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Facile ultrasensitive monitoring of mercury ions in water by fluorescent ratiometric detection

Research Article

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Abstract: Prospects for analytical application of 2,5-diphenyloxazole-substituted 3-hydroxychromone for detection of mercury ions are presented. Sensitivity and selectivity for a number of metal ions both in methanol solution and in the plasticized polymer are outlined. Ultrasensitive and highly selective fluorescent ratiometric response of the polymer film containing the title compound for mercury ions in water media is revealed. Reversibility of ratiometric response to mercury ions and influence of plasticizer's content in the polymer film on the optical feedback are also discussed.

Keywords: *Chemosensing polymer composition • Mercury ions • Ratiometric fluorescence detection • 3-hydroxychromones • Minimal permitted concentration (MPC)*

1. Introduction

Attention to the problem of controlling hazardous heavy metals ions has grown significantly for the past few decades. Among different transition metals, mercury is one of the most widespread toxic elements which impacts human and ecosystem health. The United States Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) ranks mercury and its compounds on the third place in the "Priority List of Hazardous Substances" and the European Water Framework Directive (2000/60/EG) defines these species as one of the thirty "precarious dangerous pollutants". The biological targets and toxicity profile of mercury species depend on their composition [1,2]. Mercury easily penetrates human gastrointestinal tract, crosses blood-brain barrier and targets the central nervous system. Neurological problems caused by mercury intoxication are manifold and include prenatal brain damage, immune system dysfunction, cardiovascular diseases, cognitive and motion disorders, and they result in the damage of vision and hearing impairment, blindness and death [3-6]. The global cycling of mercury and its deleterious effect on human health provides the scientific community with a challenging task: to develop new mercury detection methods, which are cost-effective, facile, rapid and applicable to the environmental and biological milieus for reliable risk assessment.

Today's leading molecular sensors for mercury ions include those with an optical feedback because of their special features giving them preferences in the most cases [7-11]. Although mercury(II) ion does not have its own optical spectroscopic signature because of its closed-shell d^{10} configuration, the detection following altering fluorescence or UV–vis absorption spectroscopy resulting from a Hg(II)-induced perturbation of an organic chromophore, is arguably best suited for monitoring Hg(II) in either environmental or biological contexts. Fluorescence-based methods present many advantages: fluorescence measurements are usually very sensitive, low-cost, easily performed, and versatile. Furthermore, a lot of opportunities exist for modulating the photophysical properties of a luminophore (for example, introduction of proton-, energy- and electron-transfer processes; fluorescence quenching connected with the heavy-atom effect; fluorescence ignition at the destabilization of a fluorescence-quenching $n\pi^*$-excited states [12,13] *etc.*) which open a wide number of possibilities for efficient fluorescent chemosensing materials design.

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Two different approaches exist for mercuric ion sensing by fluorescence spectroscopy: turn-off sensors rely on the fluorescence quenching upon specified analyte addition to the initial fluorophore, turn-on sensors, on the other hand, are based on the fluorescence ignition in the same conditions. For fluorescent detection of Hg(II), the emission enhancement is preferable to depletion because it lessens the chances of false positive results and is more amenable to multiplexing: the simultaneous use of several detectors that uniquely respond to different competing analytes. Hg(II) is a heavy metal ion, which, according to literature, quenches fluorescence by a number of pathways, hence, achieving turn-on feedback can pose a significant challenge [14-19]. However, due to the nature of analytical signal in intensometric methods they bear some disadvantages - concentrations of both a sensor and analyte should be calibrated and correlated with the fluorescence response. Their use is hardly possible in objects like living cells or tissues for *in vivo* or *in vitro* analysis and for other highly inhomogeneous natural media. An alternative approach to fluorescence sensing consists of monitoring the luminescence intensity at two different wavelengths before and after addition of the analyte [20]. Usage of the ratio of emission intensities can signal to a researcher, what type of changes occurs in the microenvironment of the fluorophore molecules independently from its concentration. Ratiometric fluorescent monitoring is less prone to artifacts, it is superior for studies of inhomogeneous samples and it facilitates analyte quantification in such intricate objects as living, dynamic, and non-equilibrium systems.

