

Absorption and Fluorescence Spectroscopy of Tetraphenylporphyrin[§] and Metallo-Tetraphenylporphyrin

Introduction

The word *porphyrin* is derived from the Greek *porphura* meaning purple, and all porphyrins are intensely coloured¹. Porphyrins comprise an important class of molecules that serve nature in a variety of ways. The Metalloporphyrin ring is found in a variety of important biological system 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 synthesized are the basic structure of biological porphyrins which are the active sites of numerous proteins, whose functions range from oxygen transfer and storage (hemoglobin and myoglobin) to electron transfer (cytochrome c, cytochrome oxidase) to energy conversion (chlorophyll). They also have been proven to be efficient sensitizers and catalyst in a number of chemical and photochemical processes especially photodynamic therapy (PDT). The diversity of their functions is due in part to the variety of metals that bind in the “pocket” of the porphyrin ring system (Fig. 1).

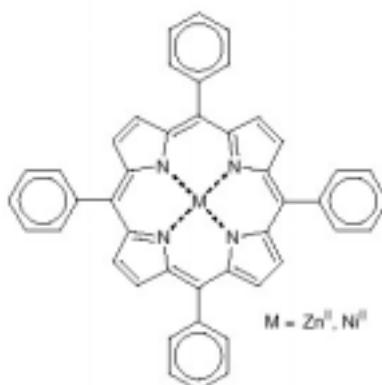


Figure 1. Metallated Tetraphenylporphyrin

Upon metalation the porphyrin ring system deprotonates, forming a dianionic ligand (Fig. 2). The metal ions behave as Lewis acids, accepting lone pairs of electrons

[§] We all need to thank Jay Stephens for synthesizing the H₂TPP

from the dianionic porphyrin ligand. Unlike most transition metal complexes, their color is due to absorption(s) within the porphyrin ligand involving the excitation of electrons from π to π^* porphyrin ring orbitals.

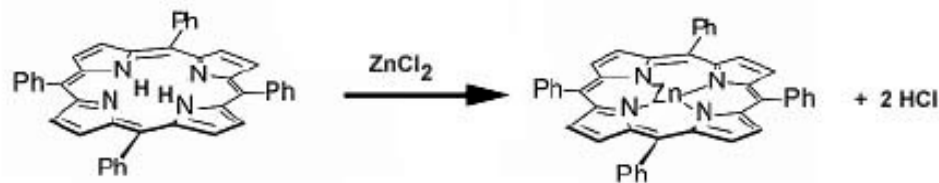


Figure 2. Synthesis of Zn(TPP)

The electronic absorption spectrum of a typical porphyrin consists of a strong transition to the second excited state ($S_0 \rightarrow S_2$) at about 400 nm (the Soret or B band) and a weak transition to the first excited state ($S_0 \rightarrow S_1$) at about 550 nm (the Q band). Internal conversion from S_2 to S_1 is rapid so fluorescence is only detected from S_1 . The B and the Q bands both arise from π - π^* transitions and can be explained by considering the four frontier orbitals (HOMO and LUMO orbitals) (the Gouterman four orbital model)

Gouterman Four-Orbital Model

Martin Gouterman first proposed the four-orbital model in the 1960s to explain the absorption spectra of porphyrins¹. According to this theory, the absorption bands in porphyrin systems arise from transitions between two HOMOs and two LUMOs, and it is the identities of the metal center and the substituents on the ring that affect the relative energies of these transitions (Figure 3 and 4). Mixing splits these two states in energy, creating a higher energy $1 e_u$ state with greater oscillator strength, giving rise to the Soret band, and a lower energy $1 e_u$ state with less oscillator strength, giving rise to the Q-bands.

