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Sol-Gel Derived Nanostructure Optical Chemosensor Based on 4'-(4-methyl phenyl)-2,2':6',2"-terpyrine for Selective Determination of Mercury (II) Ion

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Abstract

A solution chemistry study was conducted spectrophiotometrically to examine interaction between different cations and methyl-phenyl terpyridine compounds. A new versatile optical sensor based on silica for the highly sensitive and selective determination of mercury ion (Hg^{2+}) based on a change in the absorption spectrum of a sol-gel film in an aqueous solution was proposed. A film was prepared composed of tetraethoxysilane (TEOS) and methyl-phenyl terpyridine (MPTPy) as chromoionophore and ethylene glychol (ETG) as surfactant additives. The influence of different parameters was studied for the sensitivity, linear range, and selectivity of the film. Satisfactory analytical sensing characteristics for determining Hg^{2+} ions were obtained in terms of selectivity, reversibility, and reproducibility with an excellent detecting range. In addition, the optical film responds to Hg^{2+} ion reversibly over a wide dynamic range of 1.0×10^{-8} to 1.0×10^{-3} mol/L with a response time of 5 Min. The proposed sol- gel film has been successfully applied to directly determine Hg^{2+} ion in spiked samples.

Keywords: Chemosensor, Mercury (II) ion, Sol-gel film, Chromoionophore.

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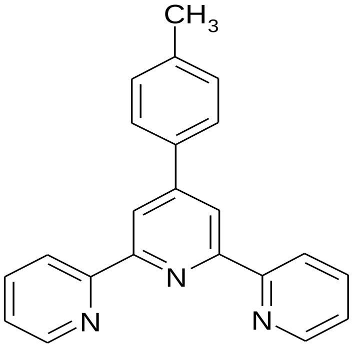
Introduction

In many areas of applied analytical chemistry, such as clinical, process control, environmental samples, food and beverage, determination of ionic species concentration requires a simple and rapid method in aqueous media. The design of discriminating and sensitive optical sensors is still considered as an important emerging frontier in the field of analytical chemistry, and it has attracted the attention of scientific researchers mainly due to the need for easy, fast, and cost-effective monitoring of environmental samples such as for heavy metal ions in aqueous solution in real time. Optodes contain a sensing membrane that has a selective property in reacting with the light source, analyte, detector, and wavelength selection device. The analyte's reaction with a specific indicator (or the analyte itself) causes a spectral shift in absorption or emission, which directly or indirectly measures the analyte concentration. Addition of reagent, further sampling or dilution is usually not required. In the last decade, many efforts have been made to develop optical molecular chemosensors for Hg (II) ion,While these sensors suffer from limitations such as narrower linear dynamic range and high detection limit [1-5].

One of the most extensive and important classes of different ligands in in coordination chemistry is 2,2' :6',2″-Terpyridine (terpy) and its derivatives [1,2]. The popularity of terpy as an attractive ligand for scientists is easy to understand. It is straightforward to synthesize, commercially available and while various terpy derivatives, especially those that can be substituted at the 4' position, are also easily available [3]. Terpy, usually in a tridentate fashion; can bind to both metal ions with low and high oxidation states [2].

We have recently reported different molecular structures and crystallographic symmetries with the crystal structures of 4'-chloro-2,2':6',2"-terpyridine Pb (II) complexes in which π-π interactions and hydrogen bonding have an important effect on the formation of supramolecular networks with special properties [9,10]. To extend our findings and studies in the field of supramolecular chemistry of the tridentate ligand, 4'-(4-methylphenyl)-2,2':6',2"-terpyridine (Mephtpy) (Scheme.1), study in the coordination, and surface electrochemistry [11-15].

In this research, the application of this compound for constructing selective sol-gel based sensor for Hg^{2+} ion is presented. The aim of this research work is to introduce a new and specific method in different sample solutions for the selective determination of mercury ions. Recent findings show that The use of this terpyridine derivative (Mephtpy) for the manufacture of optical sensors is limited [16,17]. Recently, selective sensors for important anions, cations and drugs substances have been reported in various experimental samples [8-10].



Scheme 1. Chemical structure of terpyridine derivative (Mephtpy).

