CHAPTER

1

Porphyrins and Metalloporphyrins: A General Outlook

1.1 Introduction

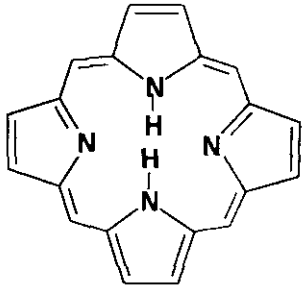
Metalloporphyrins in association with protein globule performs several important biochemical functions in nature. Hemoglobin, myoglobin, chlorophyll, cytochromes, catalase and paroxidases are well known examples, the chemistry of which relates principally to the redox property of corresponding metalloporphyrins and also their ability in transportation, storage and activation of molecular oxygen. Over the years a great deal of concerted efforts have brought to light substantial understanding of the structure –function relationship in these natural porphyrins [1-7].

Interest in metalloporphyrins are not confined only in the biological field as these compounds are equally important from chemical, industrial and technological point of view. During the last three decades synthetic porphyrins have been widely studied for various applications spanning the whole chemical and biological fields[8-16]. Metalloporphyrins are widely and intensely investigated in the area of catalysis and also as models and mimics of enzymes like catalase, paroxidases, P450 cytochromes or as transmembrane electron transport agents [8-10]. They have also been used as NMR image enhancement agents[15], nonlinear optical materials[16] and DNA-binding or cleavage agents[12, 13]. Large numbers of patents have been lodged for the use of porphyrins as radio diagnostic agents and in photodynamic therapy (PDT), foodstuff antioxidants, semiconductors or electrochromic materials[8,11].

Their applicability is so broad that they find a place even in beauty shops as body deodorants and stimulants of hair growth [8].

1.2 The Ubiquitous Porphyrin System

Porphyrin is an ubiquitous molecule present in almost all living organisms in one form or other. The basic unit of porphyrin consists of four pyrrolic units linked by four methine bridges. It is an 18-electron system and hence exhibits aromaticity[17]. There are also several porphyrin-like compounds, structures of some of which are given in **1-5**. The highly conjugated π system is the origin of the strong colour of these compounds and cause for their characteristic electronic and redox properties.



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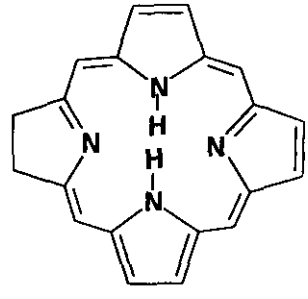
Porphyrin



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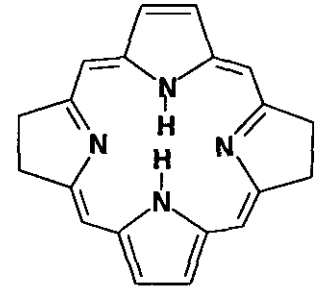
Chlorin



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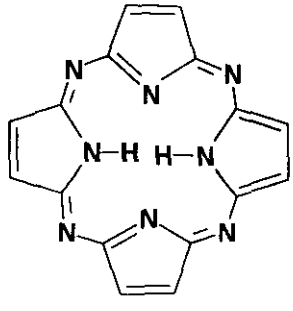
Bacteriochlorin



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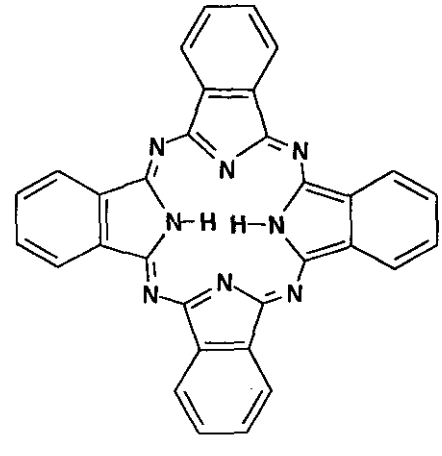
Porphyrazine



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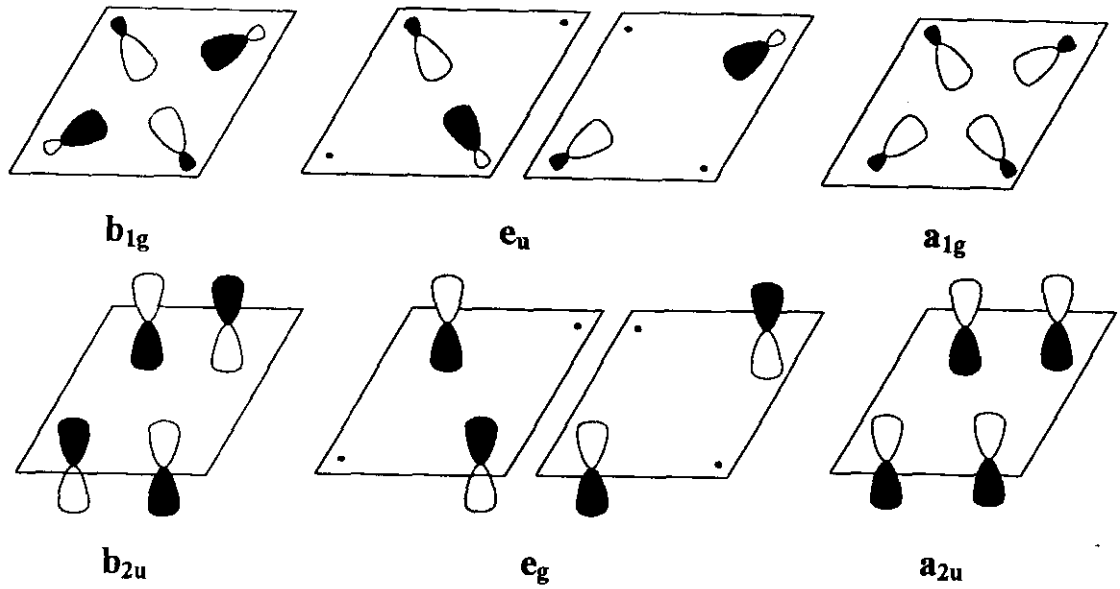
Phthalocyanine

The porphyrin ring provides a vacant site at the its center, ideally suited for metal incorporation. With very few exceptions the porphyrinato dianion acts as a tetradentate ligand with metal ions[18]. Thus the minimum coordination number of the metal ion possible in a metalloporphyrin is four. The extensive electronic delocalisation, which occurs in the porphyrinato ligand, leads to a substantial planarity of the macrocycle and an essentially square planar environment for the metal ion in four-coordinate complexes. Coordination number greater than four is also possible through ligation of suitable moieties either neutral or anionic. The five coordination complexes have generally a square–pyramidal geometry with the single axial ligand occupying the apex of the square pyramid. The two ligands of the six-coordinate metalloporphyrins are found on the opposite sides of the porphynato plane yielding complexes with tetragonal/octahedral geometries [18].

