



Development and characterization of newly engineered chemosensor with intracellular monitoring potentialities and lowest detection of toxic elements

Tahir Rasheed^a, Chuanlong Li^a, Li Fu^a, Faran Nabeel^a, Chunyang Yu^a, Lidong Gong^b, Yongfeng Zhou^{a,*}

^a School of Chemistry & Chemical Engineering, State Key Laboratory of Metal Matrix Composites, 800 Dongchuan Road, Shanghai 200240, China

^b School of Chemistry and Chemical Engineering, Liaoning Normal University, 850 Huanghe Road, Dalian 116029, China

ARTICLE INFO

Article history:

Received 30 August 2018

Received in revised form 18 September 2018

Accepted 22 September 2018

Available online 25 September 2018

Keywords:

Rhodamine

Fluorescent

Colorimetry

High sensitivity

Infield

Intracellular monitoring

ABSTRACT

The widespread existence of potentially toxic heavy elements have become one of the serious environmental concerns around the globe. Thus, it is highly important to develop efficient and selective chemical sensors to detect such potentially toxic elements. Herein, we developed a rhodamine-2-amino-5-bromopyrimidine based chemosensor (RBP) for the selective detection of toxic elements using Hg^{2+} and Cr^{3+} as model elements in combination with other competitive ions such as Al^{3+} , Ag^+ , Ca^{2+} , Ba^{2+} , Cd^{2+} , Fe^{2+} , Fe^{3+} , Li^+ , K^+ , Mn^{2+} , Mg^{2+} , Cu^{2+} , Na^+ , Ni^{2+} , Pb^{2+} and Zn^{2+} . The newly developed RBP displayed good visibility, high sensitivity, excellent selectivity, high binding ability and low limit of detection in $\text{CH}_3\text{CN}/\text{HEPES}$ buffer (1 mM 3:2 v/v, pH 7.3) as a medium. The binding constants of RBP for Hg^{2+} and Cr^{3+} were $1.09 \times 10^7 \text{ M}^{-1}$ and $8.3 \times 10^4 \text{ M}^{-1}$, respectively. As compared to earlier reported studies, the lowest detection limits (LOD), i.e., $1.6 \mu\text{M}$ for Hg^{2+} and $4.9 \mu\text{M}$ for Cr^{3+} were recorded. RBP also show reversible binding affinity with Hg^{2+} and Cr^{3+} in the presence of ethylenediaminetetraacetate (EDTA). The binding mode between metal ions and RBP were further investigated by using density functional theory (DFT) calculations, which support the experimental findings very well. More importantly, RBP can be prepared as a test paper kit to detect the concentration of Hg^{2+} and Cr^{3+} ions by changing the color of the paper visible to naked eyes and is potential for the practical infield application. In addition, the results obtained from confocal microscopy revealed that the probe is cell permeable with low cytotoxicity and can be employed as a bio-imaging reagent for intracellular recognition of Hg^{2+} and Cr^{3+} ratification in human breast cancer cells MCF-7.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, considerable attention has been given to develop and engineer chemosensors, which can sense the toxic heavy metal ions, such as Hg^{2+} , Pb^{2+} , Cr^{3+} , Pd^{2+} , Cd^{2+} , etc. Among these environmental toxicants, Hg^{2+} and Cr^{3+} ions have received considerable attention due to their widespread contamination [1,2]. Mercury is considered as the most dangerous both in its atomic and ionic form, since it can easily be converted to methyl mercury by bacteria, which consequently accumulates through the food chain [3–5]. The acute exposure to mercury can cause diarrhea, fever, and vomiting, while its chronic exposure can cause inflammation of gums and mouth, nausea, nephrotic syndrome, parosmia, pink disease, and tremor, etc. Chromium is another environmental contaminant, which can cause hemolysis, gastrointestinal hemorrhage, acute renal failure, pulmonary fibrosis, and lungs cancer as well [6,7]. Thus, it is of great significance to develop a sensitive and selective

chemosensor, which can easily detect the Hg^{2+} and Cr^{3+} in different media. The traditional techniques like inductively coupled plasma, atomic emission, atomic absorption spectroscopies are time-consuming, tedious and costly methods to detect these ions, and are not convenient for the infield applications [8,9]. These limitations encouraged the researchers to prepare cost-effective, reversible and facile chemical sensor for the detection of these metal ions.

