

Porphyryns: fascinating molecules with biological significance

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Porphyryns (which comes from the Greek for “purple”) are a ubiquitous class of naturally occurring molecules involved in a wide variety of important biological processes ranging from oxygen transport to photosynthesis, from catalysis to pigmentation changes [1]. The common feature of all these molecules is the basic structure of the porphine macrocycle, which consists of a 16-atoms ring containing

four nitrogen atoms, obtained by linking four tetrapyrrolic subunits with four methine bridges, as shown in Figure 1.

This macrocycle is an aromatic system containing 22 π -electrons, but only 18 of them are delocalized according to the Hückel’s rule of aromaticity ($4n+2$ delocalized π -electrons, where $n=4$). The size of the macrocycle is perfect to bind almost all metal ions and indeed a number of metals (e.g. Fe, Zn, Cu, Ni, and Co) can be inserted in the center of the macrocycle forming metalloporphyryns.

Porphyryn-based fundamental biological representatives include hemes, chlorophylls, vitamin B-12, and several others. Heme proteins (which contain iron porphyryns, see Figure 2) serve many roles, like O_2 storage and transport (myoglobin and

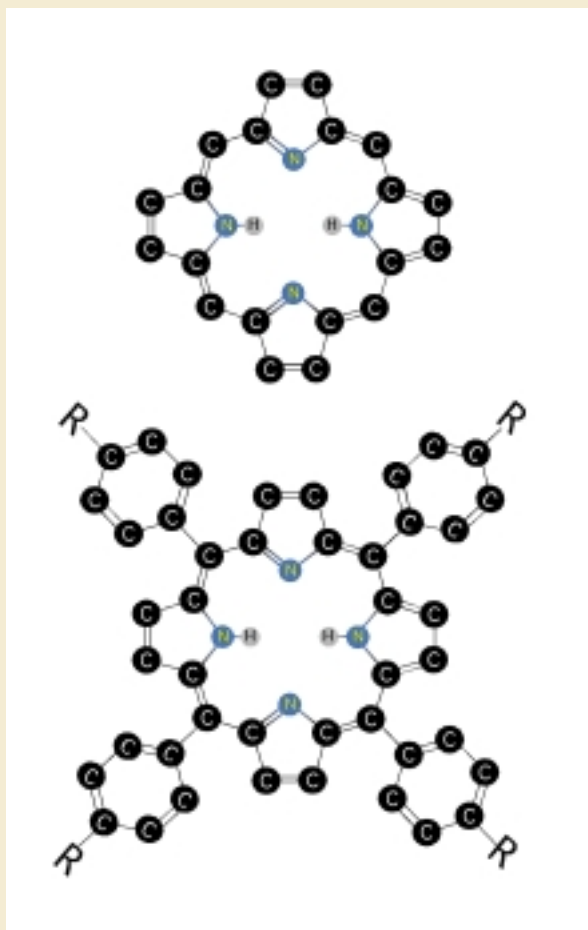


Figure 1. Structure of the porphine macrocycle (top) and of tetraphenylporphyrin (bottom). The hydrogen atoms saturating the carbon bonds are not shown. The R-groups may indicate: alkyl-, alkoxy-, amino-, carboxyl-, carbomethoxyl-, halogeno- and nitro-groups.

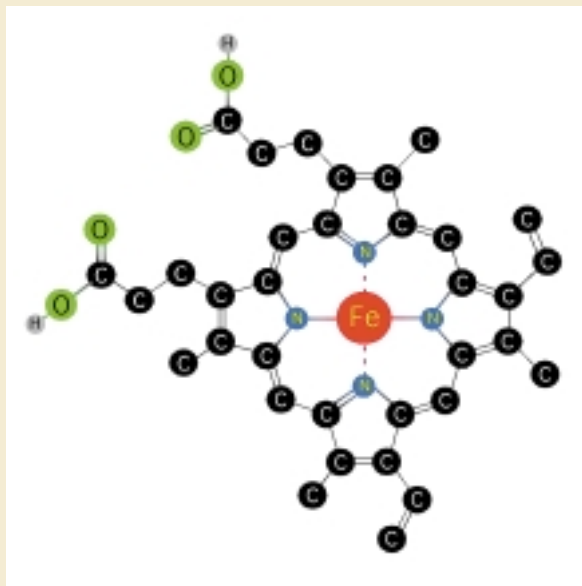


Figure 2. The structure of heme, the ligand-iron porphyrin complex in hemoglobin. The hydrogen atoms saturating the carbon bonds are not shown. Each unit of hemoglobin is composed of four subunits, each containing a heme molecule. Hemoglobin binds O_2 in the lungs and releases it in the tissue. The oxygen molecule binds directly to the iron in the heme as the sixth ligand (above the plane of the heme ring).

hemoglobin), electron transport (cytochromes b and c), and O₂ activation and utilization (cytochrome P450 and cytochrome oxidase). Chlorophylls (which have a central magnesium ion) and pheophytins (which are metal free) are found in the photosynthetic apparatus of plants and bacteria, while vitamin B-12 (which has cobalt) is present in bacteria and animals.

Given the capabilities of porphyrins to bind and release gases and to act as active center in catalytic reactions in biological systems, porphyrin-based films on metal or semiconductor surfaces are extremely appealing as chemical and gas sensors [2] as well as nanoporous catalytic materials [3] in novel synthetic bio-mimetic devices.

Moreover, the role of porphyrins in photosynthetic mechanisms indicates a good attitude of these molecules to mediate visible photon – electron energy transfer processes. As shown in Figure 3, the UV-visible absorption spectrum of the highly conjugated porphyrin macrocycle exhibits an intense feature (extinction coefficient > 200.000) at about 400 nm (the “Soret” band), followed by several weaker absorptions (Q bands) at higher wavelengths (from 450 to 700 nm). While variations of the peripheral substituents on the porphyrin ring often cause minor changes to the intensity and wavelength of the absorption features, protonation of two of the inner nitrogen atoms or the insertion/change of metal atoms into the macrocycle usually strongly change the visible absorption spectrum. For this reason, in recent years, (metallo)porphyrins and porphyrin-metal interfaces have become of major interest for applications in opto-electronics, data storage and solar

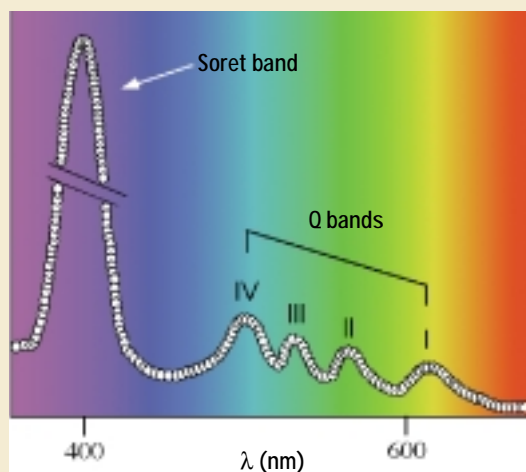


Figure 3. Typical UV-visible absorption spectrum of porphyrins [1].

cells [4] and a still increasing number of covalently linked donor-acceptor supramolecular porphyrin-based assemblies have been studied for these purposes [5].

In conclusion, the involvement of porphyrins in many biological processes and the possibility to tailor their physical and chemical properties at the molecular level – including very large dipole moments, polarizability, non-linear optical response, absorption spectrum, energy transfer and catalytic properties – make porphyrins and metalloporphyrins extremely versatile synthetic base materials for research projects in many disciplines of chemistry and physics, like electronics, opto-electronics, electrochemistry, catalysis and photophysics.

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