Up to the present time, definite success in the field of synthesis of organic compounds potentially capable for ratiometric fluorescent detection of mercury ions has been achieved. It was reported that ratiometric chemodosimeter for Hg(II) was capable of taking advantage of the known Hg(II)-induced transformation of thiourea moieties into guanidine derivatives [21]; pyrene-thymine dyad, binding Hg(II) with the lower detection limit of 100 nM [22]; dioxaoctanediamide- [23] and perylene bisimide-based ratiometric sensors [24]; dithiocarbamate-appended anthracene [25] and functionalized BODIPY chromophores [26] *etc*. All these compounds were declared as selective for mercury ions and some of them have detection limits from one to two orders of magnitude higher than mandated minimal permitted concentration (MPC) for drinking water. But they provide a response only in mixed aqueous/organic solutions, implying an organic content no less than five percent which makes them non-functional or able to provide a very poor feedback in aqueous media.

A few examples of fluorescent ratiometric Hg(II) sensors, able to operate in aqueous solutions have been reported. The coumarin-based fluorophore coordinating Hg(II) is characterized with an instability constant of 39 μM of the complex formed [27]. Two similar compounds by Nolan and Lippard based on the seminaphtofluorescein platform have their lowest detection limit of mercury ions about 50 nM. However, these compounds are not specific to just mercury(II), as other inorganic cations and anions strongly interfere with the Hg(II)-induced response. The structural complexity of these compounds makes them both challenging and expensive targets to synthesize [28,29].

Recently, scientific community witnessed dynamically growing attention to design and studies of composite functional materials. A number of approaches have been explored to improve sensing techniques using polymer-based systems [30]. For example, optical sensors sensitive to mercury(II) ions have been suggested based on composite films [31], as well as polymer-immobilized dyes [32] and nanoparticles [33].

In the past few decades, a unique family of natural and synthetic compounds, namely 3-hydroxychromones (3HC), capable for ratiometric sensing of different parameters of the fluorophore microenvironment, such as polarity, proton donor ability, presence of the surface active compounds, became the subject of extensive research. The 3HCs belong to the family of flavonoids and undergo the excited-state intramolecular proton transfer reaction (ESIPT). Thereby most of them are characterized by multi-banded fluorescence spectra, resulting from the emission of the so called “normal” (N*) (proton belongs to 3-hydroxy group) and “phototautomer” (T*) (proton belongs to 4-carbonyl group) forms [34,35]. The integral or linear intensities of their emission bands can serve as an analytical signal for various practical applications [36,37]. The most recent effort of researchers in this field was directed at the synthesis of 3HC derivatives with highly efficient fluorescence and improved solvatofluorochromic ability [38,39], as well as at some more specific features like concurrent intramolecular H-bonding [40,41]. An advantage of molecules of 3HC derivatives lies in their ability to frequently demonstrate high affinity to metal ions in solutions acting as effective organic ligands. Spectral properties of 3-hydroxychromone complexes with metal ions differ significantly from those of unbound dyes molecules [42-47]. In particular, their absorption and fluorescence parameters considerably depend on the nature and concentration of a metal ion, as well as on a few other factors such as solvent and temperature. This opens a possibility to apply these compounds as prospective fluoroionophores for qualitative and quantitative detection of metal ions in solution.

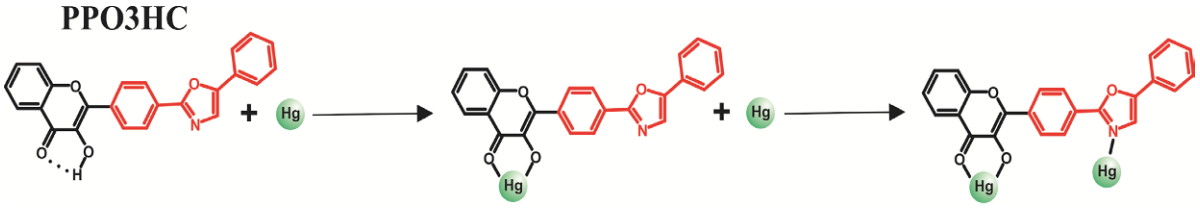

Figure 1. Complexation of **PPO3HC** with Hg(II) ions [48].

In our previous communication, we have reported the spectral behavior and a possibility to form different types of complexes with Hg(II) ions for a series of heterocyclic 3HC derivatives [48]. In the present paper, we further develop this topic in the context of prospects for their analytical applications in qualitative and quantitative detection of mercury ions in water media.