Experimental

Reagents

Reagents grade tetraethoxysilane (TEOS), hexadecyl trimethyl ammonium bromide (HDTMABr), and ethanol were prepared from Merck and used without further purification. Nitrate salts of the highest degree of purity and without further purification except for vacuum drying were all purchased from Merck. The terpyridine derivative (MPTPy) was synthesized and used after recrystallization. Deionized water was used in all stages of this research work. The stock Hg^{2+} aqueous Solution (1.0×10^{-4}M) was prepared by dissolving proper amounts of $Hg(NO_3)_2 . 2H_2O$ in deionized water. Working standard solutions of Hg^{2+} ions were prepared by diluting the stock solution before use.

Instrumentation

All Absorbance measurements were performed with a Perkin-Elmer double beam spectrophotometer with quartz cells. To measure pH at standard room temperature, a Metrohm combined pH glass electrode was used.

Preparation of sol-gel based optode films

The general procedure to prepare the sol-gel films was to mix thoroughly 3ml of TEOS and 1mg of hexadecyl trimethyl ammonium bromide (HDTMAB) with 3 mg of MPTPy and solvent mediator in the 5ml of ethanol. Chromoionophore (MPTPy)(1mg) was added to this mixture and the prepared solution was mixed well. The resulting mixture was cast into two identical membranes of 5-µm thickness on two glass plates mounted in a UV-visible quartz cell using a laboratory-made spin-on-device. All blank reference membranes were prepared using the same technique, except without using MPTPy. Then the glass plate covered with the membrane was placed vertically inside the quartz cell containing 2 ml of aqueous sample solution., and the blank membrane (without chromoionophore) covered on the glass plate was placed in the resulted reference cell. Finally, the sample cell was titrated with standard anion solutions.

Results and discussion

Solution studies

To reach a convincing conclusion about the selectivity and stability of a new compound, in the stage of preliminary studies, the visible-UV spectrum of MPTPy with various important anions was studied in acetonitrile solution. A rapid color change occurred upon addition of Hg^{2+} ion when a 1.0×10^{-6} M solution of MPTPy in acetonitrile was titrated with standard solutions of various cations (Figure 1). According to Figure 1, the increase in the absorption band of the complex at the wavelength of 466 nm and the decrease in the absorption UV-band of the Hg^{2+} complex at the wavelengths 322 and 385 nm can be seen.

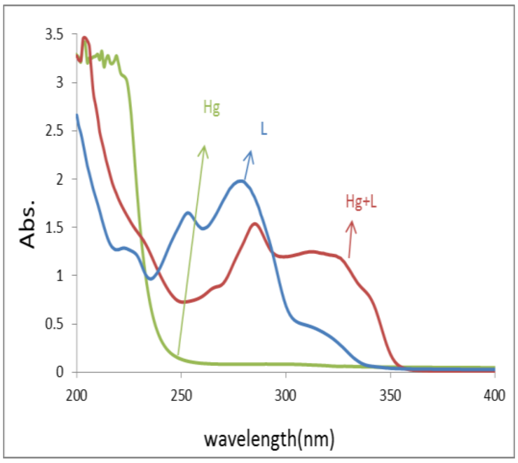


Figure 1. Uv-vis absorption spectra due to the interaction between 5×10^{-5} mol/L solution of MPTPy ligand with Hg^{2+} in acetonitrile solvent.

The titration absorption spectra for Hg^{2+} ion and MPTPy was shown in figure 2.

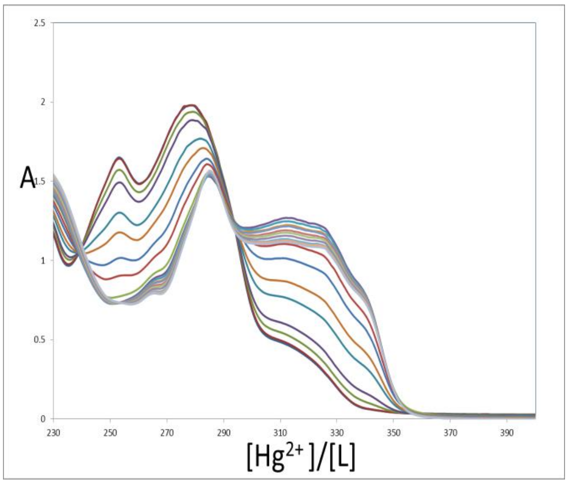


Figure 2. Absorption spectra for the titration of MPTPy ligand (5×10^{-5} mol/L) in acetonitrile solution with the increasing amounts of Hg^{2+} ions (1.0×10^{-3}) mol/L

The mol- rato plot for determination of stoichiometry between Hg^{2+} and MPTPy was shown in figure 3. The stoichiometry was 1:1.

