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## A new quinoline-based chemosensor in ratiometric sensing of $\mathrm{Hg}^{2+}$ ions

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A new quinoline-based chemosensor **1** has been designed and synthesised. Its metal ion-binding properties have been documented in organic and aqueous organic solvents. While chemosensor **1** recognises  $Hg^{2+}$  ions ( $K_a = 2.15 \times 10^4 M^{-1}$ ) by exhibiting ratiometric change in emission in CHCl<sub>3</sub>/CH<sub>3</sub>OH (1:1, v/v), under similar condition both Zn<sup>2+</sup> and Cd<sup>2+</sup> ions are sensed by significant non-ratiometric increase in emission with measurable red shift. In DMSO/H<sub>2</sub>O (5:95, v/v), the sensor **1** exhibits a greater selectivity towards  $Hg^{2+}$  ions ( $K_a = 9.20 \times 10^3 M^{-1}$ ) over the other metal ions examined.

Keywords: mercury recognition; zinc and cadmium sensing; quinoline-based receptor; ratiometric fluorescence; ratiometric absorbance

Design and synthesis of simple molecular architectures that can detect and sense the heavy transition metal ions are of particular interest in the field of supramolecular chemistry (1). Of the different metal ions,  $Hg^{2+}$  gains special importance due to its biological and environmental significances (2). Mercury ion  $(Hg^{2+})$  is considered to be dangerous as it can accumulate in the human body and affects a wide variety of diseases even in a low concentration, such as prenatal brain damage, serious cognitive disorders and Minamata disease (2). Therefore, the selective detection of  $Hg^{2+}$  ions in both organic and semi-aqueous environment is of paramount interest. To date, a number of receptor modules have been reported, which recognise Hg<sup>2+</sup> ions by colour and fluorescence changes (3, 4). Of the different fluorescent probes, the ratiometric probes for the detection of  $Hg^{2+}$  ions are considerably important, and they are relatively less in number (5). Moreover, nearly all ratiometric chemosensors show interference with Ag<sup>+</sup> and Cu<sup>2+</sup> and low sensitivity (5). The ratiometric chemosensors provide advantages over the conventional monitoring of fluorescence intensity at a single wavelength. A dual emission system can reduce the measurement errors because of the factors such as photo transformation, receptor concentrations and environmental effects (6).

During the course of our work on the fabrication of receptor modules of different architectures for both cations and anions (7), we report in this study a simple easy-to-make structure **1** that is found to be capable of sensing  $Hg^{2+}$  ions in organic solvent (CHCl<sub>3</sub>:CH<sub>3</sub>OH = 1:1, v/v) by exhibiting high ratiometric change in both fluorescence and absorbance. In contrast, among the other metal ions

examined, only  $Zn^{2+}$  and  $Cd^{2+}$  ions increased the emission of **1** greatly in non-ratiometric fashion in CHCl<sub>3</sub>/CH<sub>3</sub>OH (1:1, v/v), and thus, they are differentiated from Hg<sup>2+</sup> ions in this study. Furthermore, in DMSO/H<sub>2</sub>O (5:95, v/v), the receptor **1** is noted to be only responsive to Hg<sup>2+</sup> ion as observed from a greater quenching of emission over the other metal ions studied. In the design **1**, the role of quinoline ring in binding of metal ions was established by considering the model compound **2**.



Synthesis of **1** was achieved by the reaction sequences as depicted in Scheme 1. Piperazine was first allowed to stir with chloroacetyl chloride in the presence of  $Et_3N$  in dry  $CH_2Cl_2$  to afford the diamide **3**, which on subsequent reflux with 8-hydroxyquinoline and anhydrous  $K_2CO_3$  in dry  $CH_3CN$  gave the compound **1**. Use of 1-naphthol instead of 8-hydroxyquinoline under similar condition gave the compound **2** in good yield. Compounds **1** and **2** 

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Scheme 1. Syntheses of receptors 1 and 2.

were characterised by <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass and FTIR analyses (Supplementary Information, available online).

