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2016

# Water Soluble Cationic Porphyrin Sensor for Detection of Hg2+, Pb2+, Cd2+, and Cu2+

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# Repository Citation

Zamadar, Matibur; Orr, Christopher; and Uherek, Miranda, "Water Soluble Cationic Porphyrin Sensor for Detection of Hg2+, Pb2+, Cd2+, and Cu2+" (2016). Faculty Publications. 80. [https://scholarworks.sfasu.edu/chemistry\\_facultypubs/80](https://scholarworks.sfasu.edu/chemistry_facultypubs/80?utm_source=scholarworks.sfasu.edu%2Fchemistry_facultypubs%2F80&utm_medium=PDF&utm_campaign=PDFCoverPages)

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# *Research Article* **Water Soluble Cationic Porphyrin Sensor for** Detection of  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Cd^2$ <sup>+</sup>, and  $Cu^{2+}$

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Received 8 March 2016; Accepted 17 April 2016

Academic Editor: Sher Bahadar Khan

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Here we report the sensing properties of the aqueous solution of *meso*-tetra(N-methyl-4-pyridyl)porphine tetrachloride (**1**) for simultaneous detection of toxic metal ions by using UV-vis spectroscopy. Cationic porphyrin **1** displayed different electronic absorptions in UV-vis region upon interacting with  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ , and  $Cu^{2+}$  ions in neutral water solution at room temperature. Quite interestingly, the porphyrin **1**showed that it can function as a single optical chemical sensor and/or metal ion receptor capable of detecting two or more toxic metal ions, particularly Hg<sup>2+</sup>, Pb<sup>2+</sup>, and Cd<sup>2+</sup> ions coexisting in a water sample. Porphyrin 1 in an aqueous solution provides a unique UV-vis sensing system for the determination of  $Cd<sup>2+</sup>$  in the presence of larger metal ions such as Hg<sup>2+</sup>, or Pb<sup>2+</sup>. Finally, the examination of the sensing properties of 1 demonstrated that it can operate as a  $Cu^{2+}$  ion selective sensor via metal displacement from the **1-Hg2+**, **1-Pb2+**, and **1-Cd2+**.

## **1. Introduction**

Due to rapid industrialization and fast growing global population, the discharge of transition and heavy metals into water resources has increased globally. Along with other chemicals, heavy metals are extremely toxic and exposure to them causes adverse effects on the environment and human health [1]. For example, a very small concentration of mercury ions  $(Hg^{2+})$ can damage the central nervous system, brain, kidneys, and liver. Additionally, it can also affect the endocrine system and the immune system  $[2-4]$ . Lead  $(Pb^{2+})$  ions can cause anemia, kidney damage, brain damage, mental-retardation, and muscle paralysis [5]. Cadmium  $(Cd^{2+})$  ion is another extremely harmful metal; it can damage the kidney's filtering system, central nervous system, and immune system and causes physiological disorders [6-8]. Copper  $(Cu^{2+})$  ions are widely distributed in plants and animals, including human beings [9]. These ions are involved in various biological processes. However, they are toxic at high concentration causing kidney and liver damage [10].

Recently, porphyrin-based probes have shown great promise for detecting heavy metal ions in solution. Porphyrin

compounds possess remarkable photophysical properties. They exhibit characteristic electronic absorptions in the Soret band region (~400 nm,  $S_0 \rightarrow S_2$ ) as well as in the Q-bands region (500–700 nm,  $S_0 \rightarrow S_1$ ). Porphyrin solutions have visible color. Most importantly, porphyrins are good functional receptors for various metal ions and can typically form a chelation complex with heavy metal ions. After complexation with a heavy metal ion, metalloporphyrin shows characteristic electronic absorption bands in the visible region which can be readily observed with UV-vis spectroscopy [11–13]. As a consequence, a number of molecular optical sensors and various detection techniques including electronic absorption, fluorescence, colorimetry, and electrochemical methods have been devised to selectively detect heavy metal ions such as  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ , and  $Cu<sup>2+</sup>$ . These methods are often found to be very effective. However, reports indicated that most of the porphyrin-based sensors focused on just single metal ion detection [14–21]. Very few examples have been reported for the simultaneous detection of multimetal ions coexisting in a sample. Chen and his coworkers reported the first porphyrin-Bodipy based ratiometric sensor for  $\text{Fe}^{2+}$  and  $\text{Hg}^{2+}$  ions [22]. The same



