

A Study of Closed vs. Open Shell Transition Metal Porphyrin Complexes

Transition metals play a critical role in a myriad of biological processes. Their ions and complexes serve as structural supports, electron transfer relays, oxygen transport and storage depots, and catalytic centres. Coenzyme B₁₂ (Figure 1) and its derivatives are prototypical examples of bioinorganic complexes constructed from a porphyrin (or more specifically a corrole) type ring system. These represent rare examples of cobalt based enzymes as cobalt is the rarest of the first-row transition metals. "Model" compounds mimicking such chemistry have served to further our understanding of many of these complex systems. Porphyrins are a class of macrocyclic nitrogen-containing pigments essential in nature and biology to which molecules such as heme (which forms an integral part of haemoglobin), vitamin B12, cytochrome P-450 and chlorophyll (photosynthesis) belong.

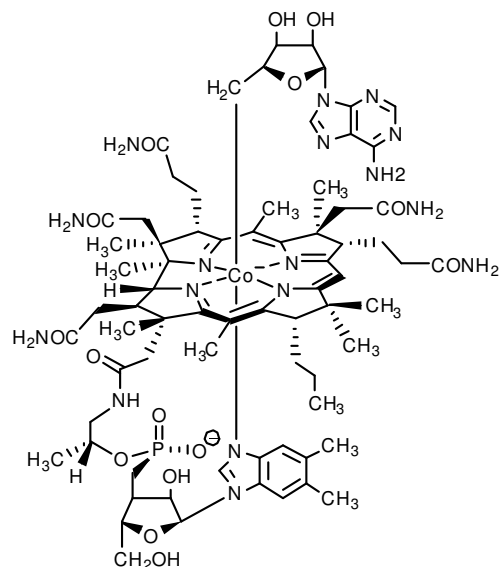


Figure 1. The naturally occurring organometallic coenzyme B₁₂ complex

All porphyrins have the ability to complex metal ions, the simplest of which being the skeletal porphine ring (Figure 2). This core ring system is planar and contains 18 delocalizable π -electrons which make it aromatic according to the Hückel rules. Porphyrins are intensely coloured materials with distinct absorption features. The name porphyrin is actually derived from the Greek word '*porphura*' meaning purple. Metalloporphyrins can be classed as either regular or irregular; the former displaying optical absorption and emission spectra determined essentially by the π -electrons of the porphyrin ring, with only minor perturbation from the electrons of the central metal ion substituent. Irregular porphyrins display extensive interaction between the π -electrons of the porphine ring and the electrons of the central metal ion.

The electronic absorption spectrum of a typical regular porphyrin such as zinc(II)-5,10,15,20-tetraphenylporphyrin (ZnTPP) consists of several π - π^* absorption bands. The closed shell Zn(II) metal ion causes weak perturbations to the porphine ring π -orbitals and their absorption spectra. Two weak transitions to the first excited singlet state ($S_0 \rightarrow S_1$) occur in the region 500-600 nm and are commonly known as the 'Q' bands (Q – quasi allowed). The lowest-energy transition is attributed to the lowest singlet excited state and is denoted by Q(0,0). The higher-energy band at relatively constant energy separation from Q(0,0) is its vibrational overtone (higher by about one mode of vibrational excitation, c.a. 1250 cm^{-1}) and is denoted by Q(1,0). A strong transition to the second excited state ($S_0 \rightarrow S_2$) known as the 'Soret' band occurs in the region of ~ 420 nm and is denoted by B(0,0). High resolution spectra in the vapour phase or at low temperature show another band about 1250 cm^{-1} to the blue; it is attributed to addition of one mode of vibrational excitation and is denoted by B(1,0). Internal conversion from S_2 to S_1 is rapid so fluorescence is only detected from the $S_1 \rightarrow S_0$ relaxation process. Theoretical analysis of the Soret

