CHAPTER I

INTRODUCTION

The word *porphyrin* is derived from the Greek *porphura* meaning purple [1], and all porphyrins are intensely colored. Porphyrins comprise an important class of molecules that serve nature in a variety of ways. A free-base porphyrin in which metal is inserted in its cavity is called *metalloporphyrin*. The Metalloporphyrin ring is found in a variety of important biological systems where it is the active component of the system or in some ways intimately connected with the activity of the system. Many of these porphyrins are the basic structure of biological porphyrins which are the active sites of numerous proteins, whose functions range from oxygen transfer and storage (haemoglobin and myoglobin) to electron transfer [2] (cytochrome c, cytochrome oxidase) to energy conversion (chlorophyll). Chlorophyll is a chlorin pigment, which is structurally similar to and produced through the same metabolic pathway as other porphyrin pigments such as heme. At the center of the chlorin ring is a magnesium ion. The chlorin ring can have several different side chains, usually including a long phytol chain. There are a few different forms that occur naturally (**Figure 1.1**).

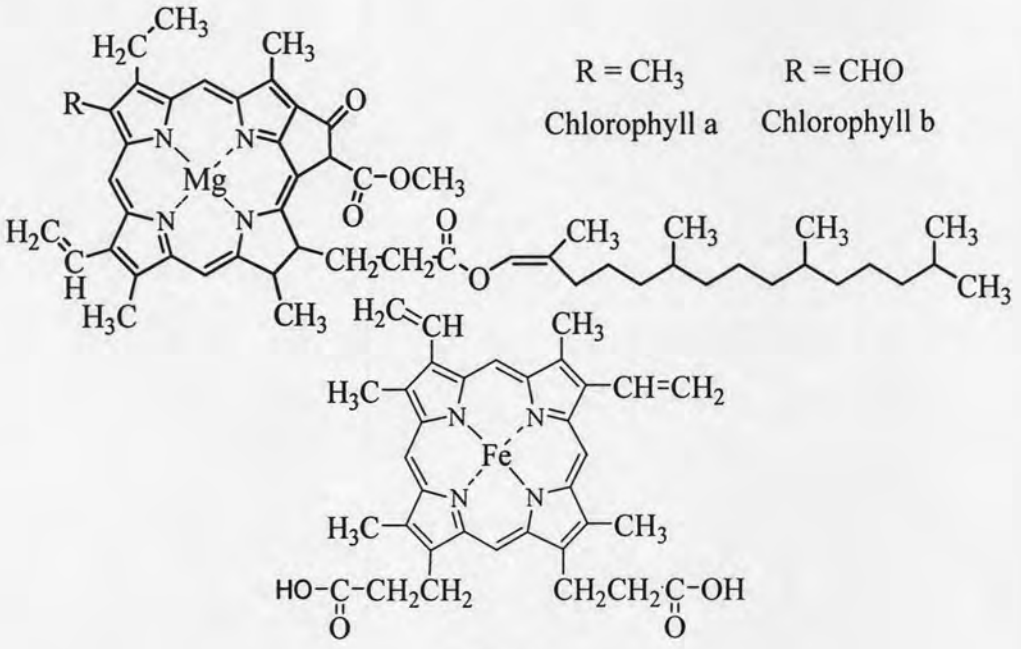
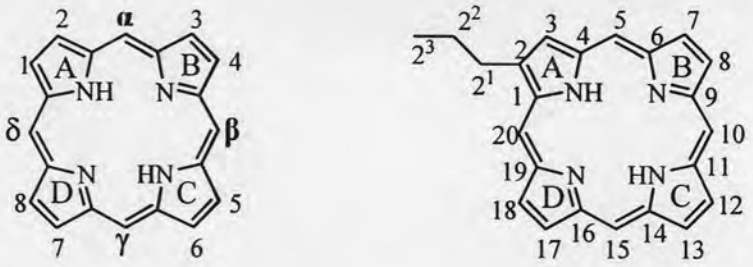


Figure 1.1 Structure of chlorophyll and heme

In addition, porphyrin plays a number of critical biological roles such as molecular binding [3], reaction catalysis [4], and light harvesting [5]. They also have been proven to be efficient sensitizers and catalyst in a number of chemical and photochemical processes especially photodynamic therapy (PDT) [6].

1.1 Structure and Nomenclature

The basic structure of the porphyrin nucleus is a cyclic tetrapyrrolic system consisting of a 20 carbon skeleton, four pyrrolic subunits linked together by single-atom bridges (methine bridges) between the alpha positions of the five-membered pyrrole rings. The nomenclature most generally used in porphyrin chemistry was developed by Hans Fischer. In this system, the pyrrolic position are numbered from 1 to 8 and the bridging (meso) positions named α, β, γ, δ. Fischer's system is based on a very large number of trivial names and a numeration scheme, shown in **Figure1.2** for the unsubstituted porphyrin ring system, which is simple but incomplete, are used. The availability of a more systematic nomenclature has helped interdisciplinary communication, and has considerably diminished the need for new trivial names. These recommendations provide for naming porphyrins, hydroporphyrins, ring contracted or expanded porphyrins, porphyrins fused with other rings, skeletally replaced porphyrins and porphyrin-metal coordination complexes together with corresponding linear arrangements of three and four pyrrole rings. The application of these recommendations permits these substances to be named more systematically using fewer trivial names. The inability of the Fischer system to name the large number of synthetic and newly isolated porphyrins led to the adoption of a systematic nomenclature based on 1-24 numbering system (**Figure 1.2**). Developed by a joint commission on biochemical nomenclature, consisting of the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Biochemistry (IUB).



Fischer IUPAC

Figure 1.2 Fischer nomenclature and IUPAC nomenclature

A comparison of the 1-24 numbering scheme with the Fischer numeration for the unsubstituted porphyrin nucleus is given in **Table 1.1**.

Table 1.1 Comparison of the 1-24 numbering scheme with the Fischer numeration for the unsubstituted porphyrin nucleus

Recommended:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Fischer:	-	1	2	-	α	-	3	4	-	β	-	5	6	-	γ	-	7	8	-	δ	-	-	-	-

The 1-24 numbering system is adopted for the porphyrin nucleus. The 2,3,7,8,12,13,17 and 18 positions have commonly been referred to generically as "*beta*-positions" (*i.e.*, of the pyrrole rings). Similarly, positions 1,4,6,9,11,14,16 and 19 have been referred to generically as "*alpha*-positions," while those at 5,10,15 and 20 are referred to generically as "*meso*-positions." However, in order to avoid possible ambiguity with stereochemical designations the use of these generic terms is discouraged.

Porphyrins are highly colored and they show a characteristic intense Soret band at around 400 nm with very high extinction coefficients. Porphyrins also have four satellite bands between 450-700 nm known as Q bands. The Soret band is a major characteristic of the optical spectra of the porphyrin macrocycle as it disappears with the disruption of the macrocycle. The intensity and wavelength of the absorption bands changes with variations in the peripheral positions of the porphyrin macrocycle. Protonation of two of the inner nitrogen atoms or insertion of a metal into the porphyrin cavity also changes the visible absorption spectrum. The NMR spectrum of the aromatic tetrapyrrole shows anisotropic effects [7, 8]. The ring current generated

by the applied field induces a local magnetic field similar to that in benzene. The NH protons, inside the porphyrin ring system are therefore shifted upfield to as high as -5 ppm in porphyrins whereas the deshielded *meso*-protons appear at very low field ($\delta \sim$ 10 ppm) [9], the pyrrolic protons are also deshielded and tend to resonate at δ 8 to 9, versus $\delta \sim 6$ ppm in pyrrole. Although the aromaticity of these porphyrin systems makes their NMR spectra a challenge to assign, the tendency toward aggregation in some cases makes for even more complicated spectra.

