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## Naphthalene and pyrrole substituted guanidine in selective sensing of Cu<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup> and CN<sup>-</sup> ions under different conditions

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#### ABSTRACT

Naphthalene and pyrrole substituted guanidine **1** has been designed and synthesised. Compound **1** efficiently distinguishes  $Cu^{2+}$ ,  $Hg^{2+}$  and  $Pb^{2+}$  ions by exhibiting different responses in fluorescence. While compound **1** exhibited *turn-on* emission selectively in the presence of  $Hg^{2+}$  and  $Pb^{2+}$  ions in CH<sub>3</sub>CN and CH<sub>3</sub>CN–H<sub>2</sub>O (1:1, v/v), respectively, it showed decrease in emission upon interaction with  $Cu^{2+}$  ion in CH<sub>3</sub>CN. Furthermore, the Cu-**1** ensemble has been established as a potential probe for selective detection of CN<sup>-</sup> ion over a series of other anions involving colour change (in ordinary light: colourless to light yellow and under UV light: colourless to sky blue). Theoretical insight has been invoked to understand the mode of metal–ligand interaction.



Naphthalene and pyrrole substituted guanidine **1** has been designed and synthesised. It efficiently distinguishes  $Cu^{2+}$ ,  $Hg^{2+}$  and  $Pb^{2+}$  ions by exhibiting different responses in fluorescence. The Cu-**1** ensemble has been established as a potential probe for selective detection of  $CN^{-}$  ion over a series of other anions involving colour change.

#### Introduction

Design and synthesis of new architectures capable of sensing multiple metal ions of biological significance draw attention in supramolecular chemistry research. Of the different transition metal ions, copper, mercury and lead ions are considered to be important due to their pivotal roles in biological system. Copper being essential element in our life is linked with a variety of fundamental physiological processes in organisms. It causes environmental pollution and also serves as catalytic cofactor for a variety of metalloenzymes (1). Exposure to high levels of copper can cause gastrointestinal disturbance and liver or kidney damage (2). Excess accumulation of copper may cause Wilson's disease (3). Various metalloenzymes involve Cu<sup>2+</sup> as catalytic

cofactor, such as superoxide dismutase, tyrosinase and cytochrome oxidase (4).

Similarly lead is associated with digestive, neurologic, cardiac diseases and mental retardation (5,6). Lead is a highly toxic heavy metal ion. The accumulation of lead in the environment causes lead pollution. It is associated with a number of developmental disorders in children including slowed motor responses, decreased IQs and hypertension (6).

On the other hand, mercury is also a toxic metal ion. Its accumulation in low concentration in the human body causes a wide variety of diseases, such as prenatal brain damage, serious cognitive disorders and Minamata disease (7). The toxicity of mercury in living systems is

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Figure 1. Structure of compound 1.

attributed to measurable affinities of the thiol group containing proteins and enzymes that results in the malfunctioning of the living cells (8).

Therefore, the detection and sensing of these toxic metal ions by a simple synthetic system is highly desirable. Multi-ion recognition with a single molecular probe is recently becoming popular due to some advantages such as cost reduction and more efficient analysis. The literature survey reveals a series of examples on selective sensing of  $Cu^{2+}$ ,  $Hg^{2+}$  and  $Pb^{2+}$  ions by artificial fluororeceptors (9). Fluororeceptors are attractive due to the simplicity, high sensitivity and real-time detection. In this manuscript, we wish to report the synthesis of a guanidine-centred pyrrole receptor 1 (Figure 1) that behaves as an efficient fluorimetric sensor for Hg<sup>2+</sup>, Cu<sup>2+</sup> and Pb<sup>2+</sup> ions. While the architecture 1 exhibits turn-on emission selectively in the presence of Hg<sup>2+</sup> and Pb<sup>2+</sup> ions in CH<sub>2</sub>CN and CH<sub>2</sub>CN–H<sub>2</sub>O (1:1, v/v), respectively, it shows decrease in emission upon interaction with Cu<sup>2+</sup> ion in CH<sub>3</sub>CN. Furthermore, the Cu-1 ensemble has been found to be a potential probe for selective detection of CN<sup>-</sup> ion over a series of other anions.