Figure 1: Structure of the cationic porphyrin (**1**).

group (Chen and his coworkers) synthesized other *N*,*N*bis(2-pyridylmethyl)amine (DPA) modified porphyrin sensors for  $Pb^{2+}$  and Cu<sup>2+</sup> ions [23]. Recently, Chen and Wang prepared azacrown[N, S, O]-modified porphyrin sensors for simultaneous detection of Ag<sup>+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup> ions [24]. However, a porphyrin-based sensor for the simultaneous detection of two or more toxic metal ions, particularly  $Hg^{2+}$ ,  $Pb^{2+}$ , and  $Cd^{2+}$  ions, has not been reported thus far. It is also worth noting that the preparation of reported porphyrinbased optical sensors often requires complex organic synthesis, which is very costly and time consuming. Furthermore, the porphyrin-based sensors are water insoluble, which limits the detection of metal ions in aqueous environment [23, 24]. Thus, finding a simple, inexpensive, water soluble, single optical chemical sensor capable of detecting any or all  $Hg^{2+}$ ,  $Pb^{2+}$ , and  $Cd^{2+}$  ions simultaneously is highly desirable.

In this paper, we report a water soluble cationic porphyrin-based optical sensor for the detection of single or multi-heavy metal ions by UV-vis absorption method. The aqueous solution of cationic *meso*-tetra(N-methyl-4 pyridyl)porphine tetrachloride **1** (Figure 1) was studied and explored as a versatile optical sensor/metal ion receptor for heavy metal ions. Cationic porphyrin **1** produced different diagnostic optical absorptions for  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ , and  $Cu<sup>2+</sup>$  in the UV-vis region indicating its ability as a potential multisignal optical sensor. Quite interestingly, we found that porphyrin **1** has the potential to behave as a single optical chemical sensor and/or metal ion receptor for detecting two or more toxic metal ions  $(Hg^{2+}, Pb^{2+}, and Cd^{2+})$ simultaneously coexisting in a water sample. Unique sensing ability of 1 for  $Cd^{2+}$  ion was investigated in the presence of metallic ions with large ionic radii. Finally, we examine the sensing properties of the aqueous solution of  $1$  for  $Cu<sup>2+</sup>$  ion. The absorption studies demonstrated that **1** can operate as a potential dual-mode  $Cu^{2+}$ -selective sensor.



FIGURE 2: Absorption spectra of  $1(5 \times 10^{-6} \text{ M})$  in H<sub>2</sub>O.

## **2. Experimental Section**

*2.1. Materials and Sample Preparation.* All reagents and chemicals were of the best available analytical reagent and were used as received without purification. Deionized  $H_2O$ was obtained from a US Filter Corporation deionization system. *meso*-Tetra(N-methyl-4-pyridyl)porphine tetrachloride was purchased from Frontier Scientific Inc., USA. Mercury (II) nitrate, cadmium (II) chloride, lead (II) nitrate, nickel (II) chloride, and sodium chloride were obtained from Sigma Aldrich, USA. Copper (II) chloride, zinc (II) sulfate, nickel (II) sulfate, iron (II) chloride, and calcium chloride were bought from Flinn Scientific Inc., USA. Potassium chloride was received from Mallinckrodt Pharmaceuticals, USA. UV-vis spectra were recorded on an Agilent 8453 single beam diode array spectrometer (Agilent Technologies, USA, model 8453). All the measurements were performed at room temperature and under an atmospheric pressure. All the metal salt solutions (1.00 ×  $10^{-3}$  M) were prepared in neutral (∼pH 7) aqueous solution. Quartz cuvettes with 1.00 cm pathlength and 2 mL volume were used for all measurements. For typical metal-binding titration, microliter amounts of standard solution of metal ion aqueous solutions were added into the cuvette containing 2 mL of solution  $1 (5.00 \times 10^{-6} \text{ M})$ and thoroughly mixed before a measurement was made.

