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Fluorimetric Chemosensors Combined with Familiar CSPT Devices for the Selective Detection of Mercury(II) Ions

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Abstract

Fluorimetric and Computer Screen Photoassisted Technique (CSPT) studies on the binding properties of three coumarin pendant arm derivatives of mixed aza-thioether macrocyclic ligands (**L1-L3**), incorporated into PVC plasticized polymeric membranes, towards a number of different metal cations were carried out. An enhanced selectivity of the ligands towards Hg^{2+} ion was detected. In particular, the DOS plasticized membrane containing **L3** and tetrakis(p-chlorophenyl)borate, TpCIPB-, as lipophilic anionic additive, displayed a strong fluorescence activation by Hg^{2+} over the wide concentration range of 10^{-7} to 10^{-3} M. The influence of the ratio among ligand and lipophilic additive on the membrane performance was tested. In addition, the CSPT measurements showed that **L3** possesses a unique selectivity towards Hg^{2+} ion with respect to several common diverse cations. Moreover CSPT technique permits to perform the fast and low cost monitoring of mercury (II) ions, by application of familiar devices and a chemometric approach.

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Keywords: mercury determination; fluorimetric and CSPT technique; mixed aza-thioether ligands.

1. Introduction

The accurate and sensitive determination of mercury at low levels in real matrices is a challenging analytical task. The environmental mercury contamination has dramatically increased in the past decades, due to the expanded use in industry and agriculture [1]. When present in the aquatic ecosystem, the mercury ions represent one of the most dangerous contaminants, due to their high toxicity and possibility to accumulate in living cells. Thus, in humans mercury accumulation hardly damages the nervous and gastrointestinal systems, and may even provoke the respiratory or kidney failures [2]. Among the standard methods of mercury analysis, Atomic absorption spectrometry, inductively coupled plasma atomic

emission spectrometry, and inductively coupled plasma mass spectrometry are the most commonly used techniques [3-5]. To respect the above mentioned methods, the development of chemical sensors, both electrochemical [6-8] or optical [9] ones, for the determination of heavy metal ions has become popular, due to the advantage of simple preparation and handling, low cost, reasonable selectivity and improved sensitivity. In the present work, three mixed aza-thioether macrocycles, having coumarin derivatives as fluorogenic fragment, were exploited as receptor units for the development of optical Hg^{2+} sensors, Fig. 1.

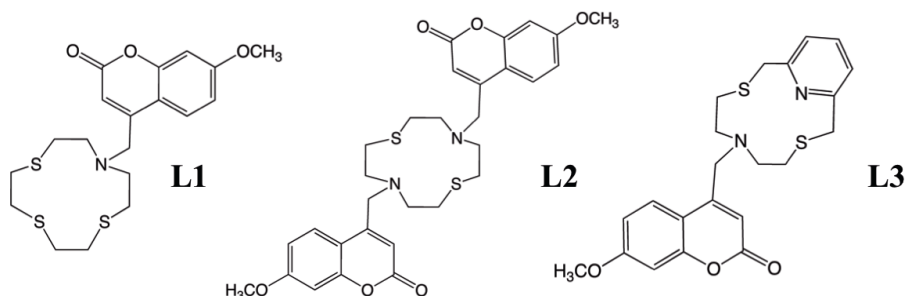


Fig. 1: The chemical structures of tested fluoroionophores **L1-L3**.

2. Experimental

High molecular weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS), o-nitrophenyl octyl ether (o-NPOE), potassium tetrakis-(4-chlorophenyl)borate (TpClPBK) and potassium tetra(bis)-3,5-trifluoromethylphenylborate ($\text{T}(\text{CF}_3)_2\text{PBK}$) were purchased from Fluka. The ligands **L1-L3** were prepared according to the literature methods at the department of Chemical and Geological Sciences of the University of Cagliari, Monserrato, Italy. Tetrahydrofuran (THF), 4-morpholinoethanesulfonic acid (MES) were purchased from Sigma-Aldrich. THF was freshly distilled prior to use. All the other chemicals were of analytical grade and used without further purification. The sample solutions for CSPT and fluorimetric measurements were prepared dissolving corresponding transition metal nitrates of given concentration in 0.01 M MES pH 5.5 background. Polymer membranes of 100 mg weight consisted of 3 wt % of ionophore, PVC/plasticizer (1:2) polymeric matrix and varying amount of lipophilic additive. All components were dissolved in 1 ml of THF and about 20 ml of the mixture were cast onto transparent glass slides. Solvent was allowed to evaporate overnight.

