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A water-soluble and retrievable ruthenium-based probe for colorimetric recognition of Hg(II) and Cys

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Abstract

A new ruthenium-based complex **1** [(bis(4,4'-dimethylphosphonic-2,2'-bipyridine) dithiocyanato ruthenium (II))] was developed as a colorimetric probe for the detection of Hg(II) and Cys (Cysteine). The obtained compound **1** can give interconversional color changes upon the alternating addition of Hg(II) and Cys in 100% aqueous solution. The specific coordination between NCS groups with Hg(II) can lead to the formation of **1**-Hg^{2+} complex, which can induce a remarkable spectral changes of probe **1**. Afterwards the formed **1**-Hg^{2+} complex can act as effective colorimetric sensor for Cys. Owing to the stronger binding affinity of sulfhydryl group to Hg^{2+}, Cys can extract Hg^{2+} from **1**-Hg^{2+} complex resulting in the release of **1** and the revival of absorption profile of the probe **1**. By introducing the hydrophilic phosphonic acid groups, the proposed probe exhibited excellent water solubility. The limits of detection (LODs) of the assay for Hg^{2+} and Cys are calculated to be 15 nM and 200 nM, respectively.

Keywords: Ruthenium, Mercury, Cysteine, Colorimetric probe, Phosphonic group

1. Introduction

Development of effective chemoprobes for sensing environmentally and biologically associated heavy and transition metal ions (ie. Hg^{2+}, Cu^{2+}, Pb^{2+}, and Cr^{3+}) have attracted considerable attention in recent years [1-5]. Mercury, as one of the most toxic species in nature, can cause serious environmental and health problems [6, 7]. In the marine environment, bacteria can transform mercury into methylmercury, a very potent neurotoxin, which can accumulate in marine food webs [8]. When ingested by humans, methylmercury triggers several serious disorders including prenatal brain damage, cognitive and motion disorders, vision and hearing loss, and even death [6, 9-11]. Various traditional techniques such as atomic absorption spectroscopy, atomic emission spectroscopy and inductively coupled plasma mass spectrometry have been applied to the detection Hg^{2+} ions [12-14]. However, these techniques usually involve sophisticated instrumentation, intricate sample handling protocols, and the need of professional operations, which limited their applications. For these reasons, colorimetric chemosensors are especially attractive because they allow naked-eye viewing the color changes triggered by target analytes without resorting to the use of sophisticated instruments [15-17]. A desirable colorimetric probe should have strong absorption band within visible region and respond specifically to the target analyte [18]. Transitional metal complexes, is a type of potent candidates for colorimetric applications because of their exceptional light-stability and visible light absorption ability arised from the ligand-to-metal charge-transfer (LMCT) transitions within the complexes [19, 20].

Due to the strong absorptions in the wavelength range of visible light and the favorable photovoltaic properties, Ru-containing dyes is a kind of useful transition metal complexes, such as N3 (bis(4,4'-dicarboxylato-2,2'-bipyridine) bis (isothiocyanato) ruthenium (II)) and N719 (Bis(tetrabutylammonium) Dithiocyanatobis(2,2'-bipyridine-4-COOH,4'-COO^-) ruthenium(II)), have been widely used as sensitizers for dye-sensitized solar cells [21]. The desirable features of Ru-based dyes also empower them to be potent chromogenic agents for colorimetric assays. Coronado et al. discovered that N719 can act effective colorimetric sensors for Hg^{2+} based on the interaction between mercury(II) ions and the NCS groups of N719 [22, 23]. Hao et al. found that the N3-Hg^{2+} complex can serve as a reversible probe for biothiols based a displacement mechanism [24].