#### **3. Results and Discussion**

*3.1. The Change of Electronic Absorption of 1 by Divalent Metal Cations.* To examine the selectivity of metal-free porphyrin **1**, the absorption spectra were recorded by adding an aqueous aliquot of the metal ions Na<sup>+</sup>, K<sup>+</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>,  $Cu^{2+}$ , Ni<sup>2+</sup>, Hg<sup>2+</sup>, and Pb<sup>2+</sup> into an aqueous solution of 1. The intensity of the absorption spectra of metal-free porphyrin **1** showed almost no change upon addition of  $Na^+$ ,  $K^+$ ,  $Co<sup>2+</sup>$ , and Ni<sup>2+</sup>. A very small reduction of intensity for the strong Soret band of 1 was observed for  $Zn^{2+}$  and  $Fe^{3+}$ metal ions (*see* Figure S1 in Supplementary Material available online at http://dx.doi.org/10.1155/2016/1905454). As shown in Figure 2, an aqueous solution of **1** exhibited a Soret band at 422 nm and Q-bands at 521, 552, and 589 nm. The intensity of the Soret band of metal-free porphyrin **1** was decreased with the appearance of a new peak at 458 nm upon addition



FIGURE 3: Absorption spectra of aqueous solution of (a)  $1 \times 10^{-5}$  M 1 and  $1 \times 10^{-5}$  Hg<sup>2+</sup> (blue curve), (b)  $1 \times 10^{-5}$  M 1 and  $1 \times 10^{-5}$  Pb<sup>2+</sup> (brown curve), (c)  $1 \times 10^{-5}$  M 1 and  $1 \times 10^{-5}$  Cd<sup>2+</sup> (pink curve), and (d)  $1 \times 10^{-5}$  M 1 and  $1 \times 10^{-5}$  Cu<sup>2+</sup> (purple curve).

of  $Hg^{2+}$  ions into the aqueous solution of 1, as shown in Figure 3(a). This new peak at 458 nm can be used as a diagnostic absorption for  $Hg^{2+}$  ions. A clear isosbestic point was observed at 432 nm which indicated that the two species (**1-Hg2+** and porphyrin **1**) were in equilibrium (*see* Figure S2 in SI). The ratio of  $I_{458}/I_{422}$  was calculated, which increased from 0 to 1.99. The detection limit (LOD) for  $Hg^{2+}$  ions with cationic **1**was determined to be 0.5 × 10−6 M under the present conditions, which is very comparable with the recent report [25]. Similarly, upon addition of  $Pb^{2+}$  ion, the absorption of the Soret band of **1** was greatly decreased and a new peak at 478 nm appeared simultaneously (Figure 3(b)). This new absorption peak is attributed to  $1\text{-}P\mathsf{b}^{2+}.$  The ratio of  $I_{478}/I_{422}$ was increased from 0 to 2.07. Well-defined isosbestic points at 374 nm and 447 nm were observed indicating that there was a simple equilibrium involved between metal-free porphyrin **1** and metal bound porphyrin, **1-Pb2+** (*see* Figure S2 in SI). The detection limit for Pb<sup>2+</sup> ions with 1 was determined to be  $0.5 \times$ 10−6 M under the present conditions. Similar detection limit was observed in [23]. As shown in Figure  $3(c)$ , upon addition of  $Cd^{2+}$  to the solution of 1, the absorbance of all the peaks decreased with a shoulder taking a shape of a peak at 447 nm. The appearance of a new absorption at 447 nm is accounted for **1-Cd<sup>2+</sup>** complex. The ratio of  $I_{447}/I_{422}$  was increased from 0 to 0.84. Interestingly, copper  $(\overline{Cu}^{2+})$  ions addition to the aqueous solution of **1** showed very marginal change of the absorption spectra of **1**. It did not produce any separate peak in the Soret band of **1**. However, an increased absorption at 552 nm was observed upon addition of increasing amount of  $Cu<sup>2+</sup>$  ions into the aqueous solution of 1. The absorption at 552 nm can be used as a diagnostic absorption for  $Cu^{2+}$  ion (*see* Figure S2). The ratio of  $I_{552}/I_{422}$  was calculated and it showed an increase from 0 to 0.05. The detection limit for  $Cu^{2+}$  ions with 1 was determined to be 1.0 × 10<sup>-6</sup> M under the present conditions, which is eight times smaller than reported [26]. All the results are tabulated in Table 1. The results indicate that the inexpensive metal-free porphyrin **1**

Table 1: The optical parameter of studied porphyrin in water.