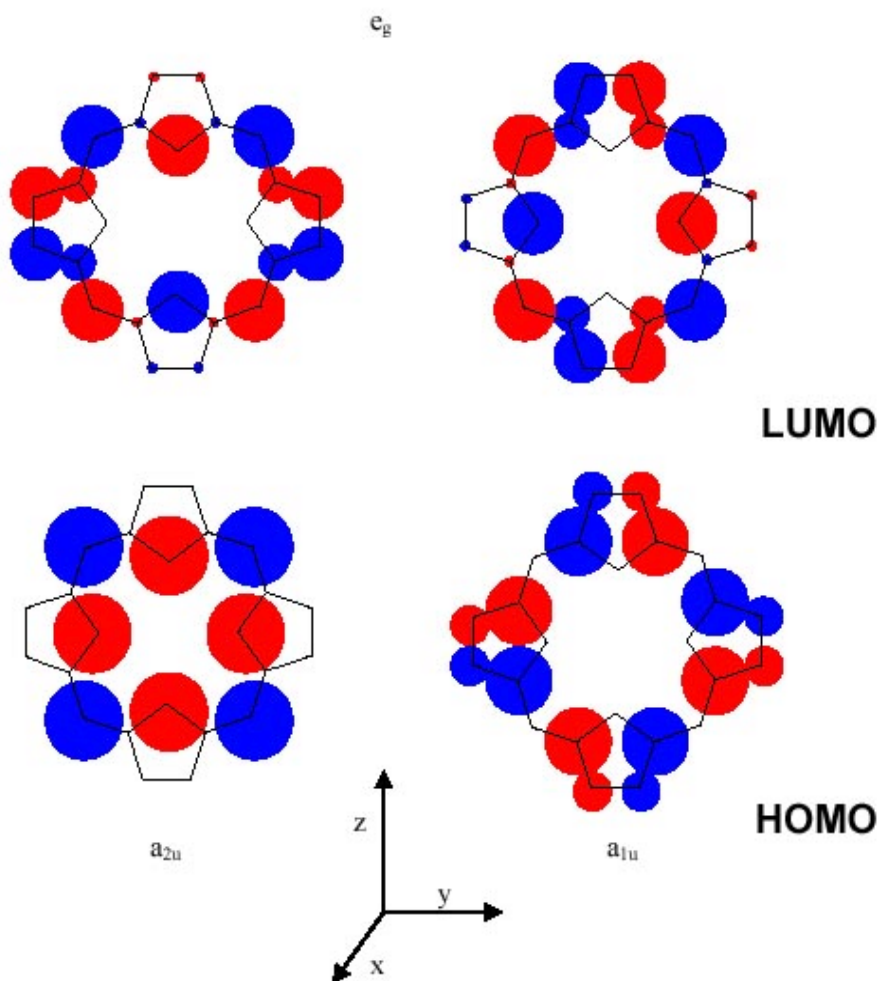


Figure 3. The Frontier Orbitals relevant to the Gouterman Four-Orbital Model

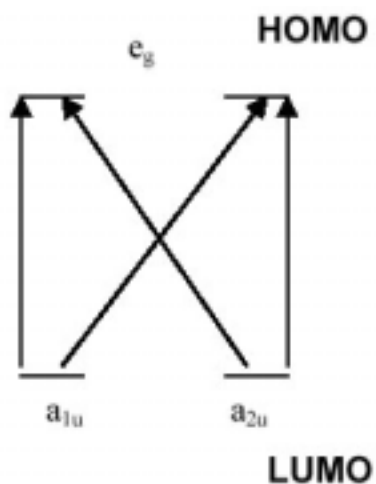


Figure 4. Orbital diagrams showing possible transitions for porphyrins. Note that while the HOMOs are shown to be degenerate in both cases, the actual relative energies will depend on the substitution of the rings.

Electronic Spectra

Metalloporphyrins can be divided into two groups based on their UV-vis and fluorescence properties². *Regular* metalloporphyrins contain closed-shell metal ions (d^0 or d^{10})—for example Zn^{II} , in which the $d\pi$ (d_{xz} , d_{yz}) metal-based orbitals are relatively low in energy. These have very little effect on the porphyrin π to π^* energy gap in porphyrin electronic spectra (Fig. 5). *Hypsoporphyrins* are metalloporphyrins in which the metals are of d^m , $m = 6-9$, having filled $d\pi$ orbitals. In hypso-porphyrins there is significant metal $d\pi$ to porphyrin π^* orbital interaction (metal to ligand π -backbonding) [Figure 6]. This results in an increased porphyrin π to π^* energy separation causing the electronic absorptions to undergo hypsochromic (blue) shifts.