By now almost all metals and some semimetals have been incorporated into porphyrin cavity [19]. The essence of bonding between a central metal atom and the porphyrin ligand is to be found in the following two types of primary interactions:σ coordination of nitrogen lone pairs directed towards the central metal atom and π interaction of metal pπ and/or dπ orbitals with nitrogen pπ orbitals[20]. The appropriate symmetry-adapted linear combinations of ligands orbitals involved in the interaction are shown schematically in **6**.

The bonding of the central metal atom to the surrounding tetradentate ligand is through interactions of dx^2-y^2 – (b_{1g}); dxz, dyz – (e_g); dz^2, s – (a_{1g}); px, py – (e_u) and pz – (a_{2u}) pairs. Each interaction may be spread out over several orbitals in the porphyrin system. In the σ system the porphyrin is clearly a donor to the metal while in the π system porphyrin has the appropriate orbitals to act both as a π-donor and as a π-acceptor.



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The symmetry adapted linear combinations of porphyrin-ligand orbitals involved in the bonding with metal orbitals.

The most useful spectroscopic technique for the study of porphyrins/metalloporphyrins is the electronic absorption spectroscopy. The normal metalloporphyrin spectrum shows an intense B(Soret) band at ~420nm and two weaker Q(α,β) bands at ~550-600nm [17,21]. These spectral absorptions arises from π-π^* transitions of the aromatic porphyrin ligand. A typical spectrum of this (for Zn^{II}) is given in **Fig 1.1**. The widely accepted model to fit this spectrum, the four-orbit model, treats the porphyrin as a cyclic polyene and emphasizes the transition between the two highest filled bonding molecular orbital levels, a_{1u}, a_{2u} and the lowest empty doubly degenerate antibonding molecular orbital levels, e_g^* [21]. The schematic representation of the porphyrin HOMOs and LUMOs are shown in 7. The allowed transitions, $a_{1u} \rightarrow e_g^*$, , $a_{2u} \rightarrow e_g^*$, are assumed to be near degenerate in energy. As consequence, the states undergo configuration interaction and give rise to new states. The resulting spectrum shows a high-energy band B in which the transition dipoles add (high intensity) and a low-energy band Q in which the transition dipoles nearly cancel (low intensity). The two Q bands are vibronic components of the same transition [21,22].

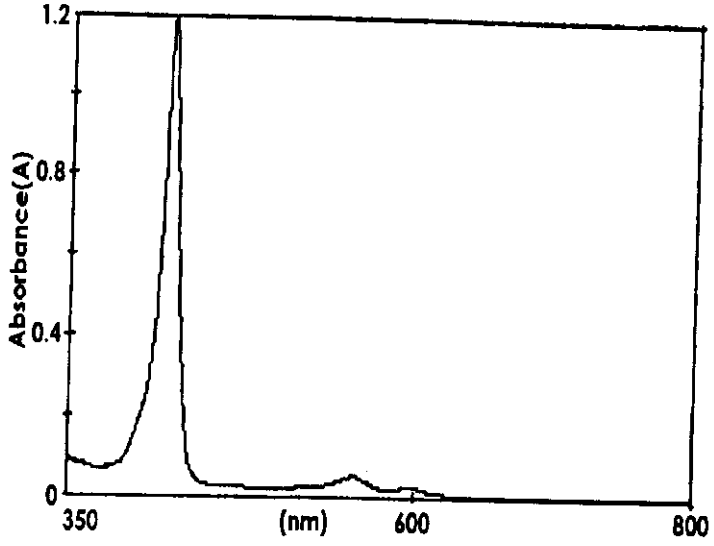
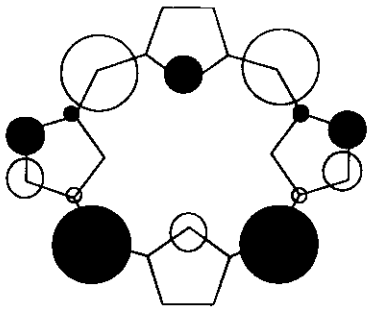
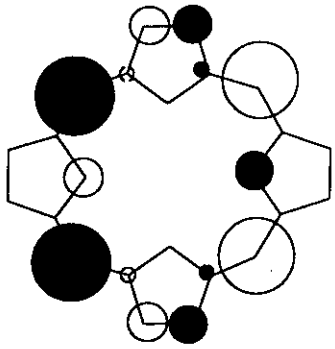


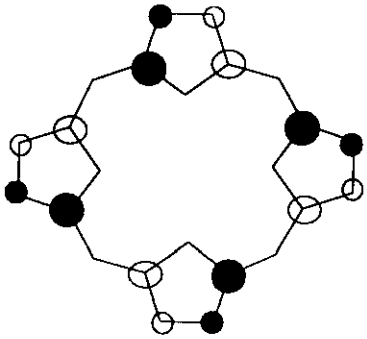
Fig. 1.1 Electronic absorptions spectrum of a Zn-porphyrin



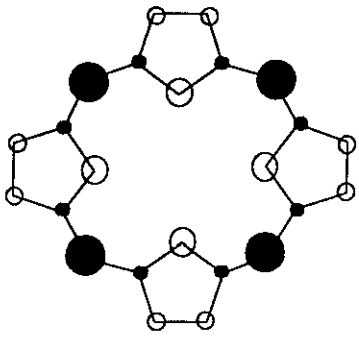
$e_g(\Pi^*_y)$



$e_g(\Pi^*_x)$



$a_{1u}(\Pi)$



$a_{2u}(\Pi)$

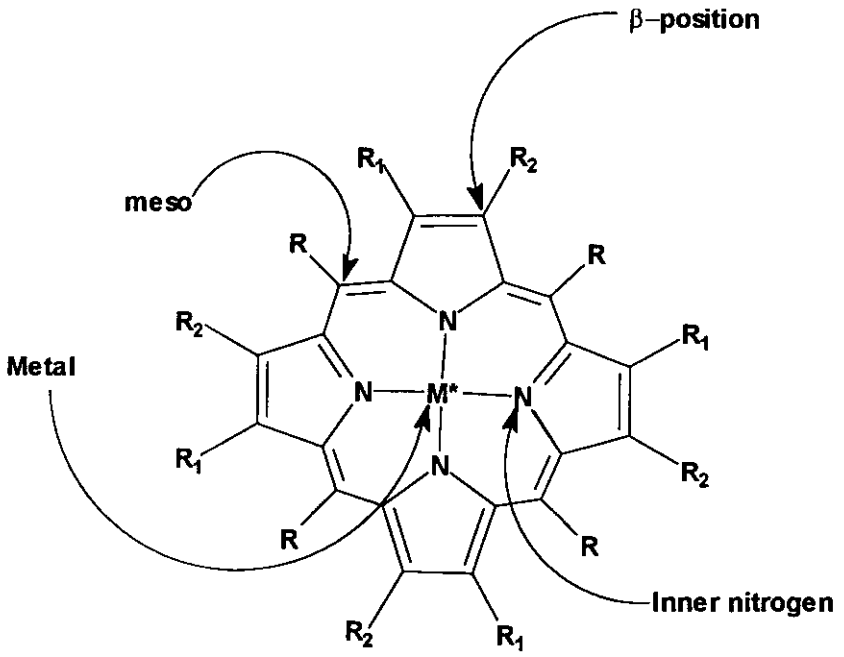
7

Schematic representation of porphyrin

HOMOs (a_{2u}, a_{1u}) and LUMOs(e_g*)

The exact positions of the spectral maxima of MPs are related to a number of parameters including metal electronegativity and metalloporphyrin molecular structure. The overlap of filled metal d orbital with the porphyrin ligand orbitals can cause some shift in the absorption bands as compared to metal-free porphyrins. Besides these absorptions some charge-transfer bands are also possible which can also shift the porphyrin π - π^* transitions significantly[17].