	Compound UV-bands [nm]	Soret band [nm]	Q-bands [nm]
		422	521, 553, 589
$1-Hg^{2+}$		422, 458	594, 639
$1-Pb^{2+}$	375	422, 478	
$1 - Cd^{2+}$		422, 447	521, 585
$1 - Cu^{2+}$	375	426	521, 552

can be used as an optical chemical sensor for detecting any of the divalent  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ , and  $Cu^{2+}$  ions in water.

*3.2. Parallel (or Simultaneous) Multi-Ions (Hg2+, Pb2+, and*  $Cd^{2+}$ ) Detection. To simultaneously (or parallel) detect two or more metal ions coexisting in a sample, an aqueous solution of porphyrin **1** was tested against a number of mixed metal ion solutions. An increasing amount of a mixture of different metal ions was added into the porphyrin **1** solution. The variation of electronic absorption of porphyrin **1** was monitored using UV-vis spectroscopy to detect all metal ions coexisting in solution. As shown in Figure 4, the intensity of absorption of **1** exhibited a gradual decrease of the most intense Soret band at 422 nm upon addition of increasing amount of a mixture of  $Cd^{2+}$ ,  $Hg^{2+}$ , and  $Pb^{2+}$ . Diagnostic absorptions for **1-Hg2+** at 458 nm, **1-Pb2+** at 478 nm, and **1-Cd2+** at 447 nm were also observed. The results revealed that the metal-free porphyrin **1** showed different absorption spectra with metal ions  $(Hg^{2+}, Pb^{2+}, and Cd^{2+})$  coexisting in an aqueous solution. Thus, porphyrin **1** represents a single molecular optical sensor which can detect and analyze metal ions, particularly  $Hg^{2+}$ ,  $Pb^{2+}$ , and  $Cd^{2+}$ , simultaneously coexisting in a sample.

*3.3. Influence of Larger Metal Ions on the Determination of*  $Cd^{2+}$ . The detection of  $Cd^{2+}$  ions has always been a challenge



Figure 4:The electronic absorption spectra of aqueous solution of **1**(5.0 × 10−6 M) upon addition of increasing amount [0, 1665, 0.333, 0.4995, 0.666, 0.8325, 0.999, 1.1655, 1.332, 1.4985, 1.665, 1.8315, 1.998, 2.1645, 2.331, 2.4975, 2.664, 2.8305, 2.997, 3.1635, 3.33, 3.4965, 3.663, 3.8295, 3.996, 4.1625, 4.329, 4.4955, 4.662, 4.8285, 4.995, 5.8275, 6.66, 7.4925, 8.325, and 9.15 (×10<sup>-7</sup> M)] of Hg<sup>2+</sup>, Pb<sup>2+</sup>, and Cd<sup>2+</sup> ions.



Figure 5:The electronic absorption spectra of aqueous solution of (a)**1-Pb2+** (5.0 × 10−6 M **1** and 5.0 × 10−6 M Pb2+) upon addition of increasing amount [0.50, 1.00, and 1.5 (×10<sup>-6</sup> M)] of Cd<sup>2+</sup> ions: the inset is the absorption of  $1-M^{2+}$  versus [Cd<sup>2+</sup>] (pink curve is the absorption at 447 nm and brown curve is the absorption at 478 nm), and (b)  $1-Hg^{2+}$  (5.0 × 10<sup>-6</sup> M 1 and 5.0 × 10<sup>-6</sup> M Hg<sup>2+</sup>) upon addition of increasing amount [0.50, 1.00, 1.50, and 2.5 ( $\times 10^{-6}$  M)] of Cd<sup>2+</sup> ions.

