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Hydrophilic Porphyrins based Chemosensors for First Transition Series Metal Ions [Chemistry]

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Assignment Title:
Hydrophilic Porphyrins based Chemosensors for First Transition Series Metal Ions

General Chemistry is a two-semester course (General Chemistry I, SCC 201 and General Chemistry II, SCC 202) required for majors in Biology and Environmental Sciences.

This lab experiment, aligned to LaGuardia Community College's Inquiry and Problem Solving Core Competency and Written Communication Ability was designed for General Chemistry I (SCC 201 Honors) course. Honors courses in LaGuardia emphasize critical thinking, analytical writing, and introduce students to research. This lab experiment provides an opportunity for students to engage in hands-on laboratory work, to develop laboratory skills, and to conduct research in the classroom by using two water soluble porphyrins to detect transition metal ions in a solution and on a paper support. Overall, this experiment was designed to meet the demand for undergraduate research experiences and to engage all the students in addressing a research question or problem that is of interest to the scientific community.

In order to demonstrate their learning, students write a formal lab report which includes an understanding of experiment procedures (methods and techniques), safety hazards, instrumentation, understanding of concepts and theories gained by performing the experiment, collecting data through observation and/or experimentation, interpretation of the data (Ultraviolet-visible spectra), analysis of the data in tables and graphs, and drawing conclusions and perspective from the experiment. The knowledge students gain during this lab experiment will be useful to connect with future chemistry courses and can also be utilized to do research. The lab write-up is deposited for the assessment of the Written Communication Ability to which SCC 201 is aligned.

This experiment also raises awareness about a global concern. Students detect transition metal ions in aqueous solutions by use of porphyrins. Due to rapid growth in technology and industrialization, transition metals are used in large amounts in a variety of electronic products. The improper preservation of the industrial wastes leads to accumulation of these metals into water resources, which can create danger to human health and the environment. Therefore, there is a need to carefully monitor and frequently detect transition metal ions content in the environment.

This lab experiment was implemented in an Honors section of General Chemistry SCC 201 and was worth about 3.5% of the final grade. The students are likely to spend 3 hours completing the experiment in the lab and another 3-4 hours completing the lab write-up.

The Program Goals that this assignment targets:

1. To provide training to the students in various lab techniques and how to utilize these techniques to conduct research.

The Student Learning Objective (s) that this assignment targets:

1. Students will have an enhanced conceptual understanding of the theory to practice relationship and will achieve higher level reasoning skills.

2. Students will be able to develop their practical competence in laboratory work.

3. Students will be able to collect data through observation and/or experimentation, preparation of solutions of known concentration, characterize the compounds by UV-vis spectra, and draw conclusions and perspective of the experiment.

4. Communicate their results through the formal lab report format of: Introduction, Chemicals, Procedure, Data, Discussion and References.

The Course Objective (s) that this assignment targets:

1. Based on the principles of environmental chemistry, students will be able to detect the transition metal ions using a porphyrin as a sensor and explore the complex connections between chemistry and real world issues.
2. Observe, collect, analyze and interpret experimental data and graph the UV visible spectra using Microsoft Excel.

Rubric for Abstract, Data and Discussion of the Experiment

Name		Excellent	Good	Fair	Poor	Score
Abstract **(5 pts)**	Briefly describe in your abstract: The statement of the experiment, the objective of the experiment, Methods used to examine the problem, Results including data in tables or graphs or picture, Conclusions, Significance of the results.					
Purpose of Experiment **(5 pts)**	What is the objective of experiment? (2 pts)					
	Which methods or techniques were used to examine the problem? (3 pts)					
Data (10 pts)	Write the observation (color change). Tabulate the data. Draw the graph. Label your UV-visible spectrum, including the wavelength and absorbance of each peak.					
Discussion **(12 pts)**	Concepts and theories gained by performing the experiment. Explanation of the data.					
Conclusion **(3 pts)**	Significance of results					
References **(2 pts)**	ACS reference style					

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Learning Objectives

a. To prepare porphyrin-based test paper using 5,10, 15, 20-tetrakis(4-sulfonatophenyl) porphyrin (TSPP) and Tetrakis (4-carboxyphenyl) porphyrin (TCPP) and to analyze transition metal ions in aqueous solutions and on paper support.

b. To understand the basic principles of Absorption Spectroscopy.

