

# A hetero-bimetallic(Cu–Ru) chromogenic and fluorogenic complex as receptor of soft metal ions

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**Abstract** A hetero-bimetallic complex of type [Cu(bpy)(NCS)( $\mu$ -NCS)Ru(bpy)<sub>2</sub>Cl]·PF<sub>6</sub> is synthesized and characterized using spectroscopic studies, elemental analyses and ESI-MS data. Owing to the presence of sulphur donor ligand in the complex, its affinity towards soft metal ions is monitored. It detects selectively Hg<sup>2+</sup> and Ag<sup>+</sup> ions over a number of environmentally relevant cations including Mn<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Co<sup>2+</sup>. The naked eye response is more pronounced for Hg<sup>2+</sup> as compared to Ag<sup>+</sup> ions. The detection limit for Hg<sup>2+</sup> ions is 1.0 ppm while for Ag<sup>+</sup> ions are 10 ppm. However, fluorescence response is exclusive to Ag<sup>+</sup> ions. The complex shows a tenfold enhancement in the fluorescence intensity upon addition of Ag<sup>+</sup> ions while no change in emission intensity is observed upon addition of other cations including Hg<sup>2+</sup>. Competitive binding experiments using fluorescence spectrometry reveal that the complex binds Ag<sup>+</sup> selectively even in presence of tenfold excess of other cations exclusive of Hg<sup>2+</sup> ions. The emission from the complex obtained by addition of Ag<sup>+</sup> ions is quenched upon addition of Hg<sup>2+</sup> ions, displaying fluorescence on–off behavior.

**Keywords** Heterobimetallic complex · Binding study · Soft metal ion · Chromogenic response · Fluorescence on–off behavior

## Introduction

The sensing of toxic species is critical of environmental monitoring, chemical processes and medical applications. The selective detection of mercury is of particular interest. It is both biologically toxic (damaging the central nervous system and creating neuropsychiatric disorders in humans) and a common environmental pollutant [1, 2]. The long atmospheric lifetime of mercury causes contamination across vast quantities of land and water [3]. To make the problem worse, bacteria convert elemental and ionic mercury to methyl mercury, adding this potent neurotoxin to the food chain [4, 5]. Thus, the design and synthesis of optical chemosensors with high selectivity and sensitivity for heavy and soft transition-metal ions, particularly mercury is demanding. It has triggered a large number of related investigations that have been recently reviewed [6]. Accordingly, the development of novel analytical methods for the sensitive and selective determination of Hg<sup>2+</sup> ions have been devised using redox [7, 8], chromogenic [9] and fluorogenic [10–12] changes. However, design and synthesis of fluorescent sensors for Hg<sup>2+</sup> ions is still continued [13, 14]. Although many investigations have been conducted to make ratiometric fluorescent sensors for metal ions [15] yet only few reports are explored for detection of Ag<sup>+</sup> ions [16]. Since heavy metal ions are known as fluorescence quenchers, therefore, discrimination between Ag<sup>+</sup> and chemically closer heavy metal ions presents a challenge.

In this context Ru(II) polypyridyl complexes have been widely employed as chromophores and fluorophores [17, 18] owing to their excellent redox and photo-physical properties, particularly absorption and emission spectra within the visible range. Herein, we report a bimetallic complex of Ru(II) and Cu(II) ions bearing 2,2′-bipyridine

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as terminal ligand and NCS as a bridging ligand, for differential colorimetric and fluorometric detection of soft metal cations. The selection of the heterobimetallic complex is made because heterodinuclear ruthenium based chemosensors are either rare or unknown. It is interesting to mention that clear detection of colour change upon binding of mercury(II) ion with such heterodinuclear complex is anticipated to make it a potential candidate since such chemosensor bears a platform of two colored centers [Cu(II) and Ru(II)]. Thus, upon binding with the cations, change in either of the two colored centers could be exploited to differentiate them from the original colour.

## Result and discussion

### Synthesis and characterization

Complex **1** [Cu(bpy)(NCS)<sub>2</sub>] was synthesized using a previously reported method with some modifications and it has been characterized [19] using single crystal X-ray diffraction data. Further reaction of complex **1** with Ru(bpy)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (generated in situ), provided another complex **2** [Cu(bpy)(NCS)(μ-NCS)Ru(bpy)<sub>2</sub>Cl]·PF<sub>6</sub> (Scheme 1). Complex **2** is purified on an alumina column using acetonitrile as eluent and the product thus obtained is characterized by physico-chemical and analytical data. Owing to the lack of suitable single crystal, its X-ray diffraction study could not be done.

