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## Photographic detection of Cadmium(II) and Zinc(II) ions

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### Abstract

The binding properties of two 2,8-dithia-5-aza-2,6-pyridinophane-based ligands, bearing respectively coumarin (HNCum) and naphthol-benzoxazole (HNBO) optically active units as pendant arms, were studied with the aim of transition metal cations selective detection. The novel all-solid-state optodes were obtained by inclusion of fluorophores inside PVC-based polymeric films. The influence of lipophilic sites incorporation and plasticizer nature on pyridinophane-based optodes response was investigated. An enhanced selectivity of the ligands towards Cadmium(II) and Zinc(II) ions was detected. Light Emitting Diode, LED 380 nm, was used as light source, and a digital camera as a signal detector. The results obtained demonstrated the suitability of the developed optodes to perform fast and low cost simultaneous monitoring of Zn<sup>2+</sup> and Cd<sup>2+</sup> ions by means of familiar devices and chemometrics.

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*Keywords:*

### 1. Introduction

The high content of transition and heavy metals in air, drinking water, soil, plants, etc. causes their consequent accumulation in humans and this phenomenon has been connected to the insurgence of allergies, tumors, and other serious diseases, such as genetic pathologies, especially in children [1,2]. To protect humans against health risks caused by multi-metal contamination, a careful monitoring of metals content in environment is required. The standard procedures of transition and heavy metals analysis employ instrumental methods, such Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma, Atomic Emission Spectrometry (ICP/AES), X-ray fluorescence (XRF), Ion Chromatography (IC), etc [3]. Despite of a high precision, these methods are often complex, time- and efforts-consuming, require sample pre-treatment, sophisticated equipment and qualified personnel involvement.

Chemical sensors, being not expensive, simple in fabrication and handling, providing notable sensitivity and rapid response time represent a valid and effective alternative to instrumental methods for environmental monitoring of metal pollution [4]. Moreover, optical chemical sensors have the advantage of simple preparation, reasonable selectivity and sensitivity, may be employed for in-field analysis of metal ions with no or minimum sample pre-treatment, simultaneous measure of several analytes, and provide the real-time results at reasonable costs. In this work, we continue our previous studies on aza-thioether macrocyclic fluorophore-based optodes [5], focusing particular attention on the detection of Cadmium(II) and Zinc(II) ions. The disposable sensors, implemented with familiar devices for signal acquisition (LED as light source and a digital camera as a signal detector) and chemometric methods for data treatment for simultaneous Cd(II) and Zn(II) detection, allowed to demonstrate the possibility to analyze real samples of environmental importance.

## 2. Experimental

Poly(vinyl chloride) (PVC) high molecular weight, tris(2-ethylhexyl) phosphate (TOP), bis(2-ethylhexyl) sebacate (DOS), o-nitrophenyl octyl ether (o-NPOE), potassium tetrakis-(4-chlorophenyl)borate (TpCIPBK), tetrahydrofuran (THF), 4-morpholinoethanesulfonic acid (MES), 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES), tris(hydroxymethyl)aminomethane (TRIS) 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 ligand HNCum was prepared according to the literature method, while HNBO was newly synthesised at the department of base sciences and foundations, Universita degli Studi di Urbino, Italy, Fig. 1.

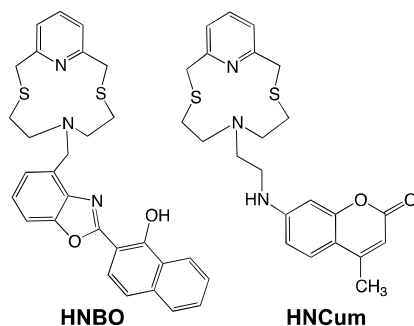


Fig. 1. The chemical structures of tested fluorophores.

To prepare optode polymeric membranes, 1- 3 wt % of ionophore, 2-8 wt% of TpCIPBK, 30-33 wt% of PVC and plasticizer, up to total weight of 100 mg, were dissolved in 1 mL of THF. 20 mL of every membrane cocktail were cast onto transparent glass slides, from 4 to 12 spots were deposited on the same slide, thus providing optical sensor arrays. Solvent was allowed to evaporate overnight. The “disposable” sensors were employed, which means that in every measurement the freshly deposited membranes were deposited and tested. For every membrane measurements were replicated twice. The membrane responses towards primary Cd<sup>2+</sup>, Zn<sup>2+</sup> ions in their individual and binary solutions, as far as towards Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup> and Pb<sup>2+</sup> as possible interfering ions were tested in 3.3×10<sup>-7</sup> - 2.2×10<sup>-2</sup> mol/L concentration range. The 1 mol/L stock solutions of metal salts were prepared dissolving corresponding amounts of metal chlorides and Pb(II) and Zn(II) nitrates in distilled water, solutions of lower concentrations were obtained by consecutive additions of calculated amounts of corresponding stock solution in 0.01 mol/L background (MES pH 5.5, HEPES pH 7.5, or TRIS pH 8.6). Blue-colored (380 nm) Light Emitting Diode, LED, was used as light source, and a digital camera as a signal detector. The measurements were performed in a transparent polystyrene cell (Katrell, model 1937). The responses of the films upon analyte addition were measured with respect to the tree main visible spectrum colors: red, green and blue. The RGB signals were evaluated after background luminosity subtraction. The videos captured by camera were transferred into the digital

signal and the film optical intensity was plotted versus analyte concentration change. In total 12 membranes of different compositions were prepared, Table 1.