The optical sensitivity of **1** towards various metal ions was investigated spectrophotometrically (fluorescence and UV titration experiments) by adding standard solutions of the cations such as Hg<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Mg<sup>2+</sup>, Ni<sup>2+</sup> and Ag<sup>+</sup> (taken as their perchlorate salts) to the fixed concentration of the chemosensor **1** in CHCl<sub>3</sub>/ MeOH (1:1, v/v). Additionally, <sup>1</sup>H NMR was studied in  $d_6$ -DMSO to understand the nature of interaction in the binding site.

Initially, we investigated the affinity of chemosensor **1** towards  $\text{Hg}^{2+}$  ion by monitoring the absorbance changes on addition of  $\text{Hg}(\text{ClO}_4)_2$  ( $c = 1.0 \times 10^{-3}$  M) to the solution of compound **1** ( $c = 4.0 \times 10^{-5}$  M) in CHCl<sub>3</sub>/ MeOH (1:1, v/v). As can be seen in Figure 1, the absorption spectrum of **1** is characterised by the presence of a typical absorption at 300 nm for quinoline. With the incremental addition of  $\text{Hg}^{2+}$  ions although the absorbance at 300 nm decreased, a new red-shifted band at ~355 nm developed with an isosbestic point at 330 nm. Such ratiometric change in absorbance was not noted with the addition of other metal ions studied (Supplementary Information, available online). However, the distinct isosbestic point in Figure 1 reveals the formation of a new species which may remain in equilibrium with the free receptor in solution.

In fluorescence, the excitation of 1 ( $c = 4.0 \times 10^{-5}$  M) in CHCl<sub>3</sub>/MeOH (1:1, v/v) at 300 nm gave sharp emission at 395 nm. This is attributed to the monomer emission of the quinoline motif. Upon gradual addition of Hg<sup>2+</sup> ions  $(c = 1.0 \times 10^{-3} \text{ M})$  (up to 10 equiv.) to the solution of **1**  $(c = 4.0 \times 10^{-5} \text{ M})$  in CHCl<sub>3</sub>/MeOH (1:1, v/v), a significant decrease in intensity of the emission at 395 nm was observed along with the appearance of a new emission centred at 482 nm. This resulted in a ratiometric change in emission and gave an isoemission point at 435 nm (Figure 2). The new emission at 482 nm is presumably attributed to the formation of excimer between the quinoline moieties that are pulled closely due to strong chelation of  $Hg^{2+}$  in the cavity of **1**. This excimer emission at 482 nm is in accordance with our previous report on quinoline-based receptor (8). Figure 3 represents the probable binding mode. Complexation-induced chairto-boat conformational switching introduces two quinolines at the close distance for the formation of excimer.



Figure 1. Change in absorption of  $1 \ (c = 4.0 \times 10^{-5} \text{ M})$  in CHCl<sub>3</sub>–MeOH (1:1, v/v) upon addition of 10 equiv. amounts of Hg(ClO<sub>4</sub>)<sub>2</sub> ( $c = 1.0 \times 10^{-3} \text{ M}$ ).



Figure 2. Change in emission of **3** ( $c = 4.0 \times 10^{-5}$  M) in CHCl<sub>3</sub>-MeOH (1:1, v/v) upon addition of 10 equiv. of Hg(ClO<sub>4</sub>)<sub>2</sub> ( $c = 1.0 \times 10^{-3}$  M).



Figure 3. Probable mode of binding of  $Hg^{2+}$  ion.

Such conformational switching in piperazine-based chemosensor for selective detection of  $Cu^{2+}$  is known in the literature (9).