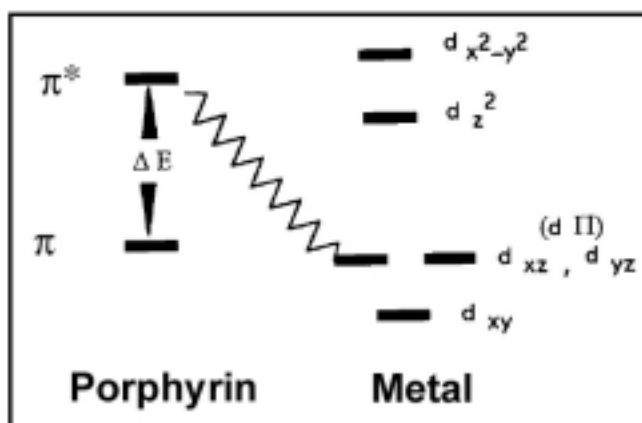


Figure 5. Molecular Orbital Diagram for metalloporphyrins. Interactions between $d\pi$ and π^* occur in hypso-porphyrins.

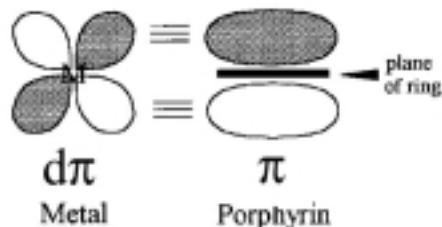


Figure 6. The $d\pi$ metal orbital overlap with the π system of the porphyrin ring.

The lowest energy excited singlet states of porphyrins can be thought of as being formed from the molecular orbitals you examined above. An excited singlet state with an $a_{1u}e_g$ configuration is formed by promoting an electron from the a_{1u} orbital to an e_g orbital. Likewise, an excited singlet state with an $a_{2u}e_g$ configuration is formed by promoting an

electron from the a_{2u} orbital to an e_g orbital. These excited singlet states mix to two new singlet states that are nearly 50:50 mixtures of the unmixed states. The closer in energy the unmixed states, the greater the degree of mixing.

An electronic transition to the higher energy mixed state, the S_2 state, is strongly allowed, whereas an electronic transition to the lower energy mixed state, the S_1 state, is only weakly allowed. The band in the uv-vis absorption spectrum due to a transition to the S_2 state is the Soret band, and the band due to a transition to the vibrationless S_1 state is the α band. The greater the degree of mixing, the less intense the α band relative to the Soret band.

In the UV-visible spectrum of porphyrin, there is also a vibronic band, the β band, that appears at slightly lower wavelengths than the α band. The β band is due to transitions to higher vibrational levels in the S_1 state and serves as a "normalization band" in porphyrin absorption spectra. As a result, the intensity of the α band relative to the β band can serve as a measure of how close in energy the a_{2u} and a_{1u} orbitals are to each other. For example, if the a_{2u} and a_{1u} orbitals have essentially the same energy, the degree of mixing will be large, the α intensity will be small, and, therefore, the α/β intensity ratio will be small. On the other hand, if the a_{2u} and a_{1u} orbitals are well separated in energy, the degree of mixing will be smaller, and the α/β intensity ratio will be larger³.