#### **Results and discussion**

#### **Synthesis**

Compound 1 was synthesised according to the Scheme 1. In synthesising 1, compound 2 which was obtained by reported procedure (10) was used as the starting material. Reaction of pyrrole carbaldehyde 2 with  $NH_2OH.HCI$ in aqueous  $K_2CO_3$  gave the corresponding oxime 3 which on reduction with HCOONH<sub>4</sub> and Pd/C in ethyl acetate yielded amine **4**. Reaction of the amine **4** with 1-naphthyl isothiocyanate introduced the compound **1** in appreciable yield. The formation of **1** as unequivocally characterised by usual spectroscopic techniques is explained according to our suggested mechanism (Scheme 2).

#### **Metal and Anion binding studies**

Metal ion binding interaction of  $1 (c = 2.50 \times 10^{-5} \text{ M})$  was examined by observing the change in its absorption and emission spectra in organic as well as aqueous-organic media. In CH<sub>3</sub>CN, on excitation at 280 nm, compound **1** displayed emission at 373 nm which was perturbed to the different extents upon titration with different metal ions ( $c = 1.0 \times 10^{-3}$  M, taken as perchlorate salts). In this regard, Figure 2 represents the change in fluorescence ratio of **1** upon addition of 3 equiv. amounts of a particular metal ion. In the experiment, while the addition of Cu<sup>2+</sup> ions to the solution of **1** in CH<sub>3</sub>CN quenched the emission (Figure 3(a)), Hg<sup>2+</sup> ions, under similar conditions, increased the emission significantly (Figure 3(b)). Other metal ions merely perturbed the emission of **1** (Figure 1S).

The selectivity in the binding of Cu<sup>2+</sup> and Hg<sup>2+</sup> ions was understood by recording fluorescence of **1** in the presence and absence of other metal ions (Figure 2S). The interference study reveals that both Cu<sup>2+</sup> and Hg<sup>2+</sup> ions mutually interfere whereas other metal ions are non interfering. In Benesi–Hildebrand plots (*11a*), the linear fit of the change in emission intensity of **1** against the reciprocal of metal ion concentration suggested the formation of 1:1 complex and the association constants were determined to be 7.59 × 10<sup>3</sup> M<sup>-1</sup> and 2.48 × 10<sup>5</sup> M<sup>-1</sup> for Cu<sup>2+</sup> and Hg<sup>2+</sup> ions, respectively (Figure 3S). The detection limits (*11b*) for Cu<sup>2+</sup> and Hg<sup>2+</sup> ions were calculated to be 5.75 × 10<sup>-5</sup> M and 9.74 × 10<sup>-6</sup> M, respectively (Figure 4S).

In UV–vis study, addition of both Cu<sup>2+</sup> and Hg<sup>2+</sup> ions resulted in sharp decrease in absorption intensity at 270 nm along with the appearance of a very weak band at 290 nm (Figure 4). In case of titration with Cu<sup>2+</sup> ions, the intensity of this weak band was increased to the small extent for which an isosbestic point at 285 nm was observed (Figure 4(a)).



Scheme 1. (i) NH<sub>2</sub>OH.HCl, K<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, 65 °C, 30 min, (ii) HCOONH<sub>4</sub>, Pd-C, EtOAc, rt, 12 h, (iii) dry CH<sub>2</sub>Cl<sub>2</sub>, 1-naphthylisothiocyanate, diisopropyl ethylamine, rt, 20 min.



Scheme 2. Probable mechanism for the synthesis of 1.



**Figure 2.** Change in fluorescence ratio of 1 ( $c = 2.50 \times 10^{-5}$  M) at 373 nm upon addition of 3 equiv. amounts of different metal ions ( $c = 1.0 \times 10^{-3}$  M) in CH<sub>3</sub>CN ( $\lambda_{ev} = 280$  nm).

In case of Hg<sup>2+</sup>, such change in absorption is small. Other metal ions did not show much interaction with **1** under similar conditions (Figure 5S). These observations indicate that the compound **1** is only capable of sensing the metal ions in the excited state rather than in the ground state.

To verify the recognition behavior of **1** towards the same metal ions in aqueous system, we performed similar study in  $CH_3CN-H_2O$  (1:1, v/v). As the compound **1** was completely insoluble in water, on compromisation we solubilised it in  $CH_3CN-H_2O$  (1:1, v/v). In this solvent combination, compound **1** exhibited an emission at 380 nm on excitation at 280 nm in the absence of metal ions. This emission was markedly enhanced with a blue shift of 18 nm upon interaction with Pb<sup>2+</sup> ions over the other metal ions examined (Figure 5(a)). Figure 5(b) which describes the fluorescence ratio of **1** at 398 nm in presence of 25 equiv. amounts of different metal ions studied represents that the compound **1** is highly sensitive to Pb<sup>2+</sup> ions (Figure 6S).

