

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

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Lab Documentation

Experimental Procedure

1. Synthesis of $\text{H}_2[(p\text{-X})_4\text{TPP}]$, (X= CN, H, CH_3 , and OCH_3)

The synthesis of the free-base porphyrins, $\text{H}_2[(p\text{-X})_4\text{TPP}]$, were performed as previously described (1). Reactant quantities were increased in order to obtain sufficient amount of product for subsequent isolation of the metallated porphyrins. All reactions were performed in a 25-mL round bottom flask fitted with a water condenser. In each synthesis 0.13 mL (1.9 mM) of pyrrole was added to 20 mL of propionic acid, followed by the addition of the required aldehyde:

for $\text{H}_2[(p\text{-CN})_4\text{TPP}]$, 0.2460 g (1.9 mM) of 4-cyanobenzaldehyde

for $\text{H}_2[(p\text{-H})_4\text{TPP}]$, 0.19 mL (1.9 mM) of benzaldehyde

for $\text{H}_2[(p\text{-CH}_3)_4\text{TPP}]$, 0.22 mL (1.9 mM) of *p*-tolualdehyde

for $\text{H}_2[(p\text{-OCH}_3)_4\text{TPP}]$, 0.23 mL (1.9 mM) of 4-methoxybenzaldehyde (*p*-anisaldehyde)

Average yields were about 35 mg (20%). All reactants are commercially available.

2. Synthesis of $[\text{Zn}^{\text{II}}[(p\text{-X})_4\text{TPP}]$.

Zinc chloride was dried at 110 °C in an oven overnight prior to use. 20 mg (~0.033 mM) of $\text{H}_2[(p\text{-X})_4\text{TPP}]$ was dissolved in 18 mL of N,N-Dimethylformamide, DMF, in a 25-mL round bottom flask containing boiling stones. Zinc chloride, 25 mg (0.18 mM), was added to the flask. A water condenser was attached to the flask and the reactants were gently refluxed for 30 minutes. The solution was decanted into a 50-mL beaker, and 4 mL of cold distilled water was added drop wise to facilitate precipitation of the product. The beaker was placed in an ice bath for 10 minutes. The product was isolated by vacuum filtration, and then washed drop wise with a 1 mL portion of cold distilled water. Products were air dried for 10 minutes, and then placed in a vacuum oven at 80 °C for 30 minutes. Average yields were about 15 mg (70%).

3. Synthesis of $[\text{Ni}^{\text{II}}[(p\text{-X})_4\text{TPP}]$.

Anhydrous nickel(II) chloride must be used. The green Ni(II) chloride hexahydrate was dehydrated by heating the crushed solid in an evaporating dish until the color was yellow-orange. Dehydrated Ni(II) chloride should be kept in an oven at 110 °C until used. The synthesis of $[\text{Ni}^{\text{II}}(p\text{-X})_4\text{TPP}]$ required 75 mg (0.58 mM) of dry nickel(II) chloride, otherwise, the synthesis is identical to that of $[\text{Zn}^{\text{II}}(p\text{-X})_4\text{TPP}]$. Average yields are about 7 mg (40%). After the 30 minute reflux yields may be increased through the utilization of a Hickman still. A Hickman still head was attached to the round-bottom flask and a water condenser was connected to the top of the still. The reaction mixture was reduced in volume to approximately 6 mL. DMF was removed from the still as it accumulated using a syringe-access sidearm. The resulting $[\text{Ni}^{\text{II}}(p\text{-X})_4\text{TPP}]$ was collected by vacuum filtration and washed as outlined (see hazards section).

4. Spectroscopy

The porphyrins can be characterized by visible absorption and ^1H NMR spectroscopy without further purification. The visible spectra (390 — 700 nm) of all compounds in DMF or CH_2Cl_2 can be obtained using any suitable spectrophotometer. The visible spectra of the unmetallated porphyrins, $\text{H}_2(p\text{-X})_4\text{TPP}$, are best obtained after isolation as solids, and then dissolved in DMF (0.1 mg/mL). The visible spectra of the metallated porphyrins can be obtained after isolation as solids, or can be taken prior to isolation after the 30 minute reflux by addition of one drop of the reaction mixture to 1mL of DMF. The NMR samples are prepared by dissolving 5 mg of compound in 0.7 mL of CDCl_3 solvent. Suitable ^1H NMR spectra were obtained after 16 scans on a 270-MHz NMR spectrometer.

