituted derivatives [65]. The Q and B bands absorptions and logarithmic coefficient values for **4**, **5** and **6** are at 666 nm (4.89), 326 nm (4.62); 673 nm (4.90), 374 nm (4.65) and 674 nm (4.85),

376 (4.56) respectively. The UV spectra of the compounds **2**, **3**, **4**, **5** and **6** are given in the Figure 3.28.

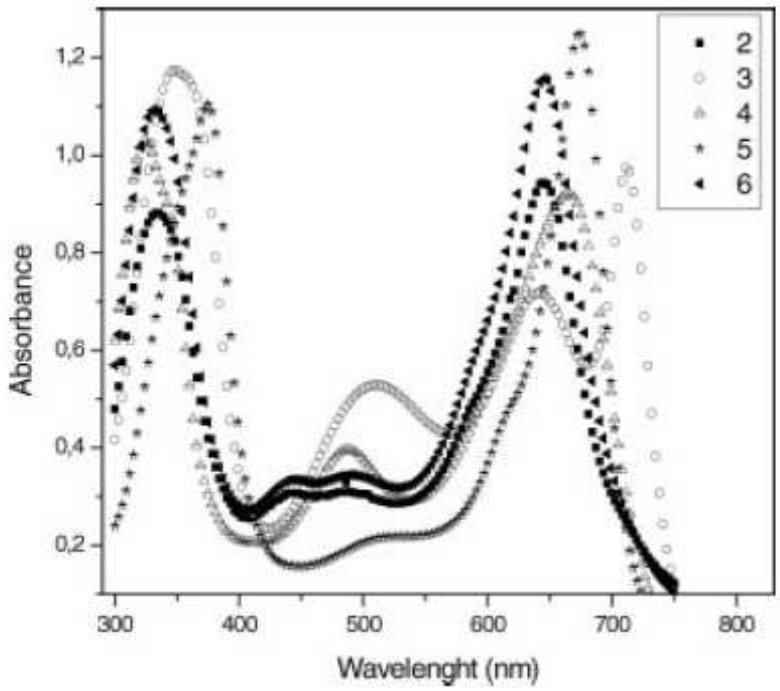


Figure 3.28 UV spectra of **2**, **3**, **4**, **5** and **6** in chloroform.

3.4.14 Metal-Linked Trinuclear Porphyrazine Dimer

This report presents the synthesis and characterization of a soluble porphyrazinedithiolate ligand and its metal complexes. As a first step toward the assembly of metal-linked multiporphyrazine arrays, we have linked two of the porphyrazinedithiolates by a metal ion (Ni(III)) to form a novel trimetallic metal-linked porphyrazine dimer [66].

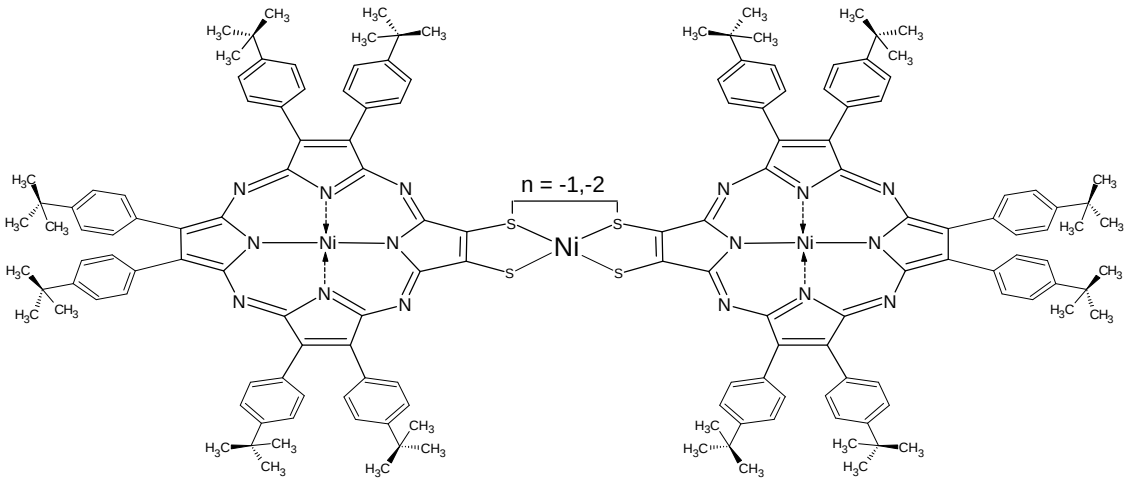


Figure 3.29 Trimetallic metal-linked porphyrazine dimer [66].

3.4.15 Dithiacrown Ether Substituted Porphyrazines

In this work gives a full account of the synthesis and physical properties of porphyrazines to which four sulfur-containing crown ether rings of various sizes are connected: dithia-7-crown-2 (**b**), dithia-15-crown-5 (**c**), and dithia-18-crown-6 (**d**). The presence of the sulfur atoms in the crown ether rings gives the opportunity to bind soft transition-metal ions.18,19 Thiacrown ethers **2**(*n*) (*n* = 1-2) containing 1,2-dicyano-1,2-dithioethene were used as the precursors for the crowned porphyrazines [67].

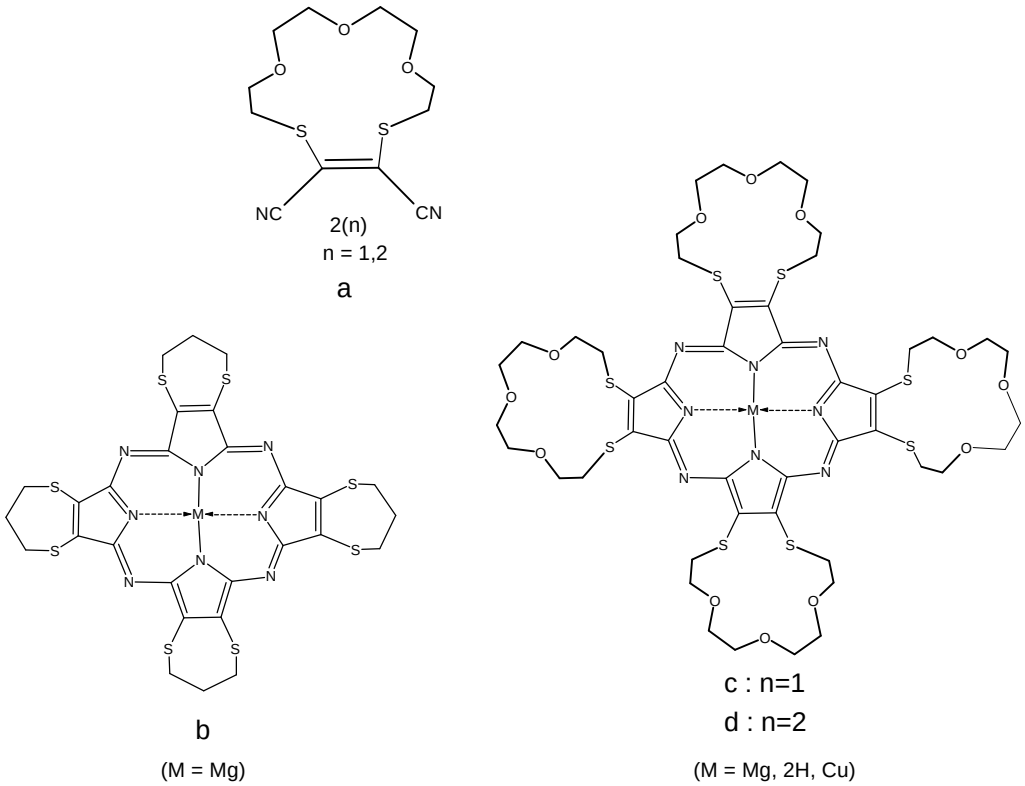


Figure 3.30 (**a**) (2(1)) : 1,2-Dicyano-3,15-dithia-6,9,12-trioxacyclopentadecene
(**b**) {Tetrakis([1,5]dithiacycloheptено)[6,7-*b*:6′,7′-*g*:6″,7″-*l*:6‴,7‴-*q*]-porphyrazinato}magnesium(II)
(**c**) {Tetrakis([1,4,7,10,13]trioxadithiacyclopentadeceno)[11,12-*b*:11′,-12′-*g*:11″,12″-*l*:11‴,12‴-*q*]porphyrazinato}magnesium(II)
(**d**) {Tetrakis([1,4,7,10,13,16]tetraoxadithiacyclooctadeceno)[14,15-*b*:14′,15′-*g*:14″,15″-*l*:14‴,15‴-*q*]porphyrazinato}magnesium(II) [67].

3.4.16 Quarternized porphyrazine ion in aqueous solution

In that study, a water-soluble quaternized cobalt porphyrazine was synthesized and used as buffer additive to separate the positional isomers of naphthalenesulfonates and chlorobenzoates employing ion-exchange electrokinetic chromatography [68]. The structure of [octakis(2-trimethylammoniumethylthio)porphyrazinatocobalt]-octaiodide (CoPzq) is given in Figure 3.31. The structures of the analytes are given in Figure 3.32.

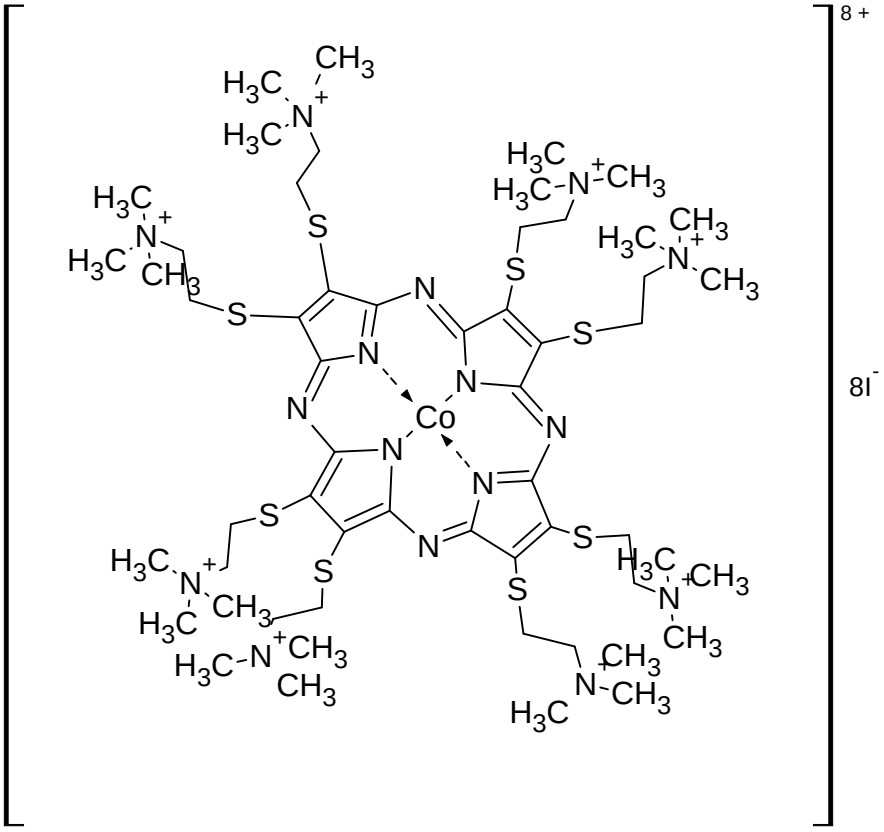
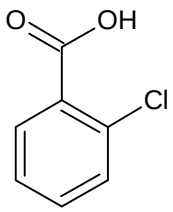
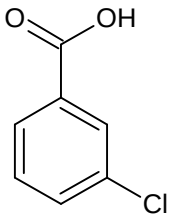


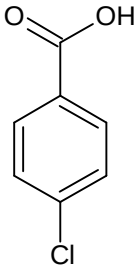
Figure 3.31 Structure of [octakis(2-trimethylammoniumethylthio)porphyrazinatocobalt] octaiodide (CoPzq) [68].



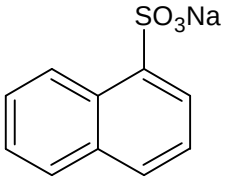
2-Chlorobenzoic acid



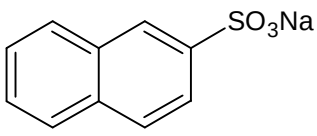
3-Chlorobenzoic acid



4-Chlorobenzoic acid



Naphthalene-1-sulfonic acid



Naphthalene-2-sulfonic acid

Figure 3.32 The structures of the analytes.

3.4.17 Phthalocyanines containing macrocycle units

A soluble metal-free phthalocyanine **5** and its metal complexes (Zn, Ni, Co and Cu) **6, 7**, **8** and **9** containing eight 16-membered tetrathiamonoaza macrocycles on peripheral substituent positions have been synthesized. The metal-free phthalocyanine **5** was synthesized from 4,5-bis{[2-(1,4,10,13-tetrathia-7-azacyclohexadecan-7-yl) ethyl]oxy}phthalonitrile **4**. The metal complexes **6, 7** and **8** were prepared by a tetramerization reaction of the phthalonitrile derivative 4 with appropriate materials (Fig.3.33). Copper(II) phthalocyanine **9** was prepared by the reaction of 4,5-bis{[2-(1,4,10,13-tetrathia-7-azacyclohexadecan-7-yl)ethyl]oxy}-1,2 dibromobenzene **3** with excess CuCN and dry quinoline (Fig.3.34). Liquid–liquid extraction of several heavy metal ions such as Ag^{+}, Hg^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} with compound **5** was also tested using picrate as the anion of the ion pair. The extraction avidity of **5** for Ag^{+} was found to be highest in the liquid–liquid phase extraction experiments [69].

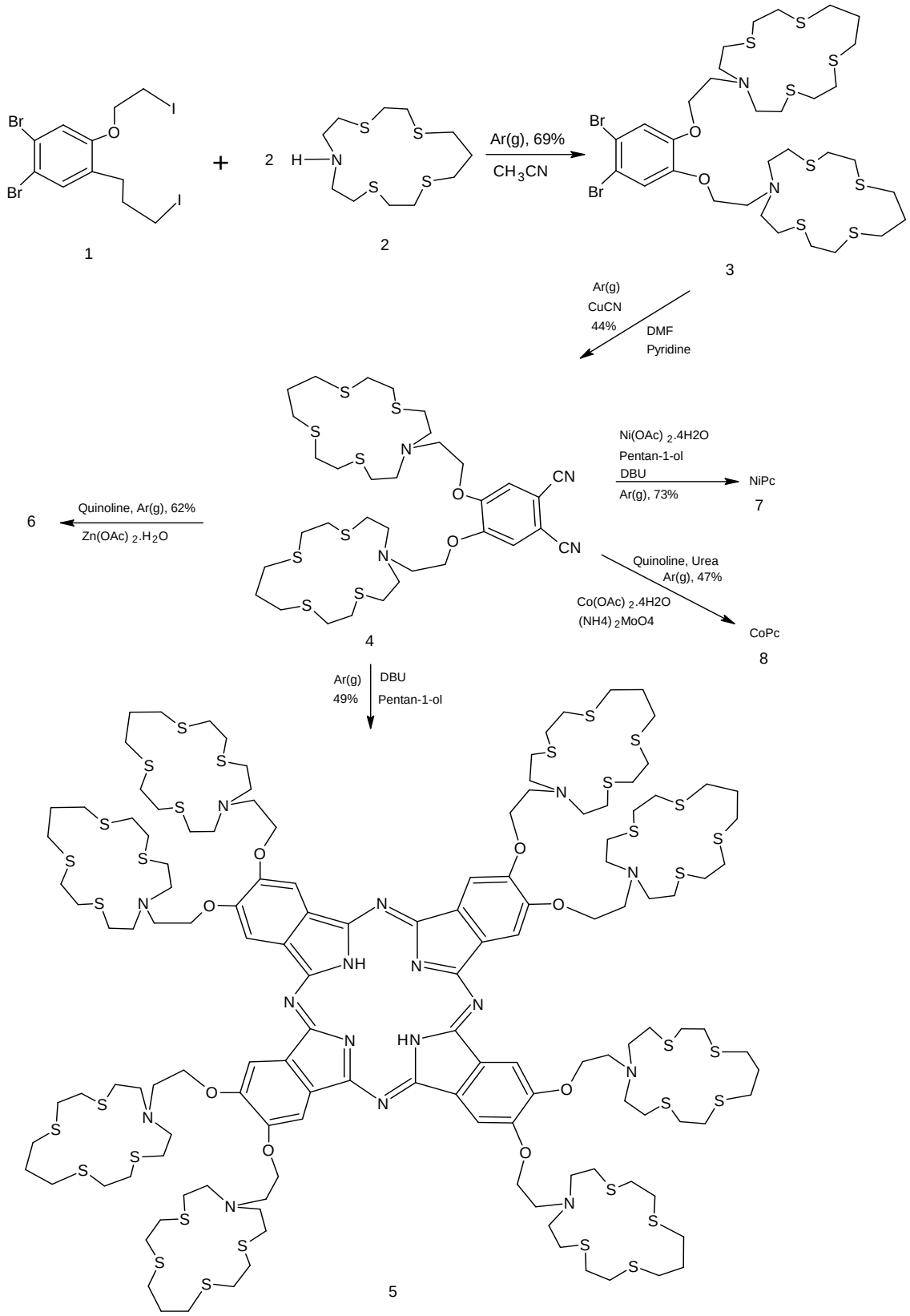


Figure 3.33 Synthesis of metal-free and metallo (Zn, Ni, Co) phythalocyanines [69].

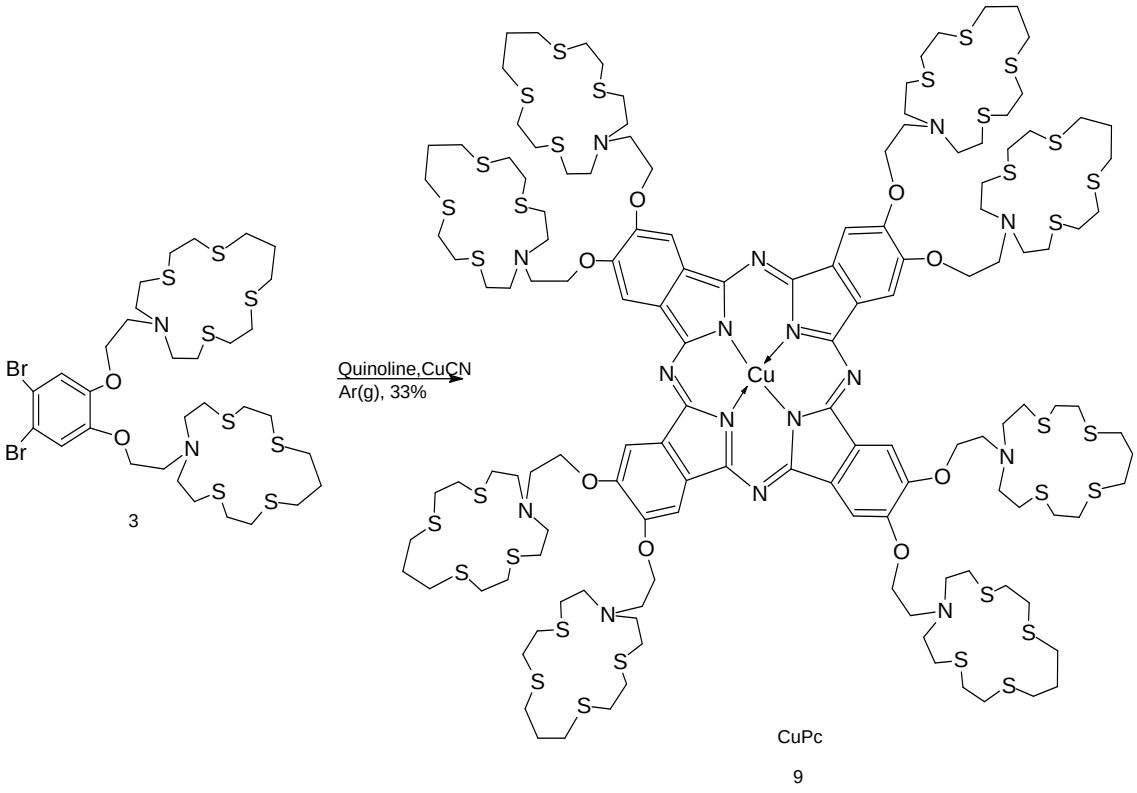


Figure 3.34 Synthesis of copper phythalocyanine [69].

3.4.18 Octakis(Octylthio)Porphyrazinatoiron Derivatives

Chlorooctakis (octylthio)porphyrazinatoiron(III) (FePzCl) was prepared by the reaction of metal-free porphyrazine with iron(II) acetate and further treatment with HCl solution (Fig.3.35). The monomeric bisaxial complex FePz(py)2 (Fig.3.36) as well as the bridged complex [FePz(pyz)]n (Fig.3.36) were formed as stable complexes by reacting FePzCl with pyridine or pyrazine, respectively. These complexes were characterized by elemental analysis and spectroscopic methods [70].