2. Experimental procedure

2.1. Subject of investigation

Complexation of 2,5-diphenyloxazole-substituted 3-hydroxychromone (**PPO3HC** – Fig. 1) with metal ions was investigated both in methanol and distilled water solutions. Synthetic procedures, purification and structure confirmation of the title compound were described in [49].

The following commercially available metal salts of analytical grade were used: mercury acetate, cadmium chloride, nickel chloride, lead acetate, zinc sulfate, copper sulfate, beryllium chloride, barium perchlorate, magnesium perchlorate. All the salts samples were additionally dried according to the procedures described elsewhere [50].

To investigate complexation in water media, the title compound was incorporated into the polybutylmetacrylate film, containing traces of di-(2-ethylhexyl-)phthalate as a plasticizer. Polybutylmetacrylate was synthesized from the monomeric butylmetacrylate by free radical polymerization. For this purpose, the mixture of initial monomer and benzoyl peroxide acting as an activator in weight proportion 200:1 was heated in a boiling water bath during 5 hours in a sealed glass tube, until solidification. The obtained polymer was dissolved in dichloromethane, then a 10^{-5} M solution of **PPO3HC** was added with a specified amount of plasticizer, di-(2-ethylhexyl-)phthalate. The resulted mixture was homogenized in the ultrasound bath, and then the solvent was evaporated at a room temperature on the horizontal flat glass surface. Commercially available monomer, polymerization activator, plasticizer and dichloromethane were of chemically pure grade and were used as received.

2.2. Spectral measurements

Absorption spectra of the title dye methanol solutions were recorded on Hitachi U3210 spectrophotometer. Fluorescence spectra were measured on Hitachi F4010 spectrofluorimeter in standard quartz cells (l = 10 mm) at 20ºC. For measurements in water, rectangular pieces of the polymeric film samples were placed into the standard plastic cell along their diagonals and they were fixed to the surface during the measurements.

Spectrophotometric and spectrofluorimetric titrations were performed in the 10 mm fluorimetric cell, initially containing 2 mL of the methanol solution of the investigated compound, with further addition of 3 to 300 µL of the methanol solution of an analyzed metal salt with a calibrated micropipette. In the case of water titrations, 2 mL of distilled water was poured into the cell with a sensing film adjusted along its diagonal, and then corresponding metal salt water solution was added in the same way. All absorption and fluorescence spectra were corrected for the dilution extent.

3. Results and discussion

Investigation of the effect of the mercury ions on the spectral behavior of some hetaryl derivatives of 3-hydroxychromone with the implementation of the quantum chemical semi-empirical and *ab initio* modeling has shown that the studied molecules could form complexes of different nature and stoichiometry at Hg^{2+} addition to their methanol solutions, depending on the nature of the fluorophore and mercury ions concentration [48].

As it was revealed in the case of **PPO3HC**, a consecutive formation of 1:1 metal:ligand stoichiometry chelate complex and 2:1 “mixed” complexes took place (Fig. 1). This compound turns out to be the most interesting and promising among the series discussed in [48]. Its π-conjugated system consists of both 3-hydroxychromone and 2,5-diphenyloxazole chromophoric fragments. The latter is known as highly efficient organic fluorophore [51]. The above mentioned two parts of **PPO3HC** molecules also act like receptors, both able to bind mercury cations at different stages of

complexation. In the first stage, it forms a highly stable chelate complex with the high equilibrium constant (log K_1=7.9±0.2). In this case, the lower detection limit for Hg^{2+} ions should be about 10^{-10} M [48], which allows sensing of these ions at nanogram scale by electronic absorption spectroscopy. The latter concentration is even lower than a mandated EPA limit of mercury content in the drinking water (2 ppb, or 10 nM) [52]. Nano- and subnanogram Hg(II) detection limits can be achieved for organic chromophores, employing such precision instrumental techniques as high performance liquid chromatography combined with a UV-vis detection, inductively coupled plasma mass spectrometry, cold vapor atomic fluorescence spectrometry and gas chromatography. However, all these methods are expensive, they require sophisticated laboratory setup, tedious sample preparation and high operating skills of the personnel. Alternatively, small-molecule ligands designed to give optical read-outs at complexation with Hg(II) can ultimately be incorporated into assay kits, portable fiber optics devices and commercial indicators, facilitating rapid Hg(II) detection even directly in the places of sampling.