Complex **2** is initially characterized by IR spectroscopy. In the IR spectrum of complex **1**, ν<sub>NCS</sub> vibration is observed at 2,081 cm<sup>-1</sup>, which upon complexation with Ru(bpy)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O appeared at 2,071 and 2,107 cm<sup>-1</sup> in the IR spectrum of **2**. Appearance of two peaks for ν<sub>NCS</sub> suggested that one NCS group is acting as bridging ligand between two metal centres while the other remains

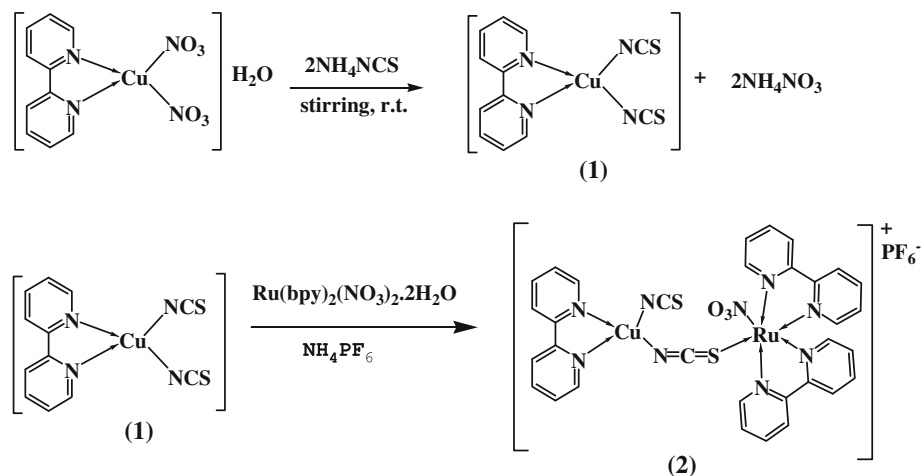
coordinated to Cu(II) ion. The peak observed at 843 cm<sup>-1</sup> is attributed to ν PF<sub>6</sub><sup>-</sup> vibration.

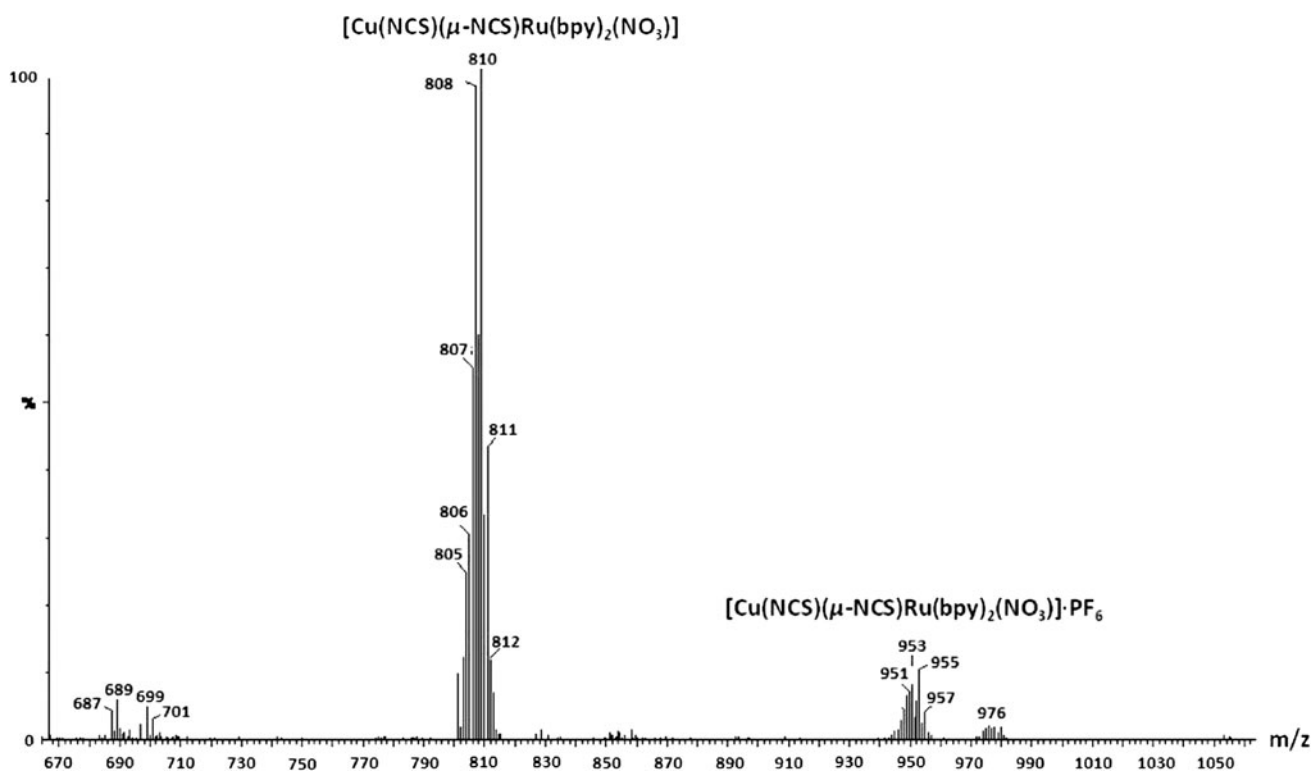
The above observation was further supported by ESI-MS data of complex **2** (Fig. 1). It showed molecular ion peak at m/z 956. Analytical data also supported the composition of complex **2** as [Cu(NCS)(μ-NCS)Ru(bpy)<sub>2</sub>(NO<sub>3</sub>)]·PF<sub>6</sub>. Though crystal of this complex could not be obtained yet being a combination of two known species [Cu(bpy)(NCS)<sub>2</sub>] and [Ru(bpy)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] its structure was supported by its mass measurement and other physico-chemical data. Its structure is proposed in support with the optimized structure for similar hetero bimetallic complex reported by us recently [20].