The synthetic metalloporphyrins have several functionalisation sites namely meso position, β (pyrrole ring) position, central metal and also the inner nitrogens (**8**)[23].



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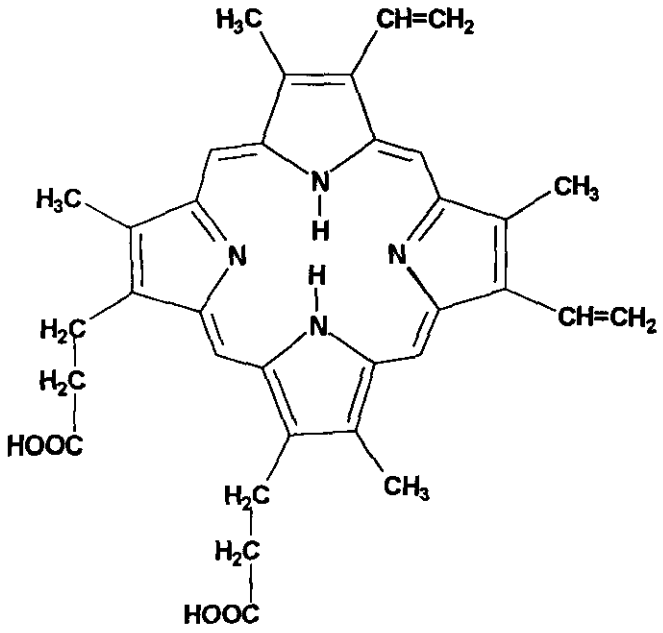
The common meso-substituted porphyrins are tetraphenyl porphyrin (R = phenyl) and ortho, meta or para substituted phenyl porphyrins. The important pyrrole substituted porphyrins includes octaethyl porphyrin (R_1 = R_2 = Ethyl) and etioporphyrin (R_1 = Ethyl, R_2 = Methyl).

1.3 Porphyrins in Life Processes

Metal complexes of porphyrins and related aromatic macrocycles are important prosthetic groups and form integral part of a wide variety of enzymes working as redox and rearrangement catalysts. Both the unique features of porphyrins mentioned earlier and controlled and cooperative interactions possible between porphyrins and the surrounding protein globule contribute substantially to the efficient functioning of these natural systems.

A large number of naturally occurring porphyrins have been isolated and characterised. Of these protoporphyrins are, by far, the most abundant and widely characterised ones. Protoporphyrin contains 4 methyl groups, two vinyl groups and two propionic acid groups. Fifteen different isomeric protoporphyrins differing in the sequence of substitution of the above groups in the eight available side chain positions are possible. Of these many possible forms, the protoporphyrin IX is the only form found in nature (**9**). It is found in hemoglobin myoglobin, heme enzymes and most of the cytochromes[3].



The chelate complex of protoporphyrin IX with Fe(II) is called protoheme or more simply heme; a similar complex with Fe(III) is called hemin or hematin. When the fifth and sixth positions of Fe-atom are occupied the resulting structure is a hemochrome or hemochromogen. It is the heme moiety, which plays the crucial role in most dioxygen mediated life processes.

The various functions of heme proteins in the transport, storage and reactions with dioxygen are made possible essentially by different and selective interactions of diverse proteins with the heme groups[7]. These differences derive from the axial ligands provided by ancillary groups of the protein and from the nature of the pockets on either side of the porphyrin. Both features create different environment about the heme so that the interaction of iron with dioxygen can achieve an extremely wide range of chemistries. Thus in blood, the tetrameric hemoglobin carries and shows cooperativity in binding of dioxygen. In the tissue, the structurally similar monomer myoglobin receives O_2 from hemoglobin and stores it for eventual reduction to water by cytochrome c oxidase in mitochondria. **Fig.1.2** shows the nature of the heme moiety buried in the protein envelope in cytochrome b_k.

Important porphyrin based natural systems are the heme enzymes, hemoglobin, myoglobin, the cytochromes and chlorophyll.

1.3.1 Enzymes

Enzymes are organic biocatalysts, which govern, initiate and control biological reactions, important for life processes. All known enzymes are proteins and some contain non-protein moieties termed prosthetic groups that are essential for the manifestation of catalytic activities[2-4]. In a variety of natural enzymes, metalloporphyrins (especially the heme system) constitute these prosthetic groups, some of which are discussed in brief.