In order to reveal the potential of sensing ability of **PPO3HC**, we studied its selectivity at binding different metal ions in the methanol solution. Fig. 2 depicts relative fluorescence quenching in both emission bands of **PPO3HC** (normal and tautomeric ones) plotted against the total concentration of the metal ions listed in the Experimental part. The upper plot represents the tendency of the compound to form two successive complexes with all the metal ions under study except barium (II). Existence of two plateaus, clearly observed for mercury ions, or less pronounced for cadmium, lead and nickel ones in the low concentration range of 10^{-3}÷10^{-9} M unambiguously points out to the occurrence of two steps of the metals ions binding to the dye. Barium ions do not reveal such a trend, which is in a good agreement with previous findings of Roshal and coworkers, who had shown Ba^{2+} ions are too large to fit into the 3HC chelate cavity [46]. The positions of titration jumps on the graphs in Fig. 2 could be considered as a measure of sensitivity to the metal ions in the study. Only for mercury and lead ions, these jumps are high enough and they differ for normal and tautomeric forms, which is an important notice for the application of the ratiometric fluorescence detection principle. In terms of ratiometric approach, the ratio of intensities in both emission bands needs to be determined. Fig. 3 illustrates a ratiometric response of **PPO3HC** to different concentrations of metal ions in solution. The ratio of intensities of the phototautomer form emission band (555 nm) to the normal one (510 nm, methanol) served as the analytical signal. In the cases of nickel and cadmium, the corresponding ratiometric function is not linear in a wide range of metal concentrations. Ba(II) demonstrated no ratiometric feedback, which is in good agreement with an above assumption that chelate complex is not formed in the case of this metal. Although according to the data presented in Fig. 2, when complexation of **PPO3HC** with Ba(II) takes place, barium ions' binding does not disturb the ESIPT process. This observation points out to the weak "outer" [46] complex formation with participation of another lone electronic pair of 3HC carbonyl group, which does not involve the intramolecular H-bonding, and it explains similar action of Ba^{2+} ions binding onto the fluorescence of both normal and phototautomer forms due to the electrochromic effect only.

At the same time, the ratiometric fluorescence response of the title compound to the mercury ions shows two distinct linear parcels. For the section corresponding to the ultralow concentrations (below 10^{-7} M), the analytical signal is explicitly higher than for any other investigated metal. As an example, Fig. 4 illustrates quenching response for both emission bands at 10^{-7} M total concentration of the investigated cations. The degree of mercury-induced quenching of the normal form is comparable with the other investigated cations, with barium predominating. Tautomeric form is quenched by Hg(II) much more efficiently than the other studied metal ions. However, it is not the relative quenching for each form $(F_0-F)/F_0$, that could be essential for ratiometric probing, but rather their ratio which retains constant and is equal to ~1,5 for Ba^{2+}, Cd^{2+}, Ni^{2+} and is slightly lower for Pb^{2+} ions with a strong prevalence of Hg(II), for which the tautomeric form is quenched 4 times more efficiently than the normal one. Absorption spectra demonstrate even greater read-out (Fig. 5).

Investigation of the prospects for **PPO3HC** as an effective chemosensor for mercury ions, which will be able to operate in water flow in the real-time and real-space mode, focused our main interest on the complexation in a water media. To withdraw from a methanol solution, which served only as a modeling solvent, the investigated fluorescent dye was incorporated into the plasticized polybutylmetacrylate (PBMA) film, allowing metal ions partial penetration into the bulk of the polymer. We have investigated the influence of the presence of several metal ions with different concentrations onto the spectral and fluorescent properties of such a composite polymeric material. We scrutinized an impact of copper, lead, cadmium, nickel, zinc, beryllium, barium and magnesium bivalent cations, besides mercury ones, on the optical properties of the polymer-dye composition under study at the same conditions. Primarily, it is worth to note the significantly better bands resolution in the