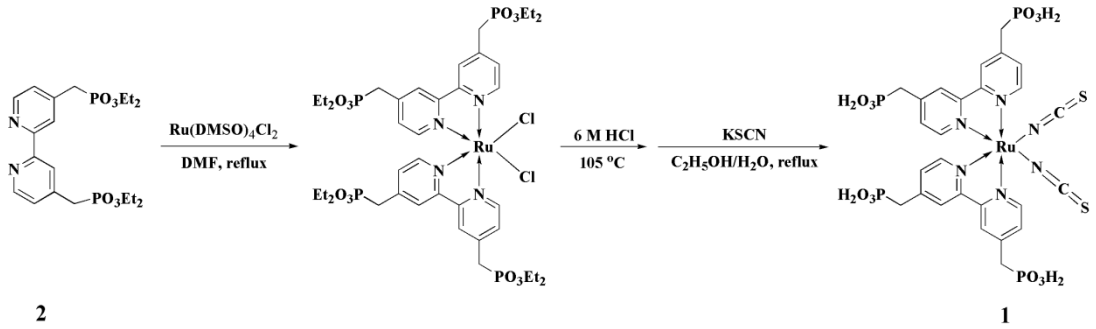
However, all these reported ruthenium-based colorimetric probes suffered the disadvantage of poor water-solubility which inevitably led to the use of organic solvents during the detection. Herein, by introducing phosphonic acid moiety which is highly hydrophilic and has been widely used for design water-soluble compounds [25-27], into the 2,2'-bipyridine ligands, we developed a water-soluble ruthenium-containing probe **1**. The synthesized probe can serve as a dual-functional sensor for recognition of Hg^{2+} and subsequently for Cys. Due to the specific recognition of Hg^{2+} by NCS group, probe **1** can bind with Hg^{2+} to form **1**- Hg^{2+} complex, which led to a color change in the dyes. Then in the presence of Cys, Hg^{2+} can be released from the complex of **1**-Hg^{2+}, resulting in the restoration of absorption profile of probe **1**.

2. Experimental

2.1. General information

All chemical reagents and solvents for synthesis were analytical grade and commercially available and used as received without further purification unless otherwise stated. Deionized water (18 MΩ cm^{-1}) from a water purification system (Simplicity Plus, Millipore Corp., Billerica, MA, USA) was used throughout. The absorbance spectra were recorded with Shimadzu UV2450 UV–vis spectrophotometer. NMR experiments were carried out on a 400 MHz Bruker spectrometer. Mass spectra (MS) were recorded on a mass spectrometer (LCQ Fleet, Thermo Fisher Scientific).

*2.2. Synthesis of probe **1***



Scheme 1. Synthesis of probe **1**.

*2.2.1. Synthesis of ligand **2***

Ligand **2** was obtained according to a five-step route according to a literature procedure [28] with slight modifications (see *supplementary information*).

*2.2.2. Synthesis of (bis(4,4'-dimethylphosphonic-2,2'-bipyridine) dithiocyanato ruthenium (II)) (**1**)*

To a solution of 4,4'-Bis(diethylmethylphosphonate)-2,2'-bipyridine **2** (0.228 g, 0.5 mmol) and LiCl (0.225 g, 5 mmol) in dry DMF (10 mL) in a three-necked flask was added $RuCl_3$ (0.163 g, 0.30 mmol) The mixture was heated at 160-170 ^oC for 6 h in the dark under flushed nitrogen. After the solution was cooled to room temperature, dichloromethane was added and the precipitate was filtered and washed with dichloromethane. After the compound was dried in a vacuum, the crude residue was purified by column chromatography on silica gel and eluted with acetone/methanol (4/6).

The obtained *cis*-dichloro-bis(4,4'-diethylmethylphosphonate-2,2'-bipyridine) ruthenium (II) (54 mg, 0.050 mmol) and KSCN (49 mg, 0.50 mmol) were dissolved in a mixture of water (5 mL) and ethanol (5 mL) in a three-necked flask. Then the mixture was heated at reflux for 12 h in the dark under flushed nitrogen. After the flask cooled to room temperature, acetone was added to the crude reaction mixture and the precipitate was filtered off and washed with acetone. The compound was then refluxed in HCl (20%, 10 mL) for 12 h. After removing solvent under vacuum, the resulting residue was then dissolved in a minimum amount of water and purified by column chromatography using Sephadex LH 20 as stationary phase and waster as eluent. ^1H NMR (500 MHz, D_2O) δ 9.19 (t, J = 5.8 Hz, 2H), 8.39 (s, 2H), 8.24 (d, J = 10.0 Hz, 2H), 7.74 – 7.69 (m, 2H), 7.60 – 7.54 (m, 2H), 7.01 (d, J = 5.8 Hz, 2H), 3.20 (d, J = 20.1 Hz, 4H), 2.95 (d, J = 20.0 Hz, 4H) (Fig. S3). MS [ESI]: m/z, calcd for $[M\text{-}NCS]^+$ 847.94; found 847.96 (Fig. S4).

