

Microscale Synthesis and Electronic Absorption Spectroscopy of Tetraphenylporphyrin $H_2(TPP)$ and Metalloporphyrins $Zn^{II}(TPP)$ and $Ni^{II}(TPP)$

Diane F. Marsh

Department of Chemistry, Riverside Community College, Riverside, CA 92506

Larry M. Mink

Department of Chemistry, California State University, San Bernardino, CA 92407

Metalloporphyrin complexes play significant roles in many biological and catalytic systems. 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). The study of porphyrins is well-suited to college and university laboratories because of their importance and several other reasons. Specifically, their synthesis involves a range of basic techniques. In addition, their high extinction coefficients require only very small quantities of product to give suitable spectra, making them amenable to current microscale methods. Interpretation of their spectra offers an introduction to molecular orbitals, molecular symmetry, and fluorescence.

Experiments have been reported for the synthesis of $H_2(TPP)$ and the iron and zinc complexes, but these require relatively large quantities of materials and solvents. For example, 300 to 500 mL of propionic acid per student was reduced to 12 mL per student in the presented microscale preparation (1, 2).

Metalloporphyrins can be divided into two groups based on their UV-vis and fluorescence properties (3). *Regular* metalloporphyrins contain closed-shell metal ions (d^0 or d^{10})—for example Zn^{II} , in which the d_π (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. 2). *Hypsoporphyrins* are metalloporphyrins in which the metals are of d^m , $m = 6-9$, having filled d_π orbitals. In hypso-porphyrins there is significant metal d_π to porphy-

rin π^* orbital interaction (metal to ligand π -backbonding). This results in an increased porphyrin π to π^* energy separation causing the electronic absorptions to undergo hypsochromic (blue) shifts.

Procedure

Synthesis of Tetraphenylporphyrin, $H_2(TPP)$ (4)

A 25-mL round-bottom flask fitted with a water condenser is heated in a sand bath or heating mantle. Propionic acid, 12 mL, is added to the flask and brought to reflux ($\approx 141^\circ C$). To the refluxing propionic acid 0.06 mL of benzaldehyde is added using an 0.1-mL graduated pipette. Pyrrole, 0.04 mL, from a freshly opened bottle or distilled at low pressure (30–40 mmHg) within a few days of use, is also added using a pipette. The color darkens to orange-yellow and becomes dark brown-black as the reaction proceeds. The reaction mixture is refluxed for a total of 30 min. After cooling to room temperature, the mixture is added to a flask containing 10 mL of methanol. This is chilled in an ice bath with stirring. Crystallization is induced by scratching the sides of the flask with a glass rod. The deep-purple crystals are filtered using a Büchner or Hirsch funnel. The crystals are washed with three 0.5-mL portions of methanol and three 0.5-mL portions of boiling-hot distilled water. The crystals are air-dried on the filtration funnel and stored in a vacuum desiccator over a drying agent until the next laboratory period. The resulting $H_2(TPP)$ is pure enough

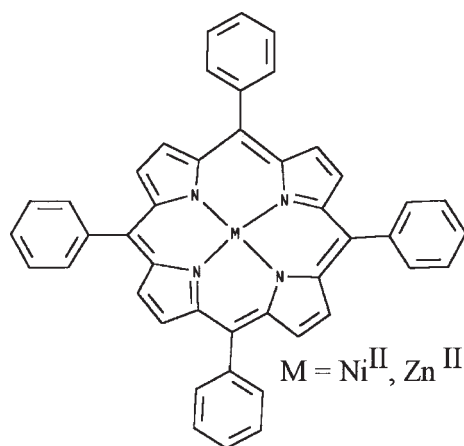


Figure 1. Metallated tetraphenylporphyrin.

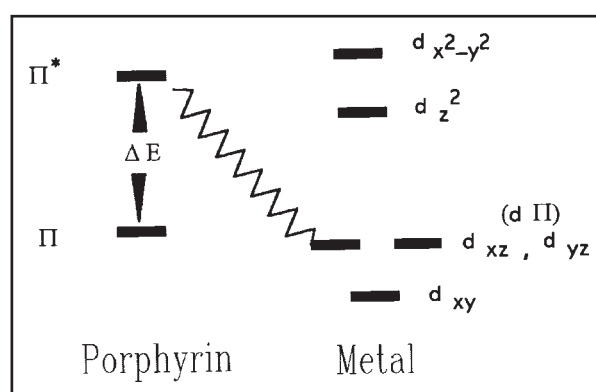


Figure 2. Simplified molecular orbital diagram for metalloporphyrins. Interaction between metal d_π and π^* porphyrin orbitals occurs in hypso-porphyrins.

for the subsequent metalation process. The average porphyrin yield is 8 mg.