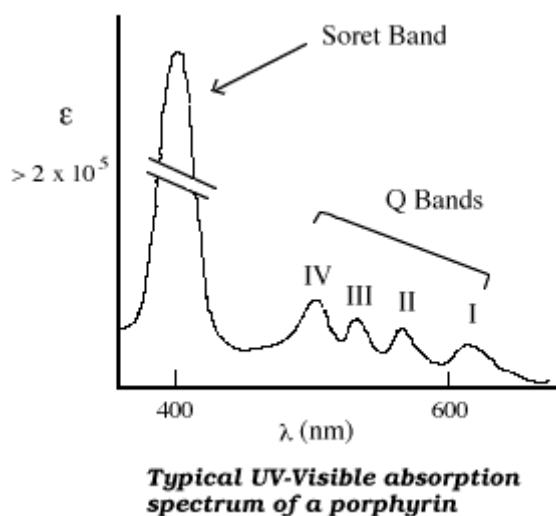


Figure 6.

Experimental

UV-Visible Spectrum

Record the Absorption Spectra of H_2TPP , TPP^{2-} , $\text{Zn}(\text{TPP})$ and $\text{Ni}(\text{TPP})$ solutions (N,N-Dimethylformamide, DMF solvent) between 300 and 900 nm using the provided solutions (to measure the Soret band). Then using record the α and β spectra between 450 and 900 nm using a solution of appropriate concentration. Save your data and with Excel convert the y-axis from absorbance to molar absorptivity. NOTE: the molar absorptivities are written on the bottle of each compound^{4,5,6,7}.

Fluorescence Spectrum⁸

Record the Excitation and Emission Spectra of deoxygenated (bubble N_2 gas into the solution for 2-3 min). DMF solutions of H_2TPP , TPP^{2-} , $\text{Zn}(\text{TPP})$ and $\text{Ni}(\text{TPP})$ using both the Soret band and the first β band (the first Q-band for H_2TPP). Record the excitation and emission spectrum of a solution of $\text{Zn}(\text{TPP})$ solution that has not been purged with N_2 .

Calculations and Comparisons:

Provide a table for the absorption spectra, including the positions of all peaks and their respective molar absorptivities. Label each peak with the appropriate designation (configuration and type, *ex.* $2 e_g \leftarrow a_{2u}$ and Soret)

Using the spectral results and your previous computational results (summarized on the last page of the lab:

Discuss the differences between the absorption spectra of the $\text{H}_2(\text{TPP})$, TPP^{2-} and the $\text{Zn}(\text{TTP})$. What changes result from deprotonation and metallation?

Convert the wavelengths for each peak in the spectra of $\text{H}_2(\text{TPP})$ and the $\text{Zn}(\text{TTP})$ and $\text{Ni}(\text{TPP})$ into kJ/mol. Likewise convert the energies of the HOMO, HOMO-1, LUMO and LUMO+1 from eV to kJ/mol.

The Gouterman Model suggests that the observed transitions in the absorption spectra arise from : $2 e_g \leftarrow a_{1u}$ and $2 e_g \leftarrow a_{2u}$ transitions. How closely do the observed energies (from the absorption spectra of each compound) compare with those calculated at the AM1 level of theory?

From the absorbance values at the α and β peak maxima, determine the α/β intensity ratio. Based on how this ratio changes upon metallation, state whether the a_{1u} or the a_{2u} orbital is higher in energy in Zn(TPP) and Ni(TPP). Compare the experimental results to your computational results.

Are there more or less peaks in the spectrum of Zn(TPP) and TPP^{2-} when compared to H_2TPP ? Why? [Hint: A general rule in spectroscopy: A simpler spectrum results from molecules with higher symmetry.]

How are the absorption spectra of Ni(TPP) and Zn(TPP) different? How can you account for the difference?