due to the very slow complexation reaction in aqueous medium at room temperature [15]. Additionally, the greatest difficulty for determining  $Cd^{2+}$  ions comes from strong interference of larger heavy metal ions. Interestingly, we found that porphyrin 1 can detect  $Cd^{2+}$  ions more effectively in presence of larger metal ions, particularly  $Hg^{2+}$  and  $Pb^{2+}$ ions. The experiment was performed by preparing a solution of **1-M2+** complexes by mixing equivalent amounts of **1** and M2+ ions in water. The changes of absorption spectra of **1- M2+** complexes were monitored by adding increasing amount of  $Cd^{2+}$  ions to see if porphyrin 1 could detect any or both metal ions simultaneously. We effectively employed very slow and more or less the similar metalation rates of metal cations  $(Hg^{2+}, Pb^{2+}, and Cd^{2+})$  with 1 to determine the presence of  $Cd^{2+}$  ion coexisting with other metal cations [15]. As shown in Figure 5(a), remarkably, very rapid change of absorption of aqueous solution of 1-Pb<sup>2+</sup> was observed upon the addition of  $Cd^{2+}$  ions. The aqueous solution of  $1-Pb^{2+}$  produced a peak at 447 nm (**1-Cd2+**) with marginal change of the absorption at 478 nm (**1-Hg**<sup>2+</sup>) upon addition of 1-2 × 10<sup>-6</sup> M of Cd<sup>2+</sup>. The detection limit for  $Cd^{2+}$  ions with 1 was determined to be  $0.5 \times 10^{-6}$  M under the present conditions, which is six times higher than reported [18]. This result indicated that cationic 1 can uniquely sense  $Cd^{2+}$  and  $Pb^{2+}$  coexisting

in a water sample. Similarly, Figure 5(b) demonstrated the simultaneous detection of **1-Hg2+** at 458 nm and **1-Cd2+** at 447 nm when the  $[Cd^{2+}]$  is around  $1 \times 10^{-6}$  M. Interestingly, in all above cases, an increased absorption of **1-Cd2+** and a decreased absorption of **1-M2+** were observed upon addition of increasing amount of  $[Cd^{2+}]$  (*see* the inset of Figure 5(a)). Typically, the absorption of **1-Cd2+** complex appeared as a tiny shoulder peak in the Soret band region of **1**(*see* Figure 3). This tiny shoulder peak of  $1$ -Cd<sup>2+</sup> rapidly turned into a very clear and sharp peak at 447 nm in the presence of metal ion with a large ionic radius. Similar observations were noticed by other researchers. The rate of complexation for smaller metal ions (Cu(II),  $Mn(II)$ , and  $Zn(II)$ ) was found to increase in the presence of metal ions with larger ionic radii [17, 27]. It is attributed to the fact that larger metal ions distort or expand porphyrin and help ease entry for smaller metal ions into its core. The increased absorption for **1-Cd2+** complex clearly revealed its unique sensing ability for  $Cd^{2+}$  ions in presence of metallic ions with large ionic radii, particularly  $Hg^{2+}$  and  $Pb^{2+}$ . However, all the metal ions sensing properties strictly depend on the presence of  $Cu^{2+}$  ion, which is discussed next.

*3.4. Strong Binding Affinity of 1 with Cu2+ Ions.* To determine the effect of divalent  $Cu^{2+}$  ions, an aqueous solution of metalfree porphyrin 1 was titrated with a mixture of  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ , and  $Cu^{2+}$  aqueous solution. The intensity of absorption of **1** exhibited a gradual decrease of the most intense Soret band at 422 nm upon addition of a mixture of  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ , and  $Cu^{2+}$ . Remarkably, no clear diagnostic absorptions for**1-Cd2+** at 447 nm,**1-Hg2+** at 458 nm, and **1-Pb2+** at 478 nm were observed in UV-visible region (*see* Figure S3 in SI). However, a shoulder peak (from 455 to 480 nm) in the diagnostic region for  $Hg^{2+}$  and Pb<sup>2+</sup> was observed indicating the presence of **1-Hg2+** and **1-Pb2+**. A clear diagnostic Qband absorption for **1-Cu2+** was observed at 552 nm. This observation leads us to postulate that  $Cu^{2+}$  ions are forming stronger complex with 1 than other metal ions and that  $Cu^{2+}$ ions are forming the complex with faster rate than the other ions. To see the strong competitive binding of  $Cu^{2+}$  ions with **1** a mixture of  $Cu^{2+}$  and other  $M^{2+}$  ions was added into the aqueous solution **1**. Porphyrin **1** exhibited no diagnostic absorptions of **1-Hg2+** or **1-Pb2+** or **1-Cd2+** upon addition of a mixture of Cu<sup>2+</sup> and Hg<sup>2+</sup> or Cu<sup>2+</sup> and Pb<sup>2+</sup> or Cu<sup>2+</sup> and Cd2+ (*see* Figure S4 in SI), respectively. Instead, diagnostic absorption of **1-Cu2+** was found increasing at 552 nm in all cases. These results indicated that all the **1-M2+** complexes which were produced almost immediately after addition of a mixture of  $M^{2+}$  ions into the solution of 1 are converted into **1-Cu2+** complex. More detailed investigations on possible displacement reactions are discussed next.