Table 1. The compositions of tested membranes based on HNCum and HNBO ligands.

Membrane #	Plasticizer	Fluorophore, wt%	TpCIPBK, wt%
Mb 1a	DOS	HNBO, 1	-
Mb 1b	oNPOE	HNBO, 1	-
Mb 1c	oNPOE	HNBO, 1	2
Mb 1	DOS	HNBO, 1	2
Mb 2	DOS	HNBO, 1	5
Mb 3a	DOS	HNCum, 1	-
Mb 3b	oNPOE	HNCum, 1	-
Mb 3c	oNPOE	HNCum, 1	2
Mb 3	DOS	HNCum, 1	2
Mb 4	DOS	HNCum, 3	8
Mb 5	TOP	HNCum, 1	2
Mb 6	TOP	HNBO, 1	5

### 3. Results and discussion

Preliminary tests on HNCum in MeCN/H<sub>2</sub>O 4:1 solutions have shown an increase of fluorescence intensity upon Cd<sup>2+</sup>-ions addition at about 430 nm. In the case of HNBO, it was found that the fluorescence activation is strongly influenced by the pH of the analyzed sample, which shifts keto-enol equilibrium in the optically active naphthol unit; the deprotonated HNBO fluorophore interacts with the analyte (mainly Cd<sup>2+</sup> and Zn<sup>2+</sup>) and this results in the increase of fluorescence emission at 418 nm (corresponding to green RGB region) and 568 nm (red RGB region) upon the complexation, Fig.2. Hence, while incorporated in PVC/ plasticized membranes, the highest luminescence response in green RGB region was expected for both fluorophores in the presence of the corresponding primary ions.

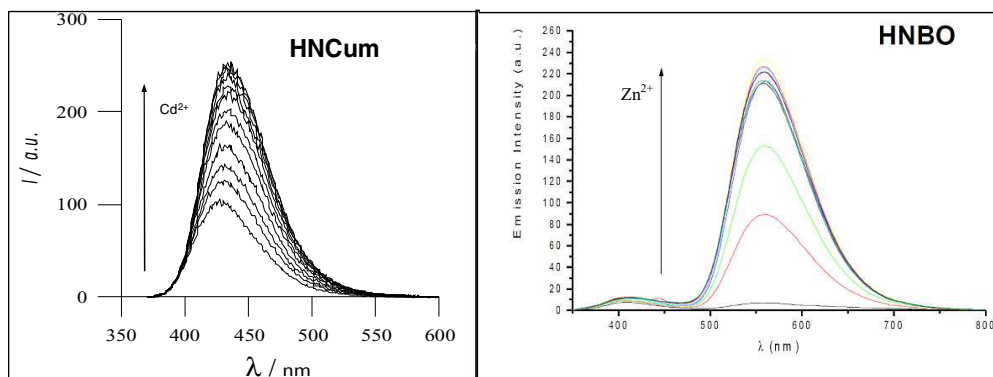


Fig. 2. Fluorescence emission of HNCum and HNBO fluorophores in MeCN/H<sub>2</sub>O 4:1 solutions upon addition of growing concentrations of Cd<sup>2+</sup> and Zn<sup>2+</sup> respectively in the concentration range from 3×10<sup>-6</sup> to 1×10<sup>-3</sup> mol/L.

The influence of background pH on the optical response of HNCum and HNBO-based optodes was first studied. At pH 5.5 in 0.01 mol/L MES background almost all tested membranes were silent, even in the presence of high concentrations (>1×10<sup>-3</sup> mol/L) of the analyte. A better behavior of HNBO-based membranes was found in TRIS pH 8.6, where the basic media promoted the deprotonation of the fluorophore and the increase of its fluorescent response toward increasing Zn<sup>2+</sup> concentration. Unfortunately, the precipitation of metallic hydroxides species did not permit to test membrane responses to analytes in a wider concentration range. We have hence performed all the following measurements in 0.01 mol/L HEPES pH 7.5 background. In order to promote initial HNBO fluorophore deprotonation, the glass slides with deposited membrane spots were initially soaked in 0.01 mol/l TRIS pH 8.6 for 15