2.3. UV-vis measurements

The detection measurements were conducted as follows. First, the stock solution of the probe **1** was prepared by dissolving the sensor compound in HEPES buffered aqueous solution (10 mM, pH 7.4). $HgCl_2$ stock solution was prepared in HEPES buffer (10 mM, pH 7.4). Before the measurements, the probe stock solution and the Hg^{2+} stock solution were diluted with HEPES buffered water (pH 7.4), and then the diluted Hg^{2+} was added into the diluted probe solution; afterward the UV-vis spectra were recorded at room temperature immediately. All spectrum tests were carried out in a HEPES bufferred (10 mM, pH 7.4) aqueous solution

2.4. HPLC conditions

Chromatographic analysis was performed using a reversed-phase (RP) HPLC system (Shimadzu 6AD, Columbia, MO) equipped with a column (Jupiter-10 μm-C18-300Å, dimension of 250 × 4.6 mm i.d.) from Phenomenex (Torrance, CA). Injection volumes were fixed at 10 μL. The mobile phases were water (mobile phase A) and methanol (mobile phase B). The flow rate was 1 mL min^{-1}, and the gradient conditions started at 0 % B, ramped to 50 % B in 20 min. Diode array detector wavelength was set 308 nm.

3. Results and Discussion

*3.1. Synthesis of the probe **1***

Synthetic process to prepare probe **1** was depicted in scheme 1. Ligand **2** was obtained according to a five-step route [28]. This procedure involves oxidation of the methly groups to carboxylic acids with potassium dichromate. The subsequent esterification with ethanol, reduction of the ester to the alcohol with sodium

borohydride, substitution with hydrobromic acid, and reaction with triethyl phosphite yields the desired compound. The preparation of probe **1** relies on two steps [29]. The first consists of refluxing 2 equiv of the bidentate ligand **2** with 1 equiv of $Ru(DMSO)_4Cl_2$ in DMF to yield *cis*-ruthenium bischlorobisbipyridine complex. In the second step, the chloride ligands are substituted by thiocyanate ligands by heating the ruthenium bis-chloro complex with KSCN in DMF, and then the diethyl ester phosphonate groups were fully hydrolyzed by heating the complexes in hydrochloric acid solution. Both of the ligand **2** and the probe **1** were characterized by ^1H NMR and MS (see supporting information).

*3.2. Absorption Spectroscopy of **1** to Hg^{2+}*

The absorption response of **1** toward Hg^{2+} was investigated by UV-vis spectrophotometric titration in HEPES buffer (10mM, pH 7.4). The UV−vis absorption spectrum of **1** displayed a strong band with the absorbance peak at 514 nm ($\varepsilon = 1.4\times 10^5$ $M^{-1}cm^{-1}$), which can be attributed to metal-to-ligand charge transfer transitions (MLCT) process of ruthenium complex. Upon the addition of increasing amount of Hg^{2+}, the intensity of the absorption peak of probe **1** at 514 nm decreased gradually, while a new absorption band at 441 nm increased dramatically. A clear isosbestic point at 476 nm indicated the conversion of **1** to a new species (**1**-Hg^{2+}) during the titration (Fig. 1). The absorbance profile of probe **1** was no longer changed noticeably when the concentration of Hg^{2+} reached 30 μM. The 3:2 stoichiometry of the complexation between **1** and Hg^{2+} was confirmed with a Job's plot analysis (Fig. S5), which is in agreement with previous studies [23, 24]. Therefore the binding mode between probe

1 and Hg^{2+} can be speculated that each Hg^{2+} is tetrahedrally coordinated to three sulfur atoms from adjacent probe and one Cl^- anion.