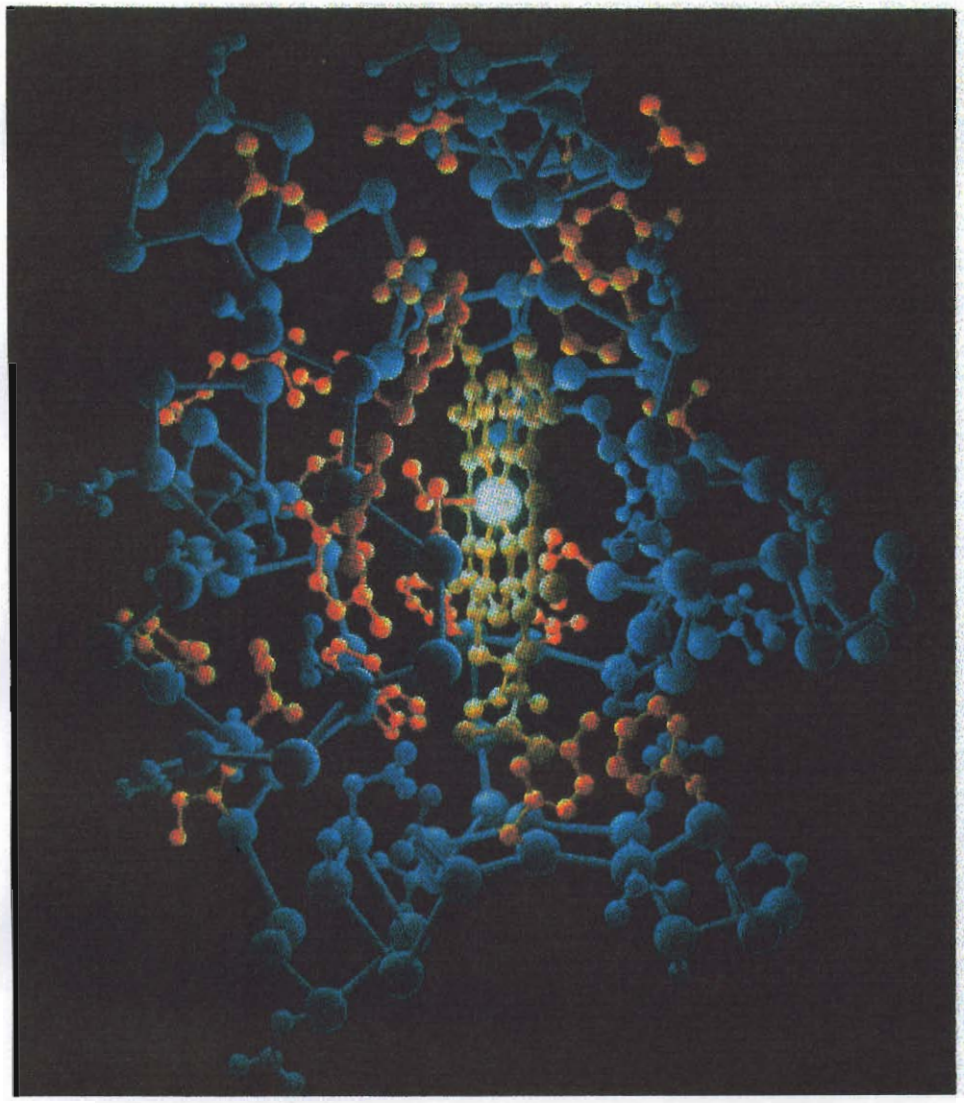


Fig. 1.2 The nature of the protein envelope around the heme moiety in cytochrome b_k (the yellow region in the centre of the system is the porphyrin ring)

Oxygenases

There are various enzymatic reactions in which one or both atoms of O_2 are directly inserted into the organic substrate molecule to yield hydroxyl groups. Enzymes catalyzing such reactions are called oxygenase, of which there are two classes: the dioxygenase catalyse insertion of both atoms of the O_2 molecules into the organic substrate, whereas the mono oxygenase insert only one [4].

Tryptophan 2,3-dioxygenase, a heme enzyme containing copper also catalyzes a step in the oxidative degradation of tryptophan[3]. In this reaction two O-atoms are introduced into the six-membered ring of tryptophan to yield an unstable, vicinal dihydroxy product, which decomposes spontaneously with cleavage of the aromatic ring into L-formylkynurenine.

The most important mono oxygenase is cytochrome P-450, found in the microsomes of liver cells[24]. The 'CO' derivative of its reduced form absorbs maximally at 450nm hence the name cytochrome P450. The reduced Fe(II) form of P450 reacts with molecular O_2 in such a way that one of the O-atom is reduced to water and the other is introduced into the organic substrate[3].

Cytochrome P450 enzymes catalyse hydroxylation of many different kinds of substrates including steroids, fatty acids, squalene and certain amino acids and thus making them more water soluble so that urinary excretion is favoured over fat storage[25]. They also promote hydroxylation of various drugs eg. phenobarbital, morphine, codeine, amphetamines and carcinogenic hydrocarbons like methyl cholanthrene[3].

Peroxidases and Catalase

Peroxidases are enzymes catalysing the oxidation of a variety of organic and inorganic compounds by H_2O_2 or related compounds. All the peroxidases, purified from plants contain hemine groups (Fe(III)-protoporphyrin IX). Peroxidases are of different types such as horseradish peroxidase(HRP), mylo peroxidase,

chloroperoxidase etc[6]. HRP is the most abundant and widely studied one and it has a histidine residue and an aquo group as the 5th and 6th ligands to Fe(III). In solutions of low pH , HRP is high-spin, but a low-spin species is formed at high pH [25].

Catalase is also a heme enzyme which catalyse the dismutation of H_2O_2 generated during various life processes. The catalase has molecular weight of about 2,40,000 and is made up of 4 identical sub-units, each containing one hemin group. Histidine and tyrosine residues are involved in the activity of the enzyme. The axial metal sites appear to be occupied by water and an amino acid residue[6].

The mechanism of the action of catalase and peroxidases are similar in the initial step via the decomposition of H_2O_2 with the formation of a high valent Fe-oxo species (compound I). Peroxidases then oxidise an electron donor species while catalase dismutate a second molecule of H_2O_2 before coming back to the initial state.

1.3.2 Hemoglobin and Myoglobin

The function of oxygen transport and storage in higher animals is provided by hemoglobin and myoglobin[2]. The former transport dioxygen from its source (lungs, gills or skin) to the site of use inside the muscle cells. There the oxygen is transferred to myoglobin for use in respiration. The myoglobin may serve as a simple storage reservoir. Other suggested functions of myoglobin include facilitation of O_2 flow within the cell and a buffering of the partial pressure of dioxygen within the cell.

The iron in hemoglobin and myoglobin is in the +2 oxidation state. The oxidised forms, Fe(III), called metmyoglobin and methemoglobin will not bind oxygen. The free heme is immediately oxidised in the presence of oxygen and water and thus renders useless for O_2 transport.

The stability of heme, Fe(II), in myoglobin and hemoglobin is a result of the protein portion of the molecule (globin), the protein chain folded about the heme reducing access to the iron and producing a hydrophobic environment[2,3]. This sterric and chemical control allows the coordination of only one O_2 molecule and does not allow the simultaneous presence of O_2 along with one or more water molecule, thereby stabilising Fe(II) in heme. This hydrophobic steric environment also keeps heme groups apart so that Fe(III)-O-Fe(III) μ-oxo formation is avoided.

In myoglobin the heme is held within a cleft in the protein (which is a 153 residue peptide) principally by non-covalent largely apolar interactions. The only covalent linkage between porphyrin and protein arises from a coordinate bond between the so-called proximal imidazole of histidine residue and the Fe(II). Hemoglobin is a tetramer composed of two similar globins of unequal length (141 residue and 146 residue peptides respectively)[2]. In spite of numerous differences in their amino acid sequences all Myogolobins and Hemoglobins have very similar tertiary structures consisting of eight helical regions A→H. The proximal histidine which is common to all functional Myogolobins and Hemoglobins is invariably the eighth residue in the helical region F. The heme is wedged in a crevise between segments E and F. Dioxygen binds on the E ('distal') side of the porphyrin[2,3,25].

The iron(II) in hemoglobin and myoglobin is in high-spin state but upon coordination of O_2 it changes to low spin[26]. This spin change is very important in the overall functions of these two moities and it is believed that the heme molecule is properly tuned by its substituents to make the spin pairing more feasible.