Introduction

Due to the rapid growth in technology and industrialization, transition metals are used in large amounts in a variety of electronic products. The improper preservation of the industrial wastes leads to the accumulation of these metals in water resources which can create danger to the environment and human health. This can lead to several diseases such as tumors, kidney and liver damage, muscle paralysis, etc. Therefore, there is a need to carefully monitor and frequently detect transition metal ions content in the environment by simple sensing devices[1-4].

Recent studies have shown that porphyrins have the potential to detect metal ions in solutions. Porphyrins possess unique optoelectronic and physio-chemical properties. They also have the ability to coordinate with wide range of metal ions, which makes this macrocycle a potential platform for diverse applications such as chemical sensors, catalyst, component to make solar cell, drug delivery vehicles, theranostics, etc[5-8]

Porphyrins: Porphyrins are naturally occurring tetrapyrrole macrocycle, where the four pyrrole subunits are connected at their α-carbon atoms via methine bridges (=CH−). The basic structure of a free base porphyrin macrocycle is shown in Figure 1. The porphyrin macrocycles are aromatic containing 11 π bonds which are conjugated. They have several distinct functionalization sites, i.e., the meso position, β-position, and inner nitrogens (Fig. 1). Porphyrins are deeply colored compounds because they are highly conjugated and they tend to absorb strongly in the visible region of the electromagnetic spectrum. Some of the examples of naturally occurring porphyrins are, heme (iron containing porphyrin) pigment in red blood cells and also chlorophyll which is a magnesium porphyrin responsible for green pigment of plants.[6]

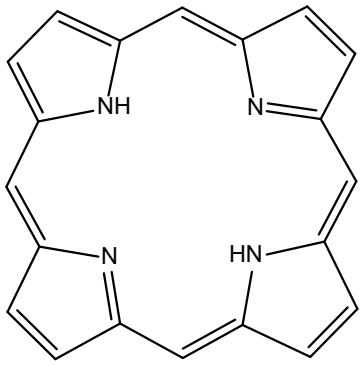


Figure 1: Structure of the porphyrin macrocycle

A typical absorption spectra of a free base porphyrin is shown in Figure 2. A very sharp intense band, also called the Soret band, appears around 400 nm in the near UV region. There are also four additional weak bands known as Q bands in visible region (490-650 nm). After coordination with a metal ion, there is slight shift in Soret band but four Q bands in free base porphyrin merge in to two Q bands.

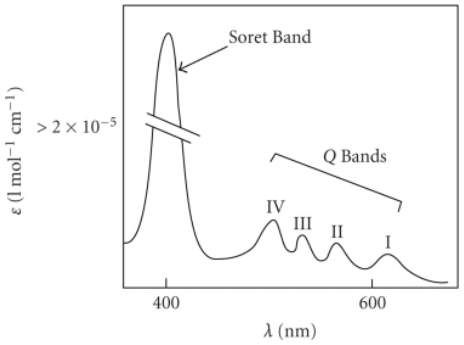
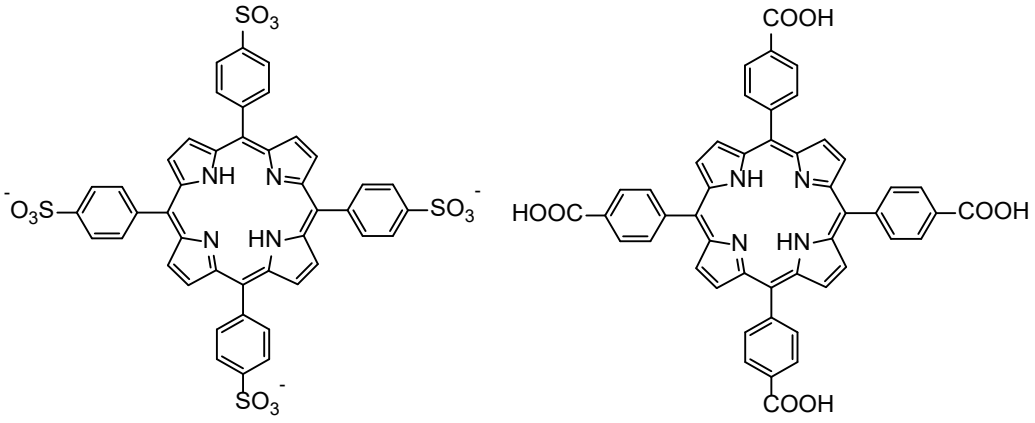