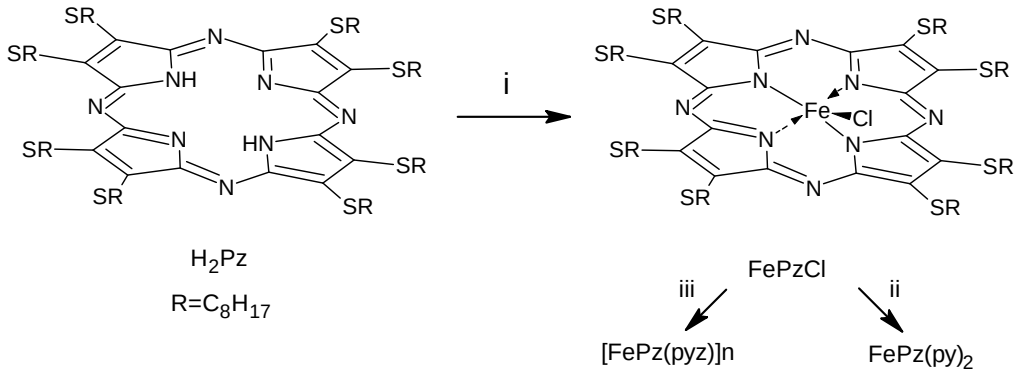


Figure 3.35 Synthesis route to new compounds: (**i**) $Fe(OAc)_2$, acetic acid, HCl; (**ii**) pyridine; (**iii**) pyrazine [70].

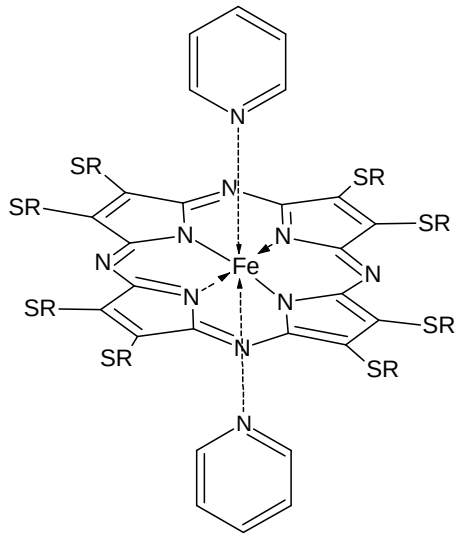


Figure 3.36 $FePz(py)_2$ [70].

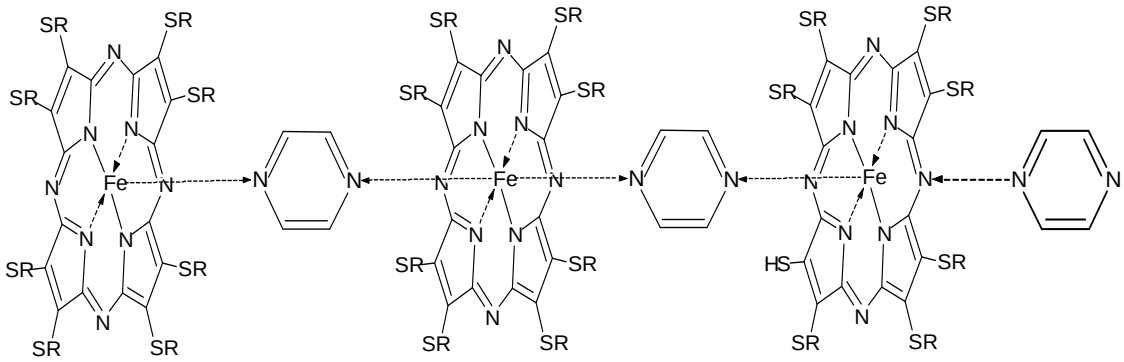


Figure 3.37 $[FePz(pyz)]_n$ [70].

3.5 Group Works in Porphyrazine Chemistry

Novel *seco*-porphyrazines substituted with (1-naphthyl), (4-tert-butylphenyl), (*p*-tolyl) and (*o*-tolyl) have been described in this section. These novel compounds have been characterized by elemental analysis, together with FT-IR, ^{1}H NMR, UV-Vis and mass spectral data.

3.5.1 Partially Oxidized Porphyrazines

The scope of the present work was to prepare metalloporphyrazinates substituted directly with eight (1-naphthyl) groups on the peripheral positions [71]. Magnesium porphyrazinate substituted with eight (1-naphthyl) groups on the peripheral positions has been synthesized by cyclotetramerization of 3,4-(1-naphthyl)pyrroline-2,5-diimine, 4-(1-naphthyl)pyrroline-2,5-diimine in the presence of magnesium butanolate. Its demetalation by treatment with trifluoroacetic acid, resulted in a partially oxidized product, namely, octakis(1-naphthyl)-2-*seco*-porphyrazine-2,3-dione (Fig.3.38). Further reaction of this product with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate led to the metallo derivatives, [octakis(1-naphthyl)-2-*seco*-2,3-dioxoporphyrazinato]M(II) (M = Cu, Zn or Co).

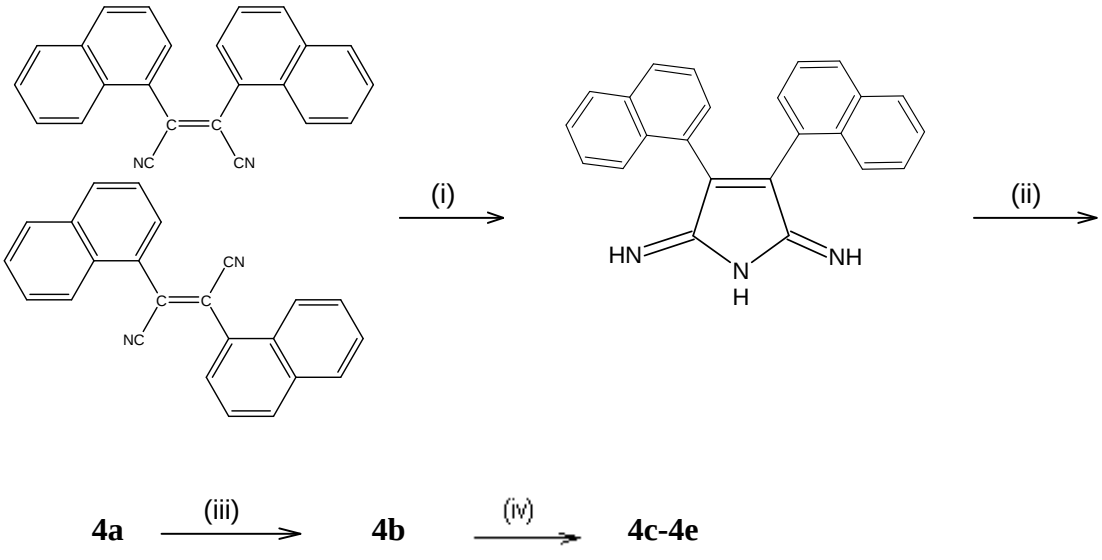
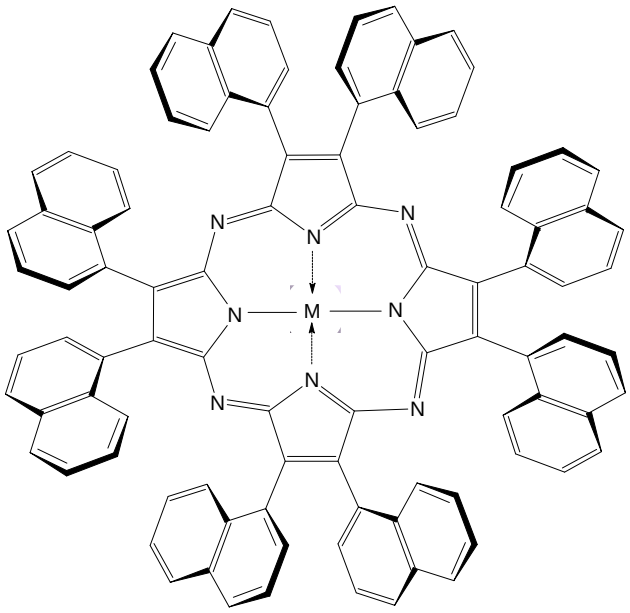
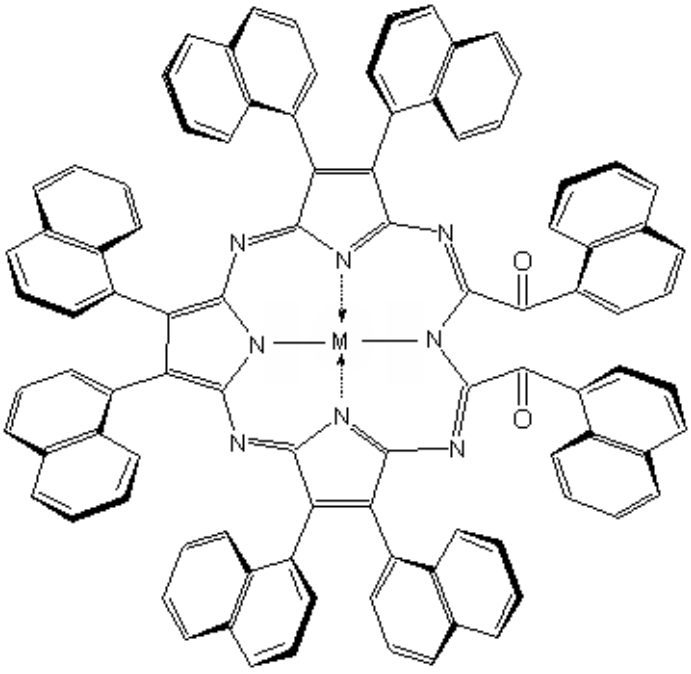


Figure 3.38 (**i**) Ethylene glycol; (**ii**) Mg turnings, I_2, *n*-BuOH; (**iii**) CF_3CO_2H; (**iv**) $CHCl_3$, EtOH and $Cu(OAc)_2$, $Zn(OAc)_2$, or $Co(OAc)_2$ [71].



M = Mg (**4a**)

Figure 3.39 [2,3,7,8,12,13,17,18-Octakis(1-naphthyl) porphyrazinato] Mg(II) [71].



M = 2H (**4b**); Cu (**4c**); Zn (**4d**); Co (**4e**)

Figure 3.40 [2,3,7,8,12,13,17,18-octakis(1-naphthyl)-2-*seco*-porphyrazine-2,3-dione] and metal derivatives [M = 2H, Cu(II), Zn(II) or Co(II)] [71].

3.5.2 Soluble Seco-Porphyrazines with Bulky Substituents

By cyclotetramerization of 3,4-bis(4-tert-butylphenyl)pyrroline-2,5-diimine in the presence of magnesium butanolate, magnesium porphyrazinate with eight (4-tert-butylphenyl) units on the periphery has been synthesized. Its demetalation by the treatment with trifluoroacetic acid resulted in a partially oxidized product, namely, octakis(4-tert-butylphenyl)-2-seco porphyrazine- 2,3-dione. Further reaction of this product with copper(II) acetate, zinc(II) acetate, and cobalt(II) acetate led to the metallo derivatives, [octakis(4-tert-butylphenyl)-2-seco- 2, 3-dioxoporphyrazinato]M(II) (M¼Cu, Zn, Co). These soluble complexes have been characterized by elemental analysis, FT-IR, 1H NMR, UV-Vis, and mass spectral data [72].

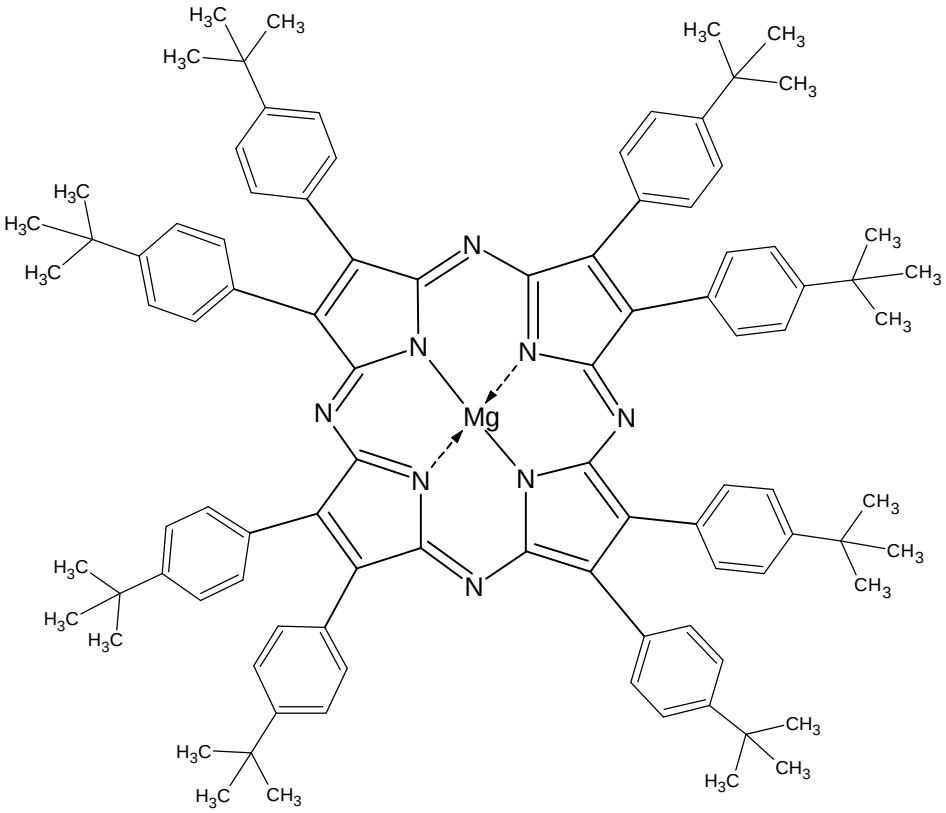
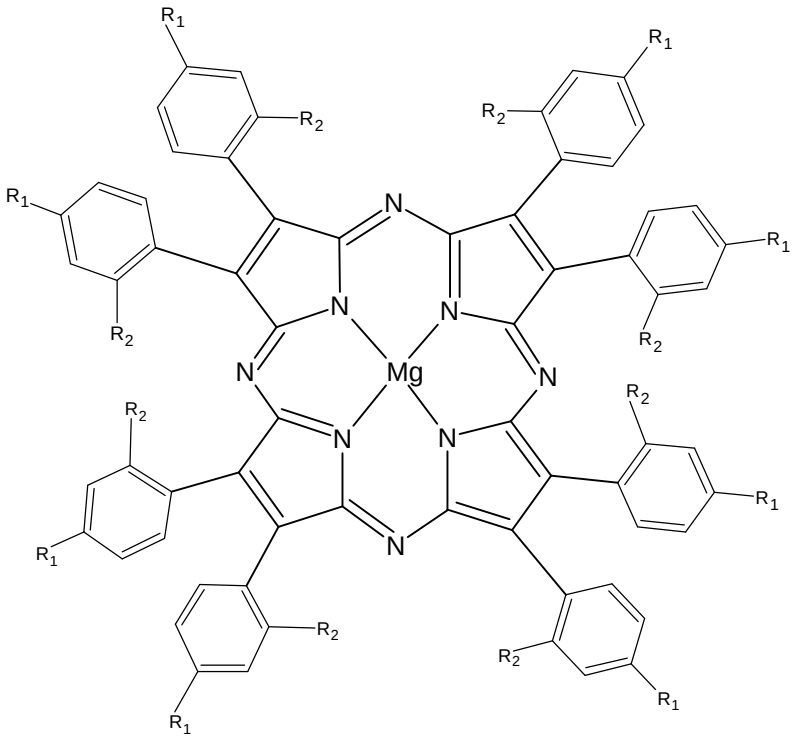


Figure 3.41 [2,3,7,8,12,13,17,18-Octakis(4-*tert*-butylphenyl) porphyrazinato] Mg(II) [72].

3.5.3 *Seco*-Porphyrazines with Eight (*p*-tolyl) and (*o*-tolyl) Units

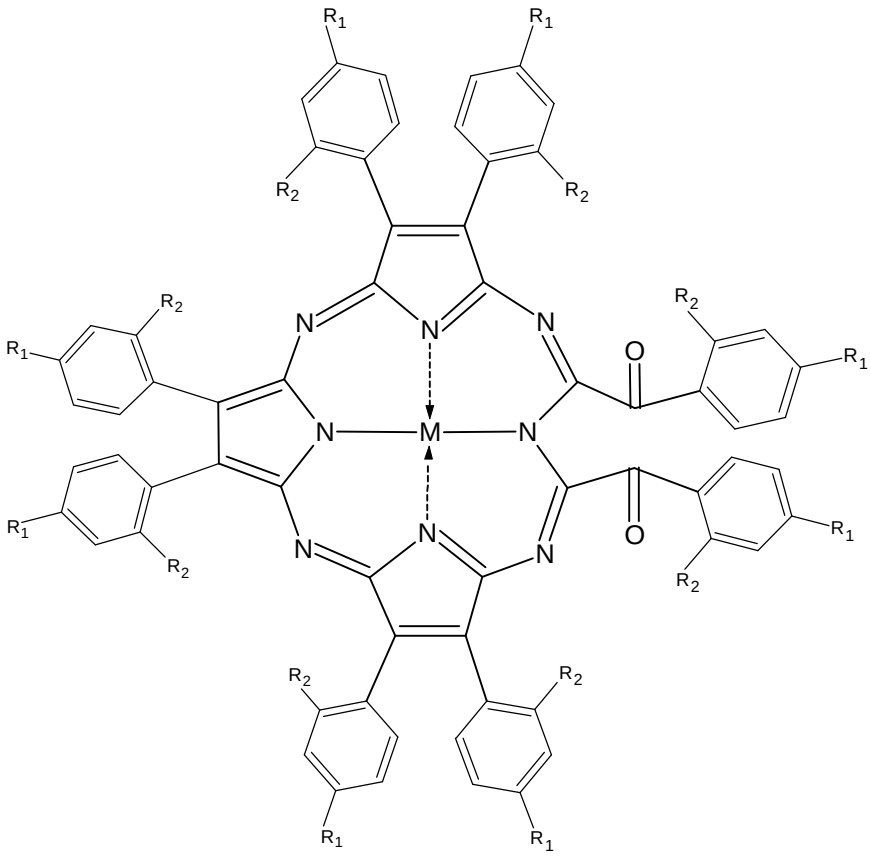
Magnesium porphyrazinates substituted with eight (*p*-tolyl) and (*o*-tolyl) units on the Peripheral positions have been synthesized for the first time by cyclotetramerization of 1,2-bis(*p*-tolyl)maleonitrile and 1,2-bis(*o*-tolyl)maleonitrile in the presence of magnesium butanolate. Their demetalation by the treatment with trifluoroacetic acid resulted in partially oxidized products, namely, octakis(*p*-tolyl)-2-*seco*-porphyrazine-2,3-dione and octakis(*o*-tolyl)-2-*seco*-porphyrazine-2,3-dione. Further reactions of these products with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate have led to the metallo derivatives, [octakis(*p*-tolyl)-2-*seco*-2,3-dioxoporphyrazinato] M(II) and [octakis(*o*-tolyl)-2-*seco*-2,3-dioxoporphyrazinato] M(II) (M = Cu, Zn, Co) [73].



5a (R_1: CH_3, R_2: H)

6a (R_1: H, R_2: CH_3)

Figure 3.42 [2,3,7,8,12,13,17,18-octakis(*p*-tolyl)porfirazinato] Mg(II) (**5a**) and [2,3,7,8,12,13,17,18-octakis(*o*-tolyl)porfirazinato] Mg(II) (**6a**) [73].



M= 2H (**5b**); Cu (**5c**); Zn (**5d**); Co (**5e**) (R_1: CH_3, R_2: H)

M= 2H (**6b**); Cu (**6c**); Zn (**6d**); Co (**6e**) (R_1: H, R_2: CH_3)

Figure 3.43 [2,3,7,8,12,13,17,18-octakis(*p*-tolyl)-2-*seco*-porphyrazine-2,3-dione] and metal derivatives {M= 2H, Cu(II), Zn(II) or Co(II)} and [2,3,7,8,12,13,17,18-octakis (*o*-tolyl)-2-*seco*-porphyrazine-2,3-dione] and metal derivatives {M= 2H, Cu(II), Zn(II) or Co(II)} [73].

3.5.4 *Seco*-porphyrazines with eight 4-biphenyl groups

The synthesis and the spectral characterization of novel seco-porphyrazines surrounded with eight 4-biphenyl groups on the periphery have been described.. The steric requirements of these groups should be the reasons leading to oxidized secoporphyrazines [74].