Myoglobin exhibits greater affinity of O_2 than hemoglobin and it is largely converted to oxymyoglobin even at low O_2 concentration in order to effect the transport of O_2 at the cell[2].

Upon the oxygenation of hemoglobin, two of the heme groups move about 100 pm towards each other while two others separate by about 700 pm due to the action of protein envelope. The net result of these combined movement is that hemoglobin

can exhibit relatively low affinity for binding the first one or two oxygen molecules. But once they are bound, the binding of subsequent O_2 molecule is greatly enhanced. Conversely the loss of one oxygen molecule from fully oxygenated hemoglobin causes the rest to dissociate more readily when the oxygen pressure is decreased[27]. It is the well-known cooperative effect exhibited by hemoglobin. The effect favours O_2 transport since it helps the hemoglobin get saturated in the lungs and deoxygenated in the capillaries.

1.3.3 The Cytochromes

The cytochromes are electron transferring proteins, containing iron porphyrin groups; they are found only in aerobic cells. Some are located in the inner mitochondrial membrane, where they act sequentially to carry electrons originating from various dehydrogenase systems toward molecular O_2. Other cytochromes are found in the endoplasmic reticulam, where they play a role in specialised hydroxylation reactions[28]. All cytchromes undergo reversible Fe(III)-Fe(II) valence changes during their catalytic cycles. In the mitichondria of higher animals, at least five different cytochromes have been identified; cytochrome b, c_1, c, a, and a_3 [5]. At least one of these, cytochrome b occurs in two or more forms (b_k and b_t). In nearly all the cytochromes both the fifth and sixth positions of the iron are occupied by the R groups of specific amino acid residues of the proteins[29]. These cyctochromes, therefore, cannot bind with ligands like O_2, CO or CN^- ; an important exception is cytochrome c oxidase which normally binds O_2 in its biological function.

The iron protoporphyrin group of cytochrome c is covalently linked to the protein via thioether bridges between the porphyrin ring and two cysteine residue in the peptide chain whereas in other cytochromes the porphyrin ring is non covalently bound. Cytochrome c is the only common heme moiety in which the heme is bound to the protein by a covalent linkage[25].

The standard oxidation-reduction potential (E_0') of various cytochromes are slightly different and it is these variations in E_0', which causes the flow of electrons through them in the respiratory chain[3].

1.3.4 Chlorophyll

Chlorophyll is the major light absorbing pigment in most green cells. Chlorophyll is basically magnesium derivative of porphyrins and some slight structural changes in porphyrin moiety results in different classes of chlorophyll viz, chlorophyll a,b,c, or bacteriochrophyll etc with slightly different photocatalytic properties[3]. All of the chlorophylls absorb light very intensely, particularly at relatively long wave length regions[30]. The light energy absorbed by a chlorophyll molecule become delocalised and spread through out the entire electronic structure of the excited molecule.

The photosynthetic pigments in the chloroplasts of plants consists of two functional units namely photosystem I and photosystem II[31]. Photosystem I contains chlorophyll and β– carotene as well as a single molecule of P700, a specialised chlorophyll a which serves as an energy trap. Photosystem I absorbes light at longer wavelengths and it is not responsible for O_2 evolution. Photosystem II on the other hand, is activated by shorter wave lengths, 670 nm and below and is responsible for O_2 evolution. It has a characteristic reactive center namely P680 a specialised chlorophyll-protein complex. Although both photosystems contain chlorophyll a and chlorophyll b the ratio of chlorophyll a to b is higher in photosystem I than in photosystem II[3]. The most significant difference between the photosystems, however, is the presence of large amounts of chlorophyll a-protein complexes absorbing at long wavelengths in photo system I and their absence in photosystem II. These two light systems, one absorbing in the region 680-720 nm (PS I) and the other at shorter wavelengths (PS II) must cooperate to yield maximal results in photosynthesis.

In addition to the above mentioned natural systems, some other macromolecules, structurally related to porphyrins are also involved in various biological processes. An example is the well known Vitamin B_{12}, which is a cobalt derivative of a 15-membered corrin ring[2]. The controlled interaction between the porphyrin-like frame work and the surrounding proteins is expected to be the crucial factor in the specific functions of these biosystems also.

1.4 Metalloporphyrins as Catalysts

Metalloporphyrin catalysis is a subject of much interest in relation to some biochemical reactions as well as organic synthesis. There is no doubt that the primary stimulus which led to the investigation of porphyrins and their metal complexes was provided precisely by their catalytic properties. The catalytic functions of metalloporphyrins have been activity investigated in the last two decades and now they have proved to be universal catalysts of many chemical, electrochemical and photochemical reactions[8].

The high catalytic activity of porphyrins is due to the aromatic character of the conjugated π system of the macroring, the conjugation of the coordinated metal atom to the π-system of the ligand and the case with which the oxidation state of the central metal atoms changes. In the planar molecules of metalloporphyrins the fifth and sixth coordination sites of the central metal ion are available for coordination of the molecules of reactants in the reaction being catalysed and the extensive conjugation within the system facilities a redistribution of the electron density in the reaction complex, which lowers the activation barrier to the reaction. It is also important that the extensive π -electron systems of porphyrins have a distinct electron-buffer character. Depending on the other reactants porphyrins can exhibit both electron-donating and electron accepting properties. It is significant that porphyrins are chemically stable in the ground state and photo excited states and also in the form of radical cations and radical anions[8,32].

Among various synthetic analogues of porphyrins, meso tetraarylporphyrins with or without substitutions at phenyl rings or β-pyrrole positions as given in **10** and **Table 1.1** are widely investigated for catalytic activities. Porphyrins with pyridine substitution at meso positions (pyridyl porphyrins) are also important catalysts.

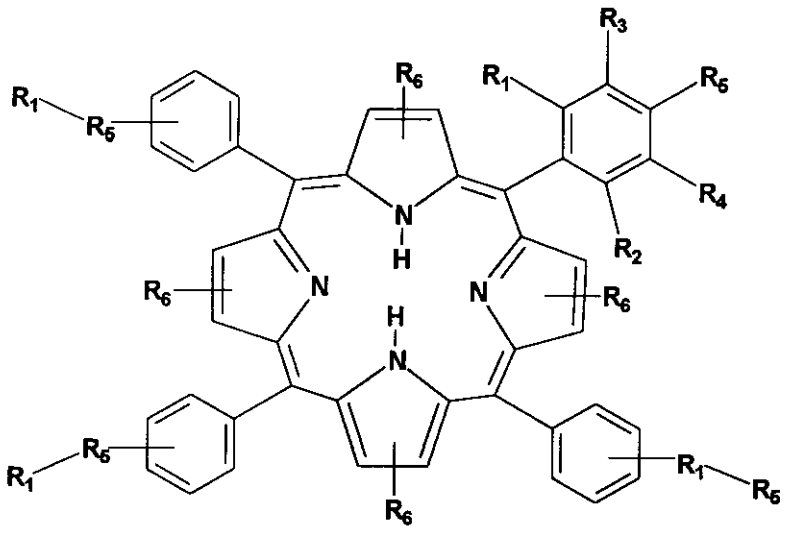


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Table 1.1 List of catalytically important meso-tetraaryl porphyrins.

