

Porphyrin: A versatile ligand from nature

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Abstract:

Nature uses large biomolecules like proteins for performing the complex biochemical reactions and processes with utmost selectivity and efficiency. It has learned to select the best configuration through time and in most of the cases retains units with optimal performances. One such unit working as a cofactor in many biomolecules are the porphyrin ring-based systems. The simple yet highly efficient tetrapyrrole ring, binds metals rather easily and has the ability to fine tune the property or reactivity of the central metal atom. Porphyrin based systems are widely available in nature in different forms of life performing jobs like electron and molecule transfer and storage to harvesting of light energy. Due to their unique properties, synthetic porphyrin-based systems are gaining popularity in various applications.

Introduction:

Ancient Greece is the place where the word porphyrin was first introduced.¹ They used the word 'porphura' for the description of color purple which describe mollusks which are used to extract Tyrian Purple, a rare purple colored pigment.² This indicates the most general and highly characteristic feature of porphyrin molecules: they are all intensely colored close towards the shade of purple.

Porphyryns are large molecules with existence both in the natural and artificial or synthetic world consist of a ring structure containing four pyrrole rings.³ It is generally crystalline in nature and the crystals are deep red or purple. Initially scientists were reluctant to believe the structure first proposed by Küster in 1913 to stable owing to the large size.⁴ Later Fischer synthesized heme from pyrrolic starting material and established the tetrapyrrole ring structure of porphyrin later confirmed by x-ray crystallography. Although minute amount product was obtained due to the low yield of the final product (0.1%), this was significant advancement in the field of synthetic organic chemistry.⁵ In fact, it created a special field in the interdisciplinary world of chemistry where organic chemists, inorganic chemist, physical chemist as well as biochemists are working together.⁶ Eventually, total synthesis of chlorophyll was accomplished in 1960 by Woodward.

The structure of the porphyrin macrocycle is simple indeed, porphyrin the unsubstituted molecule consists of four pyrrole-type residues in a plane with four methine bridging groups like bi-color beads in a necklace arranged alternately.³ The periphery of the ring is made up of carbon atoms following the common numbering system of 1 to 20. Trivial nomenclature also refers them as either the α , β or *meso* positions, carbon no 1 and 4 of the pyrrole fragments are called the α -carbons, carbons 2 and 3 are called the β -carbons, and the bridge head carbons connecting the pyrrole rings are called the *meso*-carbons.⁷

Porphyryns are versatile ligands and in nature also they appear as bound to a metal ion, iron for heme or cytochrome and Mg for chlorophyll. On chelation with metal ion the porphyrin nucleus loses two protons from

its pyrrole nitrogen atoms; the chelating species is thus a dianion, and electrostatic forces certainly contribute to the bonding. Besides earth metals (Li, Na, K) and rare earth metals, transition metals are the most studied. Apart from the alkali metals and large ions such as Pb(II), Cd(II), Ba(II), chelation with a porphyrin imposes an essential square-planar configuration upon most metal ions. Coordination to fifth and sixth axial positions can lead to square-pyramidal or octahedral complexes. More than six coordination are also possible for a number of sandwiched metalloporphyrins. Metalloporphyrins are generally low spin complexes (Co(II), Ni(II)) but depending on the metal and axial coordination of weak field ligands they can be either high spin or mixture of high and low field complexes.^{8,9}