1.2 Porphyrin Syntheses

1.2.1 Synthesis of porphyrins *via* monopyrrole tetramerization

Monopyrrole tetramerization can only produce a structurally unique product if the 3- and 4-substituents in the monopyrrole are identical. Several methods based on this strategy are well known:

1.2.1.1 The Adler-Longo's method

The most easily synthesized porphyrin is tetraphenylporphyrin (TPP, 1). The route was first reported by Rothemund [10]. In this method, pyrrole reacts with benzaldehyde in pyridine, in a sealed bomb at 150°C for 24 hours [11, 12]. A modification by Adler, Longo and their colleagues which involve the use of refluxing propionic acid [13] instead of sealed tube chemistry, reproducibly affords a 20-25% yield of TPP. The procedure employs an addition of equimolar amounts of pyrrole and benzaldehyde to refluxing propionic acid (141°C). After heating for 30 min, the mixture is allowed to cool and TPP (**Figure 1.3**) is filtered off. This method is still used widely when large quantities of porphyrin are needed and the aldehydes are capable of with standing acid conditions.

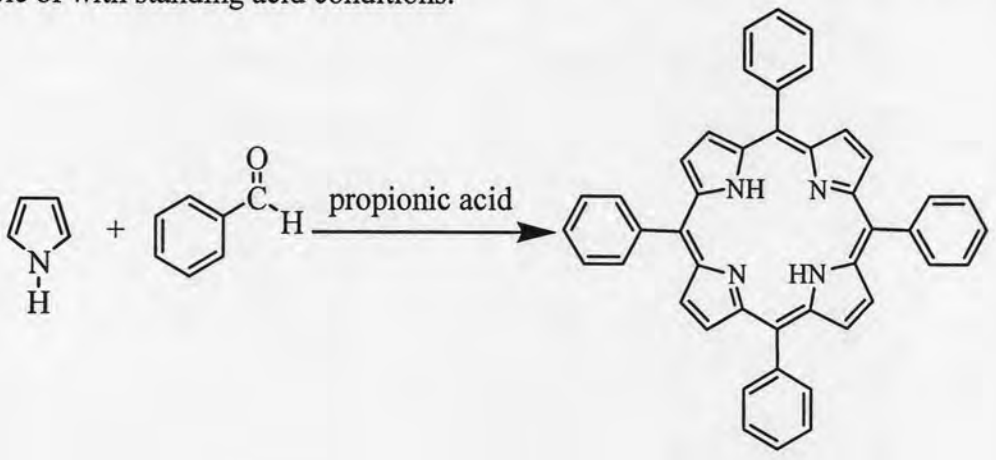


Figure 1.3 Tetraphenylporphyrin syntheses from monopyrrole using Adler-Longo's method

1.2.1.2 The Lindsey's method

The synthesis was optimized by Lindsey's group [14] which showed that excellent yields of a wide variety of tetraarylporphyrins can be obtained using a high dilution two step reaction. In the first step, pyrrole and the desired benzaldehyde react reversibly at room temperature with trace acid catalyst (usually using boron trifluoride or trifluoroacetic acid) to form the cyclic tetraphenylporphyrinogen. Secondly, an oxidant is then added to irreversibly convert the porphyrinogen to the porphyrin by using quinone such as 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). This methodology is complementary to the Adler-Longo procedure, allowing small quantities of porphyrin to be prepared from sensitive aldehyde in 30-40% yield. This method is outlined in **Figure 1.4**

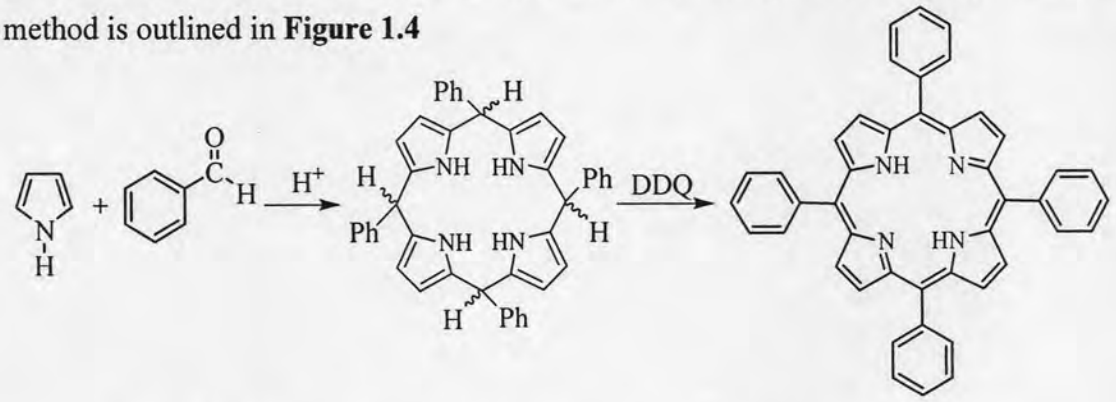


Figure 1.4 Tetraphenylporphyrin synthesis from monopyrrole using Lindsey's method

1.2.1.3 Identical 3,4-disubstituted monopyrrole

Most natural porphyrins do not contain *meso*-substituents, octaethylporphyrin (OEP) has been favored as a model for natural porphyrins more than has TPP. There bare two major synthetic routes for the OEP. Firstly, tetramerization of 2,5-di-unsubstituted pyrroles can provide the four meso methine carbons thus, cyclization of 3,4-diethylpyrrole with formaldehyde affords 55-75% yield of OEP [15] (**Figure 1.5**).

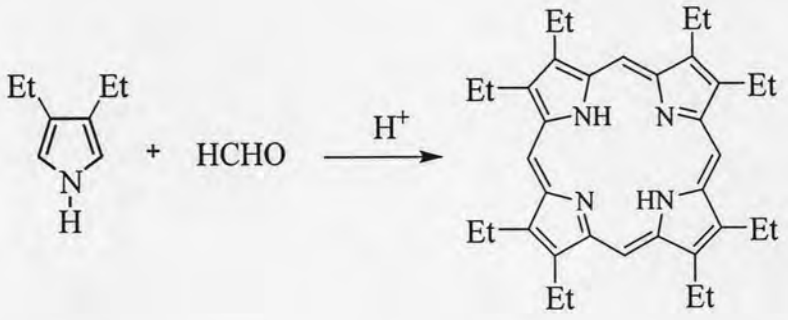


Figure 1.5 Octaethylporphyrin synthesis from 3,4-diethyl monopyrrole

Secondly, the required CH_2R groups can be attached to pyrrolic intermediates by use of the Mannich reaction of pyrrole with formaldehyde and dimethylamine [or (*N,N*-dimethylmethylene) ammonium iodide (Eschenmoser's reagent)] to give the 2-(*N,N*-dimethylaminomethyl)pyrrole. And then, 2-(*N,N*-dimethylaminomethyl)pyrrole was heated in acetic acid affords about 50% yield of OED [16] (**Figure 1.6**).