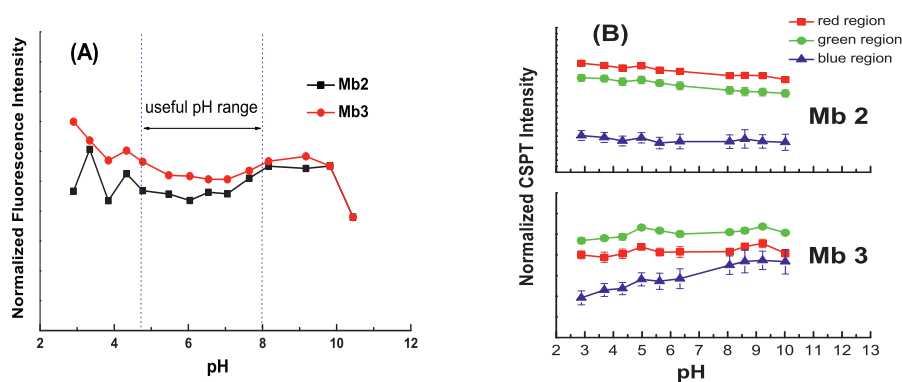


Fig. 2: Effect of the solution pH on: (A) fluorimetric response; (B) CSPT response of Mb2 (**L1**/DOS/TpClPBK) and Mb3 (**L1**/DOS).

Prior to the measurements, the membranes were soaked in a MES buffer for 10 min. For fluorimetric measurements, the coated glass was diagonally placed in a cuvette; the emission intensity was measured at 500 nm in solutions containing increasing concentrations of Hg^{2+} ions (excitation wavelength of 367 nm). In the CSPT approach, the LCD served as a polychromic light source, and the digital web-cam as a signal detector. The film optical intensity variation upon exposure to varied amounts of the target analyte was registered and transformed in analytically useful signal by home written MATLAB codes.

3. Results and discussion

At the first step of the study, we compared the complexation ability of the ligands, determined by their chemical structure. For each ligand, three membranes of different compositions were prepared by incorporation of 3 wt% of **L** in PVC plasticized with DOS or oNPOE, and containing (except the last membrane in the series) 1 wt% of TpCIPBK cation exchanger. As can be seen from the Fig.2, the film response was independent on the background solution pH in the range of 5.0-8.0 (see for Mb 2,3). An increase of the membrane fluorescence intensity emissions was detected upon increasing the Hg^{2+} concentration, indicating a neutral carrier functioning of all three ligands, **L1-L3**. In fact, addition of TpCIPB⁻ significantly stabilized in some cases the membrane responses, improving also their selectivity. The membrane Mb8 (**L3**/DOS/TpCIPBK) exhibited the greatest fluorescence response, indicating an optimal Hg^{2+} binding ability of **L3**, Fig.3A. CSPT measurements revealed instead an enhanced selectivity of oNPOE-plasticised Mb 7 containing **L3** towards Hg^{2+} ions over the other tested cations, Fig.3B.

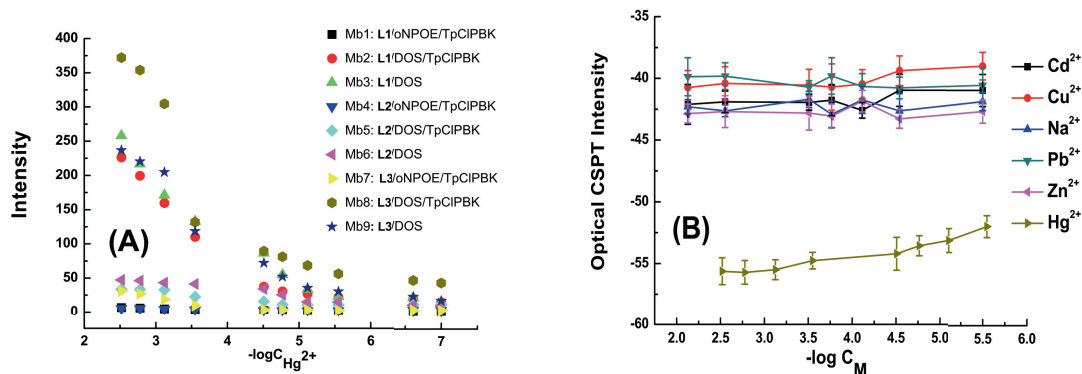


Fig. 3: (A) The fluorescence response of **L1-L3** based membranes towards Hg^{2+} ion.; (B) The CSPT response of Mb7 (**L3**/oNPOE/TpCIPBK) towards varying concentrations of Hg^{2+} and several the interfering cations.