Figure 2: Typical absorption spectrum of a free base porphyrin

Reference: https://openi.nlm.nih.gov/detailedresult.php?img=PMC2535827_MBD2008-276109.015&req=4

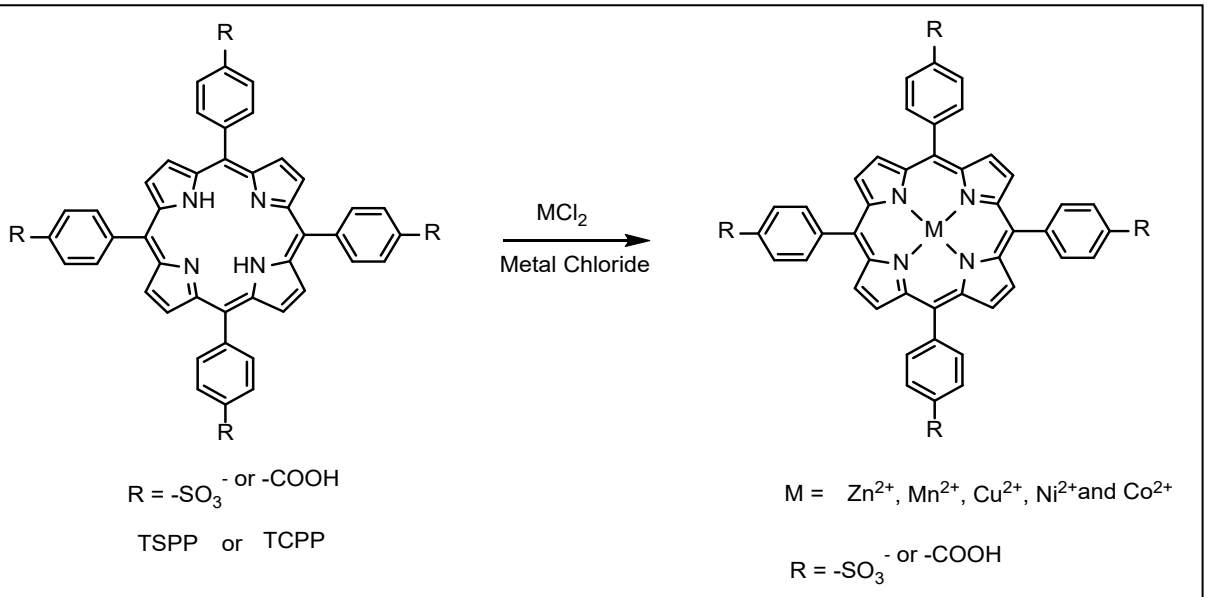
In this experiment, two free base and water soluble porphyrins,5,10,15,20-tetrakis(4 sulfonatophenyl)porphyrin (TSPP) and Tetrakis(4-carboxyphenyl)porphyrin (TCPP) (Figure 3)are used to detect metal ions both in solution phase and on chromatographic paper. The concentration of both of these porphyrins is 0.15 mM in water. The coordination reaction between metal ions and porphyrin ligand results in a color change which helps in identifying some transition-metal ions in aqueous solution (Scheme 1). The coordination of the various metals with these water soluble porphyrins (TSPP and TCPP) influences HOMO-LUMO band gap of the porphyrin which results in the different shifts of the bands in absorption spectra and different colors upon complexation.[8]



Tetrakis(4-sulfonatophenyl)porphyrin
TSPP

Tetrakis(4-carboxyphenyl)porphyrin
TCPP

Figure 3: Structures of two water soluble porphyrins TSPP and TCPP



Scheme 1: Coordination reaction between porphyrin and metal ion in aqueous solution

To test the complexation of porphyrin with metal ion on a paper support, Whatman No. 1 filter paper is used. Small circles are drawn on a paper using permanent marker and a drop of 0.15 mM porphyrin solution is deposited into that circle. Once the porphyrin drop is dry, a drop of the solution of the metal ion (0.15 mM) is added on top of it. Once the drop is dry, fluorescence is observed using 365 nm UV light.