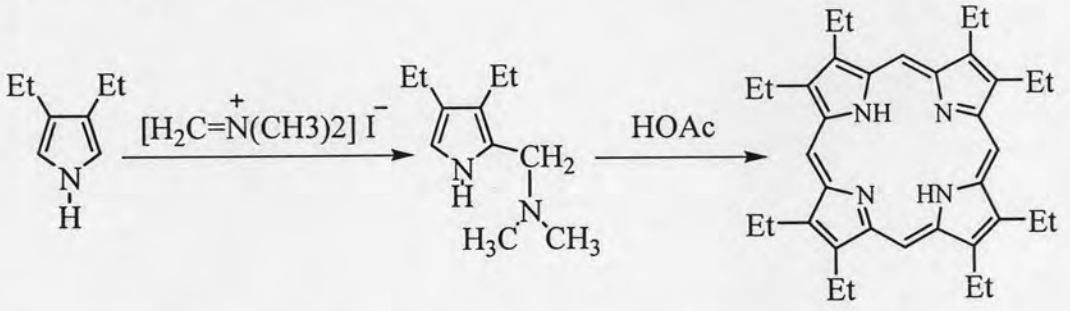


Figure 1.6 Octaethylporphyrin synthesis from 3,4-diethyl monopyrrole by *via* pyrrolic intermediates

1.2.2 Syntheses from dipyrromethanes (The MacDonald [2+2] route)

Condensation of two unsymmetrical dipyrromethanes with appropriate bridging carbons will result in two porphyrin products because the dipyrromethanes can react in two orientations (**Figure 1.7**).

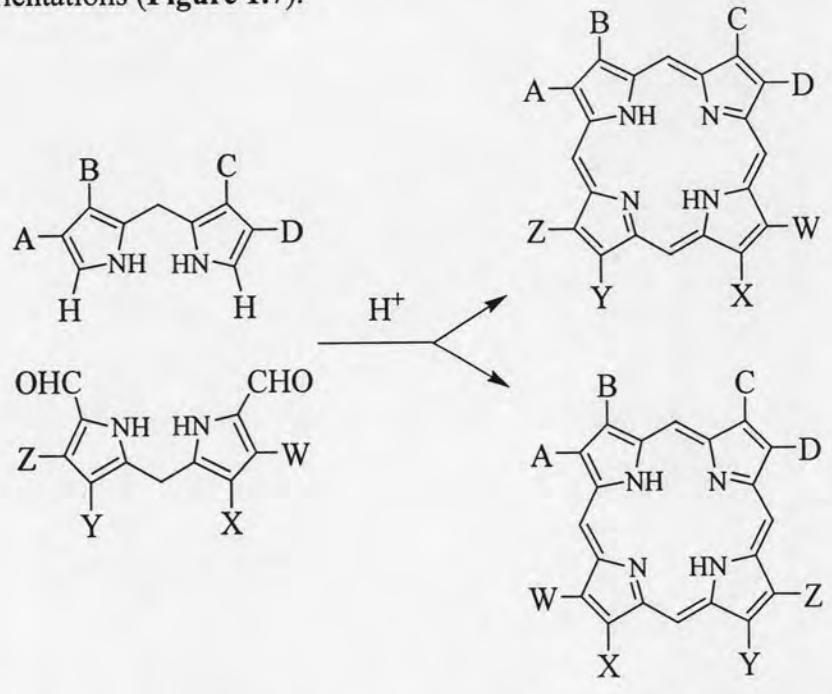


Figure 1.7 Porphyrin synthesis from two unsymmetrical dipyrromethanes by the [2+2] MacDonald route

These symmetry complications in a porphyrin synthesis involving an A-B and a C-D dipyrromethane can be avoided if the A-B or C-D unit is symmetrical.

MacDonald and coworkers [17] showed that a 1,9-diformyldipyrromethane reacted with a 1,9-di-unsubstituted dipyrromethane or 1,9-dicarboxylic acid in hydriodic acid catalyst to give pure porphyrin in over 60% yield (**Figure 1.8**).

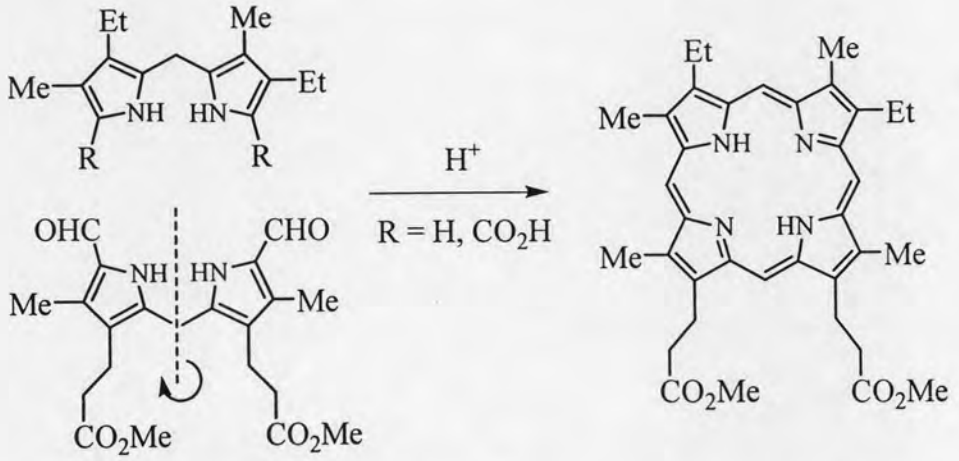


Figure 1.8 Porphyrin synthesis from symmetrical dipyrromethanes by the [2+2] MacDonald route

1.2.3 Syntheses from tripyrrolic intermediate (The [3+1] route)

The chemistry developed in the MacDonald approach is called the [3+1] route. A tripyrrane is reacted with a monopyrrole bearing the two bridging carbon atoms. This macrocyclization of a 2,5-difunctionalized monopyrrole with open chain tripyrrole to produce porphyrin has a useful application. This kind of chemistry has been facilitated by Sessler's recent advance in tripyrrane syntheses [18]. The [3+1] approach has symmetry limitations because the terminal rings of the tripyrrane are usually identical (**Figure 1.9**).

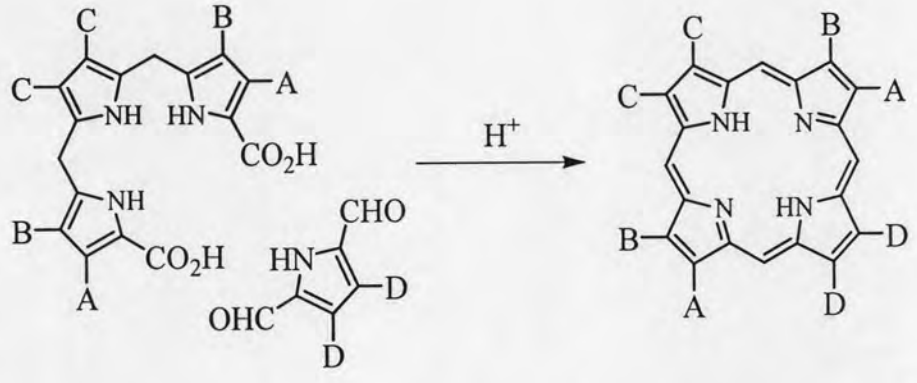


Figure 1.9 Porphyrin synthesis from tripyrrolic intermediate ([3+1] route)

In addition, the other possible isomer could be a tetrapyrrole macrocycle, in which one pyrrole ring is linked through its *α-β'* position instead of *via* a more normal *a-a'* linkage. This type of compound is called "*N*-confused porphyrin (NCP)". The new compound, *N*-confused tetraphenylporphyrin or IUPAC-recommended name is 5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin (NC-TPP) (**Figure 1.10**) was obtained using a modification of the well-known synthesis of TPP that involves the acid-catalyzed condensation between benzaldehyde and pyrrole. However, in place of propionic acid, *t*-BuOH/CH_2C1_2 (1: l) and concentrated HBr (1 equiv) were used [19].