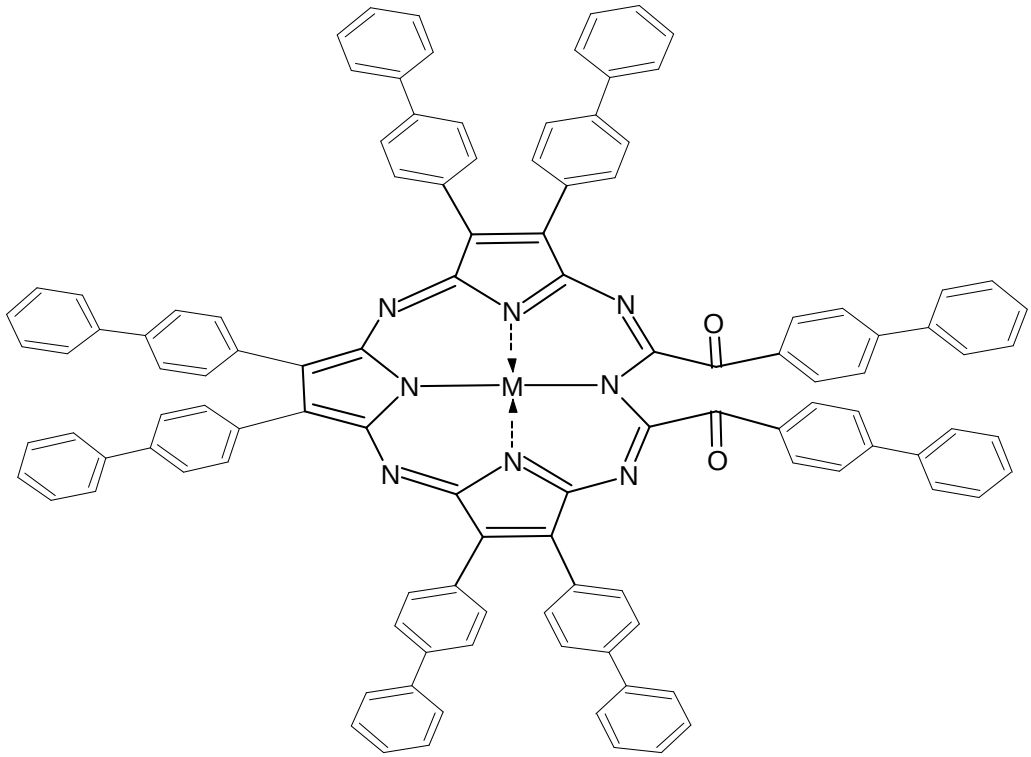


Figure 3.44 Synthesis of [2,3,7,8,12,13,17,18-octakis(4-biphenyl)-2-*seco*-2,3-dioxoporphyrazinato] {M= Cu(II), Zn(II) or Co(II)} [74].

3.6 The Aim and Scope of This Work

Porphyrazines may be considered to be structural hybrids of the well-studied porphyrins and phthalocyanines. As such, they provide an excellent opportunity to explore the subtle effects of ligand structure on the properties of coordinated metal ions in porphyrinic complexes. In addition, porphyrazines show several unique properties (optical, electrochemical, and catalytic), which make them of interest in their own right.

The synthesis of novel porphyrazines with eight (*p*-tolylmethylthio) and (*o*-tolylmethylthio) and (4-biphenylmethylthio) substituents derivatives have been the main scope of this work. Magnesium porphyrazinates have been synthesized for the first time by cyclotetramerization of 1,2-bis(*p*-tolylmethylthio)maleonitrile and 1,2-bis(*o*-tolylmethylthio)maleonitrile and 1,2-bis(4-biphenylmethylthio)maleonitrile in the presence of magnesium butanolate. The conversions of magnesium porphyrazinates into the metal-free derivatives were achieved by the treatment with relatively strong acids

(e.g. trifluoroacetic acid). Further reactions of these products with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate have led to the metal porphyrazinates (M= Cu, Zn, Co) [75].

The synthesis along with the spectroscopic properties of the novel compounds will be described.

CHAPTER 4

CHEMICALS AND EQUIPMENT

4.1. Chemicals

α-chloro-*o*-xylol ($C_9H_{11}Cl$), *α*-chloro-*p*-xylol ($C_9H_{11}Cl$), 4-chloromethyl-biphenyl ($C_{13}H_{11}Cl$), Sodium Cyanide (NaCN), Methanol (CH_3OH), Ethanol (C_2H_5OH), Iodine (I_2), Magnesium (Mg), Sodium Sulfate (Na_2SO_4), Chloroform ($CHCl_3$), Dichloromethane (CH_2Cl_2), Ammonia (NH_3), Trifluoroaceticacid (CF_3COOH), *n*-Butanol (C_4H_9OH), Diethylether ($C_4H_{10}O$), Benzene (C_6H_6), Acetone (C_3H_6O), Paraffin Oil, *n*-hexane, Cobalt (II) Acetate ($Co(OAc)_2$), Copper (II) Acetate ($Cu(OAc)_2$), Zinc (II) Acetate ($Zn(OAc)_2$), Silica Gel 60 (0.063-0.200 mm), TLC Aluminum Sheets, Parafilm, Distilled water (H_2O).

4.2. Equipment

IR (infrared) Spectrophotometer	Perkin Elmer Spectrum One FT-IR
UV/ VIS Spectrophotometer	UNICAM UV2-100
Magnetic Stirrer and Heater	IKA
Elemental Analyses	Thermo Finnigan Flash EA 1112
^{1}H-NMR Spectrophotometer	Varian INOVA 500 MHz
Mass Spectrophotometer	Bruker Daltonics MicrOTOF LC-MS

CHAPTER 5

EXPERIMENTAL PART

5.1 Synthesis of Dithiomaleonitrile Disodium Salt

Dry and powder NaCN (11 g, 0.234 mol) was stirred in DMF (70 mL) around 10 minutes. 14.11 mL (0.234 mol) CS_2 was added into that solution drop wise with stirring in ice bath for 10 minutes. Dark brown solution was stirred for extra 10 minutes and diluted to 200 mL with isobutanol and heated until all of the contents were dissolved in solvent. The solution was filtered with vacuum filtration to remove unreacted NaCN while solution was hot. Then solution was left to cool and crystallize. Needle type brown crystals were formed and filtered by vacuum filtration. The crystals were washed with diethyl ether and dried in hood.

The obtained needle type brown crystals were dissolved in 100 mL of chloroform and the dark brown solution was filtered. The solution was left to stand for 4-5 days and precipitation occurred. The precipitate having the product and sulphur was filtered and dried. Then it was dissolved in minimum methanol that can only dissolve the product and diethyl ether was added for crystallization of the product. Yellowish crystals were filtered and washed with ether and left to dry. The product was soluble in methanol, ethanol and water and insoluble in diethyl ether, chloroform and benzene [76].

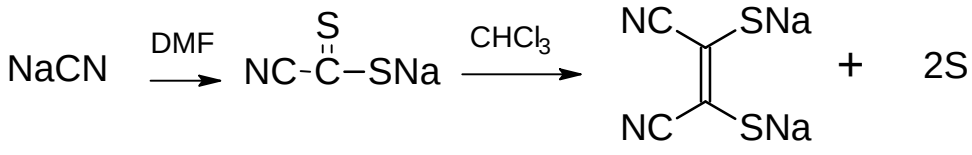


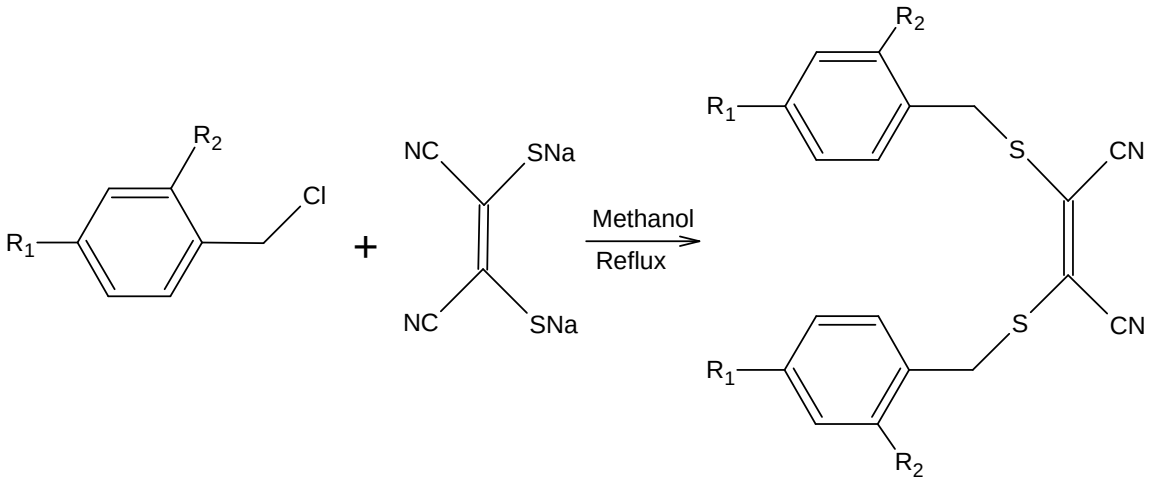
Figure 5.1 Synthesis of dithiomaleonitrile disodium salt.

5.2 Synthesis of 1,2-bis(*p*-tolylmethylthio) maleonitrile (P1)

Disodium salt of dithiomaleonitrile (1.12 g, 6 mmol) was mixed with (α-chloro-*p*-xylene) (2.11 g, 15 mmol) in methanol (50 mL) and refluxed under nitrogen for about 8 h. When MeOH was evaporated, the remaining product was treated with chloroform to remove insoluble salts by filtration. The chloroform solution was extracted several times with 15% Na_2SO_4 solution and then dried over anhydrous Na_2SO_4 overnight. After evaporation of the solvent the remaining solid product was extracted with refluxing n-hexane to remove any excess α-chloro-*p*-xylene. **P1** was yellow colored and very soluble in chloroform and dichloromethane, but insoluble in *n*-hexane. Yield: 1.64 g (78%). FT-IR, ν_{max}, (cm^{-1}): 3048-3024 (CH, aromatic), 2980-2853 (CH, aliphatic), 2210 (C≡N), 1615 (C=C, aromatic), 1513, 1448, 1379, 1320, 1242, 1175, 1154, 1097, 1040, 1022, 964, 878, 835, 803, 747, 720, 671 (Appendix A). ^{1}H NMR ($CDCl_3$, 500 MHz): δ, ppm 7.30-7.17 (m, 8H, Ar-H), 4.31 (s, 4H, S-CH_2), 2.39 (s, 6H, -CH_3) (Appendix D). MS (ESI): (m/z): 350.2 $[M]^+$ (Appendix B). Anal. calcd. for $C_{20}H_{18}N_2S_2$: C, 68.53; H, 5.18; N, 7.99%. Found: C, 68.65; H, 5.07; N, 7.85%.

5.3 Synthesis of 1,2-bis(*o*-tolylmethylthio) maleonitrile (O1)

Disodium salt of dithiomaleonitrile (1.12 g, 6 mmol) was mixed with (α-chloro-*o*-xylene) (2.11 g, 15 mmol) in methanol (50 mL) and refluxed under nitrogen for about 8 h. When MeOH was evaporated, the remaining oily product was treated with chloroform to remove insoluble salts by filtration. The chloroform solution was extracted several times with 15% Na_2SO_4 solution and then dried over anhydrous Na_2SO_4 overnight. After evaporation of the solvent the remaining solid product was extracted with refluxing n-hexane to remove any excess α-chloro-*o*-xylene. **O1** was yellow-green colored and very soluble in chloroform and dichloromethane, but insoluble in *n*-hexane. Yield: 1.75 g (83%). FT-IR, ν_{max}, (cm^{-1}): 3063-3020 (CH, aromatic), 2976-2863 (CH, aliphatic), 2209 (C≡N), 1605 (C=C, aromatic), 1494, 1461, 1380, 1242, 1170, 1120, 1094, 1049, 936, 835, 764, 742, 735, 668 (Appendix C). ^{1}H NMR ($CDCl_3$ 500 MHz): δ, ppm 7.32-7.19 (m, 8H, Ar-H), 4.36 (s, 4H, S-CH_2), 2.41 (s, 6H, -CH_3). MS (ESI): (m/z): 350.7 $[M]^+$. Anal. calcd. for $C_{20}H_{18}N_2S_2$: C, 68.53; H, 5.18; N, 7.99%. Found: C, 68.68; H, 5.26; N, 8.09%.



P1 (R_1: CH_3, R_2: H) **P2** (R_1: CH_3, R_2: H)

O1 (R_1: H, R_2: CH_3) **O2** (R_1: H, R_2: CH_3)

Figure 5.2 Synthesis of 1,2-bis(*p*-tolylmethylthio)maleonitrile (**P1**) and 1,2-bis (*o*-tolylmethylthio)maleonitrile (**O1**).

5.4 [2,3,7,8,12,13,17,18-octakis(*p*-tolylmethylthio) porphyrazinato] Mg(II) (**P2**)

Mg turnings (24.3 mg, 1 mmol) and a small I_2 crystal were refluxed in *n*-BuOH (20 mL) for about 8 h to obtain $Mg(BuO)_2$. **P2** (701 mg, 2 mmol) was added to this solution and the mixture was refluxed for about 8 h. The dark green product was filtered, washed with ethanol and water and dried in a vacuum. The crude product was dissolved in chloroform and filtered. The chloroform solution was dried over anhydrous Na_2SO_4. When the solvent was evaporated, a dark green product was obtained. Finally, pure porphyrazine was obtained by column chromatography (SiO_2, CH_3OH: $CHCl_3$, 1:50 v/v). **P2** was soluble in chloroform, dichloromethane, acetone and toluene, but insoluble in n-hexane. Yield: 449 mg (63%). FT-IR, ν_{max}, (cm^{-1}): 3050 (CH, aromatic), 2978-2880 (CH, aliphatic), 1614 (C=C, aromatic), 1519, 1465, 1366, 1271, 1184, 1126, 1090, 1044, 847, 804, 750, 725. ^{1}H NMR ($CDCl_3$ 500 MHz): δ, ppm 7.34-7.21 (m, 4H, Ar-H), 4.33 (s, 2H, S-CH_2), 2.41 (s, 3H, -CH_3) (Appendix E). MS (ESI): (m/z): 1426.6 $[M]^+$. Anal. calcd. for $C_{80}H_{72}N_8S_8Mg$: C, 67.37; H, 5.09; N, 7.86%. Found: C, 67.49; H, 5.20; N, 7.71%.

5.5 [2,3,7,8,12,13,17,18-octakis(*o*-tolylmethylthio) porphyrazinato] Mg(II) (**O2**)

Mg turnings (24.3 mg, 1 mmol) and a small I_2 crystal were refluxed in *n*-BuOH (20 mL) for about 8 h to obtain $Mg(BuO)_2$. **O1** (701 mg, 2 mmol) was added to this solution and the mixture was refluxed for about 8 h. The blue-green colored product was filtered, washed with ethanol and water and dried in a vacuum. The crude product was dissolved in chloroform and filtered. The chloroform solution was dried over anhydrous Na_2SO_4. When the solvent was evaporated, a blue-green colored product was obtained. Finally, pure porphyrazine was obtained by column chromatography (SiO_2, CH_3OH: $CHCl_3$, 1:50 v/v). **O2** was soluble in chloroform, dichloromethane, acetone and toluene, but insoluble in *n*-hexane. Yield: 414 mg (58%). FT-IR, ν_{max}, (cm^{-1}): 3063-3014 (CH, aromatic), 2954-2868 (CH, aliphatic), 1654 (C=C, aromatic), 1599, 1488, 1461, 1425, 1379, 1299, 1216, 1185, 1096, 1016, 940, 880, 790, 760, 726, 686, 660 (Appendix G). ^1H NMR ($CDCl_3$ 500 MHz): δ, ppm 7.35-7.22 (m, 4H, Ar-H), 4.39 (s, 2H, S-CH_2), 2.44 (s, 3H, -CH_3). MS (ESI): (m/z): 1426.2 $[M]^+$ (Appendix I). Anal. calcd. for $C_{80}H_{72}N_8S_8Mg$: C, 67.37; H, 5.09; N, 7.86%. Found: C, 67.52; H, 5.18; N, 7.73%.

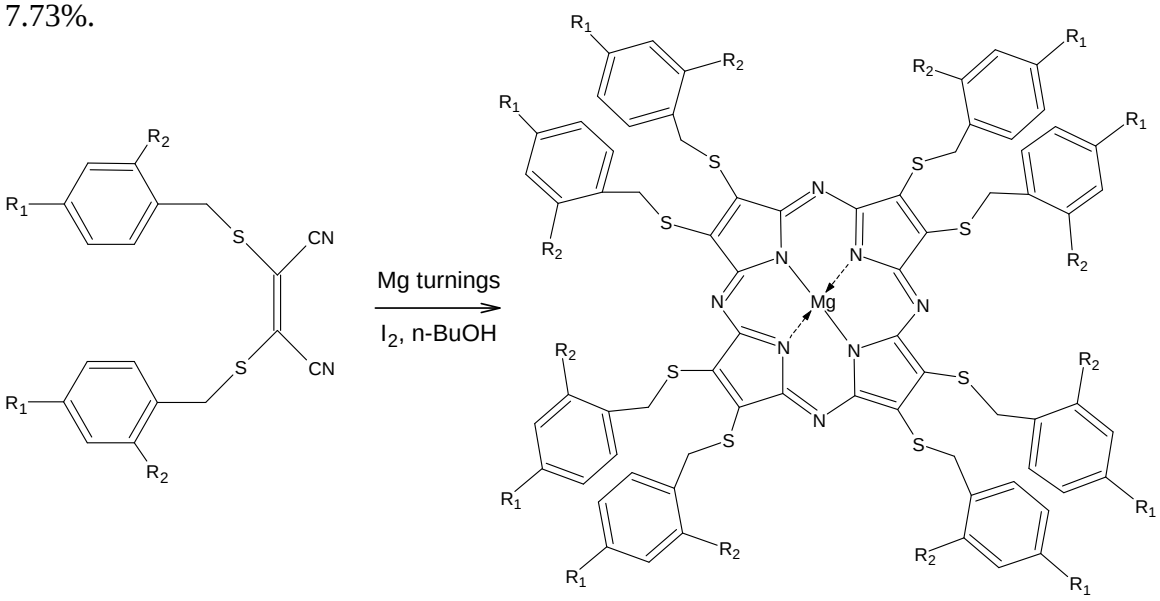
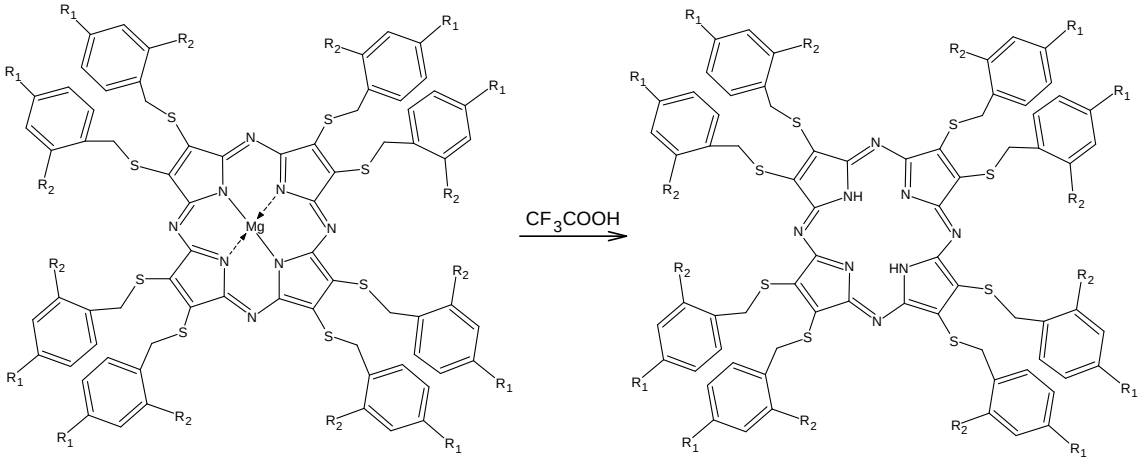


Figure 5.3 Synthesis of [2,3,7,8,12,13,17,18-octakis(*p*-tolylmethylthio)porphyrazinato] Mg(II) (**P2**) and [2,3,7,8,12,13,17,18-octakis(*o*-tolyl)porphyrazinato] Mg(II) (**O2**).

5.6 General Procedure for P3 and O3

P2 or **O2** (143 mg, 0.1 mmol) was dissolved in the minimum amount of trifluoroacetic acid (~4 mL) and stirred for 3 h at room temperature. When the reaction mixture was added to ice by dropwise and neutralized with 25% ammonia solution, precipitation occurred and it was filtered. The precipitate was extracted into the chloroform and the chloroform solution was extracted with water twice. After drying over anhydrous Na_2SO_4, the solvent was evaporated to obtain the metal-free porphyrazines (**P3, O3**). **P3** or **O3** was purified by column chromatography (SiO_2, CH_3OH: $CHCl_3$, 1:50 v/v).