These two simple experiments have the potential to be used in various fields such as environment, food industry, biology and medicine.[9]

Chemicals Needed

TSPP: 5, 10, 15, 20-tetrakis (4-sulfonatophenyl) porphyrin

TCPP: 5, 10, 15, 20-tetrakis (4-carboxyphenyl) porphyrin

Nickel (II) chloride

Cobalt (II) Chloride

Zinc Chloride

Cupric chloride

Manganese (II) chloride

Equipment needed

Droppers, beaker, glass rod, filter paper, 500 mL volumetric flask

Analytical balance

UV-vis Spectrometer

Cuvettes

Experimental procedure:

Part A: Preparation of required solutions

Using a 500 mL volumetric flask, prepare an initial 0.15 mM solution of porphyrins in water, TSPP and TCPP (you should weigh out porphyrins, TSPP has a formula weight of 930.05 g/mole and TCPP has a formula weight of 790.77 g/mole. If the porphyrins do not dissolve add few drops of the base (ammonium hydroxide). The TSPP solution in water will be green but upon addition the base will change to pink. The 0.15 mM solutions of metal ion solutions, $NiCl_2$, $CuCl_2$, $CoCl_2$, $ZnCl_2$, $MnCl_2$ solutions will be prepared by weighing the exact amount of these salts in 250 mL of water. It is important to record the accurate mass to prepare the stock solution, so that you will know the exact molarity of these solutions.

Part B: Spectrophotometric study with metal ions

To study the spectroscopic changes, mix 2 mL each of prepared metal ion and porphyrin solutions in a test tube and wait for 10 – 15 min. Every metal ion has a different rate of complexation with porphyrin. In two separate test tubes, add 2 mL of each of TCPP and TSPP solution to use as a control. Please note any color change and then see the changes in UV visible spectra using spectrophotometer.

1. Instrument Settings: Turn on the UV-Vis spectrophotometer, wait for self-tests. Set Y Scale function between 0 and 1.0 on Y axis, set wavelength range between 350 and 750 nm. The baseline correction will be done with distilled water before taking the sample reading.

2. Dilute the prepared porphyrin (TSPP) and $NiCl_2$, $CuCl_2$, $CoCl_2$, $ZnCl_2$, $MnCl_2$ solutions and record the absorbance spectra for the mixed solutions. Take the sample reading. If the absorbance is still too high, dilute by adding more water.

3. Repeat step 2 using TCPP solution and $NiCl_2$, $CuCl_2$, $CoCl_2$, $ZnCl_2$, $MnCl_2$ solutions, and record the absorbance spectra for the mixed solutions of TCPP and each metal ions. Make sure you rinse the cuvette out between each measurement and then rinse with small amount of sample solution first, before filling the cuvette with the given test solution.

4. Analyze the absorption spectra for all the bands.

Part C: Investigation of complexation behavior on filter paper

Draw circle patterns on a Whatman filter paper using permanent black marker (sharpie), these patterns act as reaction wells and prevents the liquid from spreading. Add a drop of porphyrin solution prepared, both TSPP and TCPP, use them as control. Then make more circles add a drop of each porphyrin. Let the porphyrin drop dry and then add a drop of $ZnCl_2$ solution. Let it dry. Note any color change. Repeat this step using other metal solutions and both TSPP and TCPP solutions. Note any color change. Use the UV lamp to observe the fluorescence. Is it quenched by any metal ion?

Table 1

Metal Solution used	Initial color of TCPP solution	Color after adding one drop of aqueous solution of metal ion	Fluorescence quenched (Y or N)
Mn (II) Zn Co (II) Cu (II) Ni (II)			

Table 2

Metal Solution used	Initial color of TSPP solution	Color after adding one drop of aqueous solution of metal ion	Fluorescence quenched (Y or N)
Mn (II) Zn Co (II) Cu (II) Ni(II)			

Prelab Questions

1. How are porphyrins important to life?

2. Why are porphyrins deeply colored?

3. Why is there color change when metal ions coordinate with porphyrin?

4. What is the difference between the UV-vis spectra of free base and metallated porphyrin?

5. Give main sources of transition metal contamination in the water resources.

In Your Lab Report Discussion

1) Show all the calculations done to prepare 0.15 mM of porphyrin (TCPP and TSPP) and 0.15mM of metal ($NiCl_2$, $CuCl_2$, $CoCl_2$, $ZnCl_2$, $MnCl_2$) solutions.

2) Discuss the UV-visible spectra and color changes after coordination with each of metal ion you saw while adding metal into the porphyrin. Explain the bands of free base porphyrin and shift in the bands upon coordination with metal ions.

3) Explain which porphyrin (TCPP or TSPP) was more sensitive in detecting transition metal ions?

4) Reflect on the potential uses of this porphyrin test paper.

5) Explain the statement: Porphyrins have the potential to be used in bioremediation of pollutants in soil and ground water.

References:

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