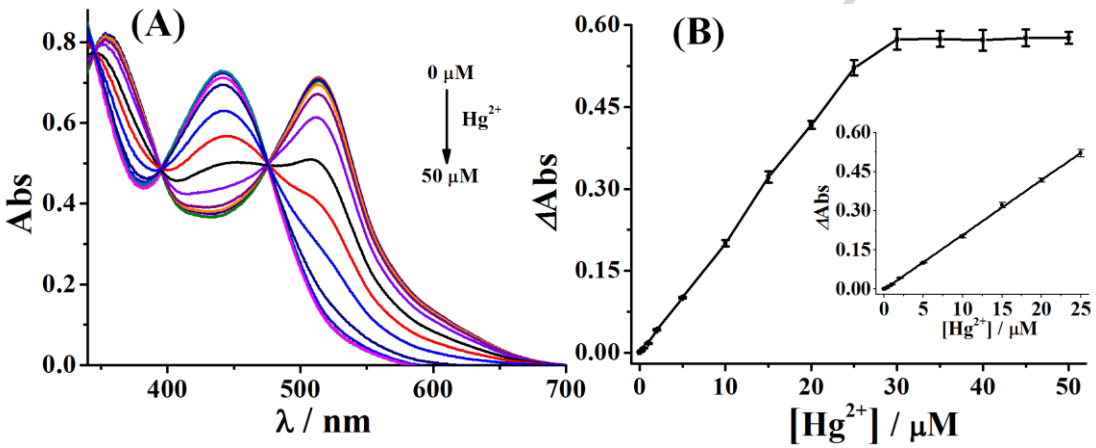


Fig. 1. (A) Absorption spectra changes of probe **1** (50 μM) in the presence of different concentrations of Hg^{2+} (0–1 equiv) in HEPES aquous buffer (10 mM, pH 7.4). (B) Absorption changes of **1** at 514 nm as function the Hg^{2+} concentration, inset shows the calibration curve.

Then the changes in the intensity of the absorbance peak (514 nm) of probe **1** were applied to quantitatively monitor the Hg^{2+}. As shown in Fig. 1B, ΔAbs of probe **1** increases linearly with the concentration of Hg^{2+} over the range from 0.1 μM to 25.0 μM which can be expressed as a linear equation of $\Delta Abs = -0.0016 + 0.02098 \times [Hg^{2+}]$ ($R^2 = 0.998$). All the RSDs (relative standard deviation) at different concentrations are less than 5.2 % indicating good reproducibility of the probe **1** for Hg^{2+} detection. The LOD (limit of detection) for Hg^{2+} was determined as 15 nM (S / N = 3). And this value is matchable to the maximum allowable level (10 nM) for Hg^{2+} in drinking water set by the US Environmental Protection Agency (EPA) [30], indicating that the

proposed assay can be a potential tool for environmental monitoring.

To evaluate the selectivity of the proposed probe **1** for Hg^{2+}, optical responses of **1** to other metal cations including Ag^{+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pd^{2+} and Zn^{2+} were measured. As shown in Fig. 2, only the addition of Hg^{2+} induce a dramatic change in the absorbance profile of probe **1**, and no significant signal changes were observed upon addition of other metal cations, indicating the specific coordination between sulfur atom of the probe's NCS groups with Hg(II). The excellent selectivity of probe **1** for Hg^{2+} could also be observed from the photographic images (inset of Fig. 2), only Hg^{2+} induced an apparent colour change from red to yellow which can be easily discriminated with the naked eye. Moreover, competition experiments were conducted. As shown in Fig. 3, either in the absence or in the presence of other cations, significant spectral changes were always observed for probe **1** upon addition of Hg^{2+}. The results indicate that none of these anions interfered with the sensing of Hg^{2+}. Therefore, probe **1** can act as a highly selective colorimetric probe for Hg^{2+}.