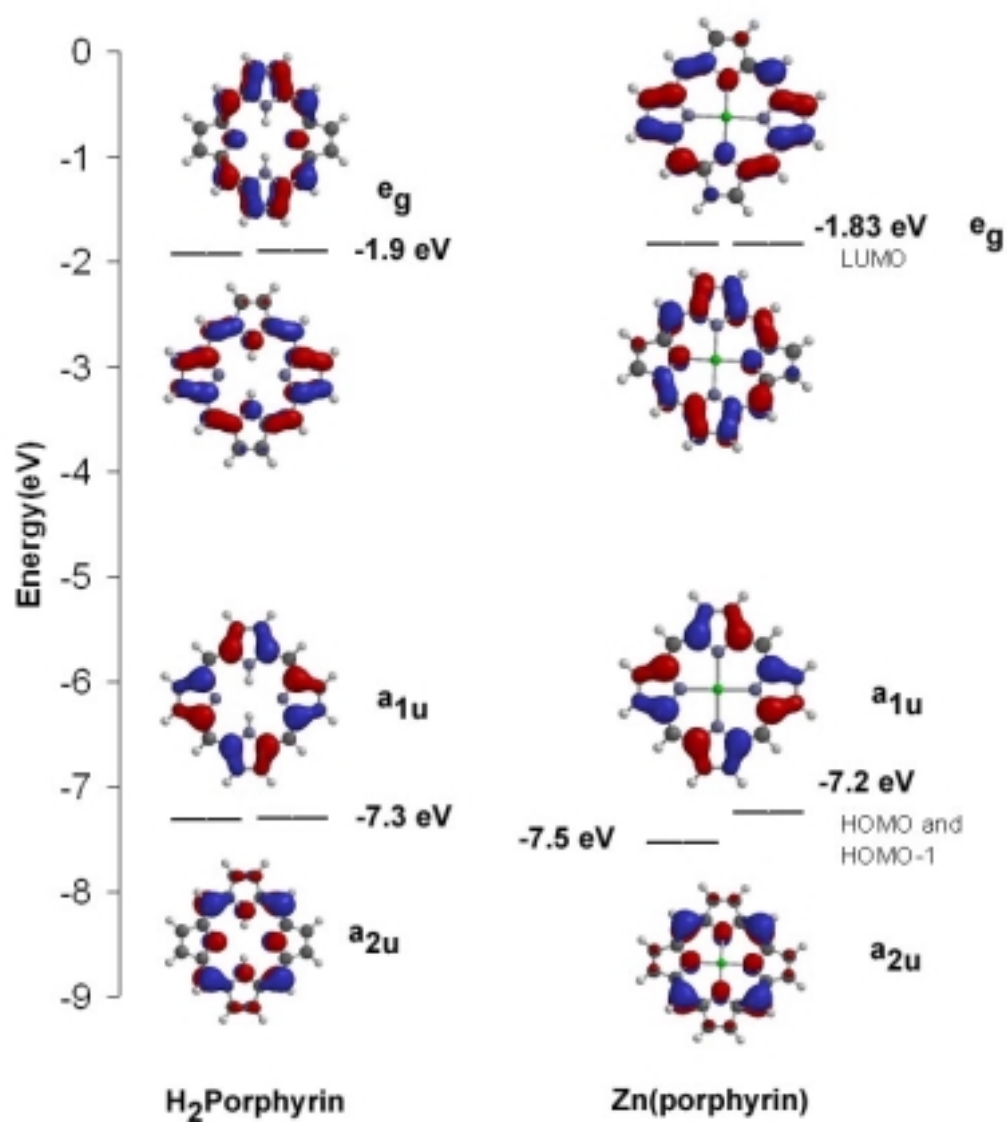
Construct a table with summarizes the luminescence spectra results. Include the excitation wavelengths and the positions of the emission peaks.

Was there a substantial difference between the fluorescence spectrum of the deoxygenated Zn(TPP) solution and the Zn(TPP) solution that was air saturated? How do you account for this behavior?

Discuss the similarities and differences in the excitation and emission spectra of the porphyrin compounds. Are all of the compounds luminescent? If No, Explain why.

What are the differences in luminescence (relative to H_2TPP) upon deprotonation and metallation with Zn(II) and with Ni(II).

