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A Highly Selective Colorimetric Aqueous Sensor for Mercury

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Abstract: A new colorimetric mercury sensor is reported based on binding to terpyridine derivatives. It is able to selectively detect Hg^{II} ions over a number of environmentally relevant ions including Ca^{II}, Pb^{II}, Zn^{II}, Cd^{II}, Ni^{II}, Cu^{II}, and others. The response time upon exposure to Hg^{II} is instantaneous. By the "naked eye," the detection limit of Hg^{II} is 2 ppm (25 μM) in solution. With a spectrometer, this detection limit is increased down to 2 ppb (25 nM), which is the current EPA standard for drinking water. The significant problem of mercury poisoning requires new methods of detection that are sensitive and selective. Here we report a new simple system that takes advantage of the unique optical properties generated by terpyiridine–Hg complexes.

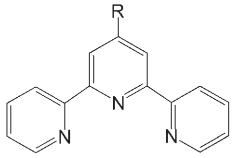
Keywords: colorimetric chemistry · mercury · polymers · sensors · terpyridine

Introduction

Mercury poisoning remains a significant threat to human health, yet global mercury emissions continue to rise.[1] In the United States, nearly 87 % of mercury emissions result from solid waste incineration and the combustion of fossil fuels.[2] The long atmospheric lifetime of mercury causes contamination across vast quantities of land and water.[3] To make the problem worse, bacteria convert elemental and ionic mercury to methyl mercury, adding this potent neurotoxin to the food chain.[4–6] Mercury poisoning causes serious sensory, motor, and cognitive disorders in human beings.[5]

Knowing the seriousness of this problem, significant research efforts have been devoted to improving mercury detection.[7–9] Current industrial approaches rely on costly, time-consuming methods like atomic absorption/emission spectroscopy or inductively coupled plasma mass spectroscopy, which are not very amenable to portable, convenient "in-the-field" detection. Therefore, many laboratories have focused on "colorimetric,"[10–18] redox active,[19,20] and/or fluorescence[6,9,19,21–29] chemosensors in the hope of developing new mercury sensors. Many of these suffer from competing metal ions, are incompatible with aqueous media, and/or have slow Hg^{II} response times. In all cases, it is critical to selectively detect mercury in the presence of other environmental metals especially Pb^{II} and Cu^{II}. Recent reports suggested that nitrogen binding sites are a good choice[19] for the selective recognition of heavy metals such as Cd^{II}, Pb^{II}, and Hg^{II}.

In this communication, a new colorimetric mercury sensor is reported based on binding to terpyridine derivatives (**1a**–**d**). It is able to selectively detect Hg^{II} ions over a number of environmentally relevant ions including Ca^{II}, Pb^{II}, Zn^{II}, Cd^{II}, Ni^{II}, Cu^{II}, and others. The response time upon exposure to Hg^{II} is instantaneous. By the "naked eye," the detection limit of Hg^{II} is 2 ppm (25 μM) in solution. With a conventional spectrometer this detection limit is increased down to 2 ppb (25 nM), which is the current EPA standard for drinking water.[30] Initially it was surprising to discover that **1** appears to be a sensitive and selective colorimetric sensor for Hg^{II}; however, as this report shows, **1** is a simple yet effective molecular scaffold to detect Hg^{II}.



1a R=H
1b R=-$O(CH_2)_3$-CH_3
1c R=-$(OCH_2CH_2)n$$OCH_3$
1d R=MMA-based polymer

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

Results and Discussion

The selectivity of **1a–d** (the syntheses of which have been previously reported[31–34]; note that the different molecules have no observable differences in the reported experiments except for the "dip-stick" analysis, see below, in which the polymer sample **1d** produced more uniform films) for Hg^{II} over a number of environmentally relevant metals ions such as Ca^{II}, Ba^{II}, Pb^{II}, Co^{II}, Cd^{II}, Ni^{II}, Mg^{II}, Zn^{II}, and Cu^{II} was investigated and the results are shown in Figure 1. The addition of HgCl$_2$ in water to a solution of **1** in DMSO/water (1:3.5) caused the immediate appearance of a pink color. Conversely, addition of the other metals to solutions of **1** resulted in little or no color change, except for Cu^{II} which turned slightly blue as expected. More importantly, the introduction of a tenfold excess of these competing heavy metals to a solution of **1** did not impact the ability of Hg^{II} to induce the pink color. The pink color only occurs in the presence of Hg^{II} with or without competing metal ions. The pink color results from binding of Hg^{II} to **1** and the absorption coefficient (ε) of Hg^{II}–**1b** is 133 times larger ($4\times10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$) than that of Co^{II}–**1b** ($0.3\times10^2\,\mathrm{L\,mol^{-1}\,cm^{-1}}$) at 557 nm.