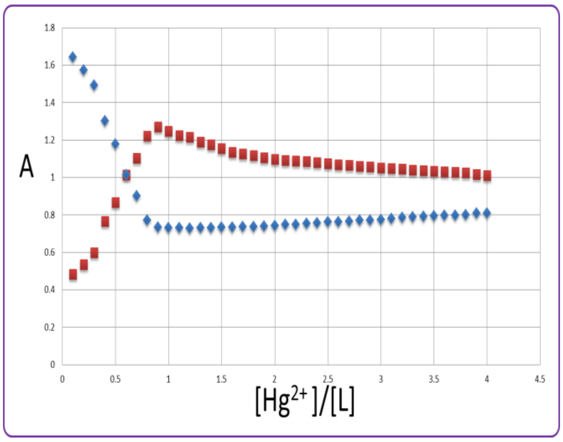


Figure 3. The absorbance versus Hg^{2+} mol ratio plot to ligand measured at 253 and 312 nm in acetonitrile solution.

While spectral changes, in adding other actions, including Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Fe^{2+}, and Zn^{2}+ in the sensing solution were not observed. This high selectivity of the desired compound is due to the formation of a new adduct between Hg^{2+} ion and Fe (III) in the center of the terpyridine units [12]. Therefore, according to this selectivity of MPTPy compound, it was expected to act as a selective chromoionophore for Hg^{2+} in the preparation of sol-gel optical electrode.

Operation principle

The change in absorption spectrum based on the response mechanism of the optical sensor can be described as follows. When the sensor thin film makes effective contact with Hg^{2+} ions with different concentrations in the aqueous solution phase (aq) and L in the sol-gel thin film (s), with the formation of an m: n complex, an equilibrium system is established [13-14]:

$$m\ Hg^{2+}(aq) + n\ MPTPy\ (sol\text{-}gel\ film) \leftrightarrow \quad Hg^{2+}{}_{(m)}\ (MPTPy)_n\ (s) \qquad (1)$$

Where, K is the equilibrium constant. The difference between concentrations and activities is ignored. The value of K can be defined using the law of mass action as follows:

$$K= [Hg^{2+}{}_{(m)}\ (MPTPy)_n]\ (sol\text{-}gel\ film)/\ ([Hg^{2+}\ (aq)]^m[MPTPy]^n) \qquad (2)$$

In the membrane phase, the relative absorption intensity is described as the ratio of uncomplexed MPTPy, $[MPTPy]_{org}$, to its total amount, $[C_T]_{org}$, so that:

$$\alpha = [L]_{org} / [C_T]_{org} \qquad (3)$$

In practice, by measuring the absorbance intensity of the optical sensor, the value of α was determined during the titration of the membrane with Hg^{2+} ions, A in λ = 466 nm,

$$\alpha = (A-A_0)/(A_I-A_0) \qquad (4)$$

Where A_I and A_0 are the limiting absorption intensities of the optical sensor at α =1 (totally complexed MPTPy), and α =0 (uncomplexed MPTPy), respectively. The relationship between the concentration of Hg^{2+} ion in the aqueous sample solution, Hg^{2+} and α – value, can be obtained from Eq. (2) and (3) as follows:

$$\alpha^n/(1-\alpha) = 1/(K[C_T]^{n-1}[Hg^{2+}]^m) \qquad (5)$$

To quantitatively determine the concentration of mercury ion using the proposed optical sensor, equation 5 can justify this process as a basis.

Response behavior of sol- gel film

It is well known that the sol-gel film composition may greatly affect the working concentration range, and the response characteristics of the optical sensors [15,18, 19].

The prepared sol-gel sensor was used for the titration of mercury ions in aqueous solution, and the results of the titration response of this sensor are shown in Figure 4.

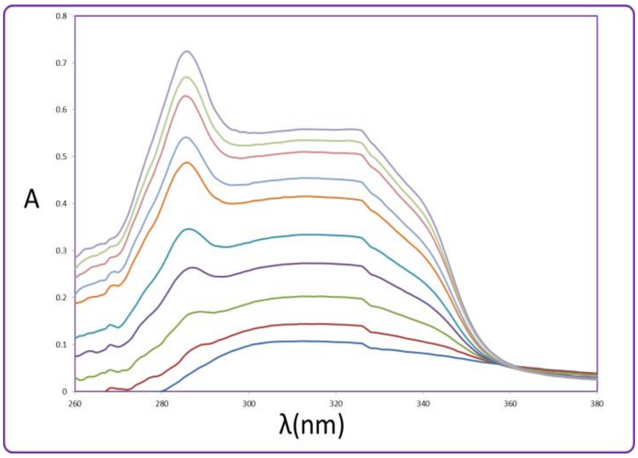


Figure 4. Absorption spectra for the titration of sol-gel thin film with the increasing amounts of Hg $^{2+}$ ions (1.0 × 10^{-3}) mol/ L in aqueous solution.