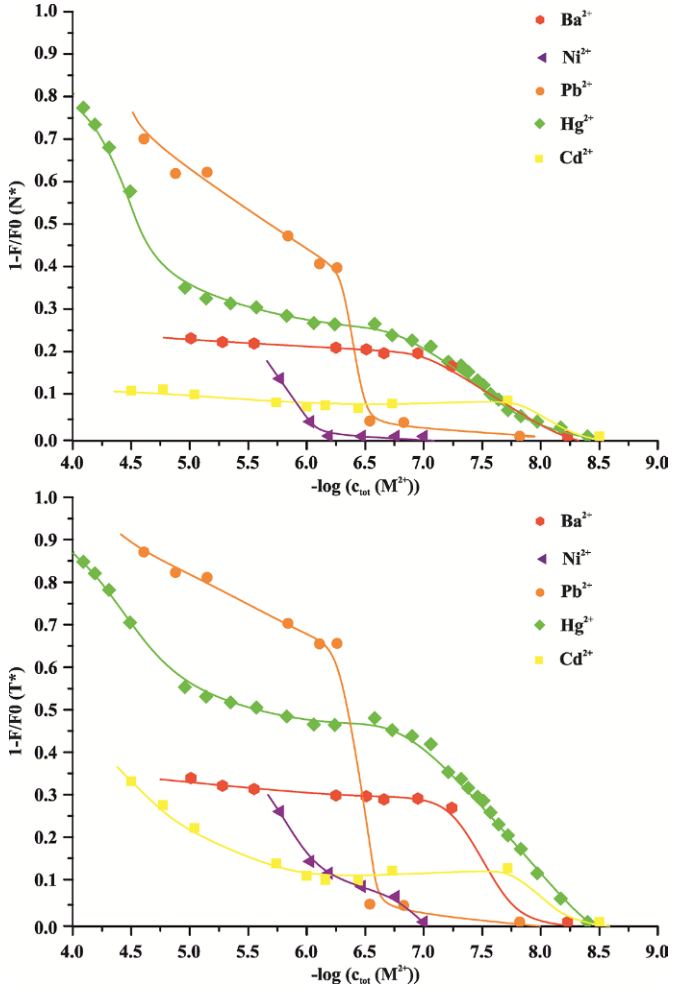

Figure 2. Relative fluorescence quenching of phototautomer (T*) and normal (N*) forms upon metal ions addition to the dye solution in methanol (λ_{ex} = 380 nm).

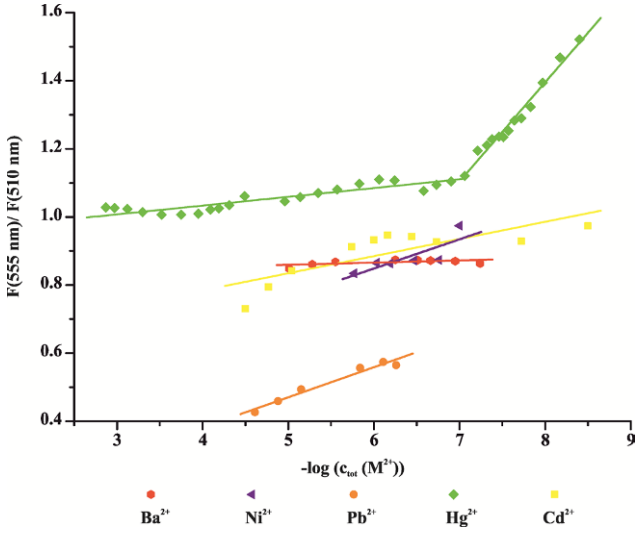

Figure 3. Ratiometric response (phototautomer to normal forms emission intensity ratio) to metal ions addition to the **PPO3HC** solution in methanol.