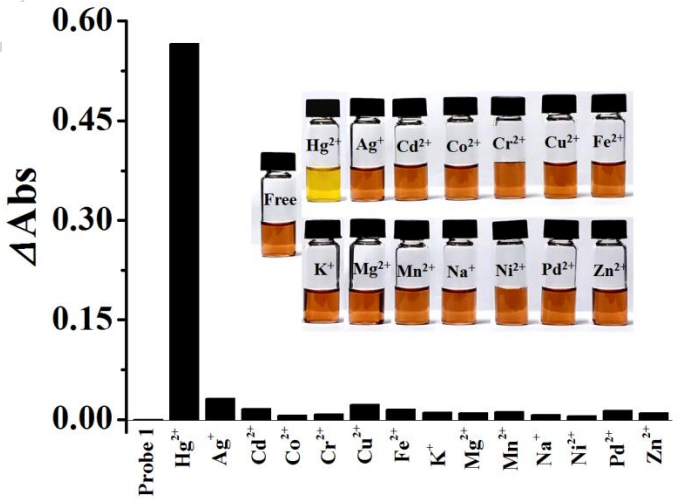


Fig. 2. Absorption response of **1** (50 μM) upon the addition of various ions (100 μM) in HEPES aquous buffer (10 mM, pH 7.4) (the inset shows their corresponding

photographic images).

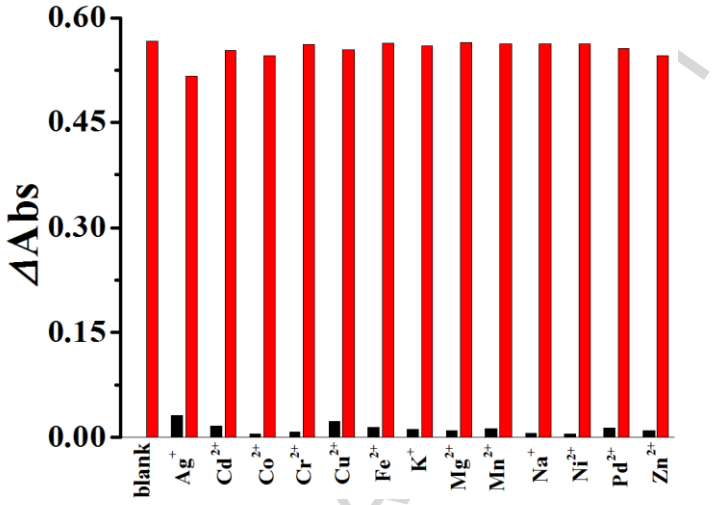


Fig. 3. Absorption responses of **1** (50 μM) in the presence of different ions (100 μM) (dark bars), followed by addition of Hg^{2+} (50 μM) (red bars) in HEPES aquous buffer (10 mM, pH 7.4).

To explore the potential applications of probe **1** for the simple and convenient monitoring of Hg^{2+}, we employed probe **1** to prepare filter paper-based test strips for the direct detection of Hg^{2+} as performed in previous studies [18, 31]. Here, the test strips were prepared by immersing the filter paper into an aqueous solution of **1** (0.1 M) and then dried in air. Then the as-prepared test strips were immersed into the aqueous solution of Hg^{2+} with different concentrations. As illustrated in Fig. 4, upon the presence of Hg^{2+}, obvious colour changes of the test strips from red to yellow were observed and the discernible concentration of Hg^{2+} can be as low as 20 μM.

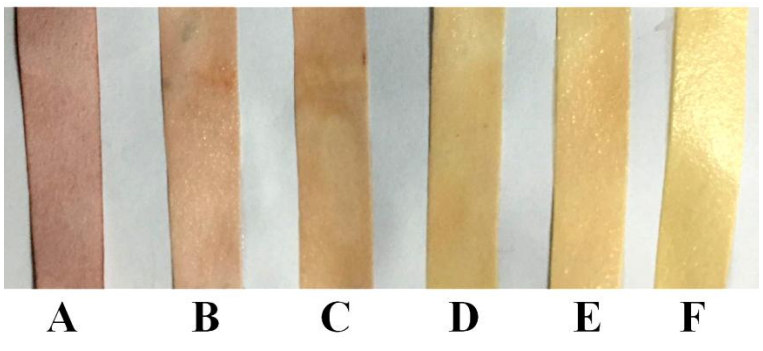


Fig. 4. Photographic images of filter paper-based test strips of **1** for various concentrations of Hg^{2+} : (A) blank, (B) 20 μM, (C) 50 μM, (D) 80 μM, (E) 100 μM, (F) 150 μM.