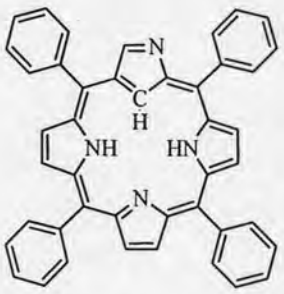


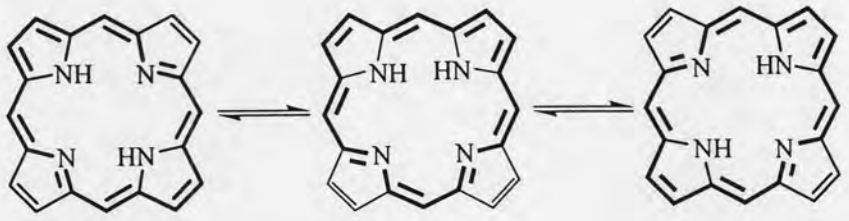
Figure 1.10 Structure of 5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin or *N*-confused tetraphenylporphyrin (NC-TPP)

The spectroscopic data obtained were consistent with the formulation of TPP. For example, the ^{1}H NMR spectrum of NC-TPP revealed characteristic high field shifts for two inner NH and β-H of "confused pyrrole" (at -2.5 and -5.1 ppm, respectively) and the outside α-H in this pyrrole appeared as a singlet at 8.68 ppm. The Soret and Q-band of NC-TPP in CH_2C1_2 were broadened and shifted to longer wavelengths at λ_{max}= 438 and 725 nm, respectively as compared to those of TPP at 419 and 647 nm.

1.3 Reactivity Profile

The aromaticity of the porphyrin macrocycle largely determines its chemical reactivity of which electrophilic substitutions are the best reactions. The porhyrins contain 22 conjugated π–electrons, 18 of which are included in any delocalization pathway shown in **Figure 1.11**. As they follow Hückel's rule, porphyrins have aromatic properties. The tautomeric forms with *trans*-NHs are generally the most favored. Substitution at the porphyrin periphery or at the inner nitrogen atoms can induce a preferred *trans*-NHs delocalization pathway which is often a determinant of chemical reactivity. The less favored *cis*-NH tautomers are believed to be intermediates in a stepwise N-H migration mechanism [20]. The most favored *trans*-

NH tautomer of chlorins bears the imine type nitrogens on the reduced pyrrole unit and the opposite ring.

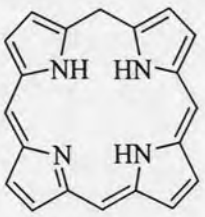


trans-NH *cis*-NH *trans*-NH

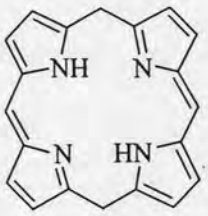
Figure 1.11 Delocalization pathway in porphyrins

In general, the electronics most reactive sites at the periphery are the α, β, γ, and δ position in the Fischer nomenclature or the 5, 10, 15, and 20 positions in IUPAC nomenclature (**Figure 1.2**). These sites, designated as the *meso* positions, are sterically less accessible when one or two of the abutting β-positions are substituted. The β-pyrrollic 2, 3, 7, 8, 12, 13, 17, and 18 positions are usually sterically less congested, and are the preferential reaction sites of porphyrins in the presence of bulky reactant species. The most reactive, electron-rich and least sterically hindered, sites at the periphery of chlorin are the two methine bridges adjacent to the reduced pyrrole rings.

Electrophillic additions can take place at the β-β' peripheral double bonds leading to chlorins, bacteriochlorins, or isobacteriochlorins, with retention of the 18π aromatic delocalization pathway. Additions to the *meso* positions can also occur, with formation of phlorins, porphodimethanes (**Figure1.12**), or expanded "homo-type" macrocycles.



5,22-dihydroporphyrin
(formerly named phlorin)



5,15-dihydroporphyrin
(formerly porphodimethene)

Figure 1.12 Structure of phlorin and porphodimethene

Porphyrins undergo halogenation at the peripheral unsubstituted β- and *meso*-positions; fluorination [21] and chlorination [22] are reactive at *meso*-positions,

whereas bromination [23] and iodination [24] occur mainly at the more sterically accessible β-positons. The inner nitrogen atoms of porphyrins react with electrophillic reagent and are easily protonated, unless protected by metallation.

Nucleophillic reactions are also known also the porphyrin macrocycle; the most common involve intermediate porphyrin π-cation radical [25]. Peripheral electron-withdrawing substituents and electronegative centrally chelated metal ions facilitate nucleophillic attack on the porphyrin rings.

Oxidations [26] and reductions [27] are amongst the better studied reactions of porphyrins and lead to variety of interesting new porphyrin derivatives with characteristic chemical and physical properties. Other reactions such as cycloadditions, intramolecular cyclizations, rearrangements, and dimerizations generate new porphyrin systems, many of which bear extended π-systems and novel chemical and physical properties.

1.4 Metallations and Demetallations [28]

Metallations of phophyrins can be done in various solvents with specific methods described as follows.

1.4.1 Chloroform/methanol method

A refluxing concentrated chloroform solution of porphyrin is treated with a saturated solution of the metal (II) acetate. The reaction in which the insertion of the metal into the inner core of porphyrin occurs is usually followed by visible absorption spectroscopy. After completion reaction, the mixture is concentrated and diluted with methanol to give the metalloporphyrin usually in near quantitative yield. Tetrahydrofuran can be used instead of chloroform because of good solubility and low boiling point which reduce the chance of thermal decomposition of sensitive substituents.

1.4.2 Dimethylformamide method

Dimethylformamide is uniformly good solvent for both porphyrin and metal salts (usually metal chloride). The HCl produced in the reaction escapes at the reflux temperature of the solvent. This is the method of choice for phenyl- and/or pyrrole substituted *meso*-porphyrins primarily due to their insolubility in lower boiling solvents and also their higher thermal stability. The products are crystallized by dilute water or dilute HCl to dissolve the access metal salts in the reaction mixture. A major disadvantage of DMF is that it can decompose to give dimethylamine which will

neutralize HCl produced in the reaction and can lead to complicating side reactions, if long reaction times are required. This is particularly so in the case of highly electron-deficient halogenated porphyrin systems where DMF may act as a nucleophile leading either to halogen substitution or to porphyrin destruction.

1.4.3 Acetic acid/acetate method

In this method, metal acetate salt is heated with porphyrin in acetic acid at 100°C. The product is crystallized either directly by cooling or by the addition of water or methanol. In the case of oxidizable metals with multi-oxidation state such as Mn(II) and Fe(II), the complex can be autoxidized to the more stable high oxidation state.

1.4.4 Pyridine method

This is a useful method for metalloporphyrins labile toward acetic acid since pyridine is a good solvent for porphyrins and metal salts. Pyridine forms complexes with metals of high charge and consequently retards the metallation process.

1.4.5 Metal carbonyl method

This method has been proven to be especially useful for the preparation of metalloporphyrins of VI-VIII metal groups. The metal carbonyl or the carbonyl chloride is heated with porphyrin in inert solvent such as benzene, toluene, or decalin.

1.4.6 Acetylacetone method

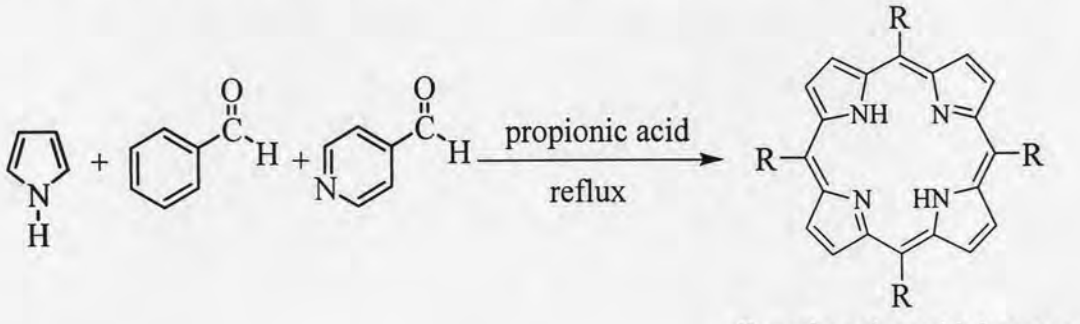
Metal acetoacetonates make very useful "carriers" due to their availability, solubility in organic solvents at the low *p*Ka of the acid liberated during the reaction. With the metal ions of high charge and small size, a weakly acidic solvent (phenol) is required to liberate the active metallating species. This method has been used with metal of groups IIIA and IIIB.