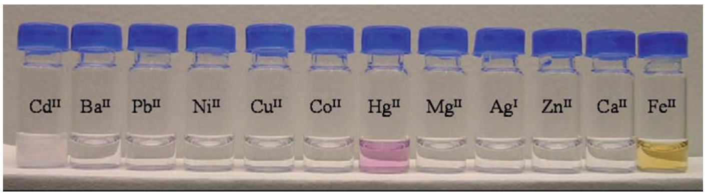


Figure 1. The specific color change to pink of **1** is only observed upon addition of Hg^{II}. This color change is also observed in the presence of competitive metal ions, even at tenfold excess. No pink color is observed for other environmentally relevant bivalent metal ions including Ca^{II}, Ba^{II}, Pb^{II}, Co^{II}, Cd^{II}, Ni^{II}, Mg^{II}, Zn^{II}, and Cu^{II}.

To determine the detection limit, the amount of Hg^{II} added to solutions of **1** was gradually decreased as shown in Figure 2 (top and middle). By "naked-eye" detection, a lower limit of 2 ppm, or 25 μM, Hg^{II} could be seen in these solutions (Figure 2, top). To further quantify the detection limit, a conventional UV/Vis spectrometer was employed to record the changes in the absorption spectra as shown in Figure 2 (middle). In this manner, the detection limit could be extended down to 2 ppb, or 25 nM, which meets current EPA standards for the maximum allowable level of Hg^{II} in drinking water.[30] The colorimetric response of **1a** and **1d** versus the concentration of Hg^{II} is shown to be linear and essentially identical in Figure 2 (bottom).

To gain some insight into the metal chelation between Hg^{II} and **1**, isothermal titration calorimetry (ITC) was performed (in triplicate) to evaluate the binding of Hg^{II} and another metal, in this case Co^{II}, with terpyridines (Figure 3). The good solubility of **1c** in 1:3.5 DMSO:H$_2$O allows metal–terpyridine association values to be reported in aqueous solutions rather than organic solvents for the first time.[35] Both Hg^{II} and Co^{II} gave the expected binding ratio near 0.5 metal ions per terpyridine ligand molecule, illustrating that even at high metal concentrations, the metal center prefers to have two terpyridine molecules chelated; this coordination was further evidenced by the crystal structure published previously.[36] In contrast, a Cu^{II}/terpyridine system can be driven to a 1-to-1 binding ratio quite easily (Supporting Information). Interestingly, from ITC, it appears that terpyridine derivatives do not have an inherent chelating preference for Hg^{II} over Co^{II} evidenced by the similar enthalpy and association constants between the two systems (Figure 3). These results suggest that the selectivity and sensitivity for Hg^{II} depends more strongly on the differences in optical properties than binding strength. Although another mechanism leading to preferential Hg^{II}/terpyridine binding cannot be ruled out.[37]

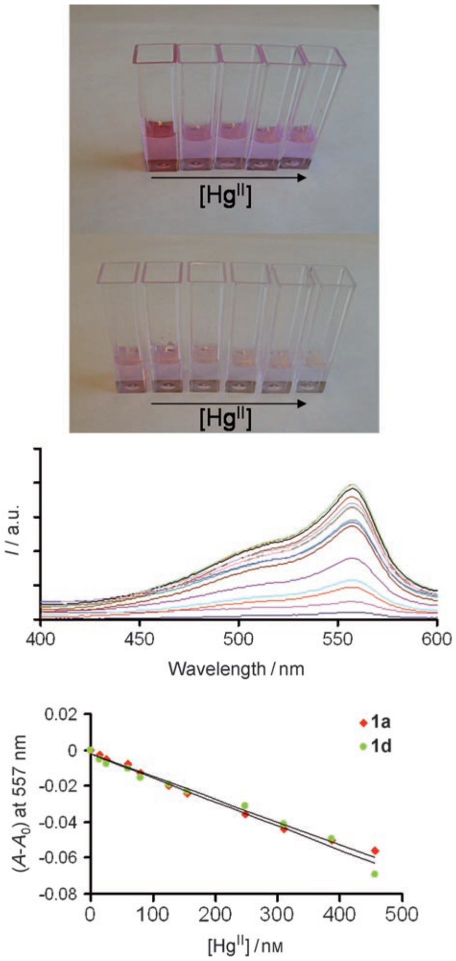
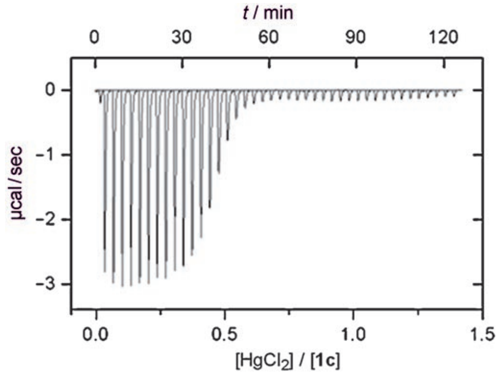


Figure 2. Top: Color change from left to right (as indicated by the arrow) due to decreasing Hg^{II} concentration. The initial volume of Hg^{II} was 2000 ppm and the final volume was 2 ppm. Middle: Absorption spectra of **1** in DMSO/water (1:3.5) with decreasing Hg^{II}. Bottom: A plot of ($A-A_0$) versus Hg^{II} concentrations for **1a** and **1d**.