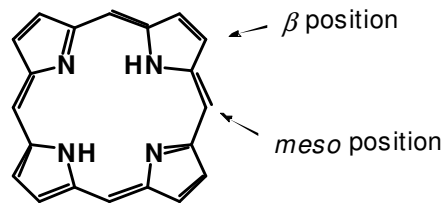
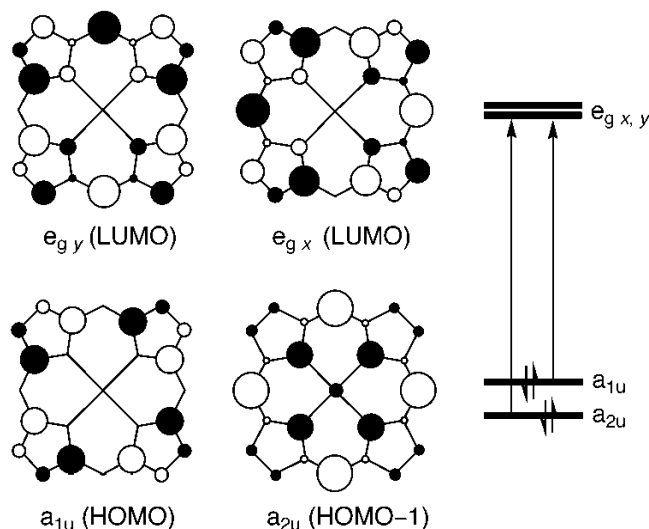


Figure 2. The free-base porphine ring with *meso*- and β -positions labelled (ring protons are omitted for clarity).

and Q bands has shown that they arise from π - π^* transitions and can be explained by considering the four frontier orbitals using Gouterman's four orbital model (Scheme 1).

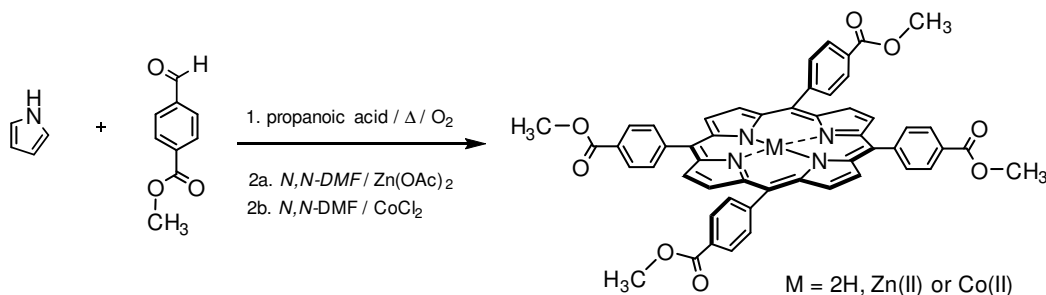
This model describes the low-lying π - π^* excited states of porphyrins in terms of the electronic transitions between the two highest occupied molecular orbitals a_{1u} and a_{2u} (HOMO and HOMO-1) to the two degenerate lowest energy unoccupied molecular orbitals e_g (LUMOs). For a porphyrin system with D_{4h} symmetry, the e_g orbitals are strictly degenerate whereas the a_{1u} and a_{2u} orbitals are non-degenerate. The electronic configuration of a ground state porphyrin is ${}^1A_{1g}$ ($a_{1u}^2 a_{2u}^2$). Accordingly, the lowest singlet excited configurations are $a_{2u}^1 e_g^1$ and $a_{1u}^1 e_g^1$. One might envision that this would lead to two absorption bands



Scheme 1. The frontier orbitals of a regular metalloporphyrin.