The demetallation process can be done to remove the metal ion from the complexes. The demetallation is favored by the presence of acid since protonation of free base drives the equilibrium in the forward direction. Metalloporphyrin stability is often defined in terms of the degree of resistance to the displacement of the metal atom by acid. Several stability classes have been identified based on the degree of completeness of the demetallation in acetic acid, aqueous HCl-dichloromethane, and sulfuric acid. While some divalent metals (*e.g.* zinc) are readily removed by trifluoroacitic acid in dichloromethane, copper requires 15-20% sulfuric in trifluoroacetic acid or sometimes even stronger conditions.

1.5 Introduction to Self-Assembly of Free-Base Pyridylporphyrin and Metallo-Pyridylporphyrin Oligomers

A significant amount of practical insight has been gained and correlated to natural chromophores by designing and comparing light harvesting porphyrin arrays and aggregates to monoporphyrin systems. Various molecular devices based on oligoporphyrins have recently been engineered and prepared, such as artificial photosynthetic systems [1], photoinduced picosecond molecular switches [29], optoelectronic gates [30], fluorescence quenching sensors [31], photonic wires [32], and cancer therapy agents [33] used in photodynamic therapy process. Several synthetic strategies have been employed to assemble porphyrin oligomer systems, *e.g.* a wide variety of porphyrin ensembles have been constructed covalently with functional porphyrin units linked through spacers [34]. More recently, self-assembly strategies have been developed to synthesize unique metalloporphyrin oligomers linked non-covalently [35] by hydrogen bonding [36], electrostatic interactions [37], and coordination using ligating porphyrins such as the oxyporphyrins [38].

Porphyrin polymers constructed through coordination bonds, namely those containing porphyrins which can coordinate to metal ions other than the four inner nitrogen atoms, have recently received much attention. In constructing coordination porphyrin polymers, introduction of the pyridyl groups at the *meso* positions has been the most common strategy (**Figure 1.13**). Mixed 4-pyridyl/phenyl porphyrins can provide connections to as many as four metal centers by coordination of the 4-pyridyl groups; depending on whether these centers lie in another porphyrin or in a coordination compound, very different ordered arrays can be constructed. A few systems using the 4-pyridyl-substituted porphyrins have been reported. Fleischer *et al.* revealed the solid and solution state structures of these coordination oligomers [39].



R = phenyl, pyridyl group

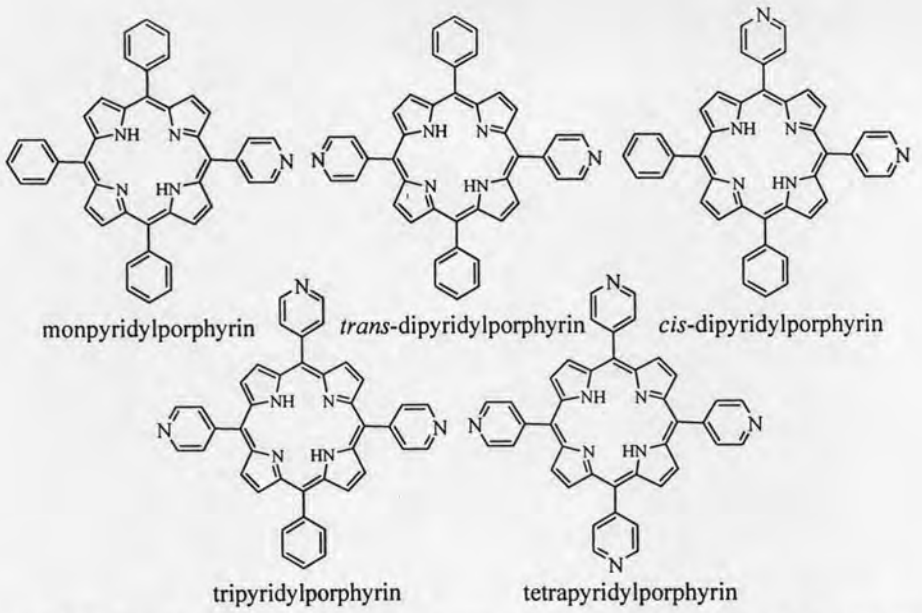


Figure 1.13 Synthesis of pyridylporphyrin and five possible pyridylporphyrin isomers

1.5.1 Self-assembly of zincporphyrin oligomers by free-base pyridylporphyrin coordination

Synthesis and characterization of discrete free-base pyridylporphyrin coordinated zinc porphyrin oligomers, such as a ZnTPP-(MPyTPP) dimer (**Figure 1.14**), and two distinct trimers, 2ZnTPP-(*cis*-DPyDPP) and 2ZnTPP-(*trans*-DPyDPP) was reported by Schachter and Fleischer [39].

The analysis of the dimer indicated that the pyridyl ring on porphyrin periphery is bound to the metal center of an adjacent porphyrin. The proton NMR showed that the resonances of bound pyridine protons of the MPyTPP were shifted upfield by the ZnTPP ring current. The β-pyrrole protons of MPyTPP also showed ring current effects as they were split (the β-pyrrole protons are generally a singlet in free-base porphyrins). The trimers showed similar proton NMR shifts with the bound *cis*-DPyDPP of the 2ZnTPP + *cis*-DPyDPP trimer resonances of the β-pyrrole, pyridyl group, and the *o*-, *m*-, and *p*-phenyl protons. These shifts indicated that the pyridine rings were bound to the zinc metal centers and, therefore, experienced a tremendous ring current effect, causing the pyridine resonances, as well as the β-pyrrole resonances, to be shifted upfield. Thus, the NMR spectra of these systems indicated that the dimer and trimers were formed in solution. Consequently, the upfield shifts of the pyridyl and β-pyrrole protons as a result of the ZnTPP ring current confirmed that the dimer and trimers were formed.

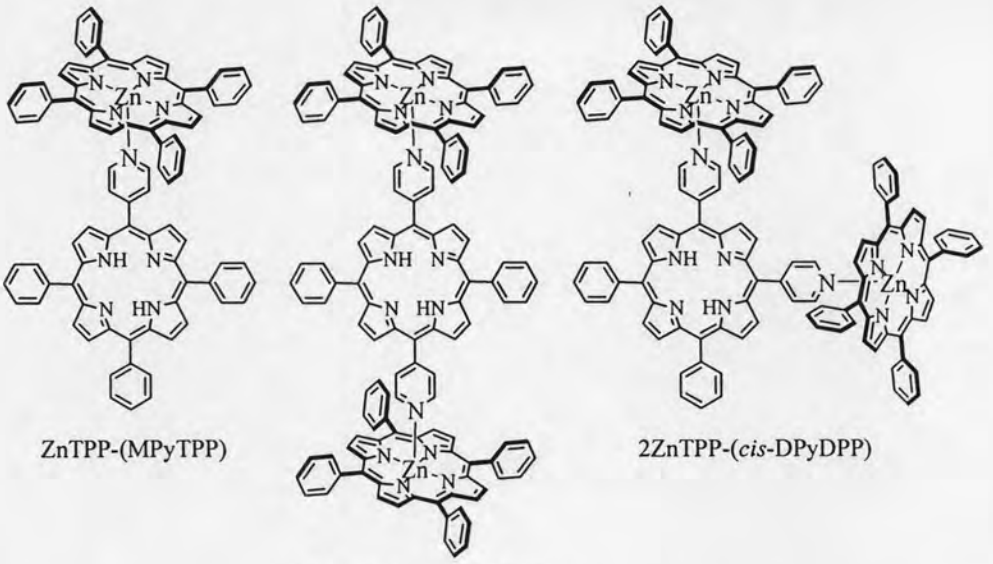


Figure 1.14 Structure of coordinated dimer and trimer pyridylporphyrin

Free-base pyridylporphyrins have been used as templates to produce porphyrin pentads (**Figure 1.15**) [40]. Tetrapyridylporphyrin (TPyP) also reacts with the cyclic zinc porphyrin tetramer to give a conformer of five porphyrins [41].