Nonionic surfactant was added to the system for two reasons: 1) to see if the DMSO concentration could be reduced and 2) to determine if the system was sensitive to amphiphilic impurities. It was determined that only 5% DMSO



	Hg^{II}	Co^{II}
Binding ratio ($[M^{2+}]$ / [**1c**])	0.45	0.41
ΔH kcal mol^{-1}	−16.2	−16.1
K_a (M^{-2})	2.3×10^{6}	9.1×10^{6}

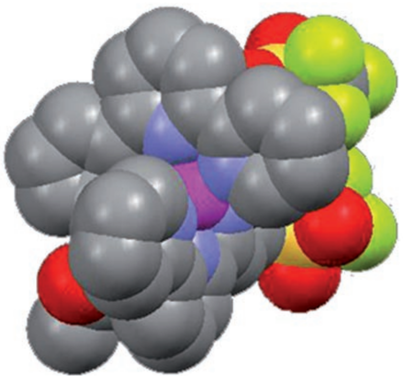


Figure 3. Top: ITC raw data of the titration of **1c** with Hg^{II}. $[\mathbf{1c}]_{initial} = 0.15$ mM and $[Hg^{II}]_{syringe} = 1.5$ mM. Also shown is a table comparing thermodynamic binding parameters of **1c** with either Hg^{II} or Co^{II}. b) Crystal structure of $[Hg(terpy)_2]$ (terpy: terpyridine) containing two $CF_3SO_3^-$ ions and one acetone molecule reported by Matković-Čalogović et al.[36]

was needed to make the system completely soluble in water and the colorimeteric "naked-eye" detection limit remained unchanged (2 ppm) in the presence of surfactant. In addition, chelation experiments with EDTA showed that the response was reversible. Upon addition of two equivalents of EDTA, the pink color disappeared. Then addition of one equivalent of Hg^{II} immediately reproduced the pink signal. This cycle was repeated three times with no observable deviations.

Motivated by the favorable features of this system in solution, the development of paper strips coated with **1d** were investigated to determine the suitability of a "dip-stick" method for detecting Hg^{II}, similar to that commonly used for pH measurements. When the litmus strips coated with **1d** were introduced into an aqueous solution of Hg^{II} ions, an immediate color change to pink was observed on contact. Determination of the detection limit for these "dip-sticks" showed a lower limit of 2 ppb. Figure 4 shows the "standard" pink colors for known concentrations of Hg^{II} in solution and three experimental "dip-sticks". The litmus paper method could detect Hg^{II} at different pH values ranging from 2.5 to 9 demonstrating that the system works over a wide range of pHs. The development of such a "dipstick" approach is extremely attractive for "in-the-field" measurements that would not require any additional equipment.

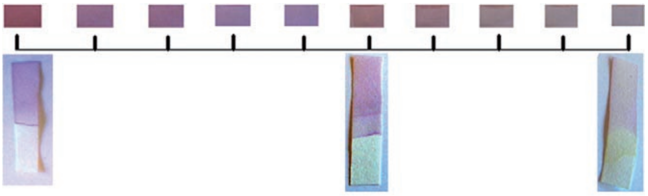


Figure 4. Demonstration of polymer **1d** coated "dip-sticks" for three different concentrations of Hg^{II}.

Conclusion

In conclusion, the ability of terpyridine to selectively and sensitively detect Hg^{II} in aqueous environments was demonstrated. A detection limit of 2ppb, the EPA standard for drinking water, was obtained using either a spectrophotometric or litmus paper method. The response time is instantaneous and the detection limit was achieved even in the presence of excess metal ion competitors of concern as drinking water pollutants. Binding data and absorption spectroscopy suggested the sensitivity arises from the large difference in the absorption coefficient for **1**-Hg^{II} complexes. Translation of the solution observations to the litmus paper method could greatly simplify in-field detection of Hg^{II} without the need for special equipment. Despite the simplicity of this system, it has an excellent detection limit and appears to be very versatile.

Experimental Section

Stock solutions of terpyridine in DMSO or DMF (42 mM) and $HgCl_2$ in water (63 mM) were made and diluted with water to the desired concentrations from 10 mM to 0.16 µM. For analar $HgBr_2$, 0.5 M HCl was used to make stock solutions due to the poor solubility of the salt. Titrations to find the lower detection limit of Hg^{II} were made by keeping the volume of terpyridine constant and varying the amount of Hg^{II}. To demonstrate the difference in coloration upon chelation with Hg^{II} over Fe^{II}. See the supporting information.

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