of very similar energy due to the $a_{1u} \rightarrow e_g$ and $a_{2u} \rightarrow e_g$ transitions however the near degenerate nature of these singlet states causes a strong configuration interaction. The resulting resonance yields the relatively weak visible Q(0,0) band, in which the transition dipoles of the two configurations are deconstructive, and the intense Soret B(0,0) band, in which the transition dipoles of the two configurations are constructive (the Q band is actually forbidden in nature however it can "borrow" intensity by vibronic coupling from the intense Soret band). The closer the energy of the configurations $a_{2u}^1 e_g^1$ and $a_{1u}^1 e_g^1$, the weaker is the Q(0,0) band. In free base and closed shell metalloporphyrins, possible transitions are confined to the delocalised π -system of the core porphine ring. The presence of open shell transition metal ions in the porphyrin core can lead to additional transitions. MLCT (d - π^*) transitions can occur between the highest occupied metal d orbital and the empty e_g orbital on the porphyrin, LMCT (π - d) transitions can occur from the a_{1u} and a_{2u} orbitals of the porphyrin to the empty d orbitals on the metal. Also, ligand field (d - d) transitions can occur via promotion of electrons within the metal d -orbital manifold. This experiment involves the synthesis of closed and open shell porphyrin complexes and photophysical characterization thereof.

Synthesis



Scheme 2. Synthesis of the free-base (1), zinc (2a) and cobaltous (2b) porphyrins.

Due to the pungent nature of propanoic acid all procedures in this synthesis should be kept inside of a well ventilated fumehood and generated waste be disposed of in a properly labelled waste container.

1. Synthesis of the porphyrin free base.

A 5-ml reaction flask will be provided by the lab instructor containing a pre-weighed quantity of methyl 4-formylbenzoate (~236 mg). To this flask add 4 ml of propanoic acid (b.p. = 141 °C) followed by 100 µl of freshly distilled pyrrole. Place a small stirring bar into the flask and reflux for at least 30 minutes. Cool the mixture to room temperature. Add the reaction mixture to 5 ml of methanol and cool in an ice bath for 5-10 min. Collect the deep violet precipitate by vacuum filtration using a Hirsch funnel. Wash with methanol and dry the product by aspiration. Record the yield and store the solid in a sealed pre-weighed glass vial.

2a/2b. Porphyrin complexation with zinc(II) and cobalt(II)

Into a 5-ml reaction flask carefully add 50 mg of H₂TPP, and 1.5 equivalents of zinc(II) acetate dihydrate (2a) or cobalt(II) chloride hexahydrate (2b). To this mixture add 2 ml of *N,N*-dimethylformamide. Reflux for 20 minutes with stirring. Remove from the heat and cool in an ice bath for 5 minutes. Add 5 ml of water to the mixture and collect the resulting solid by vacuum filtration. Dry by sequential methanol and diethyl ether washes. Record the yields for 2a and 2b and store each solid in a sealed pre-weighed glass vial.

Qualitative Analysis.

Record the UV-vis absorption and fluorescence emission spectra of the Zn(II) and Co(II) metallated porphyrin products using toluene as a solvent.

Lab Report.

1. Submit your sample, clearly labelled with the names of all group members participating in the preparation. Your written report should include a statement of milligrams product(s) obtained, balanced chemical equations for all reactions carried out and percent yield calculations. Describe any unexpected results, departures from the procedure and any noteworthy observations.
2. In your introduction discuss the relevance of the porphyrin macrocycle and its first-row transition metal complexes in biological systems.
3. Using ChemDraw present molecular representations of the free base and metallated complexes and assign their point group symmetries.
4. To develop your lab report abstract/discussion etc. construct a hypothesis based upon the comparison of open and closed shell metalloporphyrins to investigate regular and irregular porphyrin systems according to Gouterman's four orbital model.
5. Give a basic qualitative description of Gouterman's four orbital model. Construct two simple energy level schemes using ChemDraw to show Gouterman's four orbital model inclusive of both Zn(II) and Co(II) *d*-shells respectively [Hint: use the point group assignments to predict degeneracy in the 4*d* subshell and assume all 4*d*-orbitals lie within the π and π* orbitals of the porphyrin ring.]
6. Using the schemes developed in (4) discuss the observed UV-vis electronic absorption and fluorescence emission spectra for both closed shell and open shell porphyrin systems.