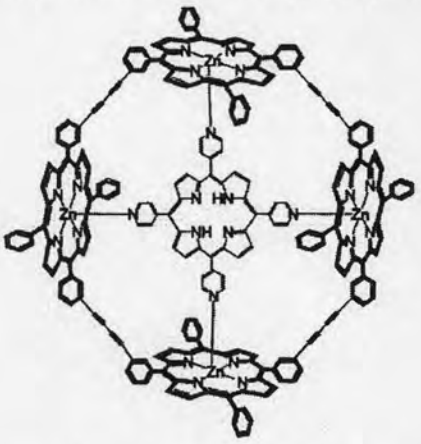


Figure 1.15 Complexation of free-base tetrapyridylporphyrin with cyclic zinc porphyrin tetramer

The association constant between TPyP and the cyclic tetramer was found to be 2×10^{10} M^{-1} at 30°C in dichloromethane. X-ray analysis established that the structure had exact crystallographic *S*4, and idealized D_{2d} symmetry. The four zinc porphyrin rings are orthogonal to the central free-base pyridylporphyrin unit and highly bowed.

The Zn-porphyrin dimers, Zn(1,4-bis[5-(10,15,20-tri-*p*-hexylphenyl porphyrinyl)]-benzene) ($[ZnHTPP]_2$), will also bind *via* one molecule of a tetrapyridyl-(4-Py or 2-Py) substituted free-based porphyrin to give the corresponding

pentamers (**Figure 1.16**) [42]. The fluorescence intensity of the parent Zn–porphyrin dimer decreases upon complexation with the tetrapyridyl-substituted free-base.

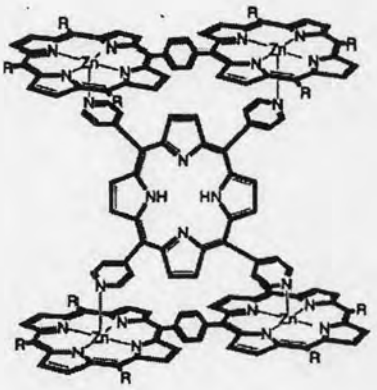


Figure 1.16 Complexation of free-base tetrapyridylporphyrin with zinc porphyrin dimers

1.5.2 Self-assembly of ruthenium- and osmium-pyridylporphyrin oligomers

Initially in the study of ruthenium porphyrin oligomers, free pyridylporphyrins were used as axial TPyP or bridging *trans*-DPyDPP ligands to construct a series of ruthenium(II) porphyrin dimers and trimers (**Figure 1.17**) [43]. In the oligomers, free pyridylporphyrins coordinate to a rutheniumporphyrin unit or bridge two ruthenium porphyrins. The X-ray structural determination of Ru(II)(OEP)(CO)(MPyTPP) was carried out. UV–Vis spectra revealed the presence of excitonic interactions between two axial porphyrin ligands in the trimers. Cyclic voltammograms of the carbonyl dimers and trimers showed no redox waves for the ruthenium(II) ions, because the ruthenium(II) oxidation state of these complexes is significantly stabilized by the coordination of the axial CO ligand.

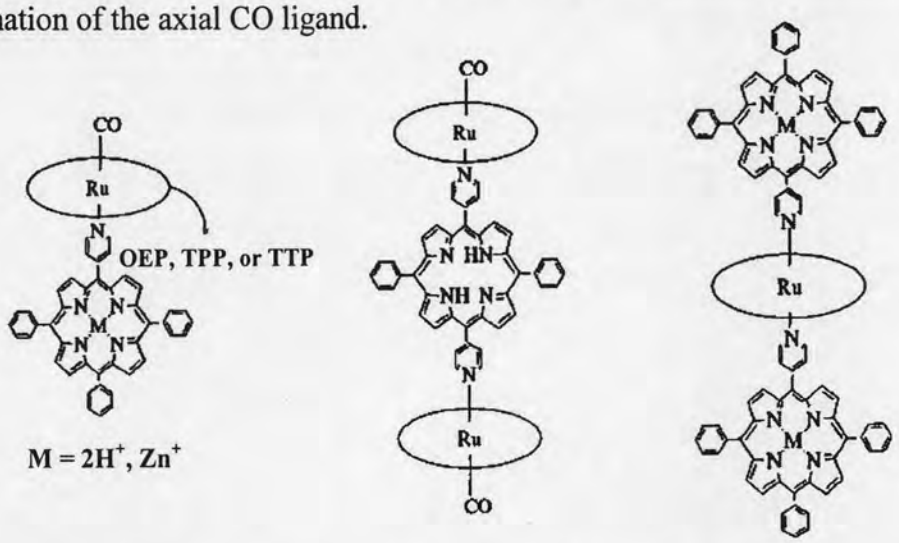


Figure 1.17 Structure of ruthenium porphyrin oligomers

The cyclic ruthenium porphyrin tetramers, $[Ru(MPyTPP)(CO)]_4$, $[Ru(MPyTTP)(CO)]_4$, and $[Ru(MPyTTP)(Py)]_4$ (**Figure 1.18**) were also synthesized [44]. The stability of the cyclic tetrameric structures was examined by variable temperature ^{1}H-NMR. The tetramers react with a large excess of pyridine to give the corresponding monomer complexes. Sharpening and increasing intensity of the Soret bands, as the monomerization reaction progressed indicates the presence of excitonic interactions between cofacially arranged ruthenium porphyrin units in these tetrameric molecules.

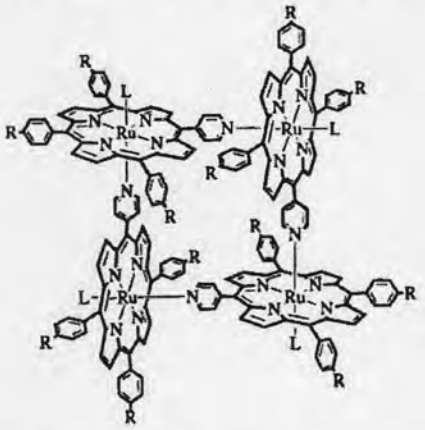


Figure 1.18 Structure of cyclic ruthenium porphyrin tetramers

Electrochemical analyses revealed the presence of interactions between the constituent ruthenium porphyrin units of the cyclic tetramers, *i.e.* the first ring-oxidation processes in the carbonyl complexes and the oxidation process of Ru(II) to Ru(III) in the pyridine coordinated complex proceeded stepwise.

A series of osmium(II) octaethylporphyrin oligomers (di-, tri-, tetra-, and pentameric porphyrins (**Figure 1.19**) has also been reported [45]. The ^{1}HNMR chemical shift difference between the inner NH protons of the constituent pyridyl porphyrins having no metal ions and those of the corresponding free porphyrin ligands, increases with the number of appended osmium OEP rings.

