



# Investigation of cobalt porphyrin doped polymer membrane films for the optical sensing of imidazole and its derivatives



Yueyang Tan, Nicole Escorcía, Alison Hyslop, Enju Wang\*

Department of Chemistry, St. John's University, Jamaica, NY 11439, United States

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## ABSTRACT

A cobalt(II) porphyrin was successfully incorporated into polymer membranes for the optical sensing of imidazole and its derivatives. This research has led to a better understanding of the behavior of Co(II) porphyrin in solution and in polymeric membranes. In aprotic dichloromethane (DCM), the Co(II) tetraphenylporphyrin (CoTPP) and Co(II) octaethylporphyrin (CoOEP) show a sensitive response to imidazole due to the strong ligation of the N-3 on the imidazole ring to the Co(II) center, which induces an absorbance change to the Soret band. However, when doped in polymeric films, only the CoTPP exhibits moderate sensitivity towards aqueous imidazole, histamine and histidine. This weakened coordination ability of CoTPP towards imidazole in the polymer films may be due to the coordination of the plasticizer, the impurities from the THF and polymer matrix at the Co(II) center. The selectivity of the polymer films towards imidazole over common anions is high. Lifetime of the cobalt(II) porphyrin incorporated polymer film was relatively short.

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## 1. Introduction

Imidazole is a planar five-membered heterocyclic ring, highly polar and ionisable aromatic compound. The physiological and pharmacological significance of imidazole and its derivatives has interested many investigators since imidazole compounds were first discovered [1–3]. Derivatives of imidazole all share the 1,3-C<sub>3</sub>N<sub>2</sub> ring. The lone pair electrons on N-3, which does not participate in the conjugated pi system, allows the unprotonated imidazole molecule to function as a ligand towards a proton or metal ion. This five-membered ring is a component of many important natural products, such as purine and nucleic acid [3], and different substituents on the imidazole ring can greatly increase its bioavailability and biological activity. For example, imidazole derivatives occur in proteins as part of the side chain of the amino acid, histidine, in nucleic acid structures as part of the purine ring, and in the vitamin B12 coenzyme. The substituted imidazole derivatives occupy an essential place in the field of medicinal chemistry [4–6].

Porphyrins are heterocyclic macrocycles composed of four pyrrole rings joined together by methylene bridges at their  $\alpha$ -carbon atoms forming an aromatic ring with 22  $\pi$  electrons [7]. The large

aromatic system allows for excitation of electrons from  $\pi$  to  $\pi^*$  porphyrin ring orbitals in the visible range. Porphyrins and their metal chelates generally exhibit characteristic sharp and intense absorption bands in the near ultraviolet to visible region. Six-coordinate metal ions bound to porphyrins have four positions occupied with the pyrrolic nitrogens in the porphyrin ring, leaving two axial ligand positions free to bind ligands. Studies of square-planar cobalt(II) complexes have been extensively reported in the literature both for their prospects as metal catalysis and as model systems for biologically active species [7–12].

Porphyrins and metalloporphyrins are excellent candidates as optical chemical sensing material because of their inherent stability, unique optical properties, and synthetic versatility. Porphyrin based sensors with different metal center have been reported to exhibit excellent selectivity for specific ions [13–21].

In our laboratory, we are investigating the strong coordination ability between Co(II)tetraphenylporphyrin (CoTPP) and imidazole which induced significant specific absorption spectra changes in organic solvent [22]. In this study, we took advantage of this strong coordination between Co(II) porphyrin and imidazole to explore the feasibility of developing high performance optical sensors for imidazole, and its derivatives, with cobalt(II) porphyrin immobilized in polymeric films. To fully understand the response mechanism, we have studied the response of two cobalt(II) porphyrin complexes toward various neutral and anion ligands in both organic solvent and polymer films.

\* Corresponding author.

E-mail address: [wange@stjohns.edu](mailto:wange@stjohns.edu) (E. Wang).

## 2. Experimental

### 2.1. Materials

2-Nitrophenyl octyl ether (*o*-NPOE), bis(2-ethylhexyl) sebacate (DOS), Tecoflex polyurethane (PU, SG-80A), high molecular weight poly(vinyl chloride) (PVC), tetrahydrofuran (THF) were obtained from Fluka, USA. 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphyrine cobalt(II) (CoTPP), 2,3,7,8,12,13,17-18-octaethyl-21*H*,23*H*-porphyrine cobalt(II) (CoOEP), dichloromethane (DCM), imidazole, benzimidazole, 5,6-dimethylbenzimidazole, *L*-histidine, histamine, *L*-alanine, caffeine, theophylline and other inorganic salts were purchased from Sigma–Aldrich. All aqueous solutions and buffers were prepared with deionized water.

### 2.2. Film preparation

The polymer membranes were fabricated according to the procedure described by Wang et al. [16]. Carriers were CoTPP and CoOEP; polymers were PVC, PU/PVC; and plasticizers were DOS and *o*-NPOE. Typically, the composition of the film was 1.2–2.4% carrier, 30% polymer and 67–69% plasticizer. The blank film solution was composed of 30% polymer and 70% plasticizer.

Membrane cocktails were prepared by dissolving a total of 200 mg of components in 2 mL THF. Aliquots of the homogeneous film solution were drawn manually into a glass pipette and 3–5 drops of the solution were deposited on glass slides (0.9 × 4 cm, 1 mm thickness) and a thin film was obtained by spin coating. The THF was allowed to evaporate overnight, leaving a thin polymer film attached to the glass slide.