M= 2H (**P3**) (R_1: CH_3, R_2: H)
M= 2H (**O3**) (R_1: H, R_2: CH_3)

Figure 5.4 Synthesis of [2,3,7,8,12,13,17,18- octakis(*p*-tolylmethylthio) H^{21}, H^{23} porphyrazine] (**P3**) and [2,3,7,8,12,13,17,18- octakis(*o*-tolylmethylthio) H^{21}, H^{23} porphyrazine] (**O3**)

5.7 [2,3,7,8,12,13,17,18- octakis(*p*-tolylmethylthio) H^{21}, H^{23} porphyrazine] (**P3**)

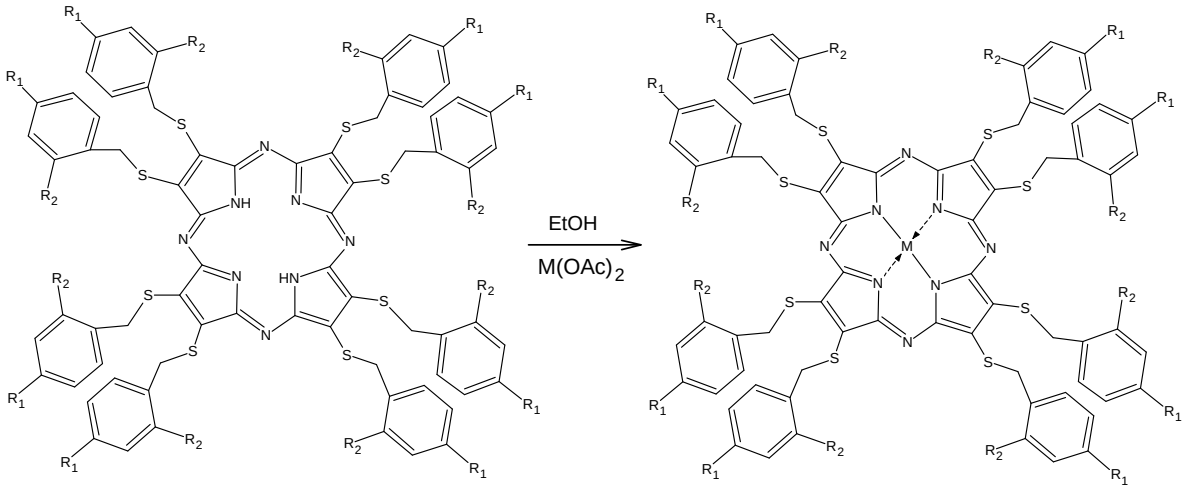
Green colored powder. Yield: 62 mg (44%). FT-IR, $\nu_{max}/(cm^{-1})$: 3330 (N-H), 3053 (CH, aromatic), 2928-2862 (CH, aliphatic), 1618 (C=C, aromatic), 1515, 1452, 1328, 1275, 1172, 1125, 1085, 1040, 847, 803, 753, 723. ^{1}H NMR ($CDCl_3$ 500 MHz): δ, ppm 7.35-7.21 (m, 4H, Ar-H), 4.34 (s, 2H, S-CH_2), 2.42 (s, 3H, -CH_3), -1,15 (br s, 2H, NH). MS (ESI): (m/z): 1404.3 $[M]^+$ (Appendix J). Anal. calcd. for $C_{80}H_{74}N_8S_8$: C, 68.44; H, 5.31; N, 7.98%. Found: C, 68.32; H, 5.44; N, 7.86%.

5.8 [2,3,7,8,12,13,17,18- octakis(o-tolylmethylthio) H^{21}, H^{23} porphyrazine] (**O3**)

Green colored powder. Yield: 73 mg (52%). FT-IR, $\nu_{max}/(cm^{-1})$: 3282 (N-H), 3045-3018 (CH, aromatic), 2924-2852 (CH, aliphatic), 1660 (C=C, aromatic), 1461, 1434, 1306, 1197, 1128, 1016, 986, 884, 840, 800, 762, 738, 685 (Appendix L). ^1H NMR ($CDCl_3$ 500 MHz): δ, ppm 7.34-7.20 (m, 4H, Ar-H), 4.38 (s, 2H, S-CH_2), 2.43 (s, 3H, -CH_3), -1,05 (br s, 2H, NH). MS (ESI): (m/z): 1404.5 $[M]^+$. Anal. calcd. for $C_{80}H_{74}N_8S_8$: C, 68.44; H, 5.31; N, 7.98%. Found: C, 68.30; H, 5.38; N, 7.83%.

5.9 General procedure for metallo porphyrazines (**P4-P6** and **O4-O6**)

P3 or **O3** (140 mg, 0.1 mmol) in $CHCl_3$ (10 mL) was stirred with the metal salt [$Cu(OAc)_2$ (182 mg, 1 mmol), $Zn(OAc)_2$ (183 mg, 1 mmol) or $Co(OAc)_2$ (177 mg, 1 mmol)] in ethanol (15 mL) and refluxed under nitrogen for about 4 h. Then, the precipitate composed of the crude product and the excess metal salt was filtered. The precipitate was treated with chloroform and the insoluble metal salts were removed by filtration. The filtrate was reduced to the minimum volume under reduced pressure and then added into *n*-hexane (100 mL) drop by drop to realize the precipitation. Finally, pure porphyrazine derivatives (**P4-P6**) or (**O4-O6**) was obtained by column chromatography (SiO_2, CH_3OH: $CHCl_3$, 1:20 v/v).



M= Cu (**P4**); Zn (**P5**); Co (**P6**) (R_1: CH_3, R_2: H)

M= Cu (**O4**); Zn (**O5**); Co (**O6**) (R_1: H, R_2: CH_3)

Figure 5.5 Synthesis of [2,3,7,8,12,13,17,18-octakis(*p*-tolylmethylthio) porphyrazinato] {M=Cu(II), Zn(II) or Co(II)} and [2,3,7,8,12,13,17,18-octakis (*o*-tolylmethylthio) porphyrazinato] {M=Cu(II), Zn(II) or Co(II)}

5.10 [2,3,7,8,12,13,17,18-octakis(*p*-tolylmethylthio) porphyrazinato] Cu(II) (**P4**)

Blue colored powder. Yield: 66 mg (45%). FT-IR, $\nu_{max}/(cm^{-1})$: 3055 (CH, aromatic), 2928-2885 (CH, aliphatic), 1642 (C=C, aromatic), 1513, 1448, 1380, 1276, 1191, 1123, 1083, 1042, 838, 802, 758, 725. MS (ESI): (m/z): 1465.2 $[M]^+$. Anal. calcd. for $C_{80}H_{72}N_8S_8Cu$: C, 65.56; H, 4.95; N, 7.65%. Found: C, 65.43; H, 4.82; N, 7.79%.

5.11 [2,3,7,8,12,13,17,18-octakis(*p*-tolylmethylthio) porphyrazinato] Zn(II) (**P5**)

Green colored powder.Yield: 56 mg (38%). FT-IR, $\nu_{max}/(cm^{-1})$: 3048 (CH, aromatic), 2925-2875 (CH, aliphatic), 1665 (C=C, aromatic), 1510, 1440, 1355, 1265, 1184, 1128, 1080, 1038, 830, 805, 767, 728. ^1H NMR ($CDCl_3$ 500 MHz): δ, ppm 7.35-7.19 (m, 4H, Ar-H), 4.35 (s, 2H, S-CH_2), 2.44 (s, 3H, -CH_3). MS (ESI): (m/z): 1467.6 $[M]^+$. Anal. calcd. for $C_{80}H_{72}N_8S_8Zn$: C, 65.48; H, 4.95; N, 7.64%. Found: C, 65.55; H, 4.83; N, 7.75%.

5.12 [2,3,7,8,12,13,17,18-octakis(*p*-tolylmethylthio) porphyrazinato] Co(II) (P6)

Blue colored powder. Yield: 63 mg (43%). FT-IR, $\nu_{max}/(cm^{-1})$: 3056 (CH, aromatic), 2936-2848 (CH, aliphatic), 1668 (C=C, aromatic), 1518, 1438, 1361, 1262, 1174, 1135, 1081, 1044, 845, 803, 758, 727. MS (ESI): (m/z): 1460.7 $[M]^+$. Anal. calcd. for $C_{80}H_{72}N_8 S_8$ Co: C, 65.77; H, 4.97; N, 7.67%. Found: C, 65.88; H, 4.86; N, 7.79%.

5.13 [2,3,7,8,12,13,17,18-octakis(*o*-tolylmethylthio) porphyrazinato] Cu(II) (O4)

Blue colored powder. Yield: 70 mg (48%). FT-IR, $\nu_{max}/(cm^{-1})$: 3052 (CH, aromatic), 2928-2868 (CH, aliphatic), 1621 (C=C, aromatic), 1493, 1458, 1355, 1258, 1212, 1188, 1091, 1041, 888, 828, 759, 735. MS (ESI): (m/z): 1465.4 $[M]^+$ (Appendix N). Anal. calcd. for $C_{80}H_{72}N_8 S_8$ Cu: C, 65.56; H, 4.95; N, 7.65%. Found: C, 65.62; H, 5.05; N, 7.54%.

5.14 [2,3,7,8,12,13,17,18-octakis(*o*-tolylmethylthio) porphyrazinato] Zn(II) (O5)

Green colored powder.Yield: 65 mg (44%). FT-IR, $\nu_{max}/(cm^{-1})$: 3055 (CH, aromatic), 2922-2864 (CH, aliphatic), 1635 (C=C, aromatic), 1495, 1448, 1352, 1260, 1214, 1193, 1094, 1038, 885, 825, 756, 736. ^{1}H NMR ($CDCl_3$ 500 MHz): δ, ppm 7.33-7.21 (m, 4H, Ar-H), 4.35 (s, 2H, S-CH_2), 2.40 (s, 3H, -CH_3). MS (ESI): (m/z): 1467.1 $[M]^+$. Anal. calcd. for $C_{80}H_{72}N_8 S_8$ Zn : C, 65.48; H, 4.95; N, 7.64%. Found: C, 65.57; H, 5.06; N, 7.53%.

5.15 [2,3,7,8,12,13,17,18-octakis(o-tolylmethylthio) porphyrazinato] Co(II) (O6)

Blue colored powder. Yield: 75 mg (51%). FT-IR, $\nu_{max}/(cm^{-1})$: 3040 (CH, aromatic), 2935-2874 (CH, aliphatic), 1632 (C=C, aromatic), 1498, 1437, 1342, 1271, 1236, 1192, 1098, 1035, 889, 823, 759, 735. MS (ESI): (m/z): 1460.6 $[M]^+$ (Appendix R). Anal. calcd. for $C_{80}H_{72}N_8 S_8$ Co : C, 65.77; H, 4.97; N, 7.67%. Found: C, 65.85; H, 4.83; N, 7.77%.

5.16 Synthesis of 1,2-bis(4-biphenylmethylthio)maleonitrile (B1)

Disodium salt of dithiomaleonitrile (1.12 g, 6 mmol) was mixed with 4-phenylbenzyl chloride (3.04 g, 15 mmol) in methanol (50 mL) and refluxed under

nitrogen for about 8 h. When MeOH was evaporated, the remaining product was treated with $CHCl_3$ to remove insoluble salts by filtration. The $CHCl_3$ solution was extracted several times with 15% Na_2SO_4 solution and then dried over anhydrous Na_2SO_4 overnight. After evaporation of the solvent the colored product was extracted with refluxing n-hexane to remove any excess 4-phenylbenzyl chloride. The product was orange colored and was very soluble in chloroform, dichloromethane and acetone, but insoluble in *n*-hexane. Yield: 2.05 g (72%). FT-IR, $\nu_{max}/(cm^{-1})$: 3056-3032 (CH, aromatic), 2921-2820 (CH, aliphatic), 2210 (C≡N), 1600 (C=C, aromatic), 1565, 1486, 1407, 1381, 1263, 1219, 1192, 1096, 1038, 1006, 964, 912, 824, 758, 730, 691 (Appendix S). ^{1}H-NMR (d-chloroform 500 MHz): δ, ppm 7.64-7.58 (m, 12H, Ar-H), 7.51-7.29 (m, 6H, Ar-H), 4.68 (s, 4H, S-CH_2). MS (ESI): (m/z): 474.2 $[M]^+$. Anal. calcd. for $C_{30}H_{24}N_2S_2$: C, 75.9; H, 4.7; N, 5.9%. Found: C, 75.8; H, 4.8; N, 5.8%.

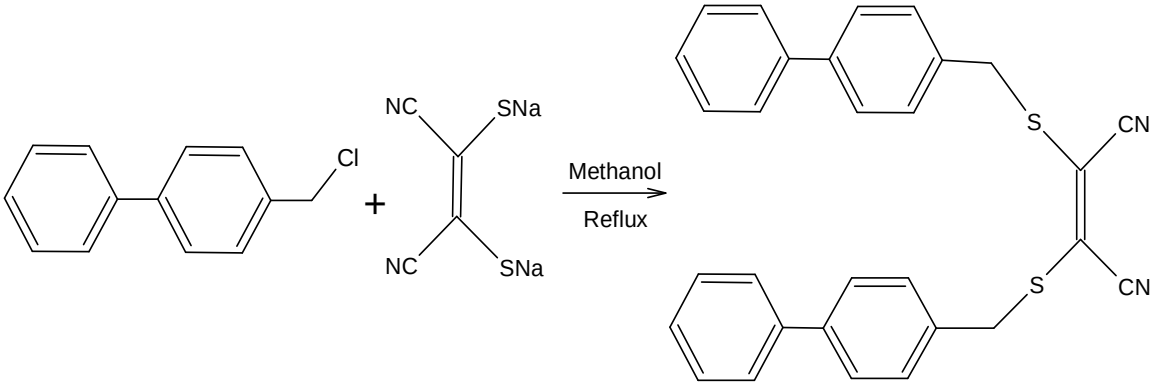


Figure 5.6 Synthesis of 1,2-bis(4-biphenyl)maleonitrile **B1**.

5.17 [2,3,7,8,12,13,17,18-octakis(4-biphenylmethylthio)porphyrazinato]Mg(II) (B2)

Mg turnings (24.3 mg, 1 mmol) and a small I_2 crystal were refluxed in *n*-BuOH (20 mL) for about 8 h to obtain $Mg(BuO)_2$. 1,2-bis(4-biphenylmethylthio)maleonitrile (**B1**) (949 mg, 2 mmol) was added to this solution and the mixture was refluxed for about 12 h. The dark green product was filtered, washed with ethanol and water and dried in a vacuum. The crude product was dissolved in $CHCl_3$ and filtered. The $CHCl_3$ solution was dried over anhydrous Na_2SO_4. When the solvent was evaporated, a colored product was obtained. Finally, pure porphyrazine was obtained by column chromatography (SiO_2, CH_3OH: $CHCl_3$, 1:30 v/v). The blue-green colored product was soluble in chloroform, dichloromethane, acetone and toluene, but insoluble in *n*-hexane. Yield: 442 mg (46%). FT-IR, $\nu_{max}/(cm^{-1})$: 3070-3030 (CH, aromatic), 2925-2845 (CH,

aliphatic), 1608 (C=C, aromatic), 1480, 1400, 1215, 1144, 1008, 848, 768, 720, 692. ^{1}H-NMR (d-chloroform 500 MHz): δ, ppm 7.78-7.33 (m, 9H, Ar-H), 4.95 (br s, 2H, CH_2-S). MS (ESI): (m/z): 1922.6 $[M]^+$. Anal. calcd. for $C_{120}H_{96}N_8S_8Mg$: C, 75.0; H, 4.6; N, 5.8%. Found: C, 74.9; H, 4.7; N, 5.7%

5.18 [2,3,7,8,12,13,17,18-octakis(4-biphenylmethylthio) H^{21}, H^{23} porphyrazine] (B3)

B2 (192 mg, 0.1 mmol) was dissolved in the minimum amount of trifluoroaceticacid (~4 mL) and stirred for 3 h at room temperature. When the reaction mixture was added to ice by dropwise and neutralized with 25% ammonia solution, precipitation occurred and it was filtered. The precipitate was extracted into the chloroform and the chloroform solution was extracted with water twice. After drying over anhydrous Na_2SO_4, the solvent was evaporated to obtain a violet colored metal-free porphyrazine. **B3** was obtained by column chromatography (SiO_2, CH_3OH: $CHCl_3$, 1:30 v/v). Yield: 105 mg (55%). FT-IR, $\nu_{max}/(cm^{-1})$: 3325 (N-H), 3062-3030 (CH, aromatic), 2928-2852 (CH, aliphatic), 1608 (C=C, aromatic), 1481, 1408, 1216, 1122, 1008, 842, 768, 723, 683. ^{1}H-NMR (d-chloroform 500 MHz): 7.76-7.35 (m, 9H, Ar-H), 5.28 (br s, 2H, CH_2-S), -1.05 (br s, 2H, NH). MS (ESI): (m/z): 1900.3 $[M]^+$. Anal. calcd. for $C_{120}H_{98}N_8S_8$: C, 75.8; H, 4.8; N, 5.9%. Found: C, 75.7; H, 4.9; N, 5.8%

5.19 General procedure for metallo porphyrazines (B4-B6)

B3 (190 mg, 0.1 mmol) in $CHCl_3$ (10 mL) was stirred with the metal salt [$Cu(OAc)_2$ (182 mg, 1 mmol), $Zn(OAc)_2$ (183 mg, 1 mmol) or $Co(OAc)_2$ (177 mg, 1 mmol)] in ethanol (15 mL) and refluxed under nitrogen for about 4 h. Then, the precipitate composed of the crude product and the excess metal salt was filtered. The precipitate was treated with $CHCl_3$ and the insoluble metal salts were removed by filtration. The filtrate was reduced to minimum volume under reduced pressure and then added into *n*-hexane (150 mL) drop by drop to realize the precipitation. Finally, pure porphyrazine derivatives (**B4-B6**) were obtained by column chromatography (SiO_2, CH_3OH: $CHCl_3$, 1:50 v/v).

5.20 [2,3,7,8,12,13,17,18-octakis(4-biphenylmethylthio)porphyrazinato] Cu(II) (B4)

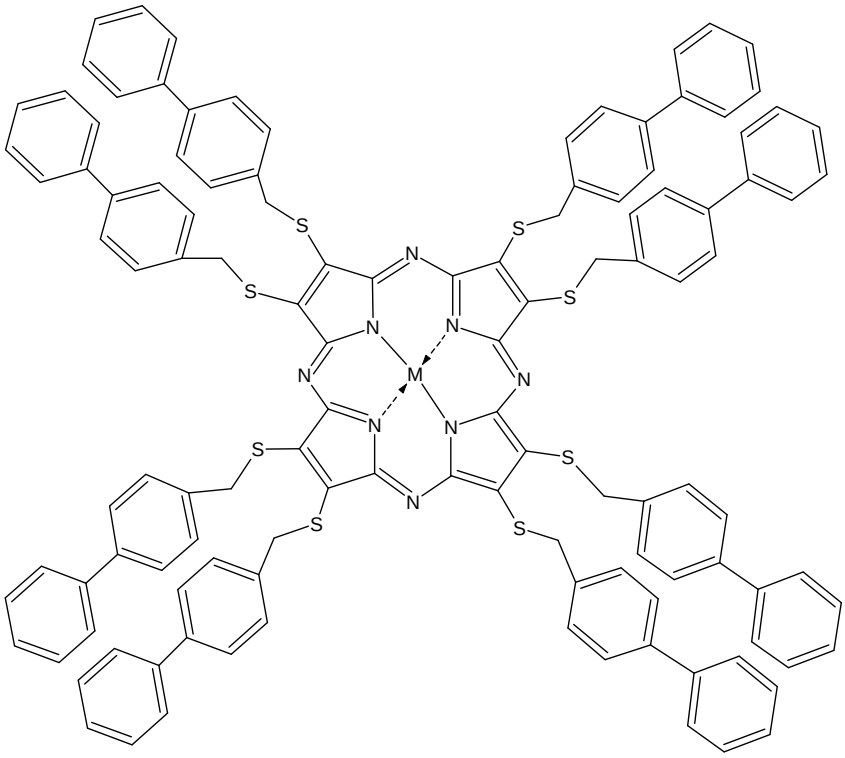
Yield: 94.0 mg (48%). FT-IR, $\nu_{max}/(cm^{-1})$: 3065-3025 (CH, aromatic), 2932-2847 (CH, aliphatic), 1620 (C=C, aromatic), 1442, 1413, 1218, 1136, 1022, 870, 755, 718, 691. MS (ESI): (m/z): 1962.3 $[M]^+$. Anal. calcd. for $C_{120}H_{96}N_8\ S_8$ Cu: C, 73.5; H, 4.5; N, 5.7%. Found: C, 73.6; H, 4.4; N, 5.8%

5.21 [2,3,7,8,12,13,17,18-octakis(4-biphenylmethylthio)porphyrazinato] Zn(II) (B5)

Yield: 102 mg (52%). FT-IR, $\nu_{max}/(cm^{-1})$: 3050-3030 (CH, aromatic), 2926-2850 (CH, aliphatic), 1654 (C=C, aromatic), 1446, 1250, 1115, 1025, 844, 758, 728, 693. ^{1}H-NMR (d-chloroform 500 MHz): 7.75-7.31 (m, 9H, aromatic H), 4.89 (s, 2H, CH_2-S). MS (ESI): (m/z): 1963.6 $[M]^+$. Anal. calcd. for $C_{120}H_{96}N_8\ S_8$ Zn : C, 73.4; H, 4.5; N, 5.7%. Found: C, 73.5; H, 4.4; N, 5.8%

5.22 [2,3,7,8,12,13,17,18-octakis(4-biphenylmethylthio)porphyrazinato] Co(II) (B6)

Yield: 90.0 mg (46%). FT-IR, $\nu_{max}/(cm^{-1})$: 3065-3020 (CH, aromatic), 2932-2855 (CH, aliphatic), 1625 (C=C, aromatic), 1476, 1408, 1215, 1146, 1009, 879, 758, 725, 684. MS (ESI): (m/z): 1957.2 $[M]^+$. Anal. calcd. for $C_{120}H_{96}N_8\ S_8$ Co : C, 73.6; H, 4.5; N, 5.7%. Found: C, 73.5; H, 4.6; N, 5.6%.