The construction of the oligomers enabled the direct observation of the tautomerism of the internal NH protons in the axial porphyrins (**Figure 1.20**). The activation energy of the tautomerism, E_a = 40.5 kJ mol^{-1}, and the exchange rate constant, k = 7200 s^{-1} are comparable with the values previously reported for various porphyrin monomers. The absorption spectra of these oligomers are essentially offset from the spectra of the constituent monomeric porphyrins. The cyclic voltammograms of all the oligomers showed the redox waves of the parent porphyrins and the osmium

ions, each current reflecting the number of constituents. The peak separations of these Os(II:III) redox waves were nearly the same among all five oligomers.

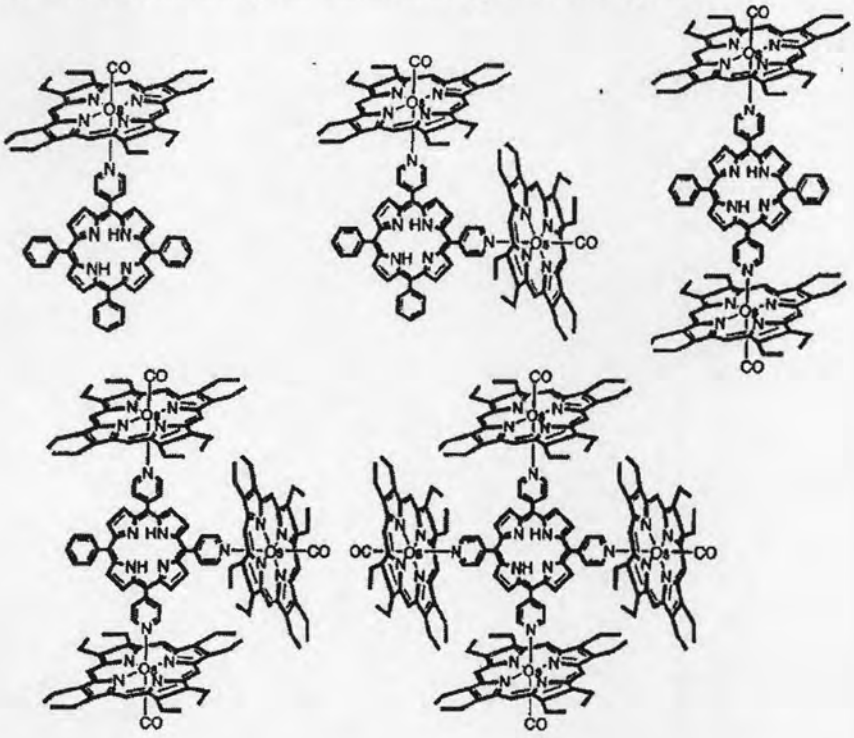


Figure 1.19 A series of osmium(II) octaethylporphyrin oligomers

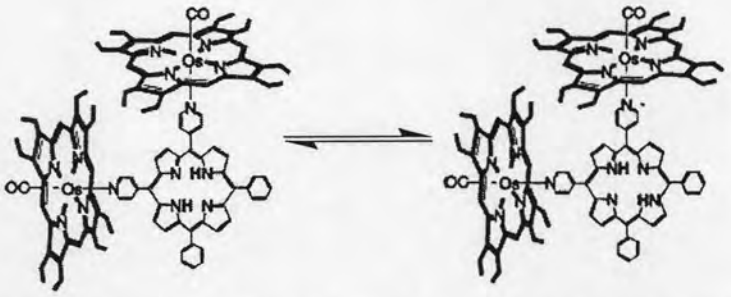


Figure 1.20 The tautomerism of the internal NH protons in the axial porphyrins

1.5.3 Multiporphyrin arrays prepared by Pd(II) and Pt(II) ions coordination

Dimers and tetramers porphyrin for ligation of *meso*-pyridylporphyrins on metal ions were synthesized by the ligation of pyridyl group on porphyrins or the corresponding zinc complexes to *cis* and *trans* square planar Pt(II) and Pd(II) arrays [46]. MPyTPP and the isomers of *cis*-DPyDPP and *trans*-DPyDPP gave discrete, ordered arrays of porphyrins involving the self-assembly of dimers and square tetramers in **Figure 1.21**.

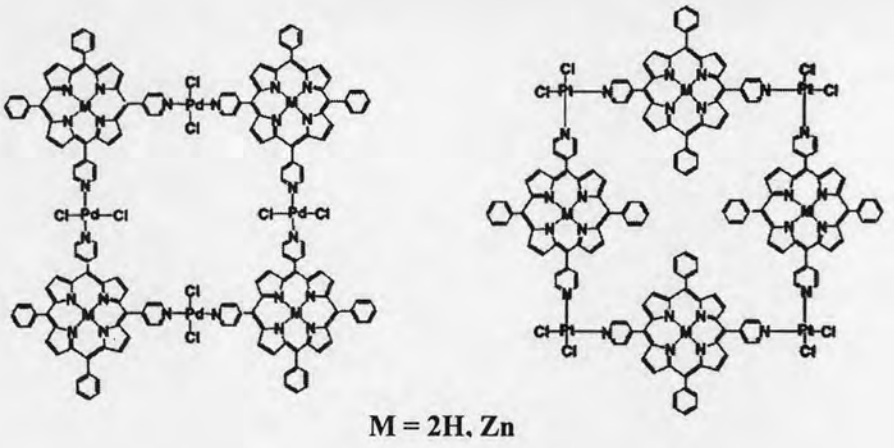


Figure 1.21 Coordination of *cis* and *trans*- pyridylporphyrin square planar Pt(II) and Pd(II) complexes

A related series of mono-, bis-, and tetrakisporphyrin assemblies (**Figure 1.22**) was also reported [47]. Porphyrin subunits assemble around the central metal ions through the pyridyl group. Tetrakisporphyrin complexes ^{1}H NMR spectra confirm the composition and general structure of the assembly. For example, in $[Pt\{(pyTP)H_2\}_4](OTf)_2$, all of the protons *ortho* to the pyridyl nitrogens appear as a single resonance (10.52 ppm, d, J = 6.0 Hz). In addition, the tolyl methyl protons give rise to only two singlets, 2.72 (s, 3H) and 2.45 (s, 6H), which can be assigned to the two symmetry-inequivalent types of tolyl groups on a single ligand. This indicates that all four porphyrins around the metal ion are identical on the NMR time scale and that the Pt and Pd ions have square planar environments in solution. For a Pd complex of the dimer, single-crystal X-ray diffraction analysis determined that in crystal the Pd bisphosphane is bridging two porphyrins.

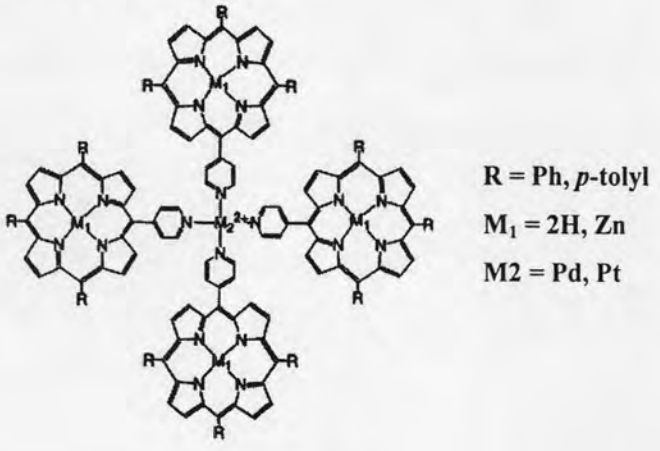


Figure 1.22 Tetrakis-pyridyltriarylporphyrin Pd(II) and Pt(II) supramolecular assemblies

1.6 Application

Porphyrins and metalloporphyrins represent a large family of functional molecular materials with high chemical and thermal stability. These compounds are objects of great interest for chemists, physicists and industrial scientists because of their potential role in emerging technologies including photoconductors, solar cells and chemical sensors. A great number of features makes porphyrins eligible as good ''sensing material'' able to detect the highly oxidizing or reducing inorganic gases, such as NO_2 [48], HCl [49], Cl_2 [50], *etc.*, and the relatively low reactive organic gases, such as volatile organic compounds (VOC) by absorption processes of the gas or vapour molecules onto the sensing layer. In order to be exploited as sensing materials, porphyrin compounds usually need to be deposited as solid films onto an appropriate substrate a large number of chemical techniques, *e.g.* solvent casting, spin coating, Langmuir–Blodgett, electropolymerization, self assembled monolayers, have been utilized and studied for this purpose [51].