Colorimetric probes based on fluorescence “on or off” signaling and visible to naked eyes are very attractive for toxic metal ion detection, which can realize infield and real-time recognition of ions in the facile and cost-effective manner. Hitherto, various researchers [10–16] have reported a number of colorimetric sensors for Hg^{2+} or Cr^{3+} ions. Among them, rhodamine and its derivatives are one of the most commonly used probes since rhodamine has excellent photophysical and spectroscopic properties [17–20]. Up till now, several rhodamine-based chemical sensors have been reported for the individual sensing of Hg^{2+} and Cr^{3+} with a broad range of binding constants values respectively [21–28]. However, to the best of our knowledge, there are very few examples of the colorimetric chemical sensors, which have the

* Corresponding author.

E-mail address: yfzhou@sjtu.edu.cn (Y. Zhou).

ability to detect Hg^{2+} and Cr^{3+} ions together. Recently Mahato and co-worker reported a “turn on” fluorescent sensor based on rhodamine, for the recognition of both Hg^{2+} and Cr^{3+} in CH_3CN -aq. HEPES buffer (1 mM, pH 7.2; 1:1, v/v) medium with binding constants $K_{\text{Hg}^{2+}} = 3.13 \pm 0.08 \times 10^5 \text{ M}^{-1}$ and $K_{\text{Cr}^{3+}} = 1.38 \pm 0.04 \times 10^5 \text{ M}^{-1}$ at 25 °C [9]. Saha and coworker prepared a similar bifunctional probe to detect Hg^{2+} and Cr^{3+} ions with $K_{\text{Hg}^{2+}} = 3.11 \times 10^3 \text{ M}^{-1}$ and $K_{\text{Cr}^{3+}} = 2.0 \times 10^3 \text{ M}^{-1}$, respectively. Das et al. reported a “turn on” chemical sensor for the detection of Hg^{2+} and Cr^{3+} in neutral water with $K_{\text{Hg}^{2+}} = 4.31 \times 10^4 \text{ M}^{-1}$ and $K_{\text{Cr}^{3+}} = 6.54 \times 10^4 \text{ M}^{-1}$. To our knowledge, these are the only reports on the bifunctional chemical sensors for both Hg^{2+} and Cr^{3+} ion detection [8].

Herein, we report a new rhodamine based colorimetric chemical sensor, which can specifically sense Hg^{2+} and Cr^{3+} in the presence of alkali metals, alkaline earth metals, and the other heavy transition metals. It shows high binding constants of $1.09 \times 10^7 \text{ M}^{-1}$ for Hg^{2+} and $8.3 \times 10^4 \text{ M}^{-1}$ for Cr^{3+} and the detection limit as low as 1.6 μM for Hg^{2+} and 4.9 μM for Cr^{3+} , respectively. To our knowledge, the work represents the highest binding constant for Hg^{2+} as a chemical sensor. In addition, the detection limits are comparable to those reported in the literature. Besides, the chemical sensor shows a “turn-on” fluorescence response visible to naked eyes: it is colorless in the absence of analytes ($\text{Hg}^{2+}/\text{Cr}^{3+}$) and change into pink color when $\text{Hg}^{2+}/\text{Cr}^{3+}$ are introduced to the RBP solution. The change of color is proportional to the concentration of ions. This recognition of Hg^{2+} and Cr^{3+} is reversible in the presence of EDTA. Furthermore, the mechanistic studies indicates that there exist an equilibrium between spirocycle closed ring and open-ring of the rhodamine moiety through photo-induce electron transfer mechanism (PET). To support the experimental findings and selective binding mechanism between RBP and analytes, DFT calculations were also employed. The most striking feature of RBP is its practical applicability as a test paper mapping kit, which can detect the concentration of Hg^{2+} and Cr^{3+} ions by changing the color of the paper. In addition, we have also shown this chemical sensor can be used for detecting the intracellular uptake of Hg^{2+} and Cr^{3+} ions by turn-on fluorescence inside the living cells through confocal laser microscope experiments.

2. Experimental section

2.1. Materials

Rhodamine B, 2-Amino-5-bromopyrimidine, Phosphorous oxychloride, Triethylamine, were purchased from Adamas and Aldrich, USA. Metal salts $\text{Ag}(\text{NO}_3)_2$, AlCl_3 , $\text{Ba}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$, $\text{Cu}(\text{ClO}_4)_2$, CdCl_2 , $\text{Cr}(\text{NO}_3)_2$, FeCl_3 , FeCl_2 , $\text{Hg}(\text{NO}_3)_2$, KCl , LiClO_4 , NaCl , $\text{Ni}(\text{ClO}_4)_2$, $\text{Mg}(\text{ClO}_4)_2$, MnCl_2 , PbCl_2 , $\text{Zn}(\text{ClO}_4)_2$, were procured from, Aldrich, USA. China. Dichloromethane (DCM), dichloroethane (DCE), acetonitrile and methanol were of analytical grade and were obtained from Shanghai Chemical and Reagents Co. All the solvents, reagents and salts were used without further purification.