The Benesi–Hildebrand plot (11a) of emission intensity of **1** against the reciprocal of Pb<sup>2+</sup> ion concentration exhibited linear relationship, indicating 1:1 stoichiometric interaction. The association constant and the detection limit have been determined (12) to be  $2.33 \times 10^3$  M<sup>-1</sup> and  $9.80 \times 10^{-6}$  M, respectively (Figure 7S). Selectivity in sensing of Pb<sup>2+</sup> ions as determined by performing competition experiments as shown in Figure 8S reveals the interference of both Cu<sup>2+</sup> and Hg<sup>2+</sup> ions.

Due to the presence of guanidine motif in the backbone, the pH effect of **1** in  $CH_3CN-H_2O(1:1, v/v)$  was investigated. As can be seen from Figures 9S and 10S, while the change in intensity of emission and absorption of **1** is merely affected up to pH 7.0, changes are considerable at higher pH. This presumably occurs due to the ester group in the structure. However, careful measurement of pH of  $CH_3CN-H_2O(1:1, v/v)$ , which was used in the present study (Figure 5) without using buffer indicated a value of ~pH 6.5. To be further confirmed with the selective interaction of **1** towards Pb<sup>2+</sup> ions in  $CH_3CN-H_2O(1:1, v/v)$ , we used tris HCl buffer and the titration output for Pb<sup>2+</sup> ions was observed to be alike (Figure 11S).

In UV-vis study, steady decrease in absorption at 273 nm was observed during titration with Pb<sup>2+</sup> ions (Figure 12S). With Cu<sup>2+</sup> and Hg<sup>2+</sup> ions, weak ratiometric response was observed (Figure 12S). Beside this, almost similar changes in absorption spectra of **1** with rest of the metal ions were observed. The absorption intensity at 273 nm was decreased gradually almost to the equal extent (Figure 12S).

In order to realise the mode of interaction of **1** with the metal ions, <sup>1</sup>H-NMR of **1** in  $\text{CDCl}_3$  was recorded in the presence of equiv. amount of  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  (Figure 6) and  $\text{Cu}^{2+}$  ions (Figure 13S). In the presence of  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  ions, small downfield chemical shift of the protons  $\text{H}_a$ ,  $\text{H}_b$ 



**Figure 3.** Change in emission of 1 ( $c = 2.50 \times 10^{-5}$  M) upon addition of 3 equiv. of (a) Cu<sup>2+</sup> ( $c = 1.0 \times 10^{-3}$  M) and (b) Hg<sup>2+</sup> ( $c = 1.0 \times 10^{-3}$  M) in CH<sub>3</sub>CN ( $\lambda_{ex} = 280$  nm).



Figure 4. Change in absorbance of 1 ( $c = 2.50 \times 10^{-5}$  M) upon addition of 3 equiv. of (a) Cu<sup>2+</sup> and (b) Hg<sup>2+</sup> ( $c = 1.0 \times 10^{-3}$  M) in CH<sub>3</sub>CN.



**Figure 5.** (a) Change in emission of 1 ( $c = 2.50 \times 10^{-5}$  M) upon addition of 25 equiv. amounts of Pb<sup>2+</sup> ( $c = 1.0 \times 10^{-3}$  M) ions and (b) change in fluorescence ratio of 1 ( $c = 2.50 \times 10^{-5}$  M,  $\lambda_{ex} = 280$  nm) at 398 nm upon addition of 25 equiv. amounts of different metal ions ( $c = 1.0 \times 10^{-3}$  M) in CH<sub>3</sub>CN-H<sub>2</sub>O (1: 1, v/v).

and  $H_c$  by 0.02–0.04 ppm was noted. This occurs likely due to electrostatic influence of the metal ion on the pyrrole motif instead of the direct involvement of pyrroles in metal coordination. Due to metal–ligand interaction, all the naphthalene protons including  $H_d$  protons of guanidine motif also underwent small downfield chemical shift (0.02–0.06 ppm). In case of Cu<sup>2+</sup> ion, while the pyrrole NH<sub>a</sub>s showed small downfield shift, the guanidine NH<sub>d</sub>s were not observed possibly due to deprotonation (Figure 13S).