Abbreviation	Substituents (as in 10)
H_2 TPP	R_1-R_5 = H, R_6 = H
H_2 TPPS	R_1-R_4 = H, R_5 = SO_3 Na, R_6 = H,
H_2 TCCP	R_1-R_4 = H, R_5 = COOH, R_6 = H,
H_2 TMP	R_1=R_2 = R_5 = Me, R_3 = R_4 = H, R_6 = H
H_2 TPFPP	R_1-R_5 = F, R_6 = H
H_2 TDCPP	R_1=R_2 = Cl, R_3 - R_5 = H, R_6 = H
H_2 Br_8TDCPP	R_1=R_2 = Cl, R_3 - R_5 = H, R_6 = Br
H_2 Cl_8TDCPP	R_1=R_2 = Cl, R_3 - R_5 = H, R_6 = Cl
H_2 Br_8TMP	R_1=R_2 = R_5 = Me, R_3 = R_4 = H, R_6 = Br
H_2 Cl_{12}TMP	R_1=R_2 = R_5 = Me, R_3 = R_6 = Cl, R_4 = H
H_2 F_8TPFPP	R_1-R_5 = F, R_6 = F

The different derivatives of H_2TPP group constituted the first generation of metalloporphyrin catalysts. The second generation of tetraaryl porphyrins have alkyl substituents at the ortho, meta or para positions of the phenyl groups of the macrocycle meso positions. The third generation is extension of the previous idea by having Br, Cl or F – atoms at the β - positions of pyrrole rings[9].

It is convenient to classify metalloporphyrin based catalysis to the following categories [8].

- Catalysis of oxidation reactions.
- Catalysis of electro chemical reactions
- Catalysis of isomerisation and polymerisation reactions.
- Catalysis of photochemical and photoelectrochemical reactions.

1.4.1 Catalysis of oxidation reactions by metalloporphyrins

Metalloporphyrins which catalyse the oxidation reactions are analogues of the prosthetic group of heme-containing enzyme which selectively catalyse various oxidation reactions[9]. Biological oxidation by heme enzymes can be classified as follows. Oxygenations of organic substrates catalyzed by cytochrome P-450; oxidations by peroxidases, oxidative chlorinations by chloroperoxidases and hydrogen peroxide dismutation by catalase. There are many metalloporphyrins which are able to reproduce and mimic all these heme enzyme mediated reactions. This similarity is one of the obvious driving forces for studying metalloporphyrin catalysed oxidation reactions. The second one arose from the necessity of producing valuable chemicals from oil derivatives by selective oxygenation reactions

Biomimetic oxygenations of organic substrates using metalloporphyrins as catalysts ideally should use dioxygen as the source of oxygen atom since O_2 is used directly by oxygenase enzymes. In most cases however, the successful metalloporphyrins that have been developed for such reactions require alternative oxidants eg. H_2O_2,

ROOH, PhIO or NaOCl since reactions using dioxygen itself either give no reaction or give predominantly the undesirable products of free radical autoxidation[33].

There are several studies on oxidation reactions catalysed by synthetic metalloporphyrins. The most important and widely studied among them are the epoxidation of olefins and hydroxylation of alkanes.

Among various MPs investigated Fe and Mn derivatives of porphyrins are found to be the most efficient catalysts in these epoxidation or hydroxylation reactions[8,9,33-43]. Also the third generation of metalloporphyrins and sterically hindered MPs are very efficient catalysts particularly in terms of specificity and selectivity of these organic transformations[44-48]. Similarly asymmetric epoxidation or hydroxylations could be carried out using chiral porphyrins[9]. A large number of studies have been also devoted for the mechanistic pathways of these various epoxidation and hydroxylations reactions[9,33,37,49-51].

Metal-porphyrin complexes also catalyse the oxidation of various drugs. For example the Fe(TPP)Cl/PhIO systems oxidise antergan to N-demetallated products[52]. Mn-porphyrin systems catalyse the oxidation of nicotine to cotinine and 3-hydroxy cotinine, two products identical to those obtained from in vivo metabolism[53]. The catalytic oxidation of acetaminophen, a well known analgesic and some antitumoral ellipticine derivatives could also be carried out by various metalloporphyrins[54]. Metalloporphyrins are also effective catalysts in oxidative N-dealkylation of tertiary amines[55], oxidative desulfurisation[56], oxidation of nitroso to nitro compounds[57], oxidation of dialkyl sulfides to sulfoxides[58] etc.

1.4.2 Catalysis of electrochemical processes by metalloporphyrins

Metalloporphyrins are widely investigated and used as catalysts for electrochemical reactions. Most studies in this field concern the catalysis of cathodic reduction of molecular oxygen in low temperature fuel cells[8]. Investigations have shown that

MPs can serve as effective and stable catalysts in this reaction and their catalytic activity is dependent on a number of factors such as the nature of the coordinated metal ion, nature of the porphyrin ligand etc[59-61].

O_2 reduction catalysed by MPs can proceed by a two electron pathway to produce H_2O_2 or by a net four electron pathway to yield H_2O[59]. It is the structural and chemial features of porphyrins that determine what pathways taken by the reaction that they catalyse. In most cases the two electron reduction was predominent. But some Co-Co cofacial diporphyrins and specially designed MPs containing cordinated Ru or Ir complexes were found to proceeded the cathodic reduction of O_2 via a $4e^-$ step[59,62-71].

In practical applications of metalloporphyrins whose electrical conductivity is low, they should be deposited on various conducting carriers. Metals and carbonaceous materials (graphite, carbon black, activated charcoal) have been investigated as carriers. MPs deposited on carbonaceous materials show the highest activity[8].

There is a method for the selective removal of N-or S-containing hetrocyclic pollutants from hydrocarbon solvents by Fe-Porphyrin system[72]. Fe(III)TPPS in solution gets electrochemically reduced to Fe(II)TPPS which has high affinity for N–or S-hetrocylic ring as axial ligands. The hetrocyclic ring coordinated Fe(II)TPPS then gets transferred to another compartment where it is subjected to oxidation to Fe(III) state again. The Fe(III)TPPS system is highly reversible with N or S coordinating ligands so that the release of this hetrocyclic pollutants from the catalyst centre is easy. Hence the selective removal and concentration of environmentally hazardous materials using Fe porphyrins can be achieved with great efficiency.

Among other electrocatalytic process occurring with participation of metalloporphyrins, mention may be made of the cathodic reduction of CO_2 [73],

cathodic reduction of HSO_3^- to H_2S [74], anodic oxidation of SO_2[8] and reduction of NO_2^- to NH_3 [75].