*3.3. Absorption Spectroscopy of **1**-Hg^{2+} to Cys*

In recent researches, the metal ions (Hg^{2+}, $Ag^{+,}$ or Cu^{2+})-based complexes have been exploited for the sensing of biothiols based on the high affinities of sulfur-bearing groups for these metal ions [32-34]. To test the feasibility of this strategy for the quantification of Cys in the proposed assay, the *in situ* generated **1**-Hg^{2+} complex was titrated with Cys in 100% aquous media. As shown in Fig. 5, the peak absorbance of **1**-Hg^{2+} at 514 nm is increased steadily with the increase in Cys concentration, and on addition of about 2 equiv of Cys the absorption profile closely matches that of probe **1**, indicating the regeneration of probe **1**. The dose-dependent absorbance changes (*Δ*Abs) shows a good linearity over a concentration range of 1.0–25.0 μM for Cys, that can be expressed as *Δ*Abs = 0.016 × [Cys] / μM - 0.051 (R^2 = 0.997), (Fig. 5 inset). The LOD of **1**-Hg^{2+} complex for Cys was calculated to be 0.2 μM.

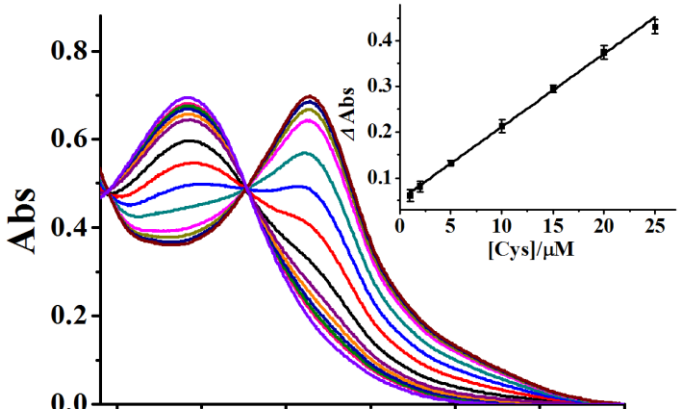


Fig. 5. Absorption spectra of **1**-Hg^{2+} complex in the presence of various concentrations of Cys (0, 0.1, 0.2, 0.5, 1, 2, 5, 10, 15, 20, 25, 30, 40, and 50 μM) in HEPES aquous buffer (10 mM, pH 7.4). Inset: calibration curve of *Δ*Abs *vs* Cys concentrations. Error bars represent the standard deviation of three measurements.