The association constant (10) between 1 and  $Hg^{2+}$  ion involving 1:1 stoichiometry, confirmed by Job plot (11) (Figure 4), was estimated as  $2.15 \times 10^4 \text{ M}^{-1}$ . On the other hand, upon gradual addition of  $Zn^{2+}$  ( $c = 1.0 \times 10^{-3} M$ ) (Figure 5) and  $Cd^{2+}$  ( $c = 1.0 \times 10^{-3}$  M) (Figure 6) ions into the solution of 1 ( $c = 4.0 \times 10^{-5}$  M), the emission at 395 nm increased to the greater extent in each case without showing any other change in the emission spectra. In the titration with other metal ions, the emission intensity of 1 was reduced, and it was found to be meaningful only in case of Cu<sup>2+</sup> and Ni<sup>2+</sup> ions (Supplementary Information, available online). However, during progression of titration although with  $Zn^{2+}$  ion the emission at 395 nm underwent a red shift of 20 nm, for  $\text{Cd}^{2+}$  it was observed to be  $\sim$  13 nm. The absence of excimer during complexation of  $Zn^{2+}$  and  $Cd^{2+}$  ions is attributed to the non-overlapping of the quinoline motifs in the  $\pi$ -stacking fashion although both the cations followed 1:1 stoichiometry in the binding process. The binding constants (10) as determined for  $Zn^{2+}$  and  $Cd^{2+}$  ions were found to be  $3.43 \times 10^3 M^{-1}$  and



Figure 4. Fluorescence Job plot for receptor 1  $(c = 4.0 \times 10^{-5} \text{ M})$  with Hg<sup>+2</sup> at 395 nm ( $\lambda_{ex} = 300 \text{ nm}$ ).



Figure 5. Change in emission of  $1 (c = 4.0 \times 10^{-5} \text{ M})$  in CHCl<sub>3</sub>–MeOH (1:1, v/v) upon addition of 10 equiv. of Zn(ClO<sub>4</sub>)<sub>2</sub> ( $c = 1.0 \times 10^{-3} \text{ M}$ ).

 $5.32 \times 10^3 \text{ M}^{-1}$ , respectively. These values are less than the binding constant value for Hg<sup>2+</sup> ion. To our opinion the cavity dimension of **1**, the ionic size of the metal ion and also metal-ligand chelation strength are the crucial points that actually regulate the conformational switching and the binding features as pointed out in Figure 3. To prove the pivotal role of quinoline ring in the binding, model compound **2** was titrated under similar condition with Hg<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> ions. Interestingly, no significant change in emission was observed (Supplementary Information, available online) in the interaction.

<sup>1</sup>H NMR analysis (Figure 7) further provided evidence that  $Hg^{2+}$  ion is effectively complexed in the cavity of **1** involving quinoline ring nitrogen as well as ether oxygen.



Figure 6. Change in emission of  $1 (c = 4.0 \times 10^{-5} \text{ M})$  in CHCl<sub>3</sub>-MeOH (1:1, v/v) upon addition of 10 equiv. of Cd(ClO<sub>4</sub>)<sub>2</sub> ( $c = 1.0 \times 10^{-3} \text{ M}$ ).



Figure 7. Partial <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO) of **1** ( $c = 1 \times 10^{-3}$  M) and in the presence of equiv. amount of Hg(ClO<sub>4</sub>)<sub>2</sub>, Zn(ClO<sub>4</sub>)<sub>2</sub> and Cd(ClO<sub>4</sub>)<sub>2</sub>.

In the presence of equiv. amount of  $Hg(ClO_4)_2$ , the signals for the protons of quinoline ring and also of  $-OCH_{2-}$ group moved downfield to the considerable extents and thus support our binding proposition as cited in Figure 3. In comparison, small change in chemical shift in the presence of equiv. amount of  $Zn^{2+}$  and  $Cd^{2+}$  ions corroborated their weak interaction.

Considering the ratiometric emission characteristics, the selectivity of **1** towards  $Hg^{2+}$  ion was realised from the plot of fluorescence ratio ( $I_{482}/I_{395}$ ) at the two wavelengths (Figure 8). As can be seen from Figure 8, the greater change in fluorescence ratio for  $Hg^{2+}$  is worth mentioning for its selective detection from the other metal ions. Such high ratiometric change in emission remained unperturbed even



Figure 8. Ratiometric fluorescent response  $(I_{482}/I_{395})$  of 1  $(c = 4 \times 10^{-5} \text{ M})$  in CHCl<sub>3</sub>–MeOH (1:1, v/v) upon addition of 10 equiv. amounts of different cations  $(c = 1 \times 10^{-3} \text{ M})$  as their perchlorate salts.