Coordination of a metal ion tends to stabilize its oxidized state relative to its reduced state; this is an electrostatic effect, the electronegativity of the ligand atoms favouring the more positively charged state of the metal ion. The greater the electron-attracting power of the porphyrin side chains, the less electronegative (less basic) the pyrrole nitrogen atoms. As the basicity (electron-donor power) of these ligand centres decreases, electron-density at the chelated metal ion also tends to decrease, so that it becomes progressively harder to remove an electron from it. With axial ligands, the greater the donor power the more negative the oxidation potential is. The intense color of the porphyrins appear due to strong electronic absorption spectra of porphyrins and metalloporphyrins. By virtue of the conjugated system with alternate single and double bonds, the π electron cloud is delocalized throughout the ring. The electronic transitions thus are dominated by strong π to π^* ligand bands. The classical explanation for the observed electronic transitions can be explained by Gouterman's four orbital model.^{10,11} The model considers the frontier molecular orbitals (FMOs) constructed from the highest occupied molecular orbital (HOMO) of a_{1u} symmetry and HOMO-1 orbital with a_{2u} symmetry and two degenerate lowest unoccupied molecular orbital (LUMO) of e_g symmetry. Through mixing of the HOMO orbitals by constructive and destructive mode different states are generated and allowing transition upon absorption of suitable amount of energy.

The very distinctive Soret or B band is resulted from the constructive mixing and dominates within the window of 350 nm to 450 nm and the peak intensity very high as the extinction coefficients may reach to the order of $10^5 \text{ M}^{-1} \text{ cm}^{-1}$. The lower energy Q bands appear through destructive mixing and appears in the 500 nm to 700 nm range with extinction coefficients reaching upto $10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Vibrionic coupling separates the Q bands in lower energy Q band (Q0) and higher energy Q band (Q1). The overall symmetry of the system definitely plays an important part as the free base with D_{2h} group is changed to D_{4h} by replacement of the two hydrogens on the opposite nitrogen by a central metal atom. Thus, the two Q bands are further split into four bands designated IV, III, II, and I. between 450 and 700 nm. The intensity and the exact positions of these bands are dependent on the concentration and the solvent. More importantly correlations have been shown to exist between the relative intensities of the four bands and the nature and positions of the porphyrin side chains.¹²

Porphyrins in Nature: The basic ring structure of the porphyrin with a metal atom at the centre appear in many important biological systems with direct or indirect role in the activity of the system. At the centre of activity of numerous proteins which are involved in important biological functions ranging from, transfer and storage of O_2 (hemoglobin and myoglobin) to transfer of electron (cytochrome c, cytochrome oxidase) to capturing

energy (chlorophyll). Although the biomolecules have different function all have porphyrin based fundamental units which include hemes, chlorophylls, vitamin B- 12, and few others.^{10,11,13-18} Heme proteins are a special class of proteins which contain iron porphyrins and perform versatile activities, like O₂ storage and transport (myoglobin and hemoglobin), electron transport (cytochromes b and c), and O₂ activation and utilization (cytochrome P450 and cytochrome oxidase). In the photosynthetic events of plants and bacteria chlorophylls are playing dynamic role having porphyrin ring with central magnesium ion or sometimes without the metal in pheophytins. Vitamin B-12 on the other hand has cobalt and is present in bacteria and animals with a very different role to perform.

Porphyrin ring and other ring like structures are preferred by the nature due to their robust coordination properties as well as fine tune the reactivity of the metal significantly throughout various biochemical events. The versatility of the ligand has been evident from its presence both in all forms of life from animal to vegetable kingdoms so far so they even share the same biosynthetic pathways.

Application: In nature porphyrins and related compounds are abundant performing complex roles ranging from solar energy transduction, electron and molecular transportation and storage, and catalysing multiple complex chemical transformations. Learning from nature, the special and unique photophysical and chemical properties of the ring and related molecules are explored.^{13,15-17,19-21}

During the 20th century, great attention has been paid to the porphyrins and their metal derivatives due to their important biological functions, unique photo-physical properties, and characteristic electronic properties. In recent years, the aforementioned features in conjunction with the high stability of porphyrins have led to applications in molecular electronics (molecule-based materials are used for electronic applications). A number of covalently linked donor-acceptor porphyrin-based assemblies have been studied for opto-electronics, information storage, and solar cells. Also, the photosensitizing properties of porphyrins has led to investigations for use as sensitizers in a variety of medical applications such as photodynamic therapy (PDT), boron neutron capture therapy, radiation therapy, and magnetic resonance imaging (MRI).²⁰

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