Hazards

Distillation of DMF should be performed in a fume hood in order to limit exposure to vapor. Exposure to CDCl_3 should be limited as much as possible. No other hazards are identified.

Results and Discussion

The absorption spectra for the unmetallated porphyrins exhibit an intense Soret band centered around 419 nm, and four less intense Q bands between 510 - 660 nm (Table 1).

Table 1. Electronic spectra of $H_2[(p-X)_4TPP]$ in (nm).

Porphyrin	Soret	Q - Bands			
		IV	III	II	I
$H_2[(p-CN)_4TPP]$	419	513	547	589	644
$H_2[(p-H)_4TPP]$	416	514	548	589	646
$H_2[(p-CH_3)_4TPP]$	418	516	550	593	648
$H_2[(p-OCH_3)_4TPP]$	421	518	555	594	652

Upon metallation the absorption spectrum is simplified. An intense Soret band and two bands of less intensity, identified as the β and α bands, are observed (Table 2).

Table 2. Electronic spectra of $[Zn^{II}(p-X)_4TPP]$, and $[Ni^{II}(p-X)_4TPP]$ in (nm).

Porphyrin	Soret	β -Band	α -Band
$[Zn^{II}(p-CN)_4TPP]$	428	560	600
$[Ni^{II}(p-CN)_4TPP]$	415	527	***
$[Zn^{II}(p-H)_4TPP]$	425	559	599
$[Ni^{II}(p-H)_4TPP]$	414	527	***
$[Zn^{II}(p-CH_3)_4TPP]$	426	560	600
$[Ni^{II}(p-CH_3)_4TPP]$	416	528	***
$[Zn^{II}(p-OCH_3)_4TPP]$	428	562	603
$[Ni^{II}(p-OCH_3)_4TPP]$	419	530	***

*** Not observed

The electronic absorptions for both the unmetallated and metallated porphyrins have been attributed to porphyrin ring based π -to- π^* electronic transitions (2, 3). For Ni(II) porphyrins as a result of extensive metal $d_\pi(d_{xz}, d_{yz})$ to ligand π^* backbonding an increased energy splitting, ΔE , for the porphyrin based π -to- π^* electronic transition occurs. The increased energy splitting results in a hypsochromic shift

(shorter wavelength) of the absorption bands. Zn(II) porphyrins display a *regular* metalloporphyrin absorption spectrum (2, 3) in which extensive metal to ligand π -backbonding is absent.

The ^1H NMR of these compounds present excellent examples of: 1) diamagnetic anisotropy, 2) electron donating/withdrawing substituent effects, 3) Spin coupling with variance in $\Delta v/J$ ratios, 4) chemical and magnetic equivalence (1). The full ^1H NMR spectrum of $[\text{Zn}^{\text{II}}(p\text{-CH}_3)_4\text{TPP}]$ is shown in Figure 2, and an overlay of the aromatic regions of $\text{H}_2[(p\text{-CH}_3)_4\text{TPP}]$, $[\text{Zn}^{\text{II}}(p\text{-CH}_3)_4\text{TPP}]$, and $[\text{Ni}^{\text{II}}(p\text{-CH}_3)_4\text{TPP}]$ is presented in Figure 3.