Synthesis of $Zn^{II}(TPP)$ (5)

Zinc chloride is dried in a 110 °C oven overnight before use. $H_2(TPP)$ (1–2 mg) is dissolved in 3 mL of dimethylformamide (DMF) in a 5-mL reaction vial containing a stir bar. Zinc chloride, 10 mg, is added to the vial. A condenser is attached, and the reactants are heated to a gentle reflux for 30 min. The resulting solution can be diluted with DMF to measure the visible spectrum.

Synthesis of $Ni^{II}(TPP)$

Anhydrous nickel(II) chloride must be used. The green Ni(II) chloride hexahydrate is dehydrated by heating the crushed solid in an evaporating dish until the color is yellow-orange. Dehydrated Ni(II) chloride should be kept in an oven at 110 °C until used. The synthesis of $Ni^{II}(TPP)$ uses 10 mg of dry nickel(II) chloride but is otherwise identical to the synthesis of $Zn^{II}(TPP)$.

Visible Spectra and Fluorescence

The visible spectra (490–660 nm) of DMF solutions (0.1 mg/mL) of $H_2(TPP)$, $Zn(TPP)$, and $Ni(TPP)$ can be obtained with any suitable spectrophotometer.

The three solutions in DMF can be tested for fluorescence with a UV lamp (short wave) in a dark room. The $H_2(TPP)$ and $Zn^{II}(TPP)$ will fluoresce, but $Ni^{II}(TPP)$ will not.

Results and Discussion

The absorption spectra are shown in Figure 3. The red-violet $H_2(TPP)$ absorbs intensely between 500 and 550 nm and more weakly around 590 and 650 nm. The more violet $Zn^{II}(TPP)$ absorbs between 550 and 600 nm, whereas $Ni^{II}(TPP)$ is red and absorbs at 525 nm.

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

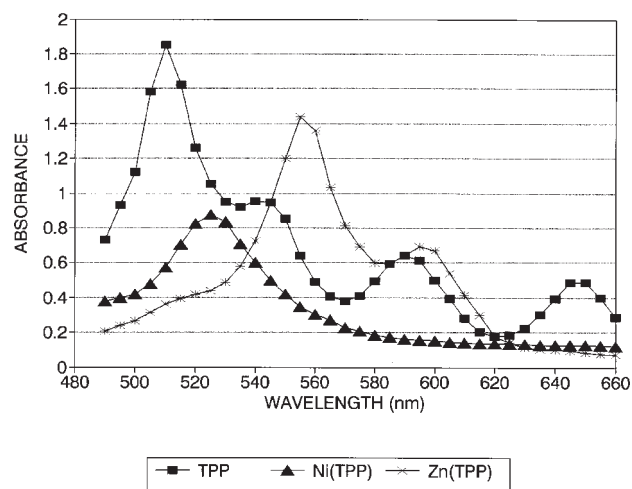


Figure 3. Absorption spectra for $H_2(TPP)$, $Ni^{II}(TPP)$, and $Zn^{II}(TPP)$. Data obtained on a Spectronic 20.

When zinc binds to the porphyrin in $Zn^{II}(TPP)$, the absorption spectrum changes owing to symmetry effects (discussed below), but the π to π^* energy gap is little affected and a *regular* metalloporphyrin spectrum results.

In contrast, the $Ni^{II}(TPP)$ peaks are shifted to shorter wavelength due to metal d_π (d_{xz} and d_{yz}) to porphyrin π^* backbonding, as shown in Figure 4. The backbonding raises the porphyrin π^* orbitals to higher energy, resulting in an increase in ΔE . The mixing of the metal d_π orbitals with the π^* orbitals on the porphyrin ring also results in a decrease in the fluorescent yield. The hypsochromic shift and loss of fluorescence are distinct characteristics of hypsochlorins.