Effect of pH, calibration curve and response time

The response of the optical sensor film was investigated under the influence of different pH values in the pH range 2.0 -12.0 for a 1.0×10^{-5} M Hg^{2+} solution (adjusted with NaOH or HNO_3), and the related results are illustrated in Figure 5. As can be seen, in the range of pH 3.0-9.0, the response of the sensor remains constant, after which, the α value changes significantly. Drift observed at higher and lower pH values could be due to the formation of some hydroxyl complexes of Hg^{2+} ion in solution and the protonation of the ion carrier, respectively.

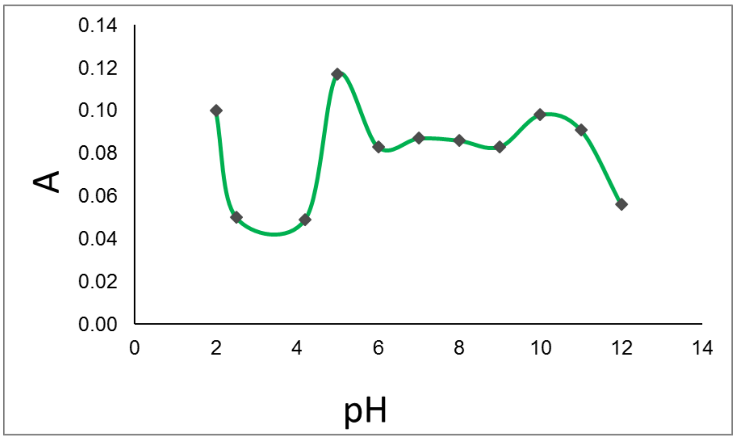


Figure 5. The effect of pH values on the response function of the Sol- gel film.

Various experiments were performed under optimal experimental conditions at different concentrations of Hg^{2+} for the optical response of the proposed Hg^{2+} selective optosensor. The calibration graph was obtained for Hg^{2+} ions at wavelength of 466 nm. For Hg^{2+} ion, the dynamic concentration ranges of the proposed sensor were 3.1×10^{-4} to 2.54×10^{-8} mol/L. The detection limit, which was 4.2×10^{-8} mol/L as determined according to the 3σ of the blank membrane film. Over the entire concentration range, the obtained static response time for the sensor is only about 60 seconds (Figure 6). Optical sensor thin films can be used if not used and stored for at least 4 weeks in a dry and dark environment.

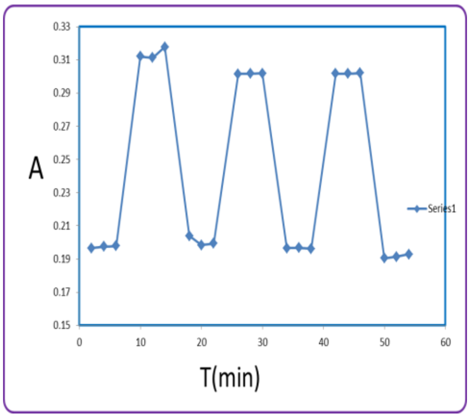


Figure 6. The reversibility of the sol- gel film from the absorbance measurements in aqueous solution of Hg^{2+} (1.0×10^{-6} mol/ L).

SEM Characterization

Figure 7 displays a typical morphology of the unmodified sol-gel film (a), the modified sol-gel based sensors with terpyridine derivative ligand (b) and sol-gel- ligand after Hg^{2+} adsorption (c) characterized by SEM technique. As shown ligand presence did not change, the morphology of sol-gel based texture, but made it more compact. However, it can be clearly seen that the therpyridine ligand dispersed homogeneously. Figure 7 c shows the surface of the film after the absorption of Hg^{2+}, which indicates the interaction of resulted ions with the active sites of the ligand on the sensor in nano dimensions.