We have then passed on to study the influence of the ratio between the content of ligand **L3** and that of lipophilic anionic sites in the membrane, on the effectiveness of Hg^{2+} determination. For this, seven new membranes all containing 3 wt% of **L3**, plasticised with DOS or oNPOE, and containing different amounts of TpCIPBK (except Mb 12 doped with $\text{T}(\text{CF}_3)_2\text{PBK}$) have been prepared, Table 1. Once again, the DOS plasticized membranes were found to be more effective for fluorimetric measurements of mercury (II) ions and the highest fluorescence intensity was shown by Mb 10.3 prepared with 8 wt % of TpCIPB⁻ anionic lipophilic sites, Fig. 4A. On the contrary, CSPT measurements of Hg^{2+} have showed that in the series of o-NPOE-plasticized membranes Mb11.1-11.3 and Mb12 the highest response towards mercury concentration variation is observed with the membrane Mb11.2, containing 5 wt% of TpCIPBK, Fig. 4B. A substitution of the TpCIPK cation exchanger with more hydrophobic $\text{T}(\text{CF}_3)_2\text{PBK}$ in Mb12 did not improve the membrane properties as it was expected, but on the contrary, resulted in the quenching of optical intensity under exposure of the membrane to the rowing concentrations of Hg^{2+} (data not shown).

Table 1. The compositions of tested membranes based on ligand L3.

Membrane	Ligand ^a	Plasticizer, wt%	TpCIPBK, wt %	Ligand : additive ratio
Mb 10.1	L3	DOS	2	1 : 0.66
Mb 10.2	L3	DOS	5	1 : 1.66
Mb 10.3	L3	DOS	8	1 : 2.66
Mb 11.1	L3	oNPOE	2	1 : 0.66
Mb 11.2	L3	oNPOE	5	1 : 1.66
Mb 11.3	L3	oNPOE	8	1 : 2.66
Mb 12	L3	DOS	3 ^b	1 : 1

^aThe amount of ligand in all membranes was 3wt%; ^bthe lipophilic additive was potassium tetra(bis)-3,5 trifluoromethylphenylborate, T(CF₃)₂PBK.

The results obtained indicate the potential utility of optical chemosensors based on aza-thioether crown ligands for mercury(II) ions detection. Further experiments on determination of mercury (II) ions content in natural and potable waters are now in progress in our laboratories.

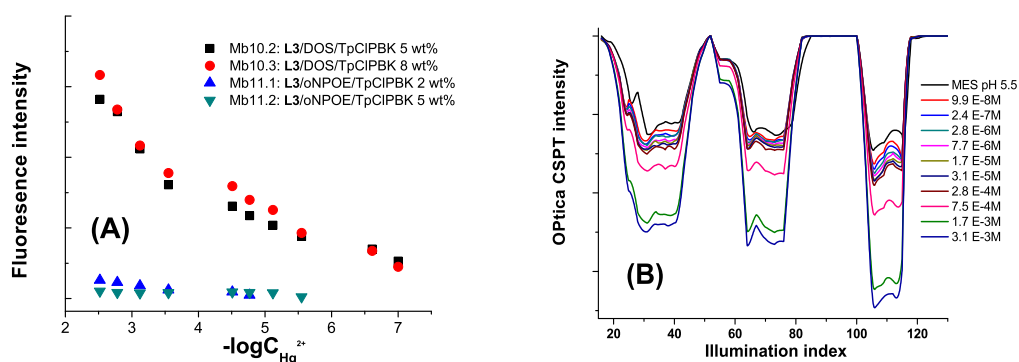


Fig. 4: (A) The fluorescence response of L3 based membranes containing different amount of lipophilic anionic sites towards Hg^{2+} ion; (B) The CSPT response of Mb 10.2 (L3/oNPOE/TpCIPBK 5 wt%) towards Hg^{2+} .

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