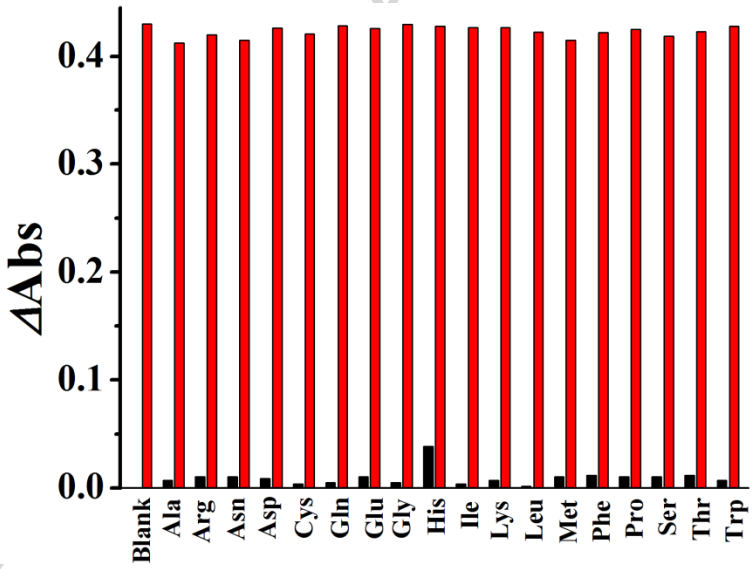
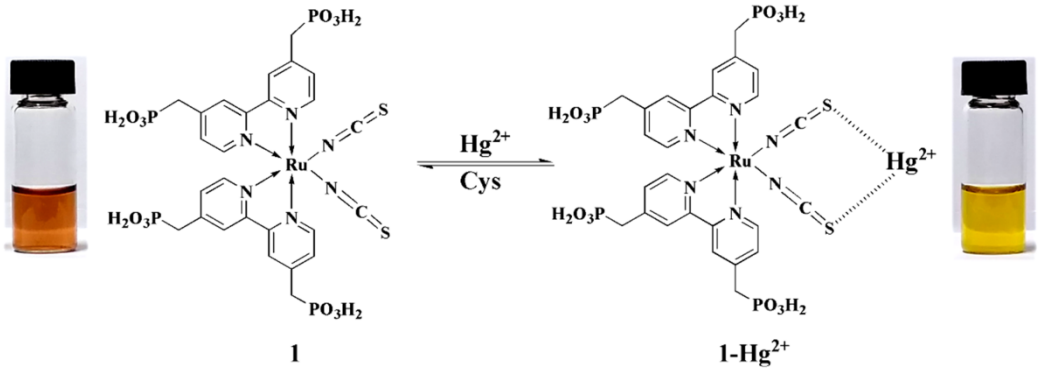


Fig. 6. Absorption changes of **1**-Hg^{2+} (50 μM) at 514 nm in the presence of different amino acids (50 μM) (low bars), followed by addition of Cys (50 μM) (high bars).

In order to evaluate the selectivity of the proposed **1**-Hg^{2+} complex for Cys, absorbance changes of **1**-Hg^{2+} at 514 nm were recorded in the presence of various other amino acids. *Δ*Abs of **1**-Hg^{2+} did not change distinctly in the presence of the other amino acids. It is probably due to that these amino acids do not have any significant

interaction with Hg^{2+}. However, in presence of Cys, *Δ*Abs dramatically changed (Fig. 6). Hence, the proposed **1**-Hg^{2+} has high selectivity for Cys among other amino acids. To explore whether the **1**-Hg^{2+} complex could maintain its sensing response to Cys in the presence of various other relevant amino acids, competition experiments of **1**-Hg^{2+} complex were conducted. Fig. 6 (red bars) shows the *Δ*Abs of **1**-Hg^{2+} to Cys in the presence of various other species. The results indicated that none of the other amino acids interfered with Cys detection. All other amino acids only caused very weak background signal, while upon consequently addition of Cys to each mixture, immediate absorbance response was achieved. These results strongly suggest that **1**-Hg^{2+} complex is a potent colorimetric assay for Cys monitoring with high specificity.



Scheme 2. The proposed sensing mechanism of probe **1** for Hg^{2+} and Cys.

3.4. Proposed sensing mechanism

As depicted in Scheme 2, the probe **1** alone displays red color. The addition of Hg^{2+} can cause an obvious color change from red to yellow due to the formation of **1**-Hg^{2+} complex. The further addition of Cys could release probe **1** from the **1**-Hg^{2+}complex owing to the stronger affinity of Cys to Hg^{2+}, resulting in the restoration of the absorbance profile of probe. This reversible binding process was

further investigated and confirmed by HPLC measurements (Fig. 7, black curve). Probe **1** (100 μM) alone showed a main peak with Rt (Retention time) of 13.7 min. After mixing **1** (100 μM) with Hg^{2+} (100 μM), the peak at 13.7 min was completely disappeared, and a new broadened peak at 19.8 min appeared (Fig. 7, red curve). This is attributed to the conversion of the **1** to **1**-Hg^{2+} complex. After the **1**-Hg^{2+} complex solution was further treated with Cys (2 equiv), the typical HPLC spectrum of **1** was entirely restored (Fig. 7, blue curve). Above results revealed that probe **1** can reversibly coordinate to Hg^{2+} upon the addition of Cys.