The change in the spectrum (fewer peaks) on metalation is due to increased symmetry relative to the free-base porphyrin (Fig. 5). The two hydrogens on the nitrogen atoms in the free base porphyrin reduce the ring symmetry from square (for metalloporphyrins) to rectangular—that is, from D_{4h} to D_{2h} . In general, a more symmetrical molecule gives a simpler spectrum. The 22 p_z

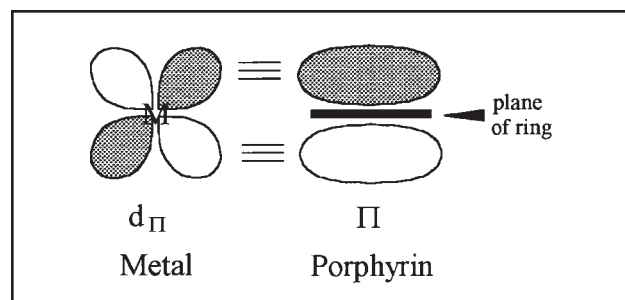


Figure 4. The d_π metal orbital overlap with the π system of the porphyrin ring.

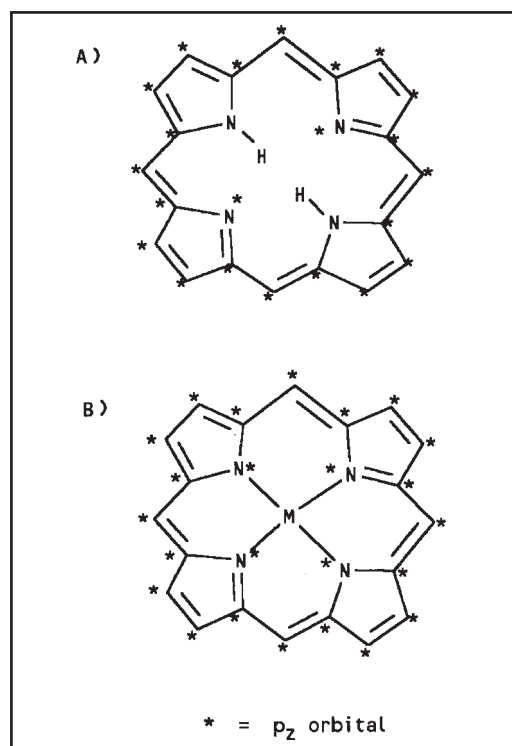


Figure 5. The position of the p_z orbitals used as a basis set for group theory. A) is the free-base porphyrin. B) is the metallated porphyrin.

orbitals in the free-base porphyrin are the basis set of orbitals combined to create the π molecular orbitals of the porphyrin ring. The point group is D_{2h} . This gives the reducible representation:

$$D_{2h} \mid E \quad C_2(z) \quad C_2(y) \quad C_2(x) \quad i \quad \sigma(xy) \quad \sigma(xz) \quad \sigma(yz) \\ \mid 22 \quad 0 \quad -2 \quad 0 \quad 0 \quad -22 \quad 0 \quad 2$$

which reduces to $5 B_{2g} + 6 B_{3g} + 5 A_u + 6 B_{1u}$. None of these states are degenerate.

After metalation the symmetry is D_{4h} , as all four nitrogens are equivalent. The resulting basis set consists of the 24 p_z orbitals.

$$D_{4h} \mid E \quad 2C_4 \quad C_2 \quad 2C_2' \quad 2C_2'' \quad i \quad 2S_4 \quad \sigma_h \quad 2\sigma_v \quad 2\sigma_d \\ \mid 24 \quad 0 \quad 0 \quad -2 \quad -2 \quad 0 \quad 0 \quad -24 \quad 2 \quad 2$$

which reduces to $6E_g + 3A_{1u} + 3A_{2u} + 3B_{1u} + 3B_{2u}$. With the increased symmetry many of the molecular orbitals are now doubly degenerate, which accounts for the reduction in the number of peaks in the visible spectrum. Compared to $Zn^{II}(TPP)$, $Ni^{II}(TPP)$ has a slight twist to give a propeller-like S_4 symmetry. The reducible representation reduces to $6E + 6A + 6B$, which is similar to the D_{4h} case.

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