Further, to understand the metal–ligand interaction, a DFT level (13) study of the complexes was conducted. The optimised geometries for  $Cu^{2+}$ ,  $Hg^{2+}$ -complexes in  $CH_3CN$ 



**Figure 6.** Partial <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (a) 1 ( $c = 7.78 \times 10^{-3}$  M), (b) 1 with Pb<sup>2+</sup> (1:1) and (c) 1 with Hg<sup>2+</sup> (1:1) ions.

and Pb<sup>2+</sup>-complex in CH<sub>3</sub>CN/H<sub>2</sub>O mixture are shown in Figure 7 with relevant details. Careful scrutiny reveals that while in Cu<sup>2+</sup>-complex the copper ion is chelated involving the ester oxygens and guanidinium nitrogens, the metal ions in both Hg<sup>2+</sup>- and Pb<sup>2+</sup>-complexes are coordinated to ester oxygens leaving the guanidium motif untouched.

To understand the photophysical properties of the metal complexes of **1**, TDDFT calculations were carried out in CH<sub>3</sub>CN for Cu<sup>2+</sup> and Hg<sup>2+</sup>-complexes and in CH<sub>3</sub>CN-H<sub>2</sub>O for Pb<sup>2+</sup>-complex. Compound **1** exhibited absorption at 267 nm indicating a transition from HOMO-1 (spread over pyrrole motif) to LUMO + 2 (spread over pyrrole and naphthalene motifs) in CH<sub>3</sub>CN (14S). In Cu<sup>2+</sup> and Hg<sup>2+</sup>- complexes, the absorptions appeared nearer to this wavelength showing marginal red shifts (Figure 14S) and validated the proposed binding structures as shown in Figure 7. Analysis of frontier orbitals

(14) (Figure 15S) shows that while in Cu<sup>2+</sup>-complex the intense transition is HOMO to LUMO + 3, the same for Hg<sup>2+</sup> complex is HOMO to LUMO + 4 in CH<sub>3</sub>CN. In Cu<sup>2+</sup>-complex, the continuous presence of electron density on the naphthalene and guanidine nitrogens shifts from naphthalene to the pyrroles. In comparison, in Hg<sup>2+</sup> complex the electron density at the guanidine motif is pulled away towards the metal and naphthalene in the associated transition.

In  $CH_3CN/H_2O$  system, the Pb<sup>2+</sup>-complex showed intense transition at 287 nm indicating HOMO-5 to LUMO transition. The occupancy of the depicted orbitals indicates that electron density is pulled away from the guanidine centre to the metal centre and nearby atoms (Figure 15S). From such ground state findings, we believe that in fluorescence (i.e. in the excited state), Hg<sup>2+</sup> and Pb<sup>2+</sup> ions-induced enhancement and Cu<sup>2+</sup>-induced quenching in emission of **1** are attributed to the manifestation of electron transfer in between the excited state of naphthalene and the metal occupied binding site in different ways for which the photo-induced electron transfer (PET) process is regulated differently.

To examine the anion sensing behaviour of the Cu- and Hg-ensembles of **1** in  $CH_3CN$ , a series of anions (counter cation: tetrabutylammonim ion) were undertaken in the study. Of the different anions, only  $CN^-$ , on progressive addition to the ensembles induced marked change in emission. While the Cu-ensemble of **1** exhibited significant increase in emission with a red shift of 52 nm on interaction with  $CN^-$  ion (Figure 8(a)), under similar conditions the Hg-ensemble showed partial decrease in emission at 373 nm (Figure 16S) and thus validated Cu-ensemble more potential in selective sensing of  $CN^-$  ions over the other anions examined (Figure 17S). In UV-vis study, in the presence of  $CN^-$ , the absorption band of the Cu-ensemble at 270 nm was intensified with a red shift of 20 nm followed by the appearance of a new band at 357 nm (Figure 8(b)).



