

Microscale Synthesis and ^1H NMR Analysis of Zn^{II} and Ni^{II} Tetraphenylporphyrins



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We present a multisection undergraduate laboratory involving the microscale synthesis and spectroscopic analysis of unmetallated porphyrins and their corresponding metalloporphyrins. We previously reported in this *Journal* (1) the microscale synthesis of the unmetallated tetraphenylporphyrins, $\text{H}_2[(p\text{-X})_4\text{TPP}]$, where $\text{X} = \text{CN}$, H , CH_3 , and OCH_3 , and the microscale synthesis (not involving isolation as solids) of the corresponding metallated tetraphenylporphyrins, $[\text{M}^{\text{II}}[(p\text{-X})_4\text{TPP}]]$, where $\text{M} = \text{Zn}$ and Ni (Figure 1).

In the previously reported laboratories (1) the unmetallated tetraphenylporphyrins were analyzed by electronic absorption and ^1H NMR (nuclear magnetic resonance) spectroscopy, and the metallated tetraphenylporphyrins were analyzed by electronic absorption spectroscopy. We now present the microscale synthesis involving the isolation of the metalloporphyrins as solids and their corresponding ^1H NMR spectra.

The Supplemental Material^W describes the procedure for the synthesis of the free base porphyrins providing sufficient quantities to enable the subsequent isolation as solids of both the corresponding zinc and nickel metalloporphyrins. A correlation of electronic absorption and ^1H NMR spectroscopic data with regard to the metal to porphyrin ring (ligand) bonding is presented. $\text{Zn}(\text{II})$ porphyrins are representative of *regular* metalloporphyrin. In *regular* porphyrins the metal is a closed-shell ion (d^0 or d^{10}), in which little metal-to-ligand π -backbonding (metal $d\pi$ to porphyrin π^*) occurs (2). $\text{Ni}(\text{II})$ porphyrins are representative of *hypsoporphyrim*. Hypsoporphyrim are metalloporphyrins in which the metals are of d^m , $m = 6\text{--}9$, having filled $d\pi$ orbitals. Hypsoporphyrim exhibit significant metal $d\pi$ -to-porphyrin π^* backbonding (1, 2).

This set of experiments is adaptable for undergraduate organic, inorganic, structural analysis, and advanced synthesis laboratories. The experiments can be presented over three laboratory sessions each of two and a half hours in duration. The first session would include the synthesis and spectroscopic analysis of unmetallated porphyrins, and the second and third sessions would involve the synthesis and spectroscopic analysis of the corresponding $\text{Zn}(\text{II})$ and $\text{Ni}(\text{II})$ porphyrins. Four porphyrin systems are presented, however, others from readily available substituted benzaldehydes and substituted pyrroles could readily be adapted.

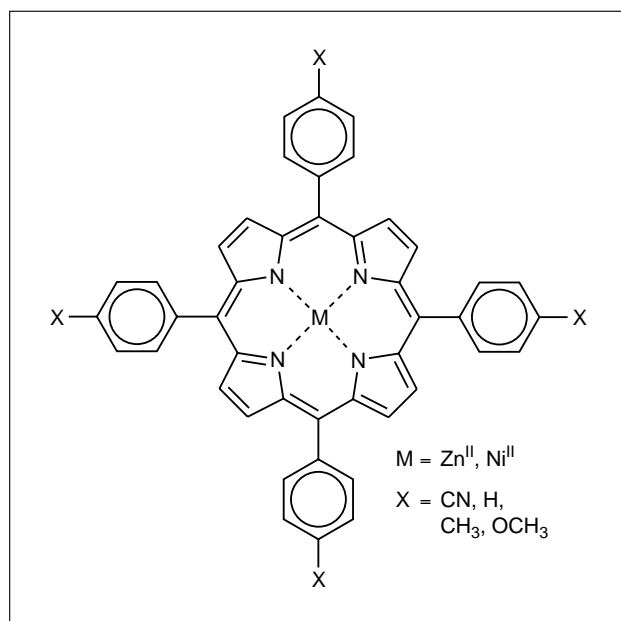


Figure 1. Metallated tetraphenylporphyrin.

Supplemental Material

The experimental procedures and tables of the NMR chemical shifts and positions of the UV-visible bands are available in this issue of *JCE Online*.

Literature Cited

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- (a) Buchler, J. W. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 1, p 389. (b) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 3, p 1. (c) Antipas, A.; Gouterman, M. *J. Am. Chem. Soc.* **1983**, *105*, 4896–4901.