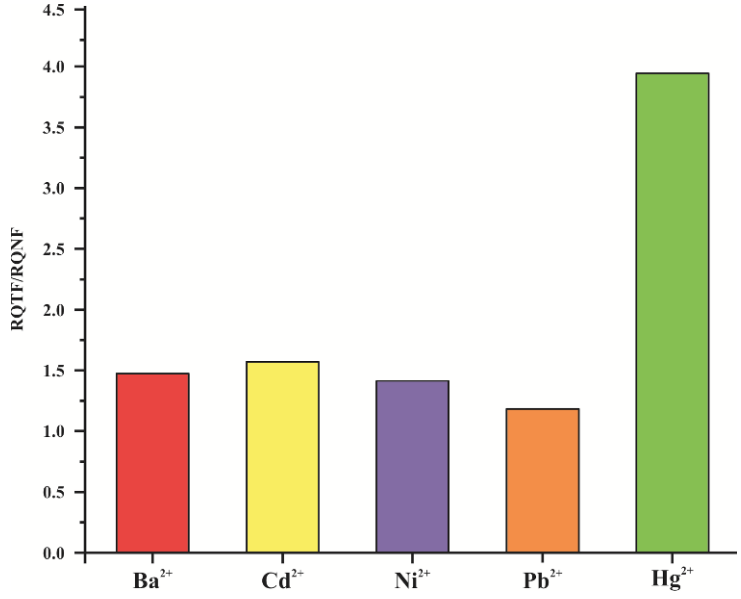

Figure 4. Ratio of the fluorescence relative quenching $\frac{(F_0^T - F^T)\cdot F_0^N}{(F_0^N - F^N)\cdot F_0^T}$ of phototautomer (RQTF) and normal (RQNF) forms with 10^{-7} M concentration of several heavy metals ions in methanol.

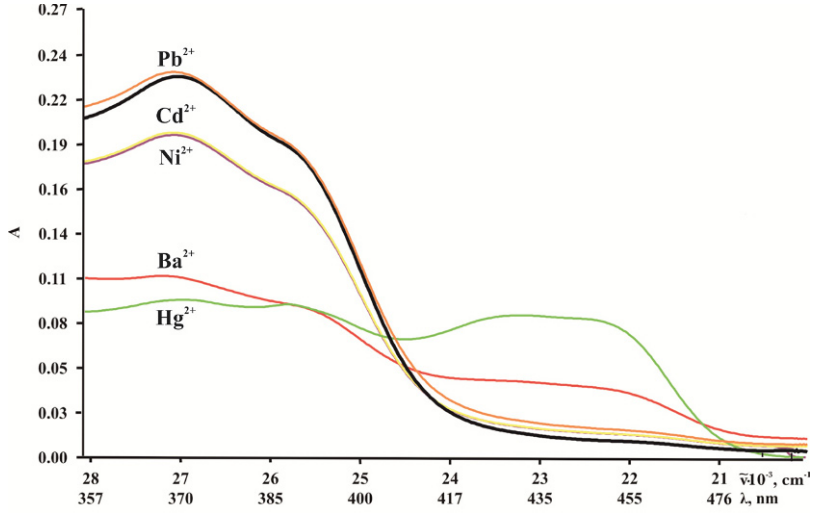

Figure 5. Absorption spectra of PPO3HC in methanol containing 10^{-7} M of various heavy metals ions [48].

fluorescence spectra of the uncomplexed polymer-incorporated **PPO3HC** due to the shift of the normal form maxima from 510 to 416 nm and from 555 to 560 nm for the phototautomer, in comparison with its solution in methanol. The emission spectra of **PPO3HC** in PBMA film dipped in water containing different concentrations of Hg (II) ions are presented in Fig. 6.

All the spectra in Fig. 6 are normalized to the maximum broad fluorescence band of the normal form (416 nm), thus changes in the phototautomer form intensity can be considered as a measure of ratiometric signal. As it follows from the data of Fig. 6, presence of mercury ions at such extra low concentration as 10^{-10} M (upper black curve) results in 15 percent relative depletion of the phototautomer form fluorescence band intensity.

Ratiometric responses, derived as a ratio of fluorescence intensities at 560 nm and 416 nm against –log c_{tot} (M^{2+}), are presented in Fig. 7 for all the investigated cations.

It needs to be noted, that the proposed polymer-based composition sensitivity to Hg(II) is several orders of magnitude higher than that to any other ionic species studied. Linearity of the ratiometric plot remains satisfactory in a wide range of concentrations (correlation coefficient reaches 0.98), strongly differing from those observed for other metals. Thus, the presence of heavy metal ions, except for mercury, should not interfere