### 2.3. Optical measurements

Absorbance measurements were recorded with a UV–Vis double beam (Cary-14) or a single beam photo-diode array (Hewlett-Packard) spectrophotometer. Polymer films on glass plates were placed in a commercial quartz cell (1 × 1 × 4 cm<sup>3</sup>) containing 3 mL test solution. The membrane coated glass slides were first soaked 20 min in distilled water to ensure a stable membrane absorbance. Then the slide was placed into the cuvette containing aqueous test solutions, the UV–Vis spectrum of the film was recorded in the presence of the test solution after 10 min. The double beam spectrophotometer was zeroed at 600 nm before the spectra was taken in the range of 350–600 nm. The calibration curves were determined by taking the spectra of the films at various concentration (1.0 M–10<sup>−7</sup> M) solutions of the target analyte to obtain the absorbance at the fixed wavelength for each set of films.

### 2.4. Selectivity towards small anions

The study of the effect of the various anions was carried out with CoTPP/DOS/PVC films. The 1.00 M stock solutions of SCN<sup>−</sup>, ClO<sub>4</sub><sup>−</sup>, salicylate, NO<sub>2</sub><sup>−</sup>, NO<sub>3</sub><sup>−</sup>, Cl<sup>−</sup>, and I<sup>−</sup> were prepared by dissolving the corresponding sodium salt in deionized water. A concentration range of 1.00 M–10<sup>−6</sup> M for the seven anions was obtained by 10-fold serial dilution from stock solution. The responses of the CoTPP/DOS/PVC film for each anion in aqueous solution were carried out after immersing the film in solution for ~10 min. The response curves for each anion and imidazole at various concentrations were established to obtain the selectivity coefficient of cobalt(II) porphyrin film in aqueous solution.

### 2.5. Porphyrin solution response towards imidazole

As the reference for the response of cobalt(II) porphyrin polymeric film to imidazole, the coordination between porphyrin and

imidazole in DCM was studied. 1.00 M imidazole solution was prepared as stock solution. A series of imidazole solutions with concentrations in the range 10<sup>−1</sup>–10<sup>−7</sup> M were diluted from the stock solutions by serial dilution method.

The 1.0 mg/mL stock solutions of CoTPP and CoOEP were prepared by dissolving 20.0 mg of the Co(II) porphyrin in 2.00 mL DCM. A standard Co(II) porphyrin solutions of 3.3 μg/mL were diluted from the 1.0 mg/mL solutions to obtain an absorbance of ≤1.

In each experiment, a solution mixture composed of 2.00 mL porphyrin solution, 300 μL imidazole solution and 700 μL DCM were pipetted directly into quartz cuvette and covered with a Teflon stopper immediately. The final concentration of Co(II) porphyrin was 2.2 μg/mL. The solution was mixed thoroughly for 10 min to achieve equilibrium. The solution composed of 2.00 mL of standard porphyrin solution and 1.00 mL of DCM was used for comparison. The absorbance spectra of these solution mixtures were measured in the range of 350–600 nm.

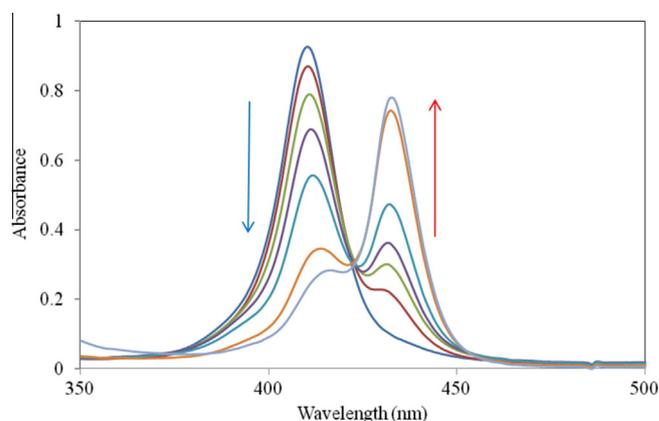
The responses of the two lipophilic imidazole derivatives, benzimidazole, 5,6-dimethylbenzimidazole, which are soluble in DCM up to 10<sup>−2</sup> M, were studied in the same procedure in the concentration range of 10<sup>−6</sup>–10<sup>−2</sup> M.

## 3. Results and discussion

### 3.1. Response in DCM solutions

As a reference, the responses of cobalt(II) porphyrins to imidazole in the polar aprotic DCM solution were first examined. DCM can fully dissolve the cobalt(II) porphyrins, as well as imidazole. As a non-coordinating solvent, DCM will not bond to the porphyrin and interfere with the coordination. A DCM solution of CoTPP has an intense Soret band around 410 nm and a weak Q band around 528 nm [21]. The addition of imidazole results in changes in the absorbance of these bands. The absorption spectra in the range of 350–600 nm with the addition of different concentrations of imidazole are shown in Fig. 1.

In Fig. 1, the band at 410 nm is from the uncoordinated CoTPP Soret band. The addition of imidazole caused a significant decrease of this peak, and an emergence of the red shifted band at 433 nm. This red shifted peak is due to the axial coordination of imidazole to the central cobalt atom of CoTPP [10]. The coordination resulted in a change in the a<sub>2u</sub> orbital energy [9] which gave rise to the changes in the spectra of the metalloporphyrin. The isosbestic



**Fig. 1.** Absorption spectra of CoTPP solution with the addition of imidazole. CoTPP concentration: 3 μg/mL. imidazole concentration: 0, 10<sup>−5</sup>, 10<sup>−3</sup>, 5 × 10<sup>−3</sup>, 10<sup>−2</sup>, 5 × 10<sup>−2</sup>, 1 M. Arrows indicates the in absorbance with increase in imidazole concentration.

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