1.4.3 Catalysis of isomerisation and polymerisation reactions by metalloporphyrins

Certain metalloporphyrins are able to catalyse isomerisation of unsaturated compounds[8]. For example, the catalytic activity of Co-porphyrins in the isomerisation of quadricyclane to norbornadiene has been well established[76].

This isomerisation reaction is symmetry prohibited and therefore proceeds at a very low rate. But Co(III)TPP and Co(II)TPP complexes increase sharply the rate of isomerisation of quadricyclane. The Co(III)TPP has greater catalytic activity than Co(II)TPP and the reaction rate depends strongly on the nature of the organic ligand.

A polymerisation process which results polymers of narrow molecular weight distribution (MWD) is in general termed as "living polymerisation". It was reported that some metalloporphyrins especially Al or Zn derivatives serve as excellent initiators for living polymerisation for some epoxides, olefines etc and the polymerisation takes place at the central metal atom of the initiator [77].

N–substituted Zn porphyrins are capable of initiating the living polymerisation of epoxides and episulphides [78,79]. It is also possible to synthesise an epoxide episulphide copolymer in a cross propagation sequence using the same porphyrins.

Since the living polymerisations initiated with porphyrins proceeds on the central metal atom of the porphyrin complex, the reactivates of the initiating and propagating species are affected by the structure of the porphyrin ligand[77].

1.4.4 Catalysis of photochemical reactions by metalloporphyrins

The most important practical application of porphyrins in photochemical reactions is the decomposition of water in order to utilise solar energy. The acridine dyes (eg. methyl viologen, MV^{2+}) widely used in early days in order to sensitise the photochemical reduction of water utilise only a limited portion of sun's rays. Porphyrins whose absorption spectra cover an appreciable portion of the spectrum of sunlight are of great interest in this respect[8]. Also MPs exhibit a very high photochemical stability.

The irradiation of a system consisting a Zn-porphyrin, MV^{2+}, EDTA, and collodial Pt results in the evolution of hydrogen with sufficient quantum yield [80,81]. In addition to Zn derivative, Mg, Sn, Ru, and metal-free haematoporphyrin system also exhibit a high activity in the H_2- evolution from water [8].

A vilogen–linked water soluble Zn porphyrin with different methylene chain lengths between porphyrin and viologen were synthesised and it has been reported that these compounds can be applied for photo induced H_2-evolution [82].

The photoelectrochemical oxidation reduction reactions catalysed by porphyrin or metalloporphyrin have been widely investigated in order to devise converters of solar energy into electrical energy [83,84]. The porphyrin coated electrode serves as the photocathode in almost all photochemical cells of the types of electrode |MP (or H_2P)|electrolyte|electrode.

The mechanism of the generation of the photocurrent as a rule involves the formation of an excited triplet state of the sensitiser (porphyrin), the migration of the triplet excited state to the MP/electrolyte interface, the generation of charges on the interface as a result of electron transfer from the photoexcited sensitiser to H^+, O_2 or an oxidant (such as methyl viologen) specially introduced into the electrolyte and finally the migration of the charges to the current measuring devices.

There are also large attempts to utilise the photochemical properties of metalloporphyrins in organic synthesis. For example it was found that irradiation by a UV- visible light, of a solution of Fe(TDCPP)OH in O_2- saturated cyclohexane led to a progressive formation of cyclohexanone [48]. Cyclooctane was similarly oxidised with formation of cyclooctanone as the major product.

1.5 References

1. T.S. Mashiko, Comprehensive Coordination Chemistry, Geoffery and Wilkinson (Ed:), Vol 2, Pergamon press, Oxford, (1987).
2. J.E. Huheey, E.A. Keiter and R.L. Keiter, Inorganic Chemistry-Principles of Structure and Reactivity (4th Edition), Harper Collins College publishers, New York, (1993).
3. A.L. Lehinger, Biochemistry (2nd Edition), Kalyani publishers, New Delhi, (1978).
4. O. Haya shi, The Enzymes, P. Boyer, H. Lardy and K. Myrback (Ed:), 2nd Edition, Academic Press, New York, Vol.8, (1963).
5. E.L. Smith, R.L. Hill, I.R. Lehman, R.J. Lef kowitz, P. Handler and A. White, Principles of Bio-Chemistry-General Aspects (7th Edition), Mc Graw-Hill Inc., Singapore, (1983).
6. G.I. Likhtenshtein, Chemical Physics of Redox Metalloenzyme Catalysis, Springer-Verlag, Berlin Heibelberg, (1988).
7. J.P. Collman, Inorg. Chem., 36, (1997), 5145.
8. O.A. Golubchikov and B.D. Berezin, Russian Chem., Rev., 55 (8), (1986), 768.
9. B. Meunier, Chem. Rev., 92, (1992), 1411
10. V.V. Borovkov, R.P. Evstigneeva, L.N. Strekova and E.I. Filippovich, Russian Chem. Rev., 58(6), (1989), 602.
11. H. Ali and J.E. vanLier, Chem. Rev., 99, (1999), 2379.
12. L.G. Marzilli, New J. Chem., 14, (1990), 409.
13. N.E. Mukundan, G. Petho, D.W. Dixon and L.G. Marzilli, Inorg. Chem., 34, (1995), 3677.
14. B.D. Berezin, Coordination Compounds of Porphyrins and Phthaloyanines, John Wiley & Sons, Chichester, U.K., (1981)
15. K.E. Keller and N.Foster, Inorg. Chem., 31, (1992), 1353.
16. K.S. Suslick, C.T. Chen, G.R. Meredith and L.T. Cheng, J.Am. Chem. Soc., 114, (1992), 6928.

17 M. Gouterman, The Porphyrins, D. Dolphin (Ed:), Academic, New York, Vol III, Part A, Physical Chemistry, (1978).

18. W.R. Scheidt, Accounts of Chemical Research, 10, (1977), 339.

19. J.W. Buchler, The porphyrins, D. Dolphin (Ed:), Academic, New York, Vol.1, Part A, Structure and Synthesis, (1978).

20. K. Tatsumi and R. Hoffmann, J. Am. Chem. Soc., 103, (1981), 3328.

21. L.J. Boucher, Coord. Chem. Rev., 7, (1972), 289.

22. M.Zerner and M. Gouterman, Theoret. Chim. Acta, 4, (1966), 44.

23. H. Ogoshi and T. Mizutani, Acc. Chem. Res., 31, (1998), 81.

24. K.E. White and M.J. Coon, Annu. Rev. Bio Chem., 49, (1980), 356.

25. M. N. Hughes, The Inorganic Chemistry of Biological Processes, (2nd Edition), John Wiley and Sons, New York, (1988).

26. M.S. Perutz, G. Fermi, B. Luisi, B. Shaanan and R.C. Liddington, Acc. Chem. Res., 20, (1987), 309.

27. M.S. Perutz, Nature, 228, (1970), 726.

28. F.S. Mathews, Prog. Bio- Phys. Mol. Biol., 45, (1985), 1.

29. T. Takano, B.L. Trus, N. Mandel, G. Mandel, O.B. Kallai, R. Swanson and R.F. Dickerson, J. Biol. Chem., 252, (1977), 776.