2.2. Instrumentation

Fluorescence spectra were recorded with a PerkinElmer LS 55 fluorescence spectrophotometer with a 10 mm quartz cuvette. The excitation and emission slit widths were set at 15 nm and 20 nm, respectively. All the absorption spectra were measured by UV-visible spectrophotometer (Schimadzu UV-2600). The pH of the solution was checked by Mettler-Toledo Delta 320 pH meter. NMR studies (^1H and ^{13}C) were performed at Bruker 500 spectrometer (Varian, USA). The studies related to Mass spectra were carried out on Q-TOF Premier Mass Spectrometer. All these measurements were performed at Instrument and Analysis Center of Shanghai Jiao Tong University.

2.3. Preparation of stock solutions

The stock solution of the chemical sensor (RBP) was prepared at the concentration of $10 \times 10^{-6} \text{ M}$ in 10 ml of MeCN and further diluted to the desired concentrations.

2.4. Preparation of ion stock solution

All the metal ion solutions were firstly prepared to the concentration of $1 \times 10^{-4} \text{ M}$ in pure water using 10 ml of water, and then further diluted with pure water to the desired concentrations. The chlorides, perchlorates and nitrates were used for the preparation of solutions of all ions. The stock solution of EDTA was prepared from Na_2EDTA in water at the concentration of $100 \times 10^{-3} \text{ M}$ and then diluted accordingly.

2.5. Emission and absorption titration experiments

All the emission and absorption titration experiments (fluorescence, UV – vis) were carried out in MeCN/HEPES (pH = 7.3, 1 mM, 3:2 v/v) buffer mixed solution. The fluorescence titration was carried out under following parameters ($\lambda_{\text{ex}} = 550 \text{ nm}$, scan speed = 500 nm/min, excitation slit = 15.0 nm, emission slit = 20.0 nm). The HEPES Buffer was used to adjust the pH value of the solution.

2.6. Calculation of binding constant using fluorescence titration data

The Eq. (1) was used for the determination of association constant, by evaluating the nonlinear least square analysis [29,30].

$$F = (F_0 + F_{\text{lim}}K_nC_M^n)/(1 + K_nC_M^n) \quad (1)$$

where F_0 , F_{lim} and F , are the intensity of emission for blank RBP, RBP saturated with excess amount of Hg^{2+} and Cr^{3+} , and RBP/metal ion complexes ($[\text{RBP} + \text{Hg}^{2+}]$ or $[\text{RBP} + \text{Cr}^{3+}]$), respectively. C_M is the concentration of metal ions, and n is the stoichiometric ratio between metal ion and RBP complex formation. K_n is the binding constant.

2.7. Calculation of binding constant using absorption titration data

The Eq. (2) was used for the determination of association constant, by evaluating the nonlinear least square analysis [29,30].

$$A = (A_0 + A_{\text{lim}}K_nC_M^n)/(1 + K_nC_M^n) \quad (2)$$

Here, A_0 , A_{lim} and A , are the intensity of absorption for blank RBP, RBP saturated with excess amount of Hg^{2+} and Cr^{3+} , and RBP/metal ion complexes $[\text{RBP} + \text{Hg}^{2+}]$ or $[\text{RBP} + \text{Cr}^{3+}]$, respectively. C_M is the concentration of metal ions, and n is the stoichiometric ratio between metal ion and RBP complex formation. K_n is the binding constant.

2.8. Calculation of lower limit of detection

The lower limit of detection (LOD) of RBP was calculated by using both the emission and absorption titration data. The emission and absorption spectrum of RBP was measured 15 times to achieve the standard deviation of blank measurement. The slope was obtained by plotting the intensities of RBP at 583 nm and 559 nm against concentration of Hg^{2+} or Cr^{3+} . The following equation was used to calculate LOD [31].

$$\text{LOD} = 3\sigma/S \quad (3)$$

where σ is the standard deviation S is the slope of the linear part (0–10 μM) of the calibration curve obtained from nonlinear least square analysis.

Download English Version:

<https://daneshyari.com/en/article/11026910>

Download Persian Version:

<https://daneshyari.com/article/11026910>

[Daneshyari.com](https://daneshyari.com)