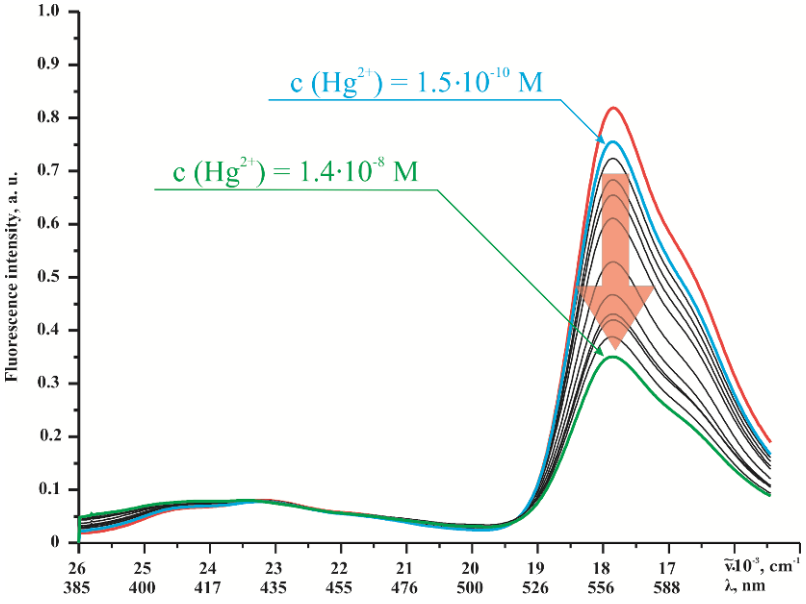

Figure 6. Fluorescence spectra of **PPO3HC** in the polymer film *versus* mercury ions concentration increase in the surrounding water solution.

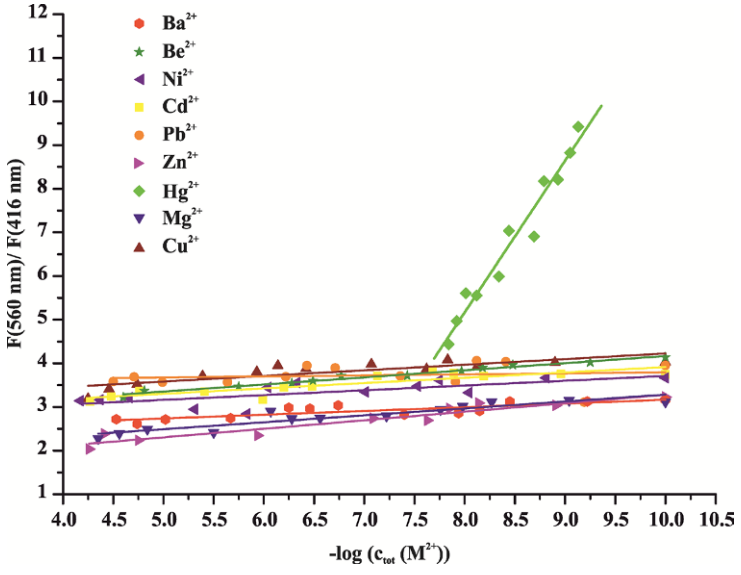

Figure 7. Ratiometric responses of **PPO3HC** in PBMA film with respect to investigated metal ions in surrounding water medium in a wide range of concentrations.

with or should not weaken the analytical signal. The time response of the polymer-dye composition was fast enough, and it normally lasted several minutes, which is significantly lower than that for the existing analogs utilizing the principle of bio-detection of mercury [53].

In our preliminary studies we have elucidated that the analytical signal of compound **PPO3HC**/PBMA composition depends strongly upon the plasticizer content, as it regulates the film density, fluidity and water penetration into its inner layers. Comparing fluorescence signals of the polymer-dye-plasticizer composition, we have optimized the contents of the latter. As optical feedback decreases ~3.5 times of magnitude while going from the di-(2-ethylhexyl)-phthalate concentrations of 1 μL to 5 μL per 100 mg of the polymer, the optimal concentration of the plasticizer appears to be near 1 μL per 100 mg. Increasing the plasticizer's contents to concentrations higher than 5 μL per 100 mg resulted in the deterioration of mechanical characteristics of the film, at concentrations of 10 μL per 100 mg and higher the film became very thin and tender, making any optical measurements hard to perform. Decrease of plasticizer contents below 1 μL per 100 mg lead to the decline of the analytical signal.