Complex **2** displayed two redox peaks (vs silver reference electrode) in DMSO (1 × 10<sup>-3</sup> M). One reversible redox peak (i<sub>p</sub>/i<sub>a</sub> = 0.61) observed at E<sub>1/2</sub> -557 mV is assigned to Cu(I)/Cu(II) couple. The other peak at E<sub>1/2</sub> 278 mV is assigned to Ru(II)/Ru(III) couple which is irreversible with an i<sub>p</sub>/i<sub>a</sub> value of 0.019 (Fig. 2).

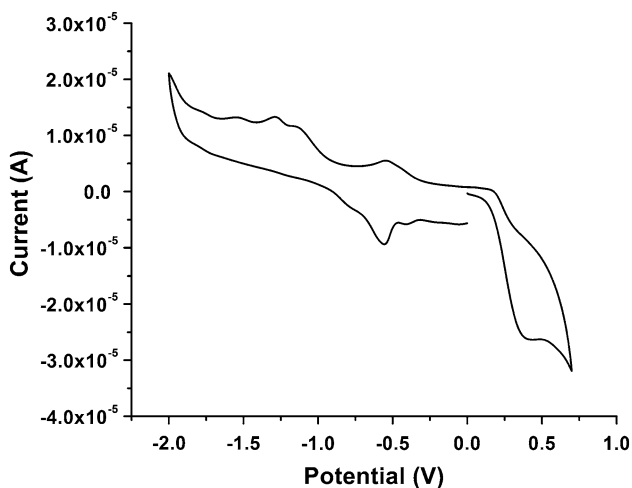
Since complex **2** contains ESR active Cu(II) ion, its ESR spectrum at 66 K was recorded. It showed typical four-lines patterns as expected from <sup>63</sup>Cu nucleus (Fig. 3). Three parallel hyperfine lines are well resolved while the fourth one is getting overlapped with g<sub>⊥</sub> signal. The complex is characterized by axial g and A tensors with g<sub>∥</sub> value (2.214) > g<sub>⊥</sub> value (2.053) suggesting that d<sub>x<sup>2</sup>-y<sup>2</sup></sub> is ground state. Although the ratio g<sub>∥</sub>/|A<sub>∥</sub>| is normally taken as an indication of the stereochemistry of the copper(II) complexes, yet it is suggested that this ratio may be an empirical indication of the tetrahedral distortion of a square planar geometry [21]. The value of |A<sub>∥</sub>| is calculated as 150 × 10<sup>4</sup> cm<sup>-1</sup> while the value of g<sub>∥</sub>/|A<sub>∥</sub>| comes out to be 147 cm<sup>-1</sup>. The values of hyperfine splitting lower than 135 cm<sup>-1</sup> are observed for square planar structures and those higher than 150 cm<sup>-1</sup> for tetrahedrally distorted complexes. Thus, data suggests that in complex **2**, Cu(II)

**Scheme 1** Synthetic strategy for complexes **1** and **2**





**Fig. 1** ESI-MS pattern of complex **2**



**Fig. 2** Cyclic voltammetric response of complex **2** in DMSO ( $1 \times 10^{-3}$  M)

ion possesses a distorted geometry as compared to its original geometry observed in the complex **1**.