**Figure 7.** (colour online) DFT optimised geometries of (a) Cu-complex in CH<sub>3</sub>CN: Cu-O1: 2.07, Cu-O3: 2.17, Cu-N1: 2.02, Cu-N2: 3.63, Cu-N3: 3.84, Cu-N4: 2.93, Cu-N5 2.81; (b) Hg-complex in CH<sub>3</sub>CN: Hg-O1: 2.82, Hg-O3: 2.34, Hg-N1: 5.17, Hg-N2: 6.79, Hg-N3: 6.84, Hg-N4: 3.94, Hg-N5: 3.40; (c) Pb-complex in CH<sub>3</sub>CN-H<sub>2</sub>O: Pb-O1: 2.29, Pb-O3: 2.29, Pb-N1: 3.44, Pb-N2: 5.22, Pb-N3: 5.51, Pb-N4: 4.47, Pb-N5: 4.73 (All distances are in Å).



**Figure 8.** (colour online) Change in (a) emission and (b) absorption spectra of the ensemble of 1 ( $c = 2.5 \times 10^{-5}$  M) with 3 equiv. amounts of Cu<sup>2+</sup> ions in CH<sub>3</sub>CN upon successive addition of 1 equiv. amount of CN<sup>-</sup> ion ( $c = 1.0 \times 10^{-3}$  M); Insets represent corresponding colour change of the 1-Cu ensemble with CN<sup>-</sup> ion under (a) UV light and (b) ordinary light.

The colour of the solution was changed from colourless to light yellow.

The Benesi–Hildebrand plot gave the association constant of  $3.95 \times 10^4$  M<sup>-1</sup> (Figure 18S) for interaction of CN<sup>-</sup> to the Cu-ensemble and the detection limit (*12*) was determined to be  $4.00 \times 10^{-7}$  M (Figure 19S).

The CN-- induced enhancement in emission of Cu-ensemble is attributed to the deprotonation of guanidine and pyrrole NHs as confirmed by <sup>1</sup>H NMR in Figure 13S due to which the metal-ligand interaction becomes stronger instead of demetallation and modifies the PET process presumably through the coordination of CN<sup>-</sup> to the organic ligand-anchored copper ion. To understand this, analysis of UV-vis spectra of 1 in the presence of <sup>n</sup>Bu<sub>4</sub>NOH and <sup>n</sup>Bu<sub>4</sub>NCN individually revealed weak absorption at 327 nm which is assumed to be due to deprotonation [although CN<sup>-</sup> acts as weak base (15)] of weakly acidic guanidine protons to the small extent (Figure 20S). Interestingly, addition of  $Cu(ClO_4)_2$  to  $CN^-$ - treated solution of 1 in CH<sub>2</sub>CN moved the absorption from 327 to 357 nm with moderate intensity. This is in accordance with the observation in Figure 8(b).

It is to note that compound **1** itself exhibited moderate quenching of emission in  $CH_3CN$  in the presence of  $CN^-$  ions (Figure 21S) and gave ~10 times lower association constant than its Cu-ensemble (Figure 22S). However, **1** did not show any noticeable interaction with other anion studied (Figure 21S). These findings indicate that **1**- $Cu^{2+}$  complex can be useful as a secondary probe for detection of  $CN^-$  ion. Of various anions,  $CN^-$  is considered to be an important due to its rapid action and extreme toxicity (*16*) that comes from its strong affinity for the heme unit in the active site of cytochrome-c oxidase enzyme. This interrupts the mitochondrial electron-transport, decreases the oxidative metabolism as well as oxygen utilisation in

living cells and thereby can directly lead to the death of human beings in several minutes.

#### Conclusion

In conclusion, guanidine-centred naphthalene-pyrrole conjugate 1 has been designed and synthesised. The compound has been obtained in moderate yield and its formation has been explained by a suggested mechanism. In CH<sub>3</sub>CN and CH<sub>3</sub>CN-H<sub>2</sub>O (1:1, v/v), compound 1 exhibited turn-on emission selectively in the presence of Hg<sup>2+</sup> and Pb<sup>2+</sup> ions, respectively. Addition of Cu<sup>2+</sup> ions in CH<sub>2</sub>CN resulted in steady decrease in emission of 1 and behaved differently from Hg<sup>2+</sup> ions. Thus, the simple compound 1 has successfully differentiated three metal ions Cu<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup> through different responses in fluorescence under different conditions. Furthermore, the Cu.1 ensemble in CH<sub>2</sub>CN has been established as good secondary probe for selective recognition of CN<sup>-</sup> ion over a series of other anions. Multi-ion recognition with such a single molecular probe is worthy and a new addendum to the existing reports in the literature (17).