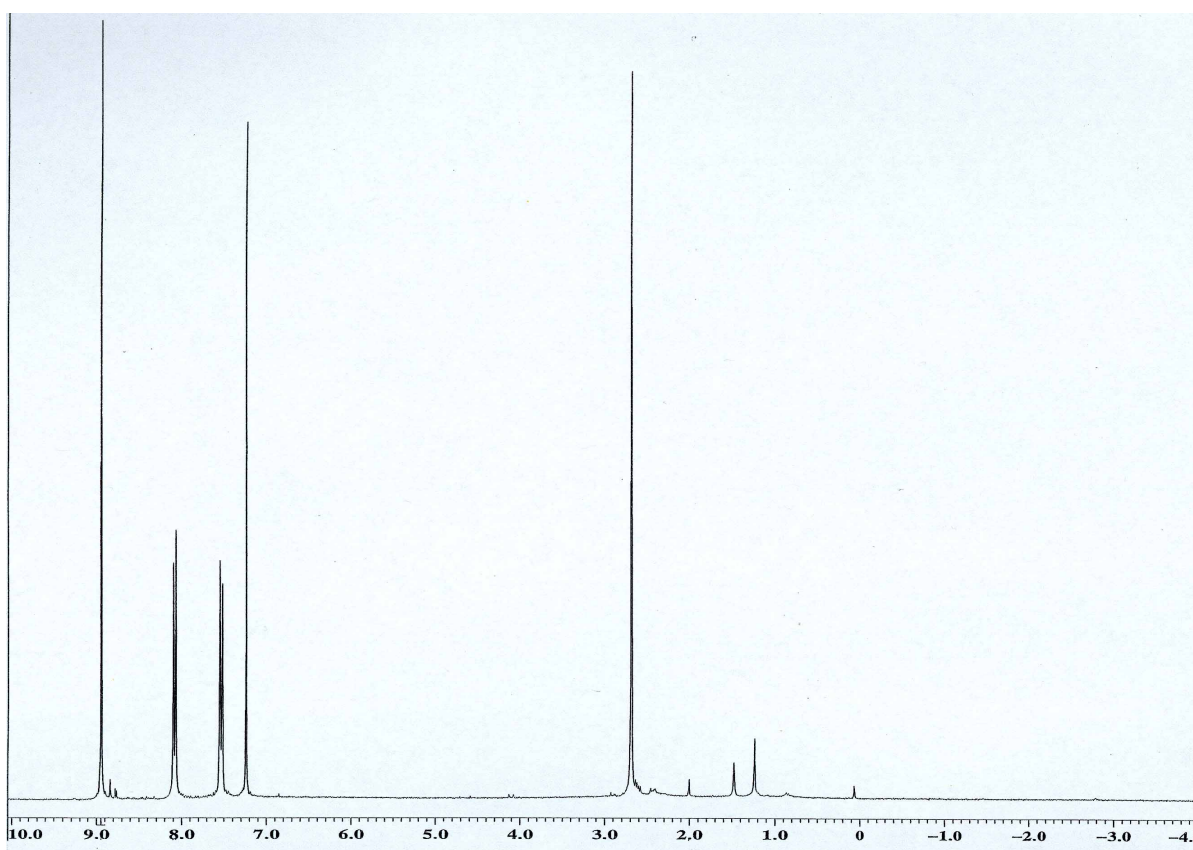


Figure 2: ^1H NMR of $[\text{Zn}^{\text{II}}(p\text{-CH}_3)_4\text{TPP}]$ in CDCl_3 . Solvent peak of CDCl_3 at 7.24 ppm. Water appears at 1.23 ppm