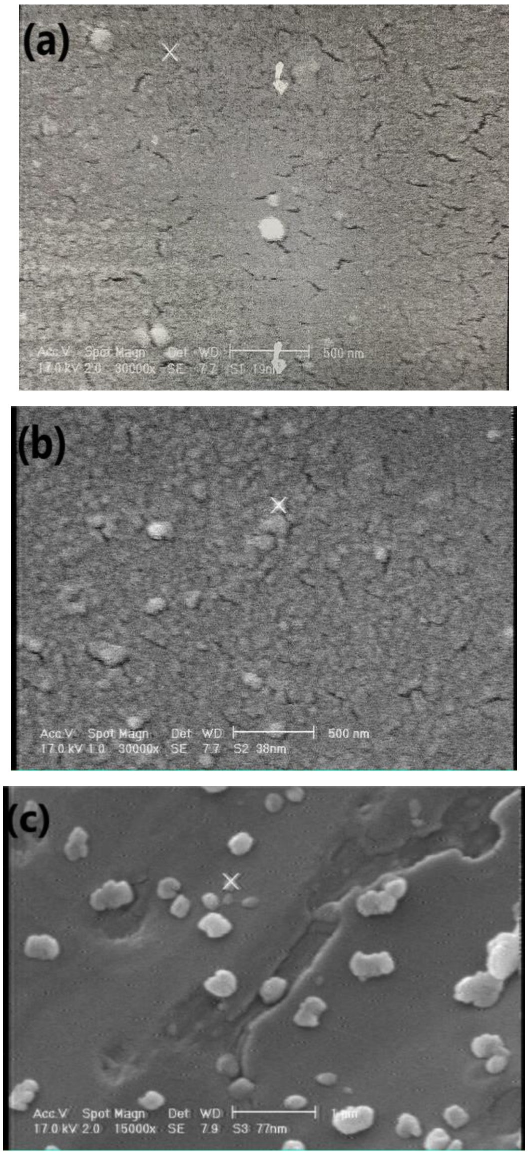
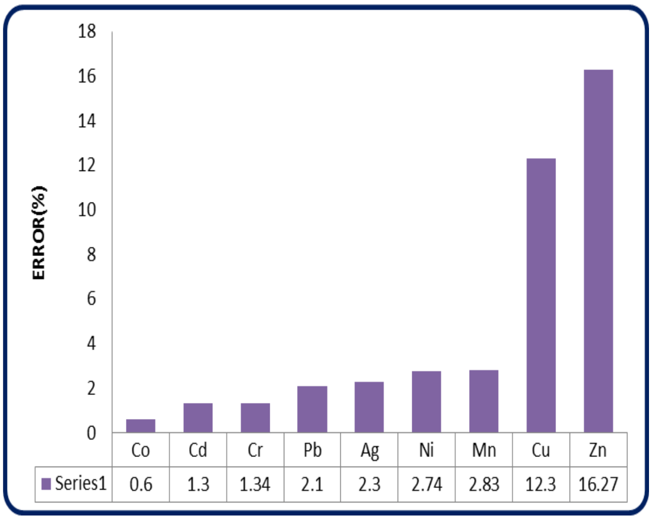


Figure 7. SEM images of (a) unmodified Sol- gel film (b): modified Sol-gel film with MphTpy ligand; (c): Sol-gel-ligand film after Hg^{2+} adsorption.

Interference tests

In the presence of different interfering ions (Figure 8), to investigate the selectivity of the proposed optosensor towards Hg^{2+}, the selectivity coefficients (K_{Hg}^{opt}), Performance description of a new sensor for an interfering ion, B, relative to Hg^{2+} ion, A, were measured by the separate solution technique (SSM) [20-28]. As seen, the selectivity pattern is $Hg^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+} > Mn^{2+} > Ag^{+} > Pb^{2+} > Cr^{3+} > Cd^{2+} > Co^{2+}$.



	Co	Cd	Cr	Pb	Ag	Ni	Mn	Cu	Zn
■ Series1	0.6	1.3	1.34	2.1	2.3	2.74	2.83	12.3	16.27

Figure 8. Effects of some diverse cations on the sol-gel sensor response to the Hg^{2+} ion.

Conclusion

The obtained results reported in this study demonstrate the ability of Mephtpy ligand to coordinate Hg^{2+} metal ions in the sol-gel derived film. The proposed Hg^{2+} ion-selective optical sensor has many advantages including selectivity, reversibility, shortest response time, and good reproducibility with an excellent detecting range. It was applied to determine the concentration of Hg^{2+} ions in a real sample.

Acknowledgements

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Declaration of Interests

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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