min, then rinsed with distilled water and immersed in HEPES pH 7.5, where the consecutive additions of CdCl<sub>2</sub> and/or Zn(NO<sub>3</sub>)<sub>2</sub> were made. The membranes selectivity tests towards several alkali-, alkali-earth, and transition metals were performed at the same conditions. No useful response was found for membranes Mb 1a, 1b, 3a, 3b without lipophilic anionic sites, while all the oNPOE-plasticized membranes showed a very low optical response, due to the fluorophores luminescence quenching by plasticizer. The DOS- plasticized membranes Mb 1-3, containing 1 wt% of fluorophores HNBO and HNCum and 2-5 wt % of TpCIPB<sup>-</sup> as lipophilic anionic sites displayed the fluorescence activation by Zn<sup>2+</sup> and Cd<sup>2+</sup> ions in the concentration range from 3.3×10<sup>-7</sup> to 2.2×10<sup>-2</sup> mol/L, indicating a neutral carrier functioning of ligands. Moreover, the membranes Mb1,2 responded to Zn<sup>2+</sup> in the presence of equal or higher concentrations of Cd<sup>2+</sup>, Fig.3. The high percentage of HNCum fluorophore (8 wt %) in membrane Mb4 provoked a complete saturation of the membrane luminescence at concentrations of Cd<sup>2+</sup> higher than 5×10<sup>-5</sup> mol/L, Fig. 3.

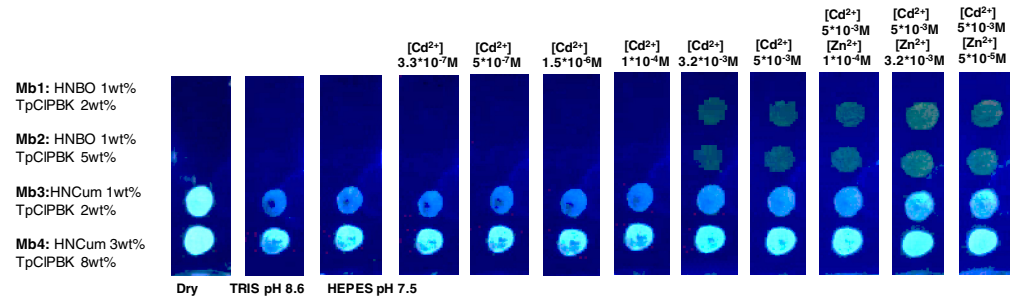


Fig. 3. The response of HNBO and HNCum-based optodes in binary solutions of Cd<sup>2+</sup> and Zn<sup>2+</sup> ions. Membranes were soaked in 0.01 mol/L TRIS pH 8.6 for 15 min, then the measurements were performed in 0.01M HEPES pH 7.5 upon excitation with a 380 nm LED.

Membranes Mb5, 6, plasticized with TOP and containing 2 and 5 wt % of TpCIPBK, respectively, showed the highest response towards cadmium and zinc concentrations variation, and a very low influence from all tested interfering species. An application of PLS2 regression method has permitted to find linear correlations for both metallic ions in their binary solutions, Fig.4. The results obtained indicate the potential utility of optical chemosensors based on pyridinophane ligands for the simultaneous Cd<sup>2+</sup>- and Zn<sup>2+</sup>-ions detection. Further tests on optodes selectivity are now in progress in our laboratories.

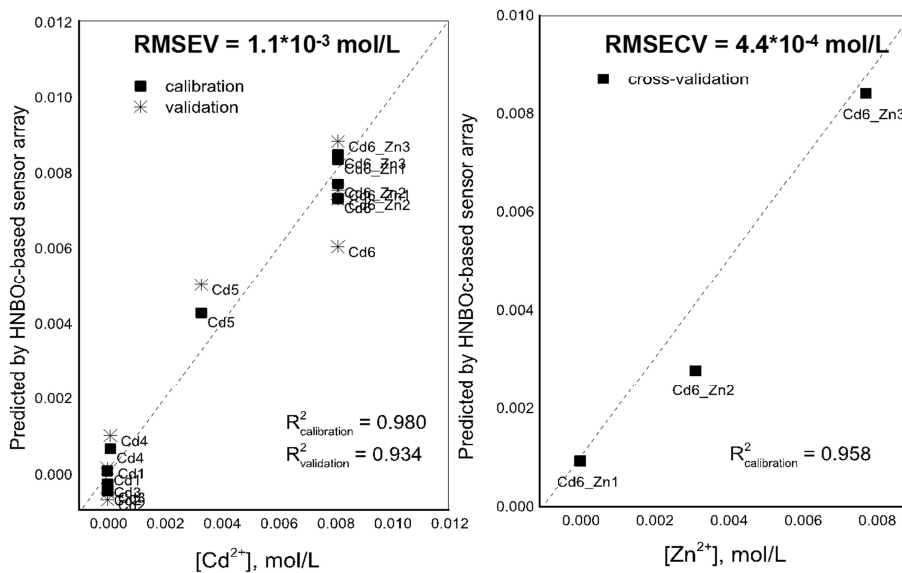


Fig 4. The PLS2 regression results of sensor array response based on Mb1-Mb4 toward Cd<sup>2+</sup> and Zn<sup>2+</sup> ions.

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