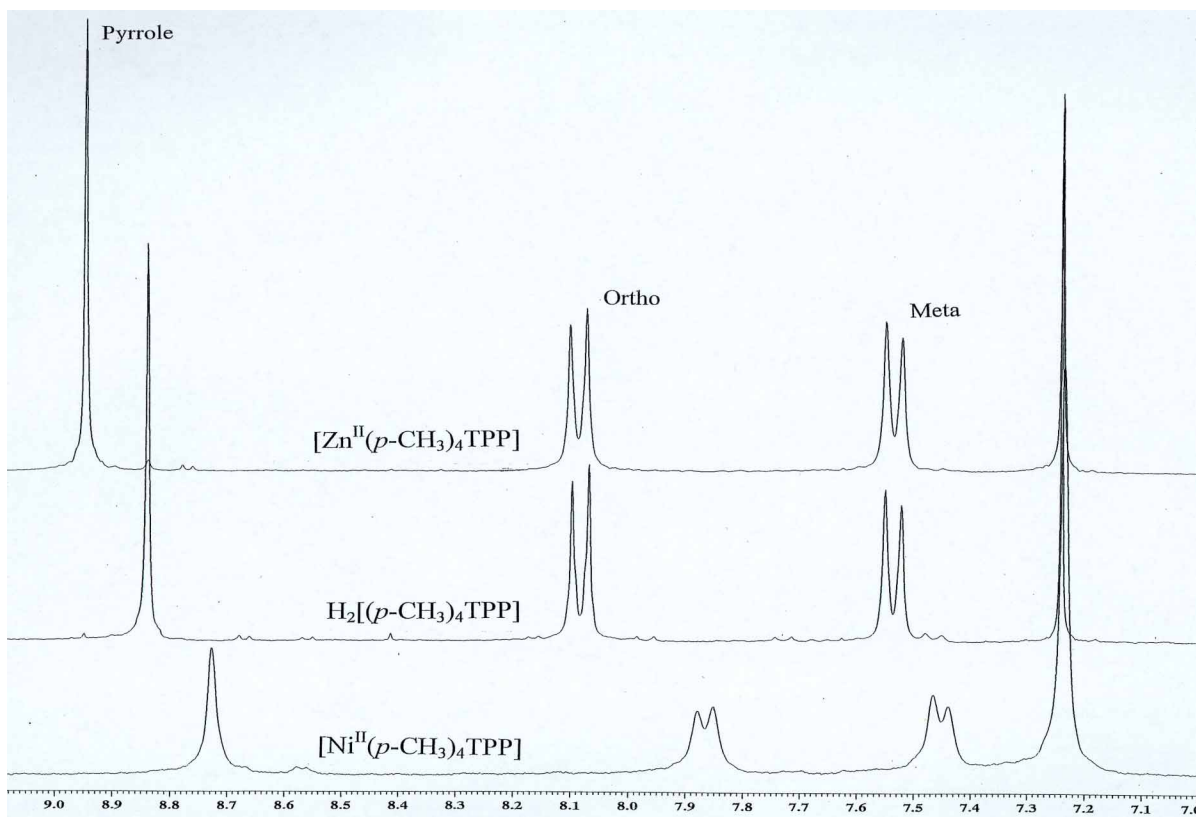


Figure 3: ¹H NMR overlay of the aromatic regions. Solvent peak of CDCl₃ at 7.24 ppm.

The ¹H NMR chemical shifts of all the porphyrins are listed in Table 3.

Table 3. ¹H NMR Chemical Shifts of all porphyrins (in ppm).

Porphyrin	H-pyrrole	H-ortho	H-meta	H-para	N-H	
H ₂ [(<i>p</i> -CN) ₄ TPP]	8.78	8.32 (J _{o-m} =8)	8.08	---	-2.90	
[Zn ^{II} (<i>p</i> -CN) ₄ TPP]	8.88	8.32 (J _{o-m} =8)	8.07	---	---	
[Ni ^{II} (<i>p</i> -CN) ₄ TPP]	8.67	8.12 (J _{o-m} =8)	8.01	---	---	
H ₂ [(<i>p</i> -H) ₄ TPP]	8.84	8.21 (J _{o-m} =8)	7.74	7.76	-2.79	
[Zn ^{II} (<i>p</i> -H) ₄ TPP]	8.94	8.32 (J _{o-m} =7)	8.07	7.75	---	
[Ni ^{II} (<i>p</i> -H) ₄ TPP]	8.73	7.99 (J _{o-m} =8)	7.67	7.68		
H ₂ [(<i>p</i> -CH ₃) ₄ TPP]	8.84	8.08 (J _{o-m} =8)	7.54	---	-2.79	-CH ₃ =2.69
[Zn ^{II} (<i>p</i> -CH ₃) ₄ TPP]	8.95	8.09 (J _{o-m} =8)	7.54	---	---	-CH ₃ =2.70
[Ni ^{II} (<i>p</i> -CH ₃) ₄ TPP]	8.73	7.86 (J _{o-m} =8)	7.45	---	---	-CH ₃ =2.62
H ₂ [(<i>p</i> -OCH ₃) ₄ TPP]	8.85	8.11 (J _{o-m} =9)	7.27	---	-2.77	-OCH ₃ =4.08
[Zn ^{II} (<i>p</i> -OCH ₃) ₄ TPP]	8.95	8.21 (J _{o-m} =8)	7.74	---	---	-OCH ₃ =4.08
[Ni ^{II} (<i>p</i> -OCH ₃) ₄ TPP]	8.74	7.90 (J _{o-m} =8)	7.22	---	---	-OCH ₃ =4.03

Chemical shifts in ppm, J_{o-m} coupling constants in Hz.

All zinc porphyrin protons exhibit downfield ¹H NMR chemical shifts, and all Ni(II) porphyrin protons display upfield chemical shifts with respect to their unmetallated porphyrin counterparts. This trend is particularly evident for the pyrrole proton resonances on the porphyrin ring that are located closet to the metal center. The protons in the zinc porphyrins are shifted downfield due to deshielding caused by the presence of the metal di-cation. The protons in the nickel porphyrins are shifted upfield as a result of shielding due to the presence of metal to ligand π-backbonding.

A nice correlation of electronic absorption and NMR spectroscopy is evident with regard to the bonding that occurs between the central metal and the porphyrin ring system.

Acknowledgment

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