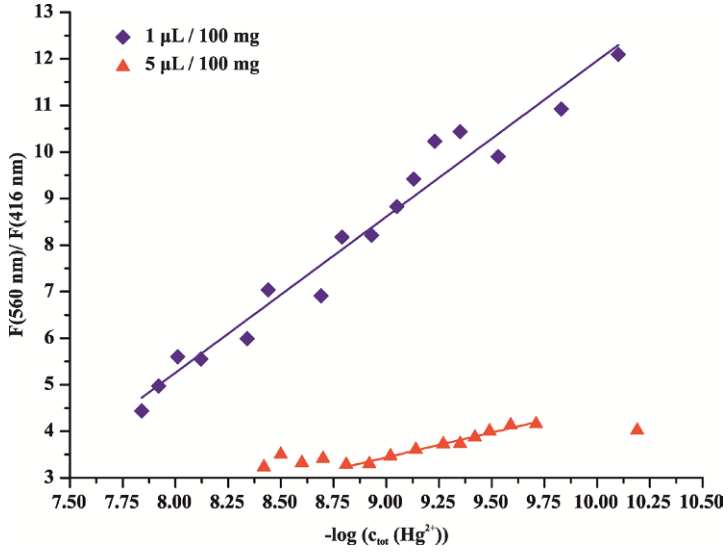

Figure 8. Ratiometric response for Hg^{2+} ions at different plasticizer concentrations.

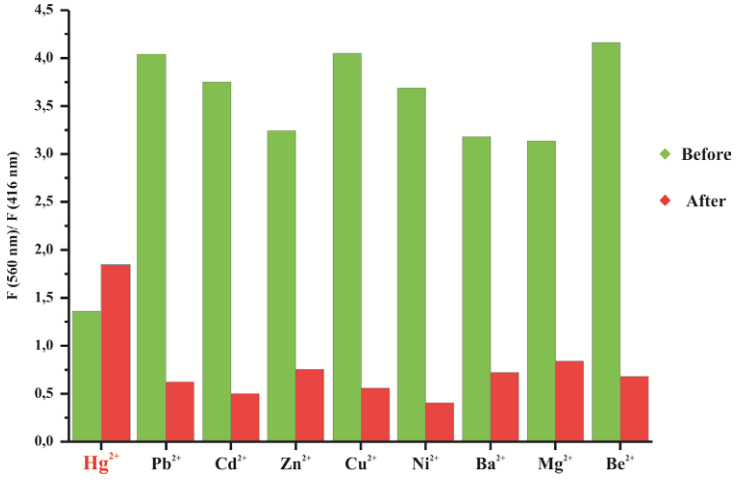

Figure 9. The ratiometric response of **PPO3HC** in PBMA film before titration (green bars, left) and after the overnight keeping in distilled water after the completion of titration experiments (red bars, right, see colors in the online version of this paper).

Reversibility is an important characteristic that allows consideration of the polymer-incorporated **PPO3HC** for further chemosensing applications. Most of the systems described before respond to Hg(II) irreversibly and should therefore be considered as Hg(II)-responsive dosimeters [25]. To test the reversibility of our polymeric composition to mercury ions, we kept the films under study overnight after the titration experiments in the freshly distilled water and then we measured their fluorescence read-out. It appeared (Fig. 9), that for all the examined metals, except for mercury, the analytical signal did not return back to its initial value, and it was preserved at the final level of titration procedure. In the case of Hg(II)-exposed film, ratiometric signal was practically restored to its initial position.

Hence, extremely high sensitivity and selectivity to mercury(II) ions in water media, short response time and good reversibility of the proposed chemosensing composition demonstrate potential for Hg^{2+} ions to be used for detection in water at real time and at real space modes.

4. Conclusions

2,5-diphenyloxazole-substituted 3-hydroxychromone reveals its high ratiometric fluorescence response to mercury(II) ions, demonstrating both ultrahigh sensitivity and selectivity while being incorporated into the plasticized polybutylmetacrylate film. The proposed chemosensing composition can be characterized with mercury ions detection limit at the level of 10^{-10} M, being 2 orders of magnitude lower than the allowed Hg^{2+} contents in drinking water. Remaining heavy metals

ions under study did not interfere with mercury-induced feedback of the proposed polymeric composition. Thus, the investigated 3HC derivative incorporated into the polymer film can be suggested as a prospective chemosensor for mercury ions detection in water in the on-line real-space mode.

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