M= Mg (**B2**); 2H (**B3**); Cu (**B4**); Zn (**B5**); Co (**B6**)

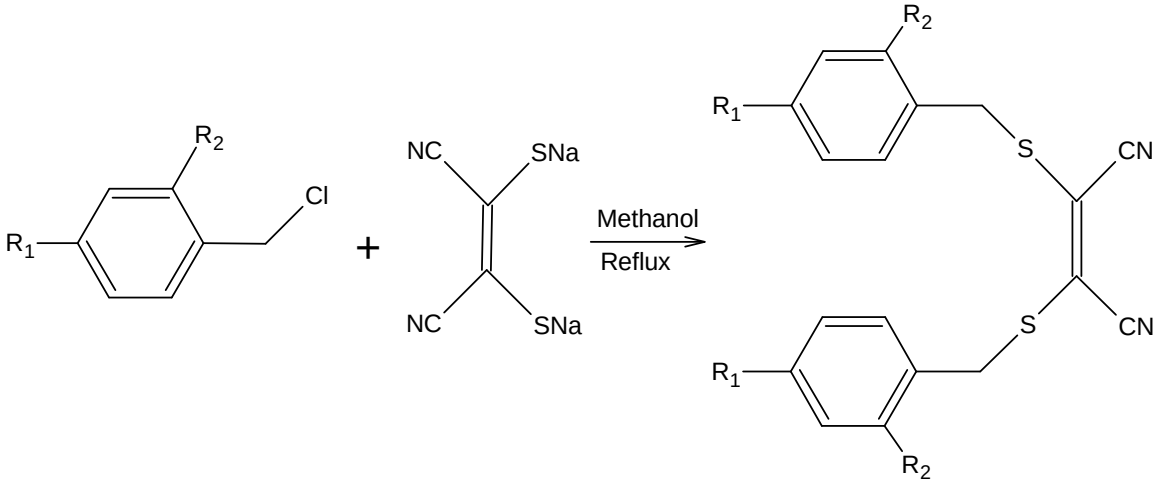
Figure 5.7 Synthesis of [2,3,7,8,12,13,17,18-octakis (4-biphenylmethylthio) substituted porphyrazines (**B2-B6**).

CHAPTER 6

RESULTS AND DISCUSSIONS

6.1 (*p*-tolylmethylthio) and (*o*-tolylmethylthio) Substituted Porphyrazines

The starting material for these novel porphyrazine structures with eight (*p*-tolylmethylthio) and (*o*-tolylmethylthio) groups bound to the periphery is 1,2-bis(*p*-tolylmethylthio) maleonitrile (**P1**) and 1,2-bis(*o*-tolylmethylthio) maleonitrile (**O1**) which were obtained from (α-chloro-*p*-xylene) and (α-chloro-*o*-xylene), respectively and the disodium salt of dithiomaleonitrile (Fig.6.1). The red brown colored products **P1** and **O1** were obtained in yield 78%, and 83%, respectively.



P1 (R_1: CH_3, R_2: H)
O1 (R_1: H, R_2: CH_3)

Figure 6.1 Synthesis of 1,2-bis(p-tolylmethylthio)maleonitrile (**P1**) and 1,2-bis(o-tolylmethylthio)maleonitrile (**O1**).

The conversion of **P1** and **O1** into **P2** and **O2** were achieved by the template effect of magnesium butanolate. In the FT-IR spectrum, the disappearance of C≡N peak at 2210 cm^{-1} is the most important clue for the macrocyclization of ligand **P1** and **O1** to form porphyrazine molecules. The cyclotetramerization gave the dark green colored **P2** in yield 63% and the blue-green colored **O2** in yield 58% (Fig.6.2). They were soluble in chloroform, dichloromethane, acetone and toluene, but insoluble in nonpolar hydrocarbon solvents such as *n*-hexane.

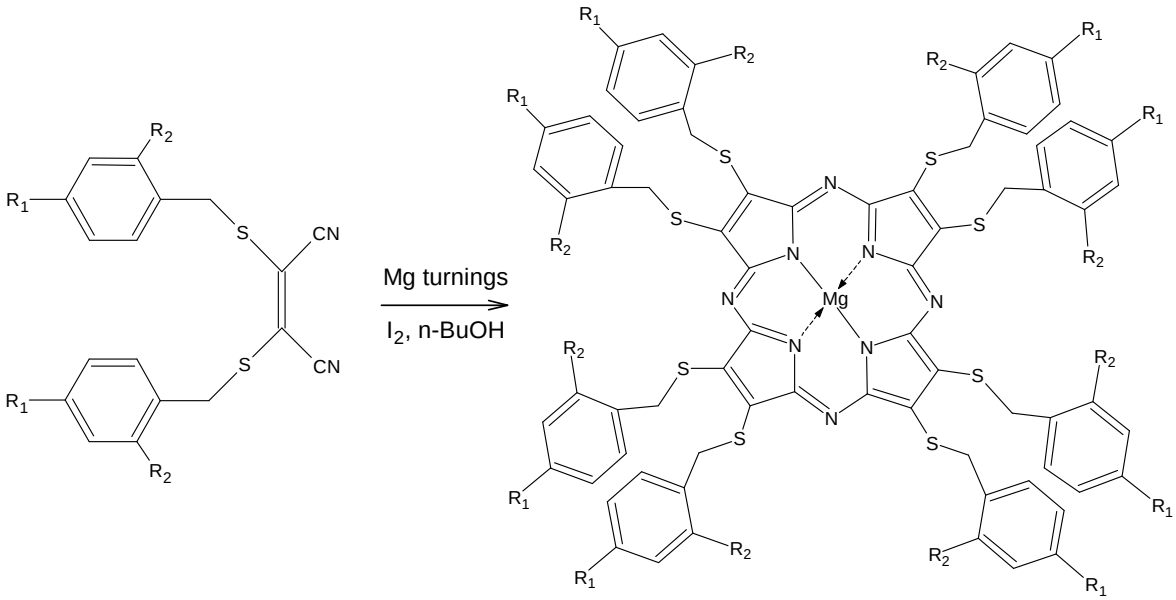
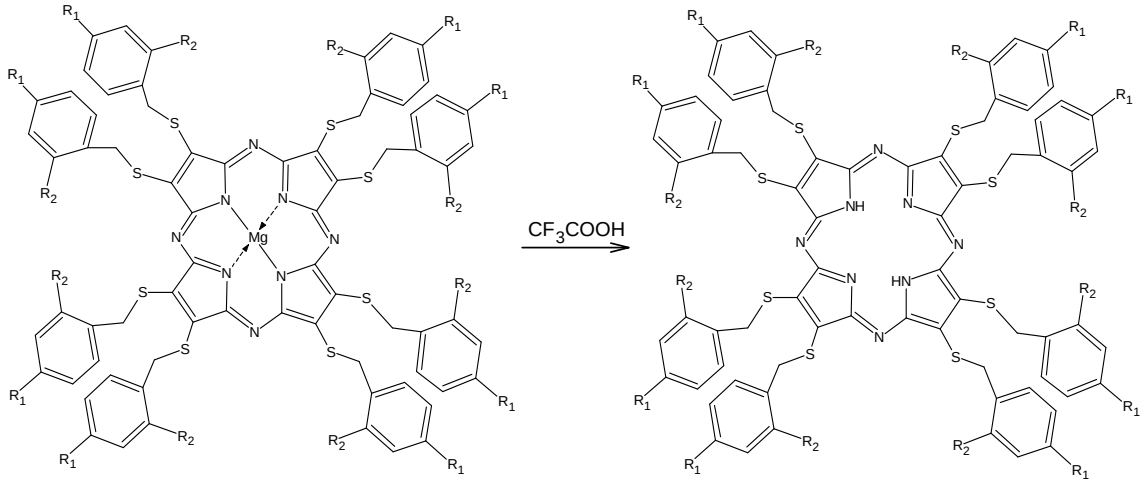


Figure 6.2 Synthesis of [2,3,7,8,12,13,17,18-octakis(*p*-tolylmethylthio)porphyrazinato] Mg(II) (**P2**) and [2,3,7,8,12,13,17,18-octakis(*o*-tolyl)porphyrazinato] Mg(II) (**O2**).

In the conversion of **P2** and **O2** into **P3** and **O3** were achieved by the treatment with relatively strong acids (e.g. trifluoroacetic acid) (Fig.6.3).



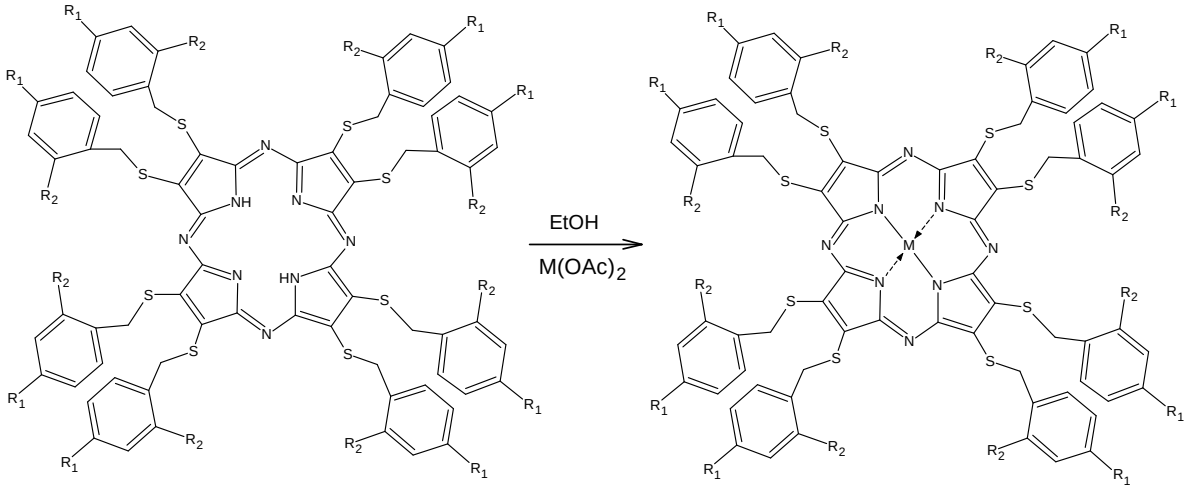
M= 2H (**P3**) (R_1: CH_3, R_2: H)

M= 2H (**O3**) (R_1: H, R_2: CH_3)

Figure 6.3 Synthesis of [2,3,7,8,12,13,17,18- octakis(*p*-tolylmethylthio) H^{21}, H^{23} porphyrazine] (**P3**) and [2,3,7,8,12,13,17,18- octakis(*o*-tolylmethylthio) H^{21}, H^{23} porphyrazine] (**O3**).

The mass spectral results have clearly indicated the change of the structure from magnesium porphyrazinates **P2** and **O2** to the demetalated porphyrazines **P3** and **O3** When magnesium metal is removed from center of porphyrazine cycle, two N atoms of pyrrole groups are protonated. In the IR spectrum, the existence of peak at 3282 cm^{-1} indicates the N-H bond stretching of H_2Pz.

The metallation reactions of the demetallated porpyrazines **P3** and **O3** with metal salts gave the metallated species **P4-P6** and **O4-O6** (Fig.6.4).



M= Cu (**P4**); Zn (**P5**); Co (**P6**) (R_1: CH_3, R_2: H)

M= Cu (**O4**); Zn (**O5**); Co (**O6**) (R_1: H, R_2: CH_3)

Figure 6.4 Synthesis of [2,3,7,8,12,13,17,18-octakis(*p*-tolylmethylthio) porphyrazinato] {M=Cu(II), Zn(II) or Co(II)} and [2,3,7,8,12,13,17,18-octakis (*o*-tolylmethylthio) porphyrazinato] {M=Cu(II), Zn(II) or Co(II)}

Elemental analyses correspond closely with the values calculated for (**P1-P6** and **O1-O6**) (Table 6.1).

Table 6.1 Elemental analyses results of the porphyrazines*

Compound	C	H	N
P1	68.65 (68.53)	5.07 (5.18)	7.85 (7.99)
O1	68.68 (68.53)	5.26 (5.18)	8.09 (7.99)
P2	67.49 (67.37)	5.20 (5.09)	7.71 (7.86)
P3	68.32 (68.44)	5.44 (5.31)	7.86 (7.98)
P4	65.43 (65.56)	4.82 (4.95)	7.79 (7.65)
P5	65.55 (65.48)	4.83 (4.95)	7.75 (7.64)
P6	65.88 (65.77)	4.86 (4.97)	7.79 (7.67)
O2	67.52 (67.37)	5.18 (5.09)	7.73 (7.86)
O3	68.30 (68.44)	5.38 (5.31)	7.83 (7.98)
O4	65.62 (65.56)	5.05 (4.95)	7.54 (7.65)
O5	65.57 (65.48)	5.06 (4.95)	7.53 (7.64)
O6	65.85 (65.77)	4.83 (4.97)	7.77 (7.67)

* Required values are given in parentheses

IR Spectra

In the FT-IR spectrum of **P1**, the stretching vibration of C≡N is observed at 2210 cm^{-1}, the aromatic and aliphatic C-H peaks are around 3048-2853 cm^{-1} and the characteristic substituted (*p*-tolyl) peak is at 803 cm^{-1} and in the FT-IR spectrum of **O1**, the stretching vibration of C≡N is observed at 2210 cm^{-1}, the aromatic and aliphatic C-H peaks are around 3063-2863 cm^{-1} and the characteristic substituted (*o*-tolyl) peak is at 735 cm^{-1}. These values comply with those reported in the literature for similar compounds [54, 57, 70]. After the conversion of **P1** and **O1** to **P2** and **O2**, the sharp C≡N vibrations around 2210 cm^{-1} disappeared. The N-H stretching absorptions of the inner core of the metal-free porphyrazines (**P3, O3**) were observed around 3330 and 3282 cm^{-1}. The FT-IR spectra of

all porphyrazines derivatives (**P4-P6, O4-O6**) showed that the aromatic and aliphatic C-H peaks are around 3063-2848 cm^{-1}, the characteristic C=C aromatic peaks are around 1605-1668 cm^{-1}, the characteristic substituted (*p*-tolyl) peaks are around 802-848 cm^{-1} and the characteristic substituted (*o*-tolyl) peaks are around 726-764 cm^{-1}.

NMR Spectra

In the ^{1}H NMR spectra of diamagnetic porphyrazines (**P2, P3, P5, O2, O3, O5**), three different types of protons are clearly seen: A multiplet around 7.19-7.35 ppm corresponding to phenyl protons, a singlet around 4.33-4.39 ppm corresponding to S-CH_2 and a singlet around 2.40-2.44 ppm for methyl protons. The ratio of the integral values 4:2:3 also confirms the proposed structures. The N–H protons of the metal-free porphyrazines (**P3, O3**) were also identified in the ^{1}H NMR spectra with the broad peaks at δ = -1.15 and δ = -1.05 ppm, presenting the typical shielding of inner core protons, which is a common feature of the ^{1}H NMR spectra of metal-free porphyrazines [53, 54, 57,76].

Electronic Spectra

Electronic spectra are especially useful to establish the structure of the porphyrazines (**P2-P6, O2-O6**). UV-Vis spectra of porphyrazine core are dominated by two intense bands, the Q band around 650 nm and the B band in the near UV region around 350 nm, both correlated to $\pi \rightarrow \pi^{*}$ transitions [58, 59]. The presence of an electron-donating unit on the periphery causes a bathochromic shift on Q bands. The UV-Vis spectra of porphyrazines (**P2, P4-P6, O2, O4-O6** in chloroform) prepared in the present work exhibited intense single Q band absorption of the $\pi \rightarrow \pi^{*}$ transitions around 676-688 nm and B bands in the near UV region around 345-378 nm (Table 6.2). As a consequence of the change in the symmetry of porphyrazine core from D_{4h} (in the case of metallo derivatives) to D_{2h}, the electronic absorption spectra of **P3** and **O3** display a split in the Q band at 652 and 708 nm and at 656 and 700 nm, respectively. UV-Vis spectra of **P2** and **O2** in chloroform are shown in Figure 6.5. An absorbance *vs.* concentration study indicated that due to the bulky (*p*-tolylmethylthio) and (*o*-tolylmethylthio) substituents, no aggregation occurred either for **P2, P3, O2** or **O3**.

Table 6.2 UV–Vis data for the porphyrazines in chloroform.

Compound	**λ/nm (log ε / dm^3 mol^{-1} cm^{-1})**		
P2	368 (4.71)	676 (4.70)	
P3	352 (4.89)	652 (4.74)	708 (4.81)
P4	348 (4.79)	676 (4.84)	
P5	360 (4.78)	676 (4.88)	
P6	366 (4.84)	646 (4.89)	
O2	376 (4.53)	680 (4.58)	
O3	354 (4.51)	638 (4.18)	715 (3.85)
O4	358 (4.41)	642 (4.38)	
O5	376 (4.45)	688 (4.42)	
O6	356 (4.49)	650 (4.40)	

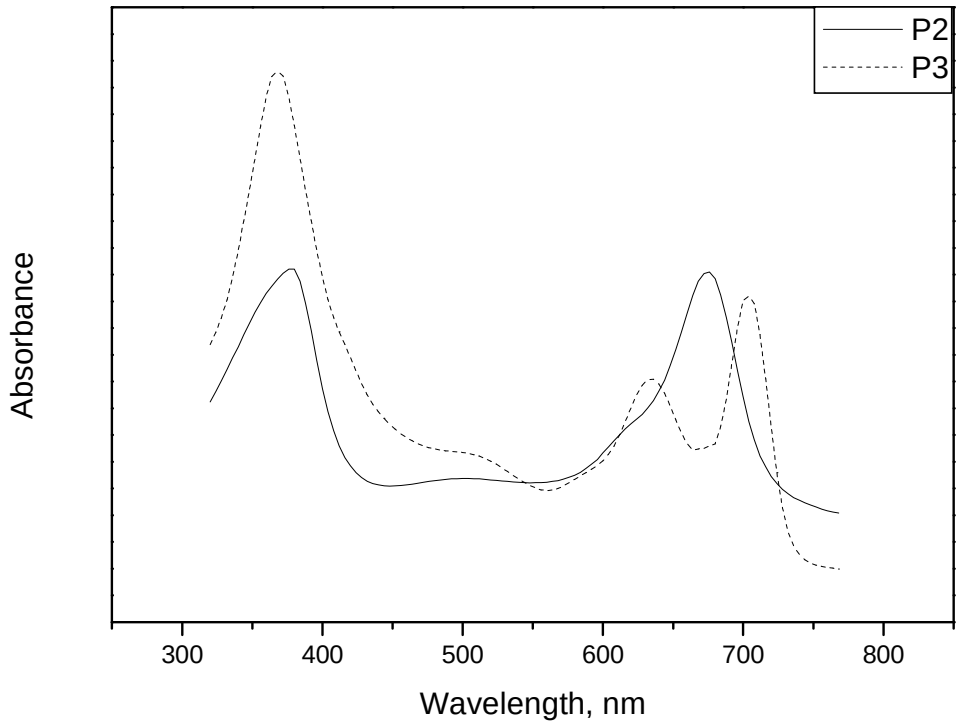


Figure 6.5 UV-Vis Spectra of **P2** and **P3** in Chloroform

6.2 (4-Biphenylmethylthio) Substituted Porphyrazines

The starting material for these novel porphyrazine structures with eight (4-biphenylmethylthio) units bound to the periphery through flexible methylthio chains is 1,2-bis(4-biphenylmethylthio)maleonitrile (**B1**) which was obtained from the disodium salt of dithiomaleonitrile and 4-phenylbenzyl chloride (Fig.6.6). The orange colored product (**B1**) was obtained in relatively high yield (72%).

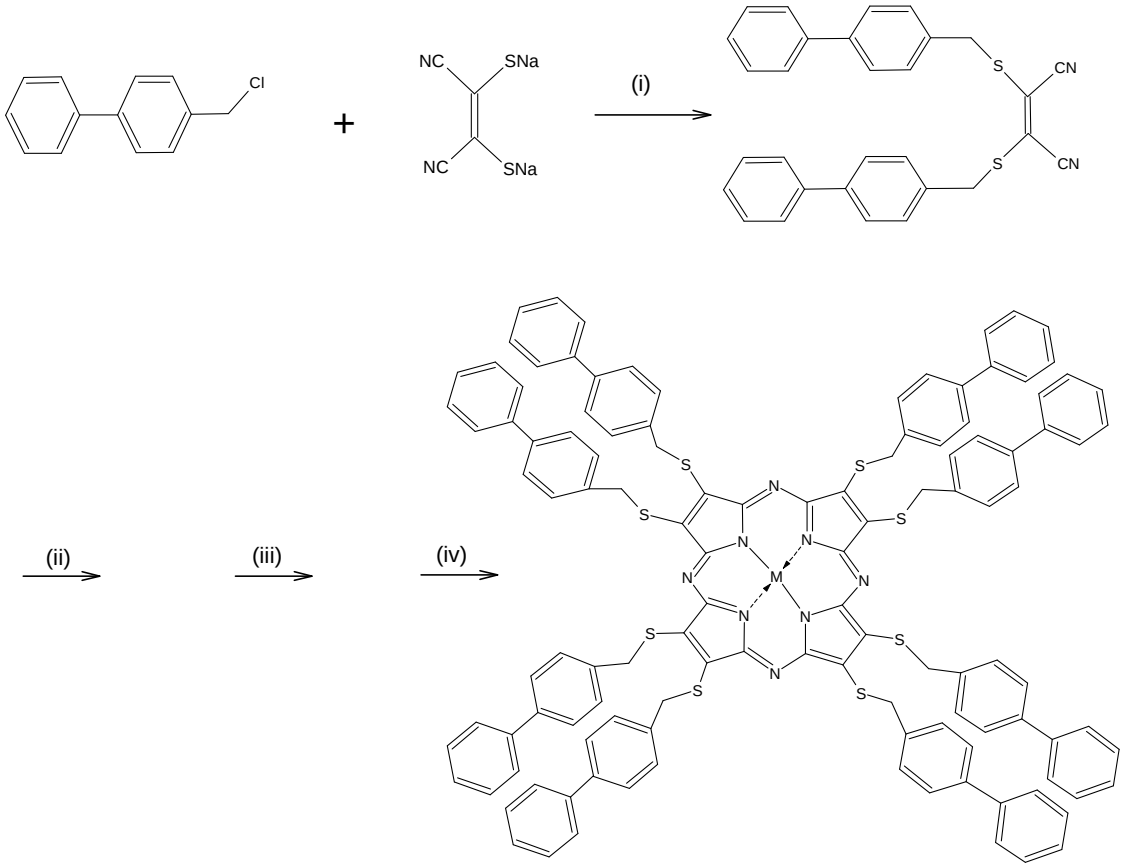


Fıgure 6.6 (i) Methanol; (ii) Mg turnings, I_2, n-BuOH; (iii) CF_3CO_2H; (iv) EtOH and $Cu(OAc)_2$, $Zn(OAc)_2$, or $Co(OAc)_2$.