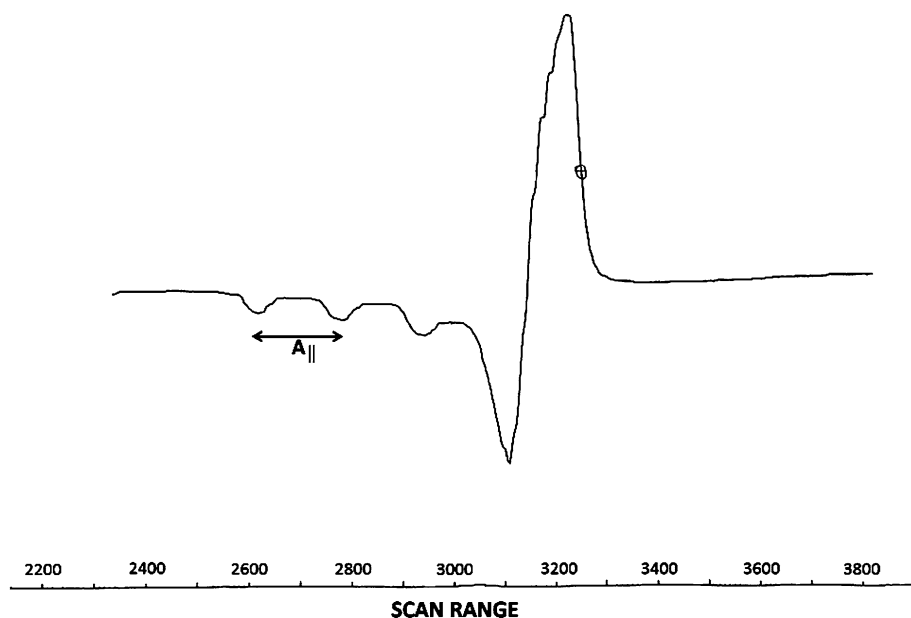
#### Cations binding studies

The absorption spectrum of complex **2** (30  $\mu$ M) shows absorption bands at  $\lambda_{\text{max}}$  360 and 510 nm. The bands observed at  $\lambda_{\text{max}}$  510 nm are attributed to MLCT transition from  $d\pi(\text{Ru}) \rightarrow \pi^*(2,2'\text{-bipyridine})$  in view of earlier