#### **Experimental**

#### **Syntheses**

#### (E)-methyl 5-((hydroxyimino)methyl)-1H-pyrrole-2carboxylate (3)

The carbaldehyde  $\mathbf{2}^{10}$  (0.53 g, 3.49 mmol) was dissolved in H<sub>2</sub>O (15 mL) at 65 °C and a solution of NH<sub>2</sub>OH.HCl (0.35 g, 5.24 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.72 g, 5.24 mmol) in 2 mL of H<sub>2</sub>O was added dropwise. The reaction mixture was then allowed to heat at 65 °C for 30 min. Then the reaction mixture was cooled to obtain white precipitate which was extracted with ethyl acetate. The organic layer was dried

over anhydrous  $Na_2SO_4$  and evaporated under reduced pressure to get **3** as crude product. Recrystallisation of the crude using diethyl ether afforded pure compound **3** in appreciable yield (0.42 g, yield 80%, mp 98 °C). Compound **3** was directly used in the next step without any characterisation. FTIR (KBr, cm<sup>-1</sup>): 3300, 1693, 1556, 1451, 1228.

*Methyl 5-(aminomethyl)-1H-pyrrole-2-carboxylate (4)* Compound 3 (1.0 g, 6.57 mmol) and HCOONH, (4.13 g, 65.7 mmol) were taken in 50 mL of ethyl acetate. Then 10% Pd-C (0.25 g) was added to the reaction mixture and the mixture was allowed to stir at room temperature for 12 h under nitrogen atmosphere. After completion of the reaction, the reaction mixture was filtered using Celite bed and washed well with ethyl acetate. Water was added to this filtrate and the solution was stirred well for 15 min. Then the organic layer was extracted, dried over anhydrous  $Na_2SO_4$  which on evaporation gave the compound **4** as crude mass. Recrystallisation of the crude using diethyl ether afforded compound 4 in pure form in 74% yield (0.66 g, mp 140 °C). Compound **4** was directly used in the next step without any characterisation. FTIR (KBr, cm<sup>-1</sup>): 3301, 1675, 1567, 1489, 1224.

#### **Compound 1**

To a stirred solution of compound 4 (0.13 g, 0.84 mmol) in 10 mL dry CH<sub>2</sub>Cl<sub>2</sub> was added 1-naphthalene isothiocyanate (0.15 g, 0.80 mmol) and diisopropyl ethylamine (0.19 mL, 1.26 mmol) at room temperature. The mixture was stirred for 20 min. Then the solvent was evaporated off and the crude mass was extracted with ethyl acetate. Evaporation of the solvent under reduced pressure gave the crude product which was purified by column chromatography using 40% ethyl acetate in petroleum ether to afford the compound 1 in 62% yield (0.24 g, mp. 104 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 9.56 (brs, 2H), 7.83 (d, 1H, J = 8 Hz), 7.78 (d, 1H, J = 8 Hz), 7.63 (s, 2H), 7.48–7.43 (m, 2H), 7.39–7.34 (m, 2H), 7.25 (merged with CDCl<sub>3</sub>, 1H), 6.90 (d, 2H, *J* = 4 Hz), 6.23 (d, 2H, J = 4 Hz), 5.06 (s, 4H), 3.83 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 184.2, 161.0, 135.1, 134.1, 131.4, 129.6, 128.4, 127.8, 126.6, 126.3, 125.4, 125.3, 123.8, 121.9, 115.6, 110.3, 51.6, 41.9; FTIR (KBr, v in cm<sup>-1</sup>): 3288, 2920, 2078, 1699, 1491, 1228; HRMS (TOF MS ES+): calcd. 499.1544 (M+K+1)<sup>+</sup>, found 499.1402 (M+K+1)<sup>+</sup>.

#### **Theoretical calculations**

Structures of compound **1** and its complexes with  $Cu^{2+}$  and  $Hg^{2+}$  were optimised in acetonitrile. Structure of **1** with  $Pb^{2+}$  was optimised in acetonitrile:water mixture. TDDFT calculations were carried out on all optimised structures in the same solvents. Gaussian program suite (*12*) was used in all calculations. For DFT and TDDFT calculations, SDD

basis set (18) and B3LYP functional (19) were employed. MaSK software (13) was used to generate the molecular orbitals. Onsager's SCRF approximation (20) with polarisable continuum method (21) was used for calculation involving solvent phase.

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