Figure 9. Change in emission of 1 ( $c = 4 \times 10^{-5}$  M) upon addition of 2 equiv. amounts of Hg(ClO<sub>4</sub>)<sub>2</sub> ( $c = 1 \times 10^{-3}$  M) in the presence of other metal ions.

in the presence of other metal ions. Figure 9, in this aspect, demonstrates the change in emission of 1 upon addition of 2 equiv. amounts of  $Hg^{2+}$  ions to the solution of 1 containing other metal ions in 2 equiv. amounts each. The interference of individual metal ion was also verified (Supplementary Information, available online), and no metal ion in the study perturbed the ratiometric sensing of  $Hg^{2+}$  ion.

The enhancement of fluorescence upon addition of  $Zn^{2+}$  and  $Cd^{2+}$  ions is explained due to the inhibition of photoinduced electron transfer (PET) process occurring in between the excited state of quinoline and binding site. Similarly, the quenching of emission in the presence of other metal ions is ascribed due to the activation of PET process. The change in emission in the presence of  $Hg^{2+}$  ion follows a different mechanism. The heavy atom effect of  $Hg^{2+}$  ion (12) quenches the monomer emission followed by the appearance of a new emission for excimer that results in from the complexation-induced pulling of the pendant quinolines.

To check the feasibility of the receptor **1** in sensing the metal ions in aqueous environment, we carried out the similar interaction study in DMSO:H<sub>2</sub>O (5:95, v/v) considering the solubility of **1** (Supplementary Information, available online). In this high-water-content solvent, the receptor **1** responded only to Hg<sup>2+</sup> ion by showing greater quenching of emission. No excimer emission was noted and to our opinion, this was due to the greater polarity of solvent system that reduced the Hg<sup>2+</sup>–ligand interaction effectively ( $K_a = 9.20 \times 10^3 \text{ M}^{-1}$ ). Beside Hg<sup>2+</sup> ion, effect of other metal ions on the emission of **1** was observed to be weak (Figure 10). In the ground state, the absorption of **1** at 300 nm underwent a considerable red shift in the presence of Hg<sup>2+</sup> ion (Supplementary Information, available online).





In conclusion, this study demonstrates an easy synthesis of simple chemosensor 1 that selectively recognises Hg<sup>2+</sup> ion with measurable binding constant value over a series of other metal ions by exhibiting a high ratiometric change in both absorption and emission in CHCl<sub>3</sub>/CH<sub>3</sub>OH (1:1, v/v) solvent. The ratiometric fluorescent response via conformational switching of piperazine scaffold is convenient in the present case for the selective detection of Hg<sup>2+</sup> ion from  $Zn^{2+}$ , Cd<sup>2+</sup> and other metal ions taken in the study. Although there are examples for ratiometric sensors of  $Hg^{2+}$  (5), the present example demands its merit for its simplicity in design and better response. Indeed, this simple quinoline-piperazine conjugate is an elegant example of PET sensor like other reported quinoline-based receptors (13) for chemosensing of Hg<sup>2+</sup> ions. In high-water-content semi-aqueous system  $(DMSO:H_2O = 5:95, v/v)$ , the chemosensor 1 also efficiently recognised Hg<sup>2+</sup> ion from the other ions by exhibiting quenching of emission to the considerable extent and validated the working ability of the receptor in aqueous system. Further exploration along this direction is underway in our laboratory.

#### Supplementary data

Figures showing the change in absorption and fluorescence spectra of **1** and **2** with the metal ions, Job plots for  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Hg^{2+}$  ions, selectivity test, experimental procedures are available.

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