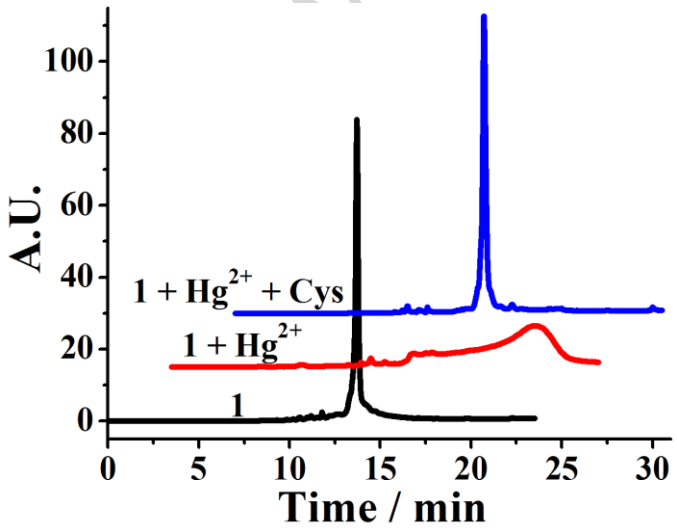


Fig. 7. HPLC chromatograms obtained by injecting a solution of HEPES buffer (10 mM, pH=7.4) containing (black curve) 100 μM probe **1**; (red curve) 100 μM **1** and 100 μM Hg^{2+}; (blue curve) 100 μM N3, 100 μM Hg^{2+} and 200 μM Cys.

4. Conclusions

In summary, we have reported a colorimetric chmosensor **1** for recognition of Hg^{2+} and Cys. By incorporating hydrophilic phosphonic groups into the bipyridine ligands of the ruthenium complex, probe **1** displays excellent water-solubility. Due to

the specific coordination of Hg^{2+} to the sulfur atom of the probe' SCN groups, **1** shows high selectivity toward Hg^{2+}. And this complexation could lead to the absorbance change of prbe **1** from red to yellow and the formation of **1**-Hg^{2+}. Moreover, the *in situ* generated **1**-Hg^{2+} complex can act as an effective chemosensor for Cys detection in aqueous solution.

Acknowledgements

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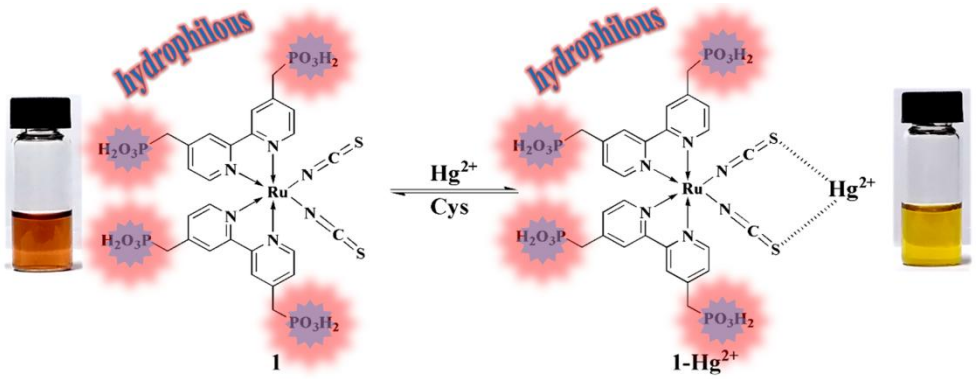

Graphical abstract

Hightlights

- A novel retrievable ruthenium-based colorimetric probe was developed for recognition of Hg(II) and Cys based on a displacement mechanism.
- The probe possesses highly sensitivity and selectivity towards the targets.
- The constructed probe displays excellent water-solubility.