Microscale Preparation of *meso*-Tetraphenylporphyrin and its Fe(III) Complex[1]

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 centers. "Model" compounds mimicking such chemistry have served to further our understanding of many of these complex systems. Porphyrins are a class of macrocylic nitrogen containing pigments essential in nature and biology to which molecules such as *heme* (which forms an integral part of hemoglobin) and *chlorophyll* (photosynthesis) belong. All porphyrins have the ability to complex metal ions, the simplest one being the periphally unsubstituted porphine ring (Fig. 1). The ring system is planar, contains 18 delocalizable π electrons which makes the compound aromatic in character, according to the Hückel rule.

Porphyrins are intensely coloured materials with distinct absorption features. The word '*porphyrin*' is actually derived from the Greek word '*porphura*' meaning purple. Metalloporphyrins can be classed as either regular or irregular and, in terms of their absorption, into three categories: normal, hypso and hyper. Hypso absorption spectra are blue shifted with respect to normal porphyrins and hyper absorption spectra show prominent extra absorption bands in the region $\lambda > 320$ nm. A regular porphyrin is one whose optical absorption and emission spectra are determined essentially by the π electrons of the porphyrin ring, with only minor perturbation from the electrons of the central metal ion substituent. In irregular porphyrins there is extensive interaction between the π-electrons of the porphine ring and the electrons of the central metal ion and its ligands.
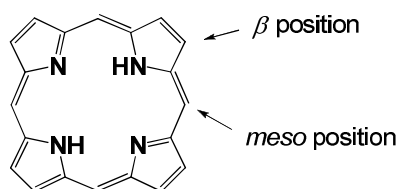

Figure 1. The porphine ring with the *meso* and β positions labelled.

The electronic absorption spectrum of a typical regular porphyrin such as Zn-TPP consists of several bands (closed shell metal ions cause weak perturbations to the porphine ring π-orbitals and their absorption spectra in general are of the normal type). Two weak transitions to the first excited 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 400 - 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 emission is only detected from S_1.

Theoretical analysis of the Soret and Q bands has shown that they arise from $\pi-\pi^*$ transitions and can be explained by considering the four frontier orbitals using Gouterman's four orbital model. This model describes the low-lying $\pi-\pi^*$ excited states of porphyrins in terms of the 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 molecule with D_{4h} symmetry, the orbitals e_g 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 $^1(a_{2u}{}^1 e_g{}^1)$ and $^1(a_{1u}{}^1 e_g{}^1)$. One might envision that this would lead to two absorption bands 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 strong electron interaction between them. 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 $^1(a_{2u}{}^1 e_g{}^1)$ and $^1(a_{1u}{}^1 e_g{}^1)$, 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 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 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 a ferric porphyrin complex. These 'heme' models can be used to illustrate the effect of the axial ligands on spin state and redox chemistry.

Microscale preparation of meso-tetraphenylporphin (H₂TPP)
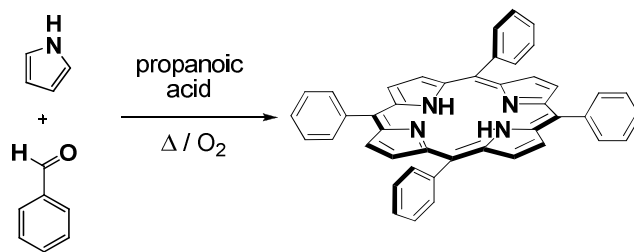
Perform this reaction a fumehood! A 50 cm^3 round bottomed flask is charged with 25 cm^3 of propanoic acid, 0.010 mol of pyrrole and 0.010 mol of benzaldehyde. Place a small stirring bar into the flask and assemble the apparatus for reflux by fitting with a reflux condenser. Heat the reaction vessel and allow to reflux for 30 minutes. Cool the mixture to room temperature and collect the deep violet coloured compound by suction filtration using a Hirsch funnel (fumehood!). Wash the deep purple product with 1 cm^3 portions of methanol until the washings are colourless. Dry the product by aspiration and record the yield. **WASTE DISPOSAL:** *The filtrate and any methanol washings should be placed in a labelled organic waste container in the hood.*

Microscale preparation of meso-tetraphenylporphyrin iron chloride [FeTPP(Cl)]

The iron porphyrin is conveniently prepared from the free-base porphyrin by a scaled-down, modified version of the procedure reported by Adler et al.[10] Into a 25 ml round bottom flask carefully add 100 mg of H_2TPP, and 1.5 equivalents of ferric chloride tetrahydrate. To this mixture add 5 cm^3 of *N,N*- dimethylforamide, and two pieces of boiling aid. Assemble reflux apparatus and bring to reflux for 10 minutes. Remove from the heat and allow to cool in an ice bath for 5 – 10 minutes. Add 5 cm^3 of water to the mixture along with 1 mL of 6 M HCl and collect the resulting solid by vacuum filtration on a sintered glass funnel. The dark brown-purple solid is washed with water until the filtrate is colorless and aspirated to dryness. Typically, isolated crude yields are greater than 90%. **WASTE DISPOSAL:** *The initial filtrate should go in container labelled aqueous waste in the hood.*

Purification and Characterization

Purify a small amount of the metallated complex by column chromatography using a pasteur filter pipette chromatography column as follows: into a glass pasteur pipette carefully place a small plug of cotton wool. Also place about 4 cm of alumina (fumehood!) in the column. Clamp the pipette upright. Use a small test tube to collect a pure fraction of the metallated TPP. To assist the flow of eluent, a rubber pasteur pipette teat may be used to apply slight pressure to the column, taking care to avoid suck back effects. This technique utilises the essential aspects of flash chromatograph (see instructor for directions). Record the UV-Vis spectrum of both the free base and metallated porphyrin products in dichloromethane.

Questions:

1. Draw a molecular representation of the metallated Fe-TPP(Cl) complex.

2. State the point group of H_2TPP and Fe-TPP(Cl).

3. Predict what reaction would take place between Fe-TPP(Cl) and $AgNO_3$ in the presence of a Lewis base such as pyridine.

4. Give three examples of the porphyrin macrocylce in nature and/or biology with a brief description of its role in each case (including the role of the metal involved).

References

1   (a) Adler, *J. Org. Chem.* **1967**, 32, 476. (b) Adler, *J. Am. Chem. Soc.* **1975**, 97, 5107. (c) Adler, *J. Inorg. Nucl. Chem.* **1970**, 32, 2443.