The conversion of 1,2-bis(4-biphenylmethylthio)maleonitrile into porphyrazine was achieved by the template effect of magnesium butanolate. The cyclotetramerization gave the blue-green [2,3,7,8,12,13,17,18-octakis(4-biphenylmethylthio) porphyrazinato] magnesium (**B2**) (Fig.6.6). It is soluble in chloroform, dichloromethane, toluene and acetone, but insoluble in apolar hydrocarbon solvents such as n-hexane. The conversion of **B2** into B**3** was achieved by the treatment with relatively strong acids (e.g. trifluoroacetic acid). The MS results have clearly indicated the change of the structure from magnesium porphyrazinate (**B2**) to the demetalated porphyrazine (**B3**). Further reaction of this product with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate has led to the metal porphyrazinates (M= Cu, Zn, Co) (**B4-B6**) (Fig. 6.6).Elemental analyses correspond closely with the values calculated for **(B1-B6)** (Table 6.3).

Table 6.3 Elemental analyses results of the porphyrazines*

Compound	C	H	N
B1	75.8 (75.9)	4.8 (4.7)	5.8 (5.9)
B2	74.9 (75.0)	4.7 (4.6)	5.7 (5.8)
B3	75.7 (75.8)	4.9 (4.8)	5.8 (5.9)
B4	73.6 (73.5)	4.4 (4.5)	5.8 (5.7)
B5	73.5 (73.4)	4.4 (4.5)	5.8 (5.7)
B6	73.5 (73.6)	4.6 (4.5)	5.6 (5.7)

* Required values are given in parentheses.

Infrared Spectra

In the FT-IR spectrum of 1,2-bis(4-biphenylmethylthio)maleonitrile (**B1**) stretching vibration of C≡N is observed at 2210 cm^{-1}, the aromatic and aliphatic C-H peaks are around 2820-3055 cm^{-1} and the aromatic C=C peak is at 1600 cm^{-1}. These values comply with those reported in the literature for similar compounds [54]. After the conversion of dinitrile derivative (**B1**) to porphyrazine (**B2**), the sharp C≡N vibration around 2220 cm^{-1} disappeared. The N-H stretching absorption of the inner core of the metal-free porphyrazine (**B3**) was observed around 3325 cm^{-1}. FT-IR spectra of all porphyrazines derivatives (**B2-B6**) showed the aromatic and aliphatic C-H peaks are around 2845-3070 cm^{-1} and the aromatic C=C peak is at 1608-1654 cm^{-1} [54].

NMR Spectra

The N-H protons of the metal-free porphyrazine (**B3**) were also identified in the ^{1}H-NMR spectrum with a broad peak at δ= -1.05 ppm, presenting the typical shielding of inner core protons, which is a common feature of the ^{1}H-NMR spectra of metal-free porphyrazines [43, 45, 46, 54, 59, 61]. In the ^{1}H-NMR spectra of diamagnetic porphyrazines **B2**, **B3** and **B5,** two different types of protons are clearly seen: A multiplet around 7-8 ppm corresponding to the phenyl protons and a singlet at 4.95 ppm (**B2**), 5.28

ppm (**B3**) or 4.89 ppm (**B5**) for methylene protons. The ratio of the integral values 9:2 also confirms the proposed structure.

Electronic Spectra

Electronic spectra are very useful to establish the structure of the porphyrazines (**B2-B6**). UV-Vis spectra of porphyrazine core are dominated by two intense bands, the Q band around 670 nm and the B band in the near UV region of around 350 nm, both correlated to $\pi \rightarrow \pi^*$ transitions [58,59]. The presence of an electron donating group on the periphery causes a bathochromic shift on Q bands. UV-Vis spectra of metallo-porphyrazines (**B2, B4-B6** in $CHCl_3$) prepared in the present work exhibited intense single Q band absorption of the $\pi \rightarrow \pi^*$ transitions around 668-680 nm and B bands in the near UV region around 344-378 nm (Table 6.4). For metal-free derivative (**B3**), Q band is split into two peaks at 652 and 715 nm as a consequence of the change in the symmetry of porphyrazine core from D_{4h} (in the case of metallo derivatives) to D_{2h}. An absorbance *vs.* concentration study indicated that due to the bulky (4-biphenylmethylthio) units, no aggregation occurred either for **B2, B3**.

Table 6.4 UV–Vis data for the porphyrazines in chloroform

Compound	**λ/nm (log ε / dm^3 mol^{-1} cm^{-1})**		
3a	378 (4.71)	668 (4.70)	
3b	336 (4.65)	652 (4.45)	715 (4.48)
3c	352 (4.28)	676 (4.30)	
3d	348 (4.40)	680 (4.36)	
3e	344 (4.33)	678 (4.38)	

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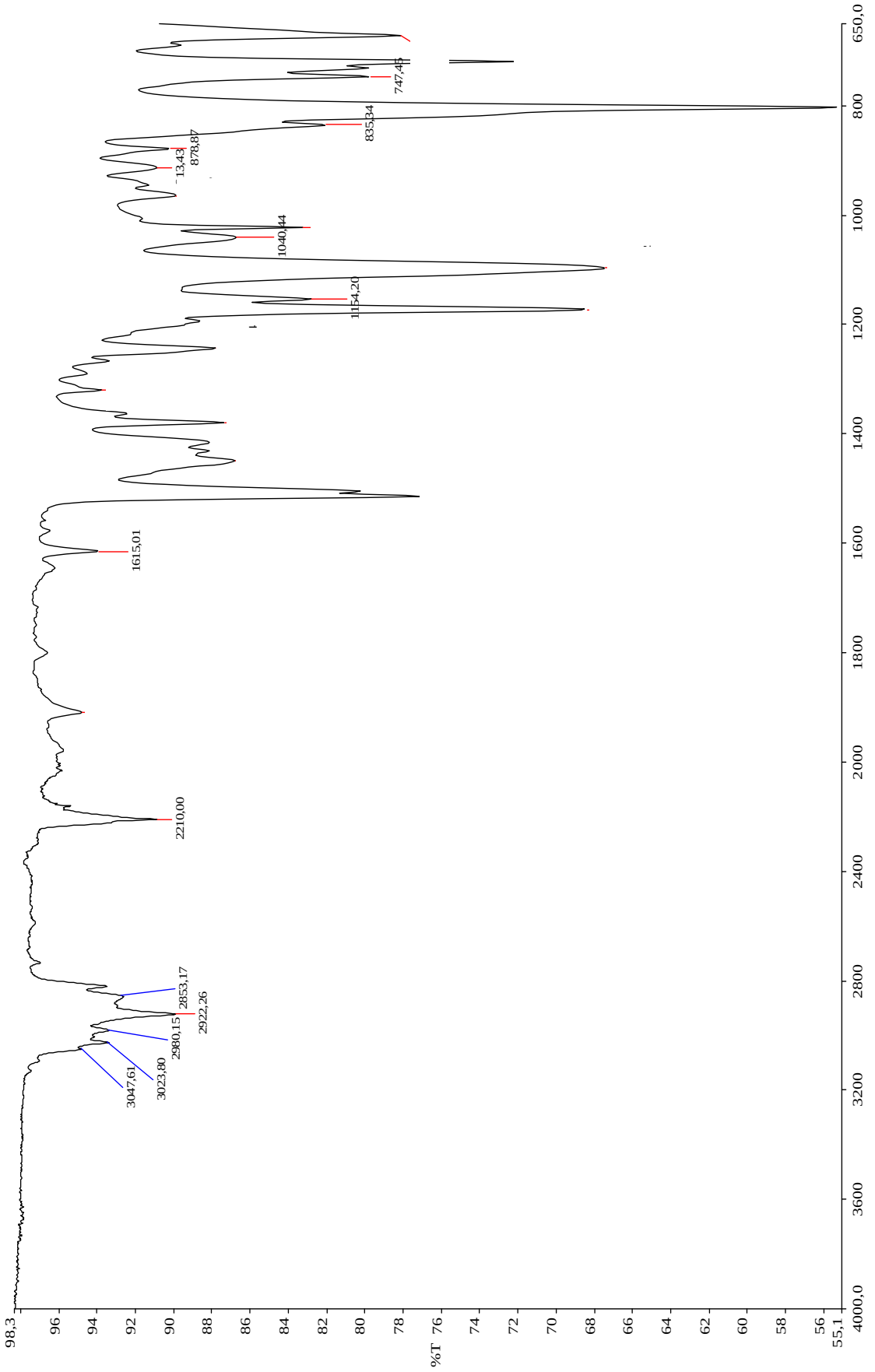
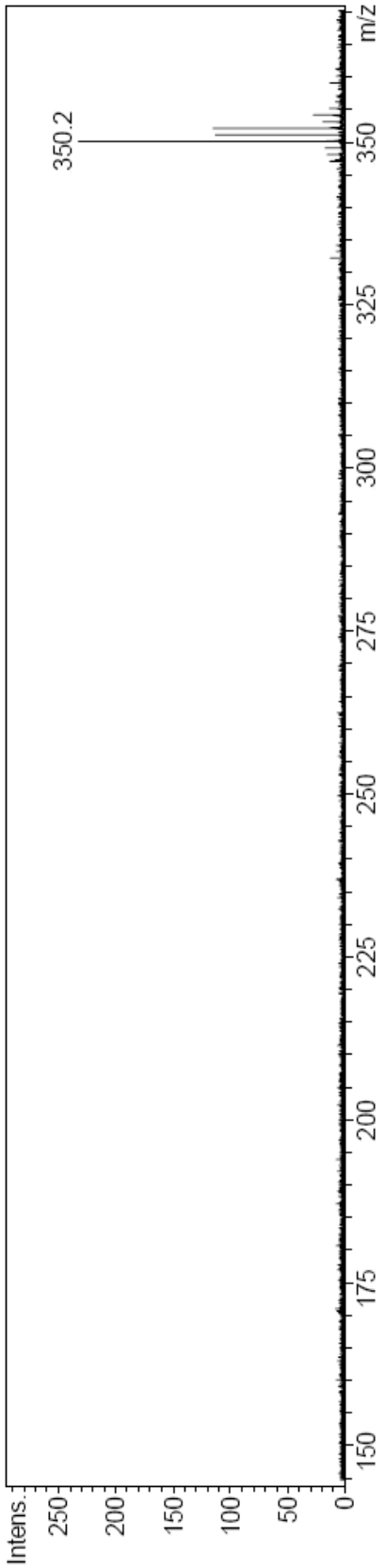
APPENDIX A



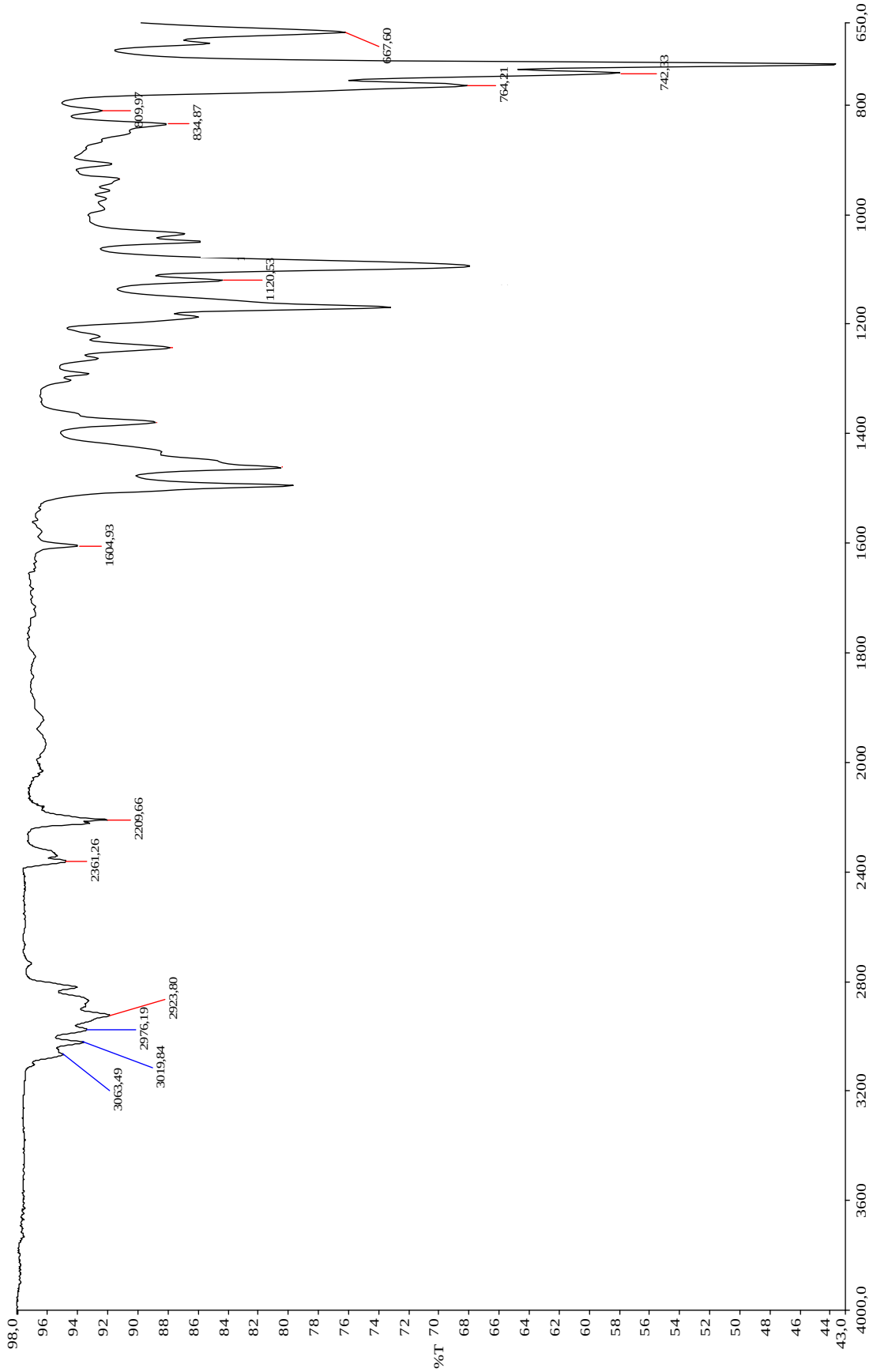
FT-IR Spectrum of 1,2-bis(*p*-tolylmethylthio) maleonitrile **(P1)**

APPENDIX B



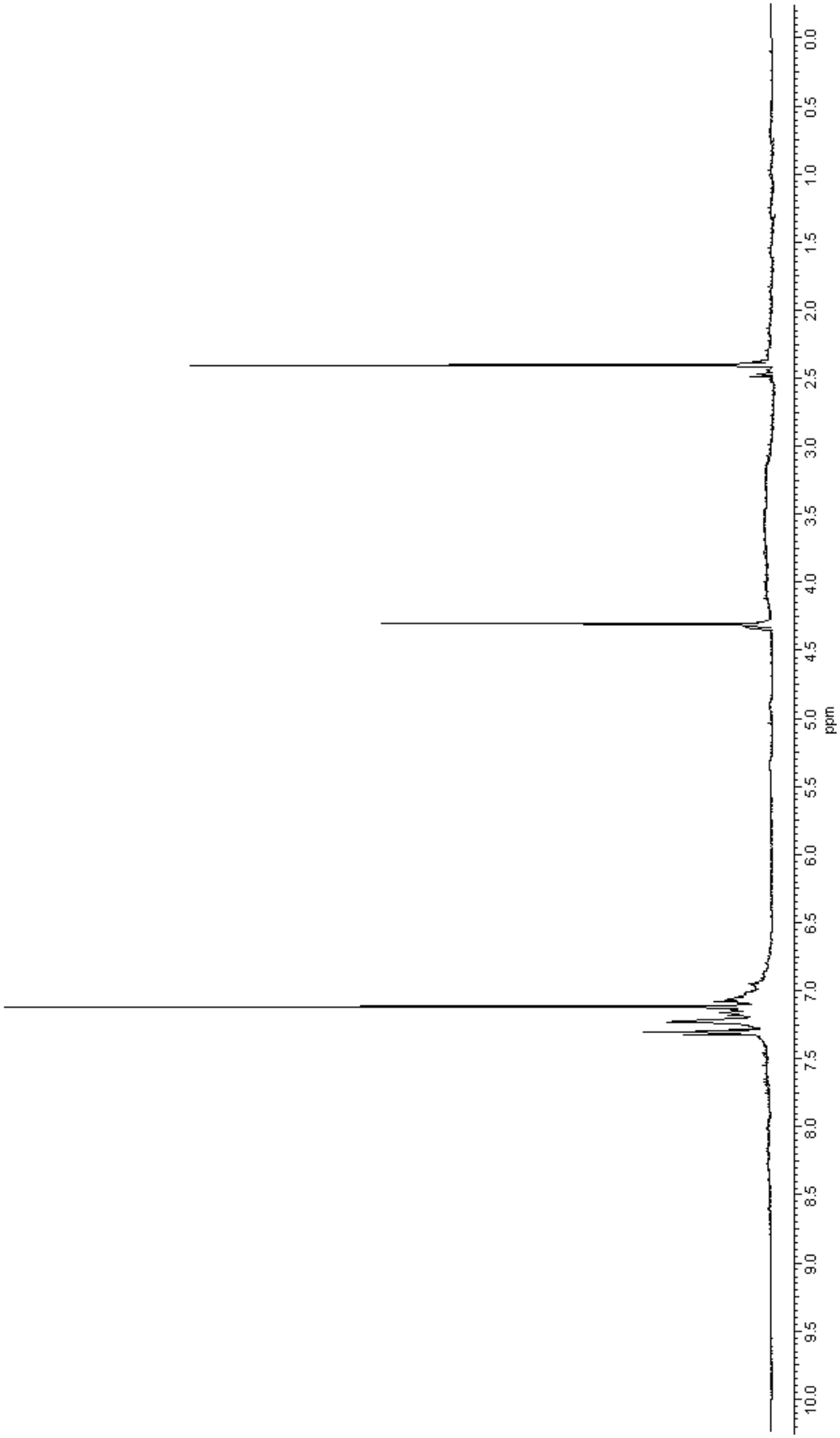
Mass Spectrum of 1,2-bis(*p*-tolylmethylthio) maleonitrile **(P1)**

APPENDIX C



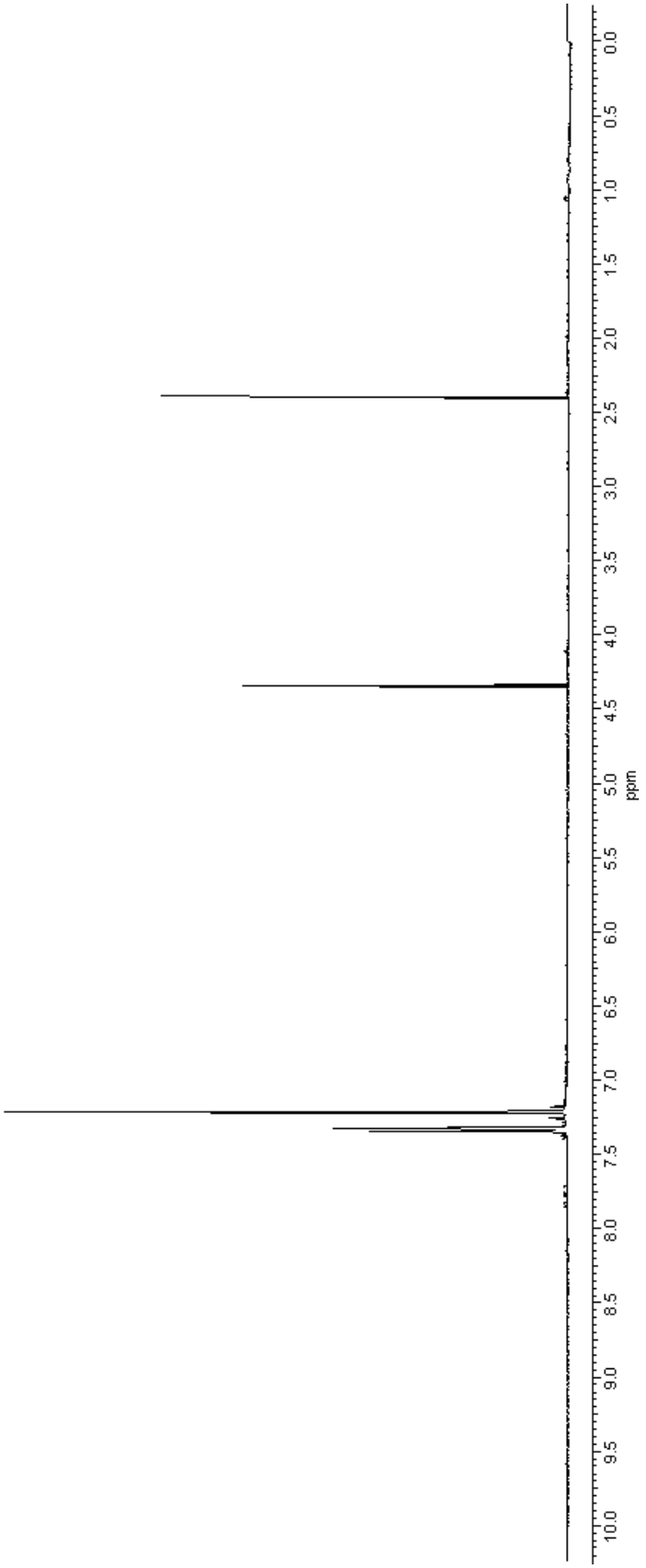
FT-IR Spectrum of 1,2-bis(*o*-tolylmethylthio) maleonitrile **(O1)**