*3.5. Displacement of*  $M^{2+}$  *from* **1-** $M^{2+}$  *by Cu*<sup>2+</sup>. To confirm the possible displacement of a  $Hg^{2+}$  from **1-Hg**<sup>2+</sup> or  $Pb^{2+}$  from **1-** $Pb^{2+}$  or  $Cd^{2+}$  from **1-Cd**<sup>2+</sup> by  $Cu^{2+}$  to form **1-Cu**<sup>2+</sup> complex, a number of displacement reactions were carried out. The experiment was performed by adding equivalent amounts

of metal cations  $(Hg^{2+}/Pb^{2+}/Cd^{2+})$  into the porphyrin 1 solution to allow **1** to form **1-M2+** complex in solution. Then, an aqueous  $Cu^{2+}$  ion was added into a  $1-M^{2+}$  solution to see if  $Cu^{2+}$  ion could displace metal ions from the  $1-M^{2+}$ complex. Figure 6(a) showed the formation of **1-Cu2+** from **1-** Hg<sup>2+</sup> complex upon addition of Cu<sup>2+</sup>. The disappearance of diagnostic absorption of **1-Hg2+** at 458 nm and appearance of **1-Cu2+** were observed. Similarly, Figure 6(b) showed the change of  $1-Pb^{2+}$  to  $1-Cu^{2+}$  with the disappearance of the diagnostic absorption at 478 nm and the appearance of the absorption peak at 422 nm. As shown in Figure 6(c), the change of **1-Cd2+** to **1-Cu2+** was observed. Diagnostic absorption of **1-Cd2+** has disappeared with appearance of **1-**  $Cu^{2+}$ . The displacement of  $Pb^{2+}$ , Hg<sup>2+</sup>, and  $Cd^{2+}$  by  $Cu^{2+}$ ion is attributed to the fact that  $Cu^{2+}$  is smaller in size compared to other metal ions. Larger size  $Pb^{2+}$ , Hg<sup>2+</sup>, and  $Cd^{2+}$  ions cannot fit into the core of the central porphyrin. The larger metal ions locate away from the central core of the porphyrin, perhaps at the periphery of porphyrin **1**, and form loosely bound  $1-M^{2+}$  complex, whereas smaller size  $Cu^{2+}$  ions can sit perfectly into the central porphyrin core and form a stable  $1-Cu^{2+}$  complex. This explains the replacement events described above. Similar observations were noticed by Jiang and Chen groups [23, 24]. Thus, this result indicates that this single optical sensor  $1$  can operate as a dual-mode  $Cu^{2+}$ selective sensor via the absorption nature of  $1$  for  $Cu^{2+}$  as well as the absorption ratio metal displacement from the **1-Pb2+**/**1-**  $Hg^{2+}/1-Cd^{2+}$ . This porphyrin 1 presented a rare example of a dual-mode multisignal system for detecting toxic metal ions  $(Pb^{2+}, Hg^{2+}, and Cd^{2+})$ , particularly for Cu<sup>2+</sup> ion [23, 24, 28, 29].