Porphrin Molecular Orbitals (AM1 level)



References:

- ¹ L. R. Milgrom, *The Colours of Life: An Introduction to the Chemistry of Porphyrins and Related Compounds*, OUP, Oxford, 1997; *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 1978.
- ² D. F. Marsh and L. M. Mink, "Microscale Synthesis and Electronic Absorption Spectroscopy of Tetraphenylporphyrin H₂(TPP) and Metalloporphyrins Zn^{II}(TPP) and Ni^{II}(TPP)", *J. Chem. Ed.*, **73**, 1181, 1996
- ³ <http://www.molecules.org/experiments/Walters/Walters.html>
- ⁴ G. H. Barnett, M. F. Hudson, and K. M. Smith, "Concerning meso-tetraphenylporphyrin purification," *J. Chem. Soc. Perkin Trans. I*, 1401-1403, 1975
- ⁵ J. Spencer Baskin, Hua-Zhong Yu and Ahmed H. Zewail, *J. Phys. Chem. A* **2002**, *106*, 9837-9844.
- ⁶ Hua-Zhong Yu, J. Spencer Baskin, and Ahmed H. Zewail. *J. Phys. Chem. A* **2002**, *106*, 9845-9854
- ⁷ Harriman, "Luminescence of porphyrins and metalloporphyrins. Part 1. - Zinc(II), nickel(II) and manganese(II) porphyrins.," *J. Chem. Soc., Faraday Trans. I*, 76, 1978-1985, 1980.
- ⁸ The quantum yield is 0.033 [J. P. Strachan, S. Gentemann, J. Seth, W. A. Kalsbeck, J. S. Lindsey, D. Holten, and D. F. Bocian, "Effects of orbital ordering on electronic communication in multiporphyrin arrays," *J. Am. Chem. Soc.*, 119, 11191-11201, 1997.

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

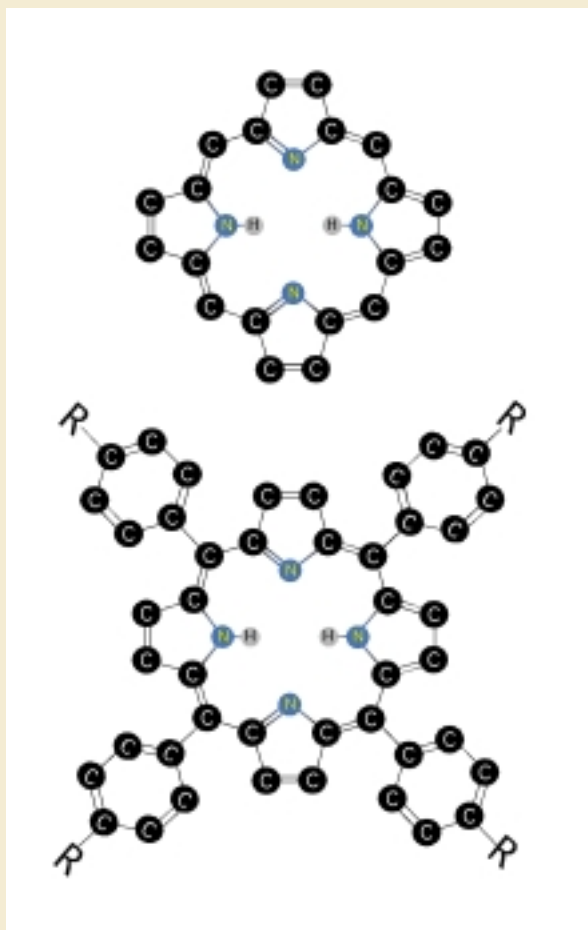


Figure 1. Structure of the porphine macrocycle (top) and of tetraphenylporphyrin (bottom). The hydrogen atoms saturating the carbon bonds are not shown. The R-groups may indicate: alkyl-, alkoxy-, amino-, carboxyl-, carbomethoxyl-, halogeno- and nitro-groups.