APPENDIX D



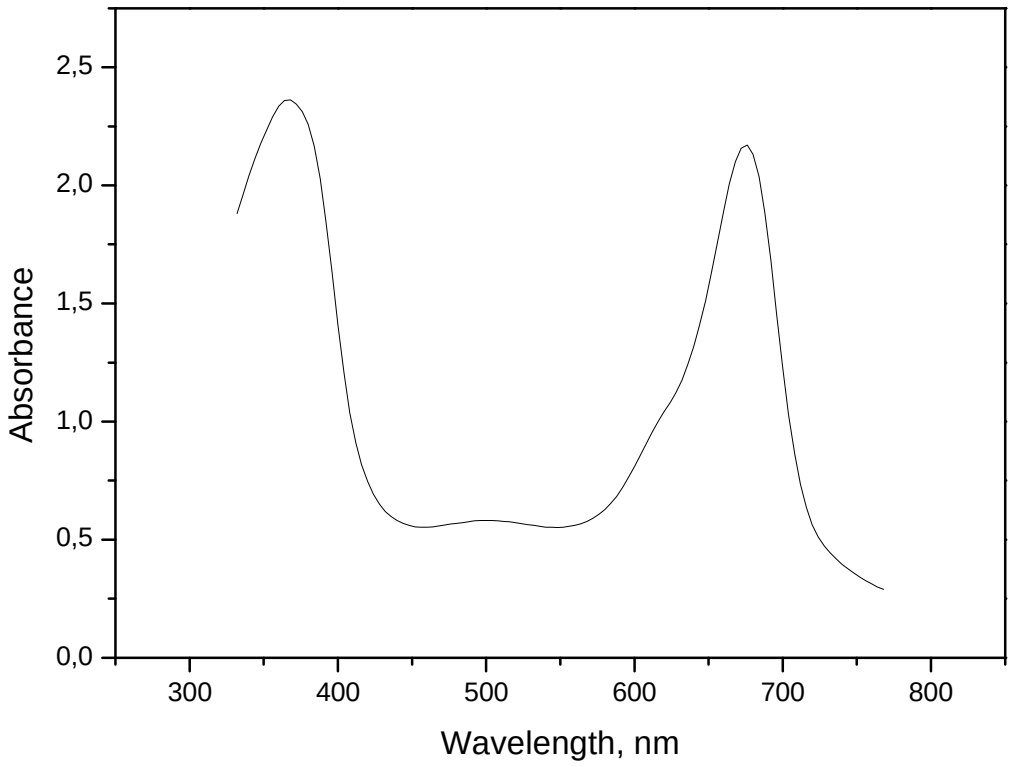
^{1}H NMR Spectrum of 1,2-bis(*p*-tolylmethylthio) maleonitrile **(P1)**

APPENDIX E



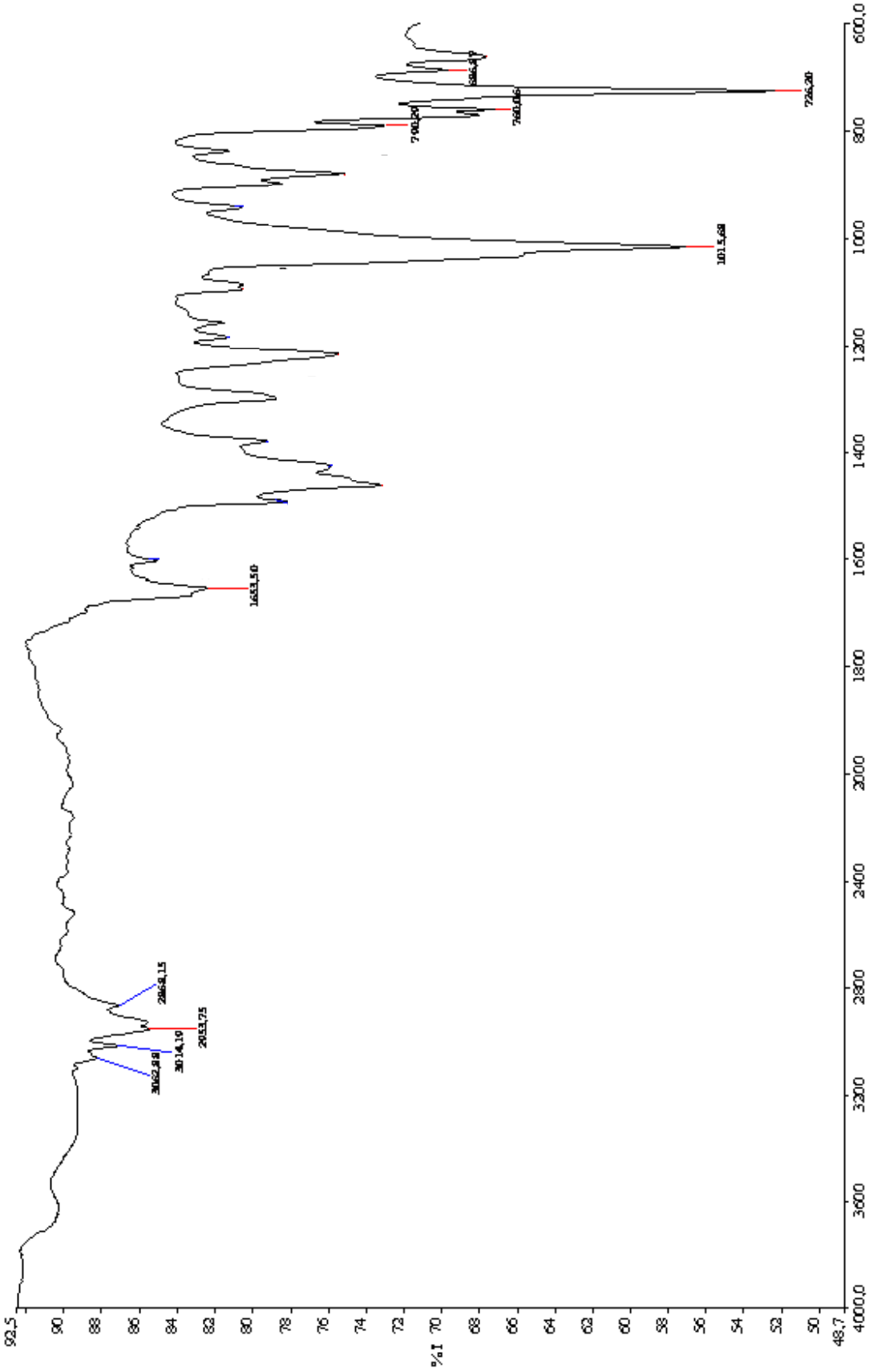
^{1}H NMR Spectrum of MgPz **(P2)**

APPENDIX F



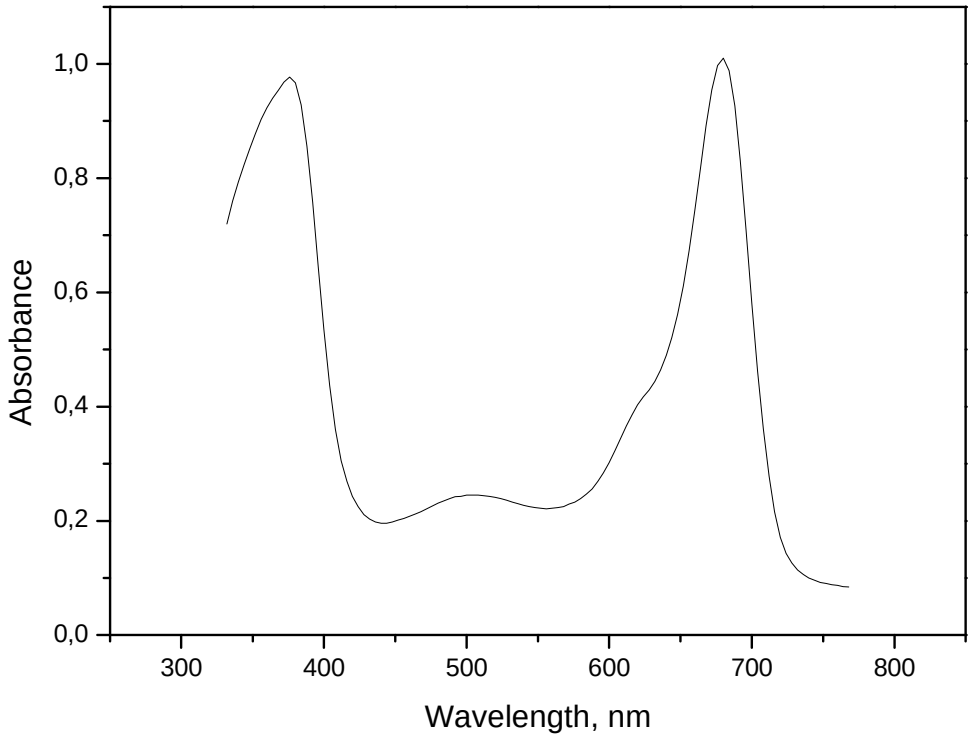
UV-Vis Spectrum of MgPz (**P2)** in Chloroform

APPENDIX G



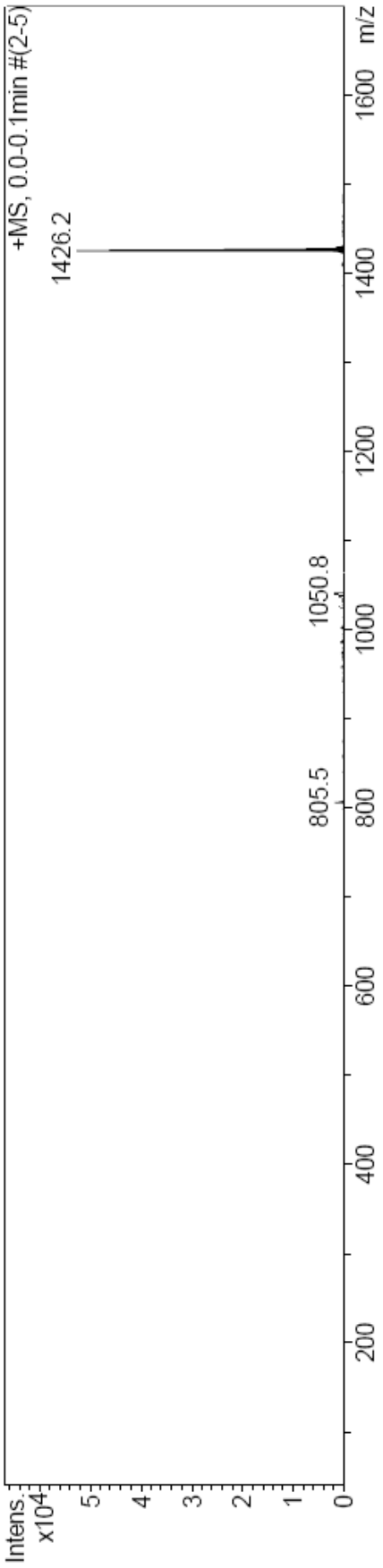
FT-IR Spectrum of MgPz **(O2)**

APPENDIX H



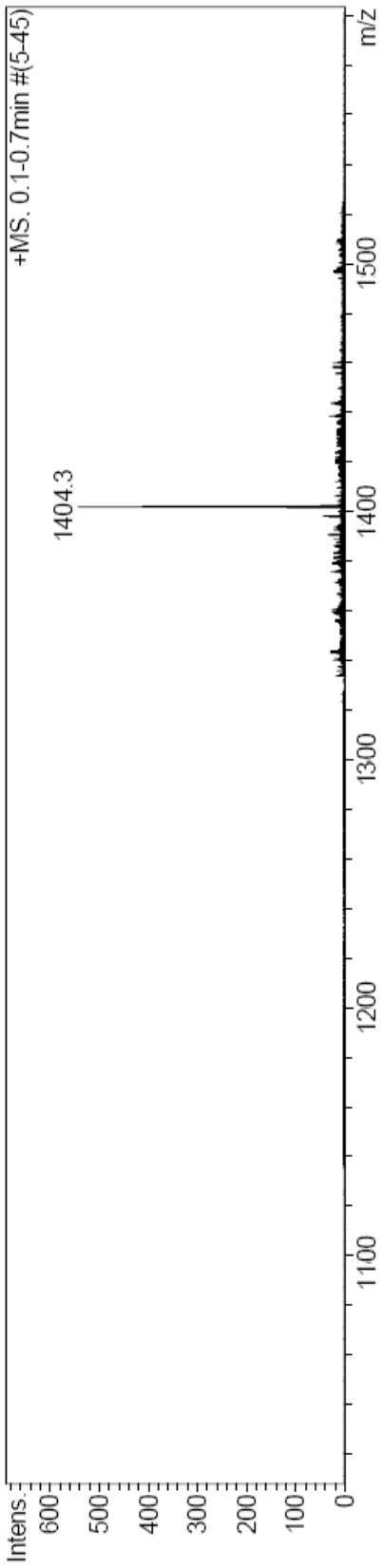
UV-Vis Spectrum of MgPz **(O2)** in Chloroform

APPENDIX I



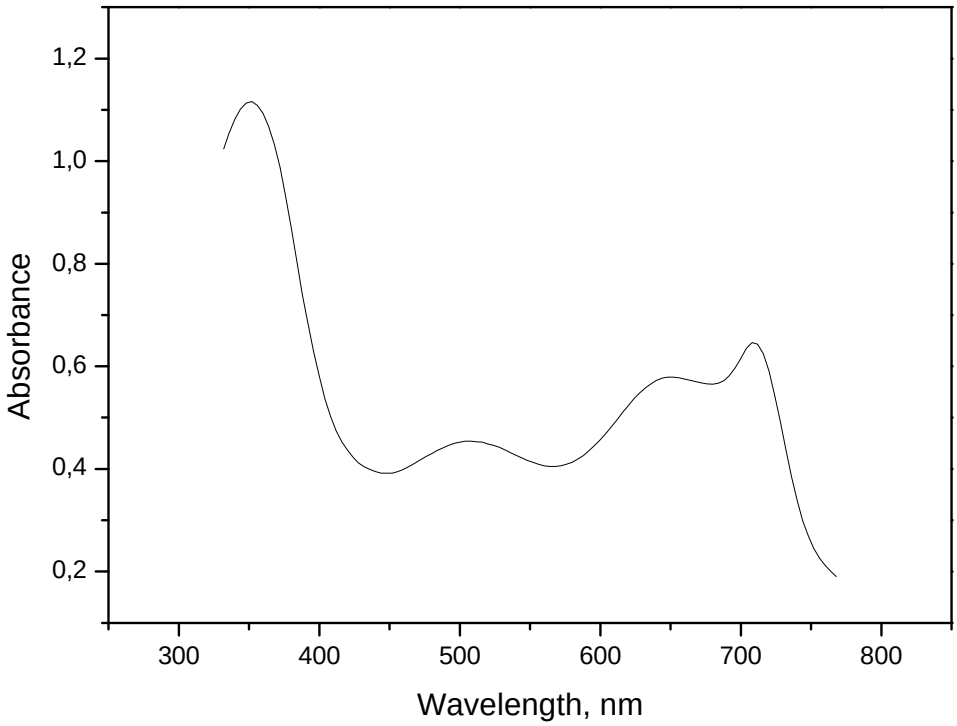
Mass Spectrum of MgPz **(O2)**

APPENDIX J



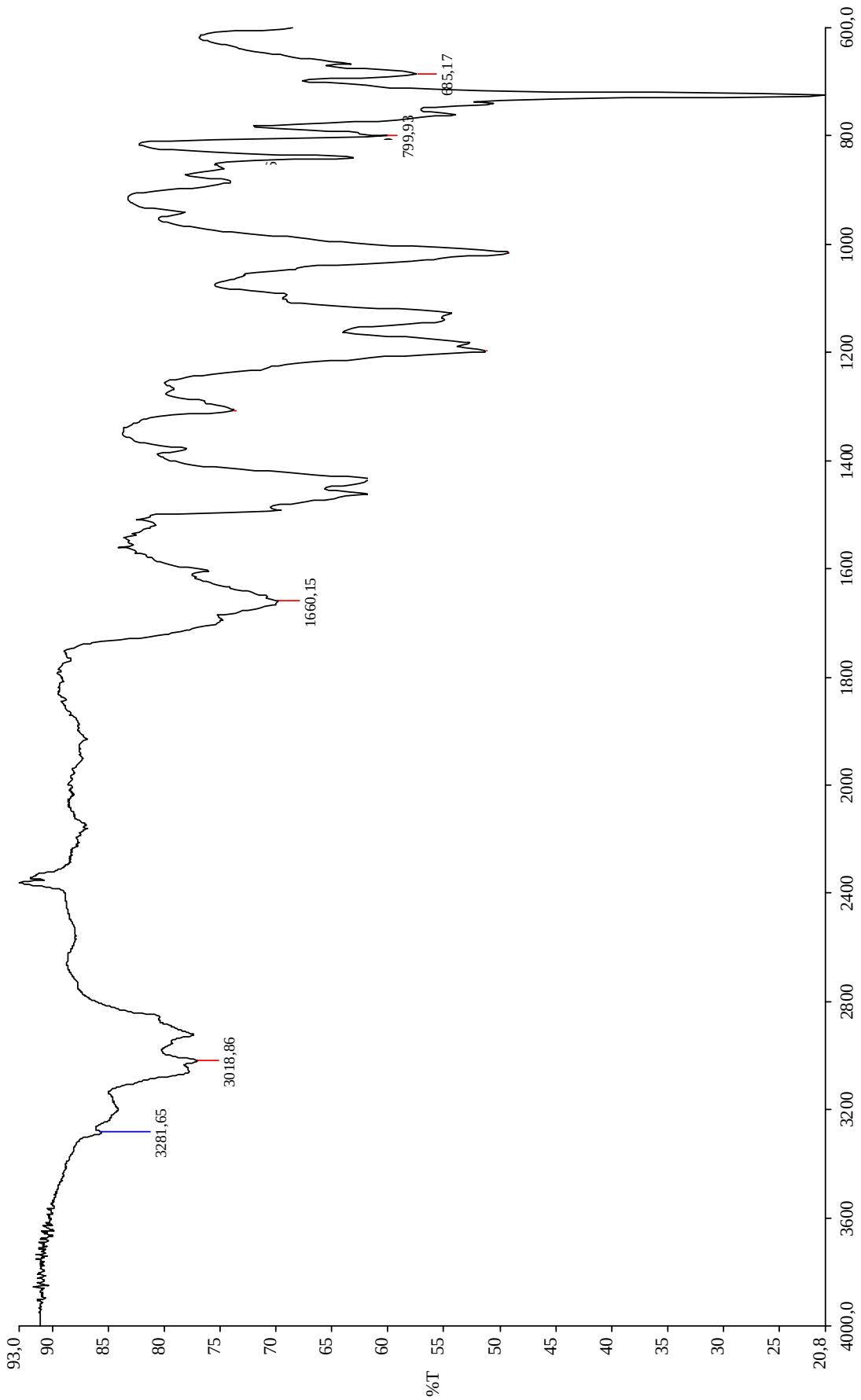
Mass Spectrum of H_2Pz **(P3)**

APPENDIX K

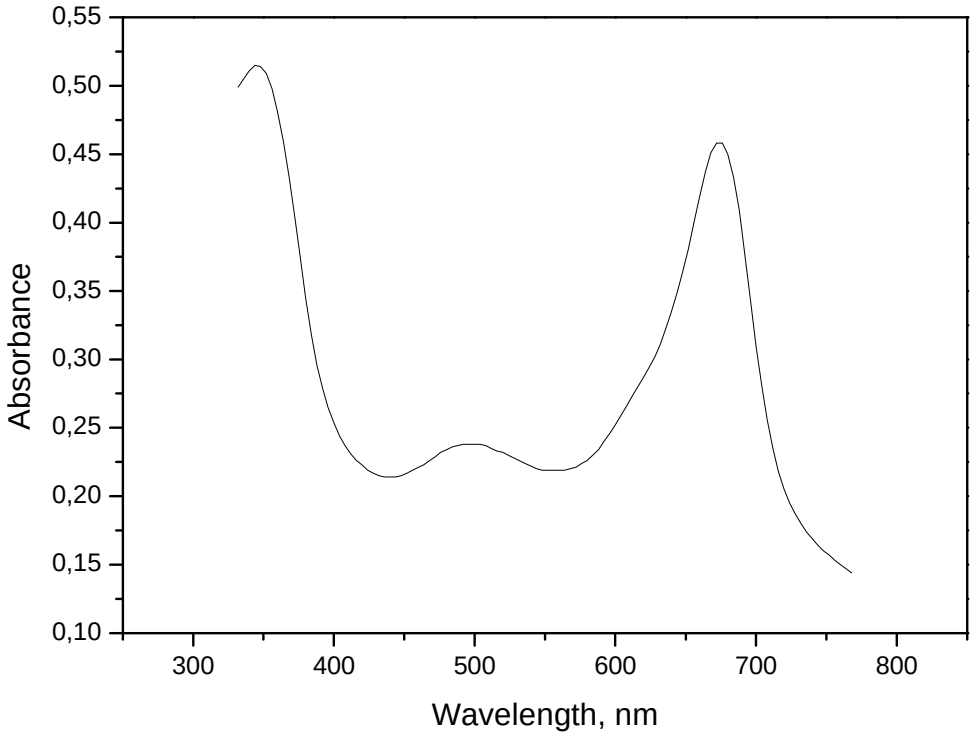


UV-Vis Spectrum of H_2Pz **(P3)** in Chloroform

APPENDIX L

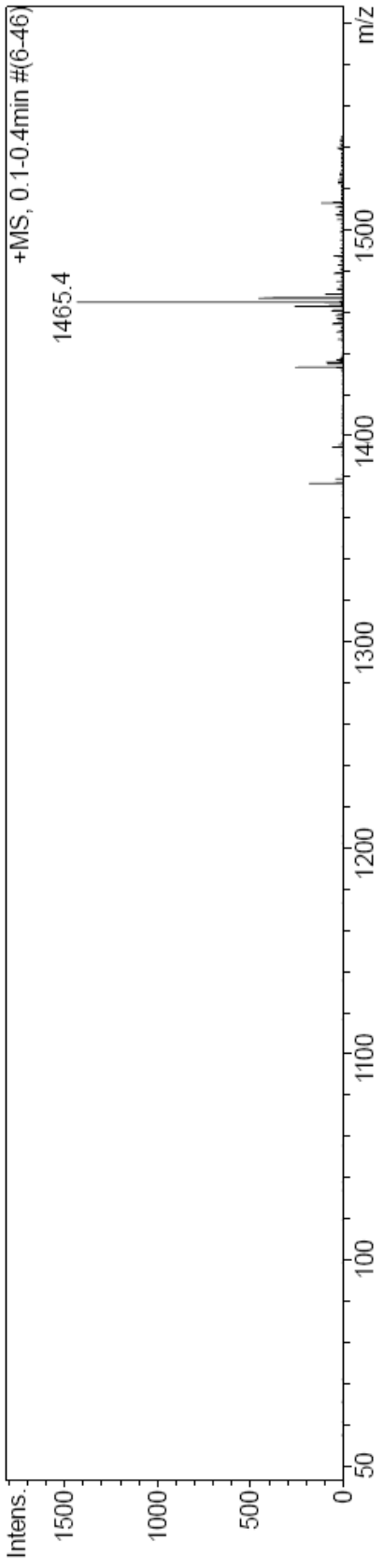

3281,65
3018,86
1660,15
799,93
685,17
%T
Wavenumbers (cm-1)
FT-IR Spectrum of H2Pz (O3)