*3.6. Preliminary Analytical Application.* The aqueous solution of **1** was challenged with wastewater sample obtained from a rural wastewater treatment facility, Nacogdoches Wastewater Treatment Plant in Nacogdoches City (East Texas), Texas, USA [30]. The wastewater sample was collected from the second treatment stage, namely, aeration chamber. A different amount of wastewater sample was added to the aqueous solution **1**. Figure 7 showed a gradual decrease of Soret band absorption of **1** at 422 nm, which slowly shifted to the red (435 nm) upon addition of increasing amount of wastewater into the aqueous solution of **1**. Similar observation was found when  $Ca<sup>2+</sup>$  ion was added into **1**, shown in Figure S5. Recent report by Onchoke and his coworkers also indicated that wastewater from Nacogdoches plant contains high concentration of  $Ca^{2+}$  ions (100 ppm) and a very small concentration of  $Cu^{2+}$  ions (0.94 ppm) and almost undetectable amount of other toxic cations, particularly cadmium (0.004 ppm), lead (0.07 ppm), and mercury (0.01 pm) [30]. A highly expensive instrument, inductively coupled plasma optical spectrometry (ICP-OES) instrument, was used for metal ions analysis [30]. Our results showed that the inexpensive, water soluble, and commercially available 1 can detect  $Ca<sup>2+</sup>$  ion in wastewater sample with satisfactory performance. To the best of our knowledge, the water soluble porphyrin-based optical sensor for determining  $Ca^{2+}$  ions has not been reported thus far.



Figure 6: The electronic absorption spectra of aqueous solution of (a) **1-Hg2+** (5.0 × 10−6 M **1** and 4.0 × 10−6 M Hg2+, blue curve), (b) **1-Pb2+** (5.0 × 10−6 M **1** and 4.0 × 10−6 M Pb2+, brown curve), and (c) **1-Cd2+** (5.0 × 10−6 M **1** and 4.0 × 10−6 M Cd2+, pink curve) upon addition of Cu2+ ions (5 × 10−6 M for **1-Hg2+** and **1-Pb2+**, 4 × 10−6 M for **1-Cd2+**).



Figure 7: The electronic absorption spectra of aqueous solution of (a)**1** (5.0×10−6 M) in DI water (black curve), (b)**1** in DI water : wastewater (15 : 1, brown curve), (c) **1** in DI water : wastewater (7 : 1, green curve), (d) **1** in DI water : wastewater (3 : 1, purple curve), (e) **1** in DI water : wastewater (1 : 1, blue curve), (f) **1** in DI water : wastewater (1 : 0.33, orange curve), and (g) **1** in DI water: wastewater (1 : 0.005, red curve).

This will be the first porphyrin-based optical sensor for  $Ca^{2+}$ . However, 1 was not able to detect  $Cu^{2+}$  due to the strong absorption of **1-Ca2+** complex in the region of **1-Cu2+**.

### **4. Conclusion**

We examined porphyrin **1** as an inexpensive, water soluble single optical chemical sensor and/or metal ion receptor for the detection of toxic metal ions. Cationic porphyrin **1** produced different electronic absorptions in UV-vis region upon interacting with  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ , and  $Cu^{2+}$  ions. This porphyrin can detect two or more toxic metal ions simultaneously coexisting in a water sample. We also found that porphyrin 1 can detect  $Cd^{2+}$  easily in the presence of metallic ions with large ionic radius, particularly  $Hg^{2+}$  and  $Pb^{2+}$ . Finally, we observed that porphyrin 1 can operate as a  $Cu^{2+}$  ion selective sensor via metal displacement from the  $1-Hg^{2+}$ ,  $1-Pb^{2+}$ , and  $1-Cd^{2+}$ . The results show that this porphyrin **1** is a promising sensor for metals ions in waste water and nutritional sample.

### **Competing Interests**

The authors declare that they have no competing interests.

#### **Acknowledgments**

Matibur Zamadar thanks The Welch Foundation Departmental Grant (AN-0008) and Michael A. Janusa, Chair and Professor of Chemistry and Biochemistry at SFASU, for support. Matibur Zamadar acknowledges support from RCA grant at the Stephen F. Austin State University Research Enhancement Program. Matibur Zamadar thanks Dr. Darrell R. Fry in the Department of Chemistry and Biochemistry at SFASU for discussion and technical assistance.

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