Porphyrins present optical absorption and fluorescence bands in the visible region related to the electronic transitions of the aromatic systems. The interactions of analytes with porphyrin thin films affect both the optically active transitions of the single molecule and the π-π interactions between macrocycles, giving rise to detectable changes of the optical absorption spectra. This property allowed to develop several opto-chemical sensing procedures [52, 53].

The self-assembled monolayer (SAM) of Cu(II) *meso*-tetra(4-sulfanatophenyl) porphyrin (CuMTSP) (**Figure 1.23**) was used as optical sensing receptor for organic gases [54]. The monolayer was deposited on a quartz substrate by immersing the substrate into its aqueous solution for 30 min at 5 °C. The thin film was used to detect the saturated vapor of ethanol, 2-propanol and cyclohexane in airflow of 15 l/min. **Figure 1.24** shows the response time of the SAM to the vapor samples which were measured at a wavelength of 514 nm.

It was observed that the SAM was sensitive to all the vapor samples, as indicated by an increase in the reflected light intensity. The SAM response was also found to be very fast with the average time to reach the maximum change in the light intensity within 15 s. The SAM also exhibited a good reproducibility, as demonstrated by almost the same response profiles during the three cycles of response

measurement. It indicated that the thin film exhibited a good sensitivity and reproducibility towards all vapor samples.

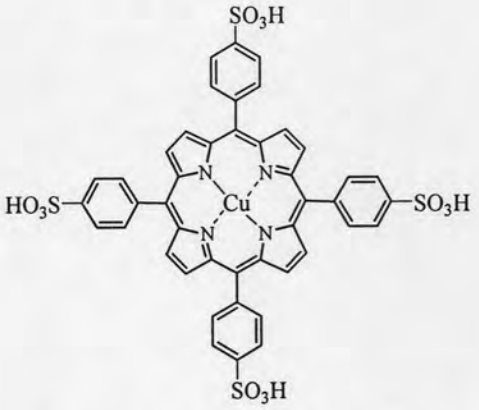


Figure 1.23 The molecular structure of Cu(II) *meso*-tetra(4-sulfanatophenyl) porphine (CuMTSP)

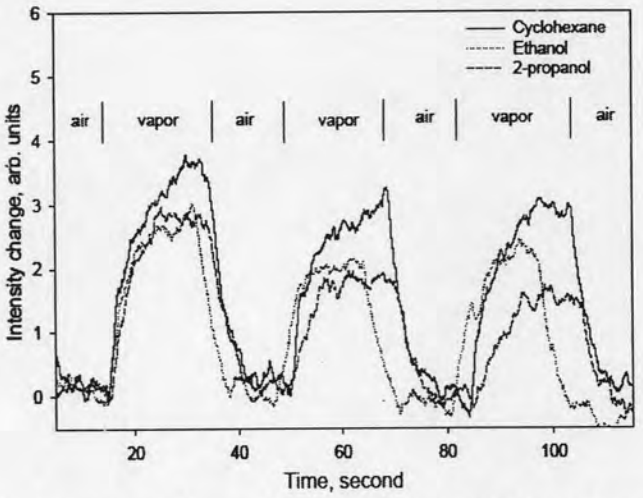


Figure 1.24 Optical response time at 514 nm of the CuMTSP thin film to saturated vapor of ethanol, 2-propanol and cyclohexane in airflow of 15 l/min

The ZnTPP thin film deposited by spin coating techniques have been used as optochemically interacting materials to detect 4-aminophenol [55], following the UV–Vis optical absorption variations obtained by the exposure of the sensing layers to vapour analyte diluted in dry-air controlled atmosphere. The dynamic responses were measured by recording the area integral of the absorption spectrum in the selected wavelength region versus time on four independent channels shown in **Figure 1.25**. The spectral regions corresponding to the 300–350 nm and 560–650 nm have a positive response, different from the 350–450 and 500–560 nm range, which show a negative.

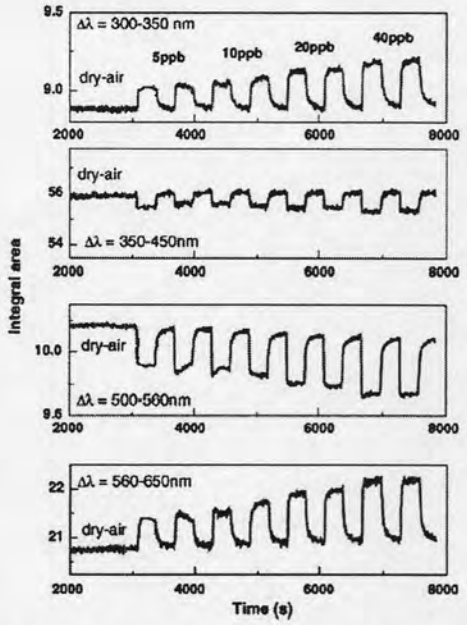
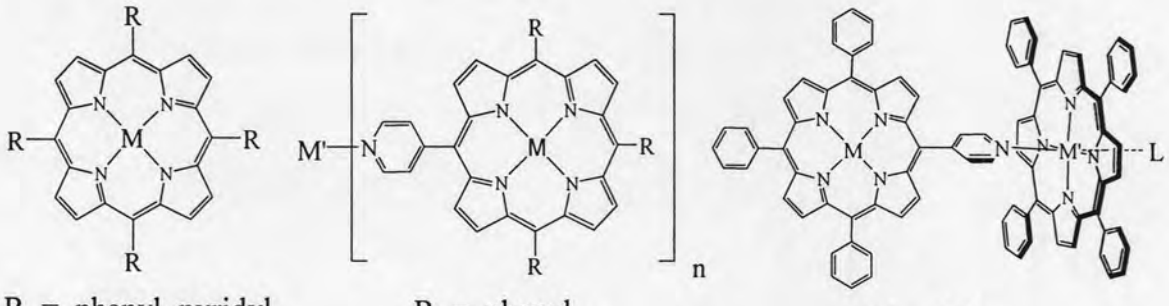


Figure 1.25 Typical dynamic responses of four analyzed spectral range in the presence of 4-amminophenolin the test chamber

1.7 Objectives

This research is aimed to synthesize various derivatives and complexes of tetraphenylporphyrin and 4-pyridyl/phenyl porphyrin isomers, the structures of which are shown in **Figure 1.26**. The spectroscopic data, especially the optical data, of the free-base porphyrins will be studied in comparison to their metal complexes. The synthesized compounds will be put to test for optochemical activity towards small volatile organic molecules for primary screening to be used as sensing materials. Furthermore, a larger array of porphyrin derivatives consisting of various free-base porphyrins and/or metal-porphyrin complexes will be prepared.



R = phenyl, pyridyl
M = 2H, Zn, Cu, Ni, Co, Fe, Mn

R = phenyl
M = 2H, Zn, Cu
M'= Cu, Pd

M = 2H
M'= Zn, Ni, Co

Figure 1.26 Structures of 4-pyridyl/phenyl porphyrin isomers and metal-porphyrin complexes