APPENDIX M



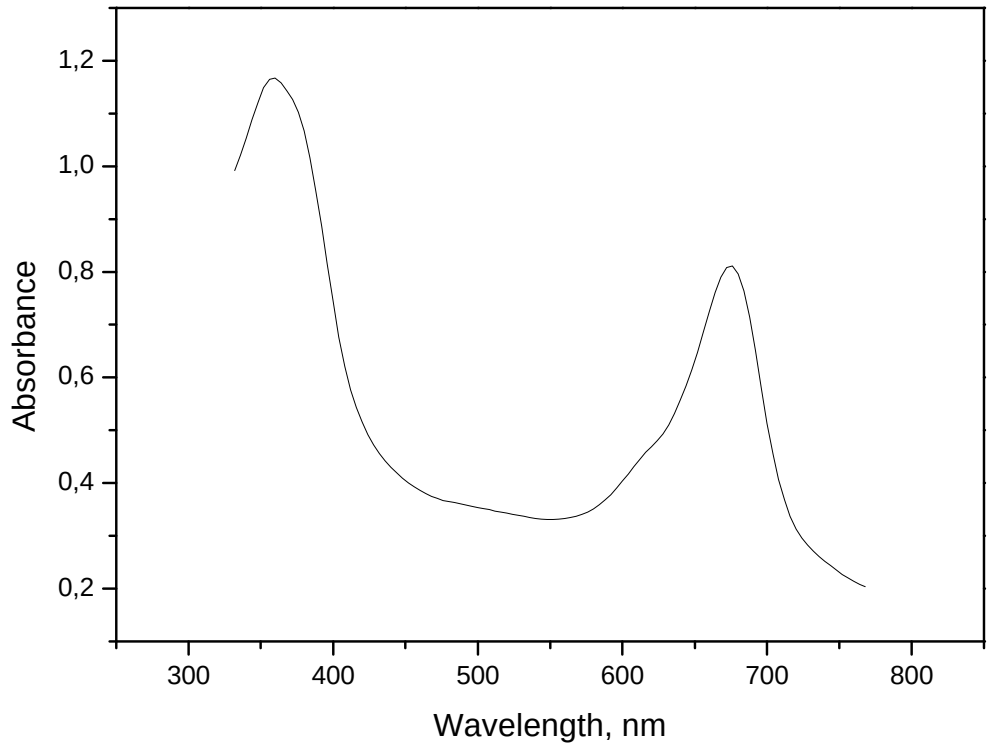
UV-Vis Spectrum of CuPz **(P4)** in Chloroform

APPENDIX N



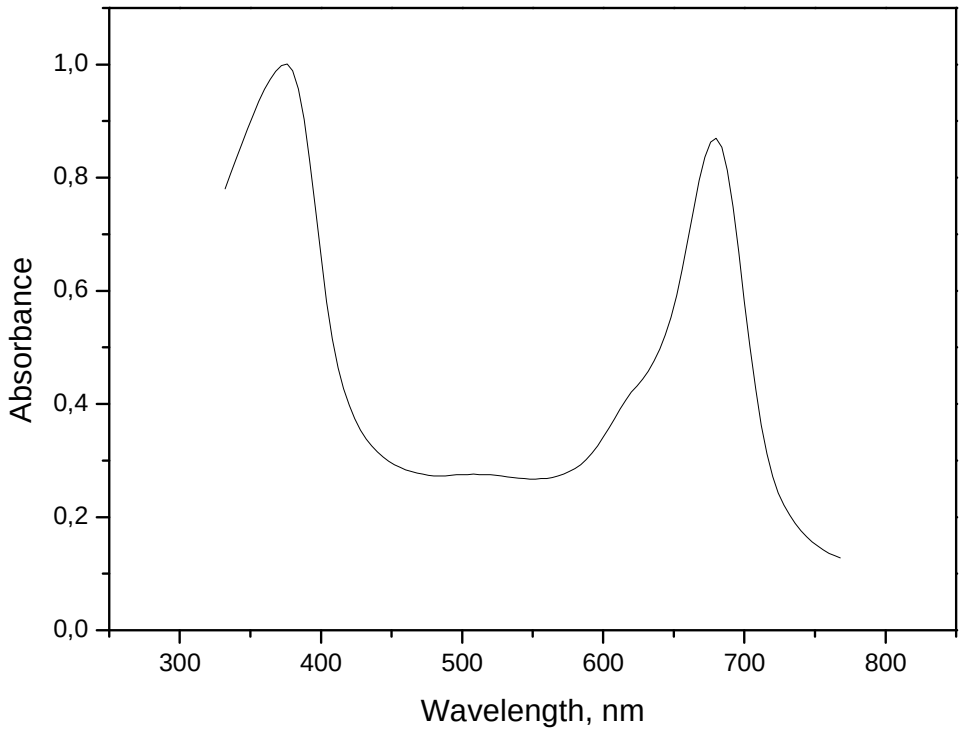
Mass Spectrum of CuPz **(O4)**

APPENDIX O



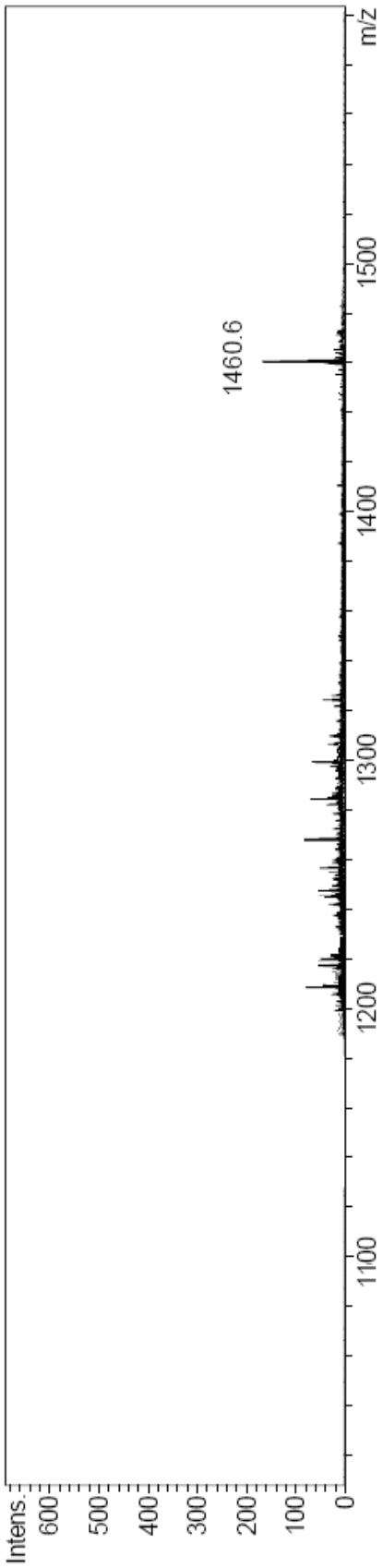
UV-Vis Spectrum of ZnPz **(P5)** in Chloroform

APPENDIX P



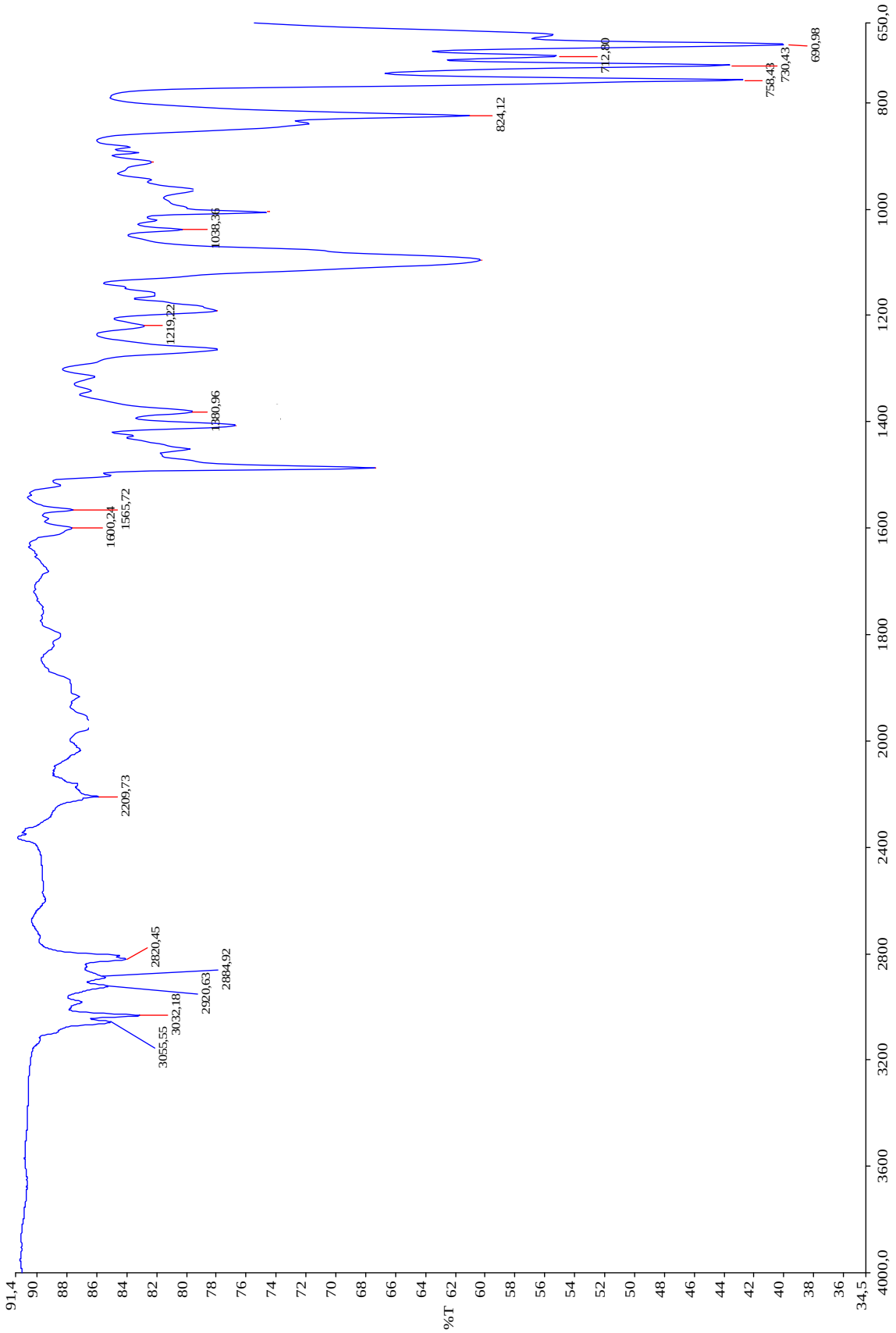
UV-Vis Spectrum of ZnPz **(O5)** in Chloroform

APPENDIX R



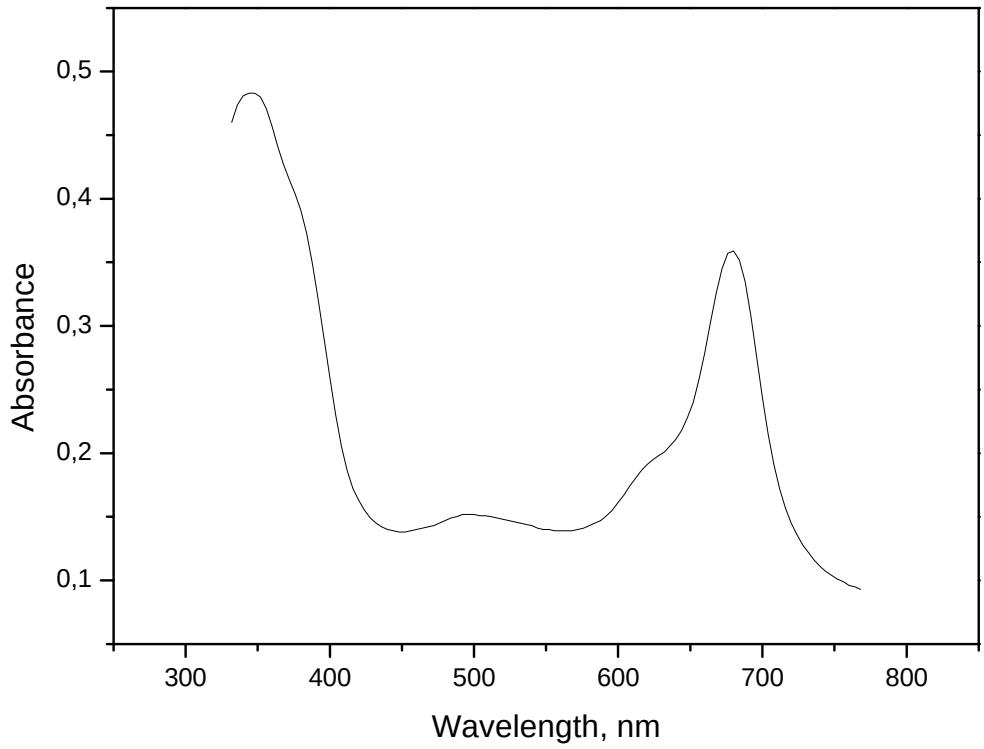
Mass Spectrum of CoPz **(O6)**

APPENDIX S



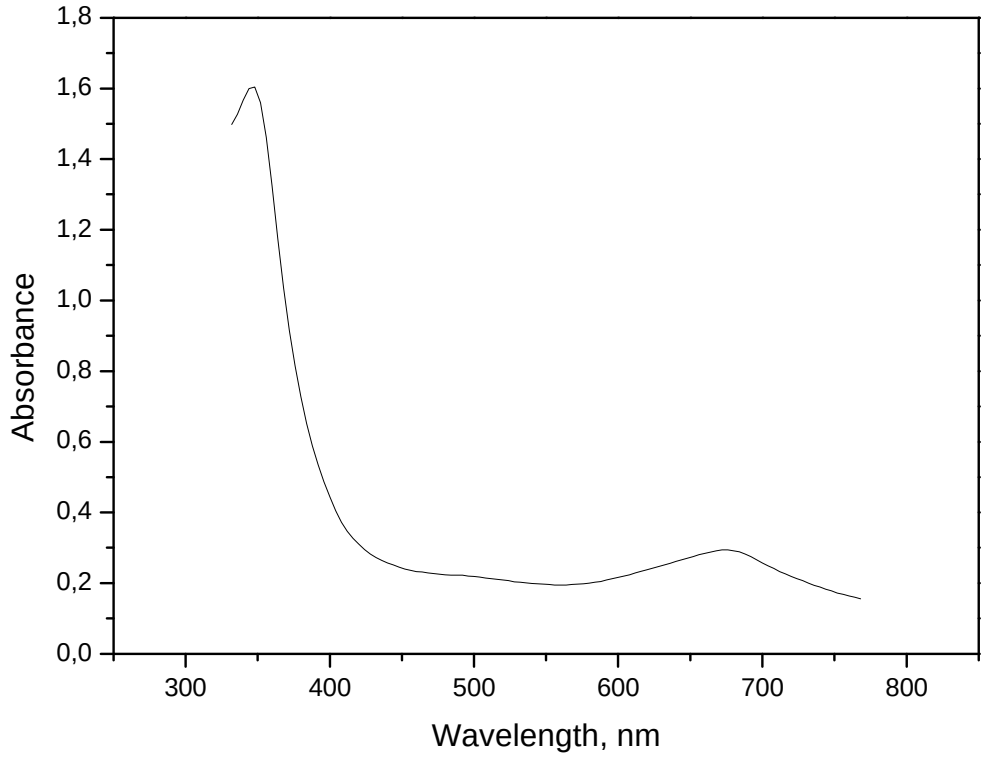
FT-IR Spectrum of 1,2-bis(4-biphenylmethylthio)maleonitrile **(B1)**

APPENDIX T



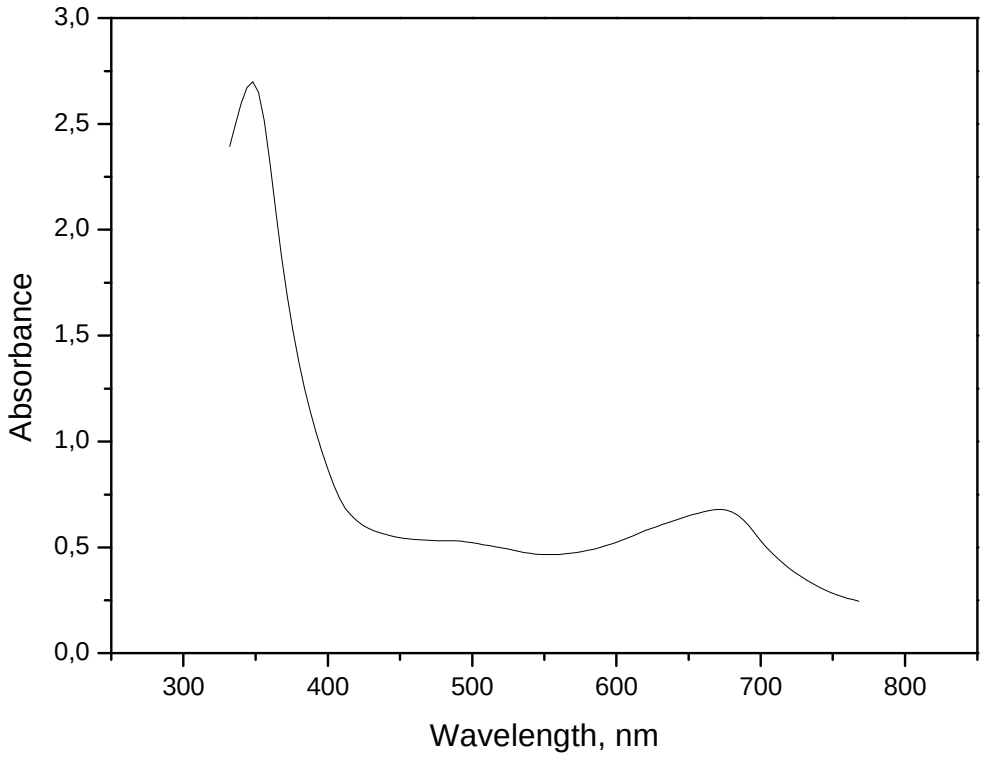
UV-Vis Spectrum of MgPz **(B2)** in Chloroform

APPENDIX U



UV-Vis Spectrum of CuPz **(B4)** in Chloroform

APPENDIX V



UV-Vis Spectrum of CoPz **(B6)** in Chloroform