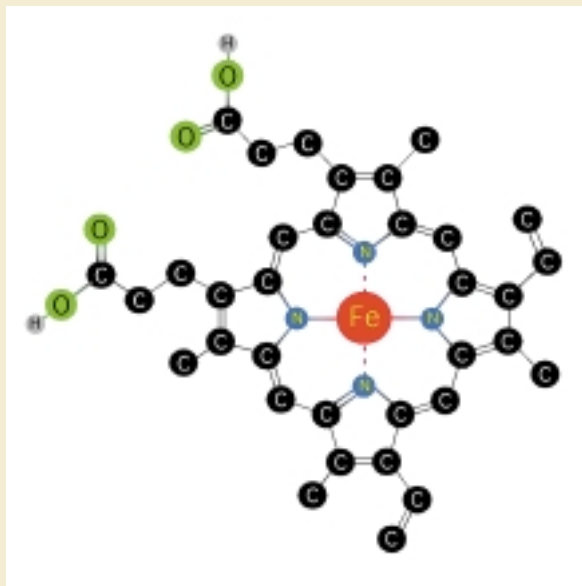


Figure 2. The structure of heme, the ligand-iron porphyryn complex in hemoglobin. The hydrogen atoms saturating the carbon bonds are not shown. Each unit of hemoglobin is composed of four subunits, each containing a heme molecule. Hemoglobin binds O_2 in the lungs and releases it in the tissue. The oxygen 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

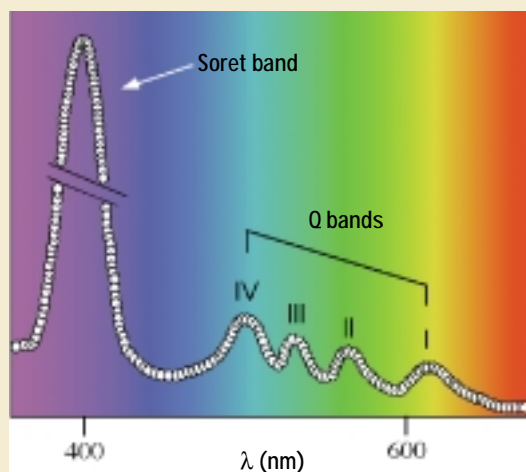


Figure 3. Typical UV-visible absorption spectrum of porphyrins [1].

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.

References

- [1] K. M. Smith, *Porphyrins and Metalloporphyrins*, Ed. (Elsevier, Amsterdam, 1975), M. Boulton et al., *J. Photochem. & Photobiol. B: Biology*, 64, 144, (2001), E.I. Sagun et al., *Chem. Phys.*, 275, 211, (2002)
- [2] J.P. Collman et al., *Metal Ions in Biology*, Vol. 2, T.G. Spiro Ed., Wiley, NY, 1 (1980), M.A. Schiavon et al., *J. Molecular Catalysis A*, 174, 213, (2001), T.H. Richardson et al., *Thin Solid Films*, 393, 259, (2001)
- [3] K.S. Suslick, et al., “Shape Selective Oxidation Catalysis” in *Comprehensive Supramolecular Chemistry*, Vol. 5, K.S. Suslick Ed., Elsevier, Oxford, 141 (1996), P. Bhyrappa et al., *J. Am. Chem. Soc.*, 118, 5708, (1996), J.A.A. Elemans et al., *Org. Chem.* 64, 7009, (1999)
- [4] K. Yamamshita et al., *J. Phys. C: Solid State Phys.*, 93, 5311, (1989), G. Stegeman and P. Likamwa, *Nonlinear Optical Materials and Devices for Applications in Information Technology*, A. Miller, K.R. Welford, B. Daino Eds., (Kluwer, The Netherlands, 1995), J. Chen et al., *Science*, 286, 1550, (1999), A. Tsuda and A. Osuka, *Science*, 293, 79, (2001)
- [5] D. Gust et al., *Topics in Current Chemistry*, 159, 103, (1991), M.R. Wasielewski, *Chem. Rev.*, 92, 435, (1992), W. Han et al., *J. Phys. Chem. B*, 101, 10719, (1997), G. Stainberg-Yfrach et al., *Nature*, 392, 479, (1998)