30. H.H. Seliger and W.D. McElroy, Light: Physical and Biological Action, Acadmic Press. New York, (1965).

31. K. Saner, Annu. Rev. Phy. Chem., 30, (1979), 155.

32. N.S. Enikolopyan, K.A. Bogdanova and K.A.Askarov, Russian Chem. Rev., 52(1), (1983),13.

33. W. Nam, H.J. Kim, S.H. Kim, R.Y.N. Ho, and J.S. Valentine, Inorg. Chem., 35, (1996), 1045.

34. J.T. Groves, T.E. Nemo and R.S. Myers, J. Am. Chem. Soc., 101, (1979), 1032.

35. J.T. Groves, and T.E. Nemo J. Am. Chem. Soc., 105, (1983), 5786.

36. C.K. Chang and F. Ebina, J. Chem. Soc., Chem. Commun., (1981), 778.

37. M.J. Gunter and P. Turner, J. Mol. Cat., 66, (1991), 121.

38. P. Battioni, J.P. Renaud, J. F. Bartoli, M. Reina-Artiles, M. Fort and D. Mansuy, J. Am. Chem. Soc.,110, (1988), 8462.

39. J.T. Goves and T.E. Nemo, J. Am. Chem. Soc., 105, (1983), 6243.

40. J.R.L. Smith and D.N. Mortimer, J. Chem. Soc., Chem. Commun., (1985), 410.

41. M.J. Nappa and C.A. Tolman, Inorg. Chem., 24, (1985), 4711.

42. P. Battioni, J.P. Renaud, J.F. Bartoli and D. Mansuy, J. Chem. Soc. Chem. Commun., (1986), 341.

43. J. Bernadou, P. Geals and B. Meunier, Tetrahedron Lett., 29, (1988), 6615.

44. P.S. Traylor, D. Dolphin and T.G. Traylor, J. Chem. Soc., Chem. Commun., (1984), 279.

45. O. Bortolini, M. Momenteau and B. Meunier, Tetrahedron Lett., 25, (1984), 5773.

46. B. Meunier, M.E. De Carvalho and M.Momentaeu, Inorg. Chem., 27, (1988), 161.

47. J.F. Bartoli, O. Brigaud, P. Battioni and D.J. Mansuy, J. Chem. Soc. Chem. Commun., (1991), 440.

48. D. Mansuy, Coord. Chem. Rev., 125, (1993), 129.

49. T.G. Traylor, C. Kim, J.L. Richards, F. Xu and C.L. Perrin, J. Am. Chem. Soc., 117, (1995), 3468.

50. J.P. Collman, J.I. Brauman, B. Meunier, T. Hayashi, T. Kodadek and S.A. Raybuck, J. Am. Chem. Soc., 107, (1985), 2000.

51. K.A. Lee and W. Nam, J. Am. Chem. Soc., 119, (1997), 1916.

52. F. Pautet, R. Barrel and M. Daudon , Pharm. Acta. Helv., 63, (1988), 140.

53. M.A. Chauncey and S.I. Ninomiya, Tetrahedron Lett., 31, (1990), 5901.

54. J. Bernadou, M. Bonnafous, G. Labat, P. Loiseau and B. Meunier, Drug Metab. Dispos., 19, (1991), 360.

55. J. Iley, L. Constantino, F. Norberto and F. Rosa, Tetrahedron Lett.,31, (1990), 4921.

56. R.S. Davidson and M.D. Walker, Tetrahedron Lett., 29, (1988), 1827.

57. K.A. Jorgensen, J. Chem. Soc., Chem. Commun., (1987),1405.

58. J.H. Ramsden, R.S. Drago and R. Riley, J. Am. Chem. Soc., 111, (1989), 3958.

59. K. Shigehara and F.C. Anson, J. Phys. Chem., 86, (1982), 2776.

60. A. Bettelheim, R. Parash and D. Ozer, J. Electrochem. Soc., 129, (1982), 2247.

61. N. Kobayashi, M. Fijihira, T. Osa and S. Dong, Chem. Lett., (1982), 575.

62. J.P. Collman, L.L. Chng and D.A. Tyvoll, Inorg. Chem., 34, (1995), 1311.

63. C.K. Chang, H.Y. Liu and I. Abdalmuhdi, J. Am. Chem. Soc., 106, (1984), 2725.

64. J.P.Collman, P.S. Wagenknecht and J.E. Hutchison, Angew. Chem. Int., Ed. Engl., 33, (1994), 1537.

65. R.R. Durand, C.S. Bencosme, J.P. Collman and F.C. Anson, J. Am. Chem. Soc., 105, (1983), 439.

66. C. Shi and F.C. Anson, J. Am. Chem. Soc., 113, (1991), 9564.

67. C. Shi and F.C. Anson, Inorg. Chem., 31, (1992), 5078.

68. B. Steiger and F.C. Anson, Inorg. Chem., 33, (1994), 5767.

69. B. Steiger and F.C. Anson, Inorg. Chem., 34, (1995), 3355.

70. C. Shi and F.C. Anson, Inorg. Chem., 34, (1995), 4554.

71. B.Steiger, C.Shi and F.C. Anson Inorg. Chem., 32, (1993), 2107.

72. C.A. Koval, S.M. Drew, R.D. Noble and J. Yu, Inorg. Chem., 29, (1990), 4708.

73. I. Bhngun, D. Lexa and J.M. Saveant, J. Am. Chem. Soc., 116, (1994), 5015.

74. M.A. Kline, M.H. Barley and T.J. Meyer, Inorg. Chem., 26, (1987), 2196.

75. M.H. Barley, K.J. Takeuchi and T.J. Meyer, J. Am. Chem. Soc., 108, (1986), 5876.

76. S. Miki, T. Ohno, H. Iwasaki and Z. Yoshida, Tetrahedron. Lett., 26, (1985), 3487.

77. T. Aida and S. Inoue, Acc. Chem. Res., 29, (1996), 39.

78. T. Aida, K. Kawaguchi and S. Inoue, Macromolecules, 23, (1990), 3887.

79. Y. Watanabe, T. Aida and S. Inoue, Macromolecules, 23, (1990), 2612.

80. J. Kiwi and M. Gratzel, J. Am. Chem. Soc., 101, (1979), 7214.

81. A. Harriman, G. Porter and M.C. Richoux, J. Chem. Soc. Faraday Tran. II., 77, (1981), 833.

82. Y. Kinumi and I. Okura, J. Mol. Cat., 52, (1989), 33.

83. T. Kawi, K. Tanimura and T. Sakata, Chem. Phys. Lett., 56, (1978), 541.

84. F.R. Fan and L.R. Faulkner, J. Am. Chem. Soc., 101, (1979), 4779.