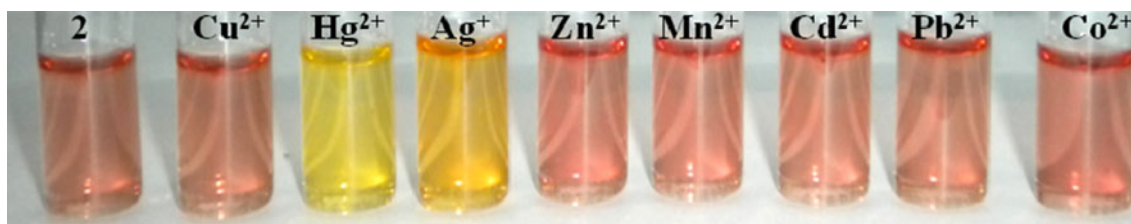
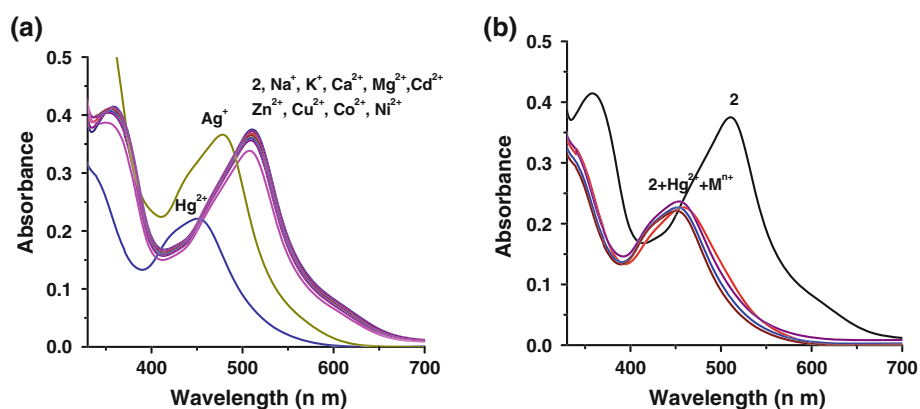
reports [22]. Complex **2** emitted at  $\lambda_{\text{em}}$  670 nm upon excitation at wavelength  $\lambda_{\text{ex}}$  510 nm. The binding affinities of complex **2** (30  $\mu$ M) for various metal ions have been investigated in aqueous-acetonitrile (1:1, v/v) solution. Upon addition of various metal ions (5 equiv) such as,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  ions, as their nitrate salts, to the solution of complex **2** the absorption spectrum is considerably modulated only in the presence of  $\text{Hg}^{2+}$  ion in which, the  $\sim 510$  nm band was hypsochromically shifted for 60 nm and appear at  $\lambda_{\text{max}}$  450 nm. The rest of the metal ions did not exhibit any significant change in the absorption spectrum of **2** (except for  $\text{Ag}^+$  ion) (Fig. 4). Binding property of complex **2** with  $\text{Hg}^{2+}$  ion is found stronger than the reported Cu–Ru complex [20]. It may be owing to the presence of a terminal NCS group attached to the Cu(II) centre in addition to bridged NCS as present in the reported complex. The absorption spectrum of **2** in the presence of  $\text{Ag}^+$  ion reveals a relatively small blue shift in the absorbance of 510 nm band along with a significant enhancement in the absorbance as depicted in Fig. 4a. Consequently, upon interaction with both  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  metal ions a visible orange color solution of **2** was changed to light yellow (Fig. 5).

The selectivity of  $\text{Hg}^{2+}$  over a number of environmentally relevant metals ions such as  $\text{Ag}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Co}^{2+}$  were investigated and the results are shown in Fig. 4b. Upon addition of  $\text{Hg}^{2+}$  to a

**Fig. 3** ESR spectral diagram of complex **2**



**Fig. 4 a** Change in absorption spectra of complex **2** ( $3 \times 10^{-5}$  M) upon addition of different metal ions (5 equiv) in aqueous-acetonitrile (v/v, 1:1). **b** Interference studies of **2** upon addition of competitive metal ions (15 equiv) to the solution of **2**-Hg<sup>2+</sup> complex in aqueous-acetonitrile (v/v, 1:1)

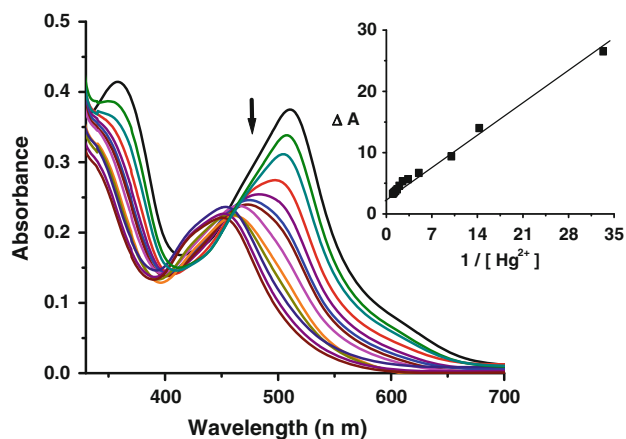


**Fig. 5** Change in colour of complex **2** upon interaction with different metal ions

solution of complex **2**-Ag<sup>+</sup>, the absorption spectra were changed and vice versa, upon addition of different metal ions to a solution of complex **2**-Hg<sup>2+</sup> no spectral changes were observed. Thus, the experimental observations clearly suggested the specificity of **2** for Hg<sup>2+</sup> ions selectively among the competitive metal ions.

To ascertain the selective binding affinity of **2** for Hg<sup>2+</sup> ion UV-Vis titration experiment was carried out in aqueous-acetonitrile (1:1; v/v). To a solution of **2** (30  $\mu$ M) equiv of Hg<sup>2+</sup> ion (2–30  $\mu$ M) were added sequentially.

Upon addition of 1 equiv of Hg<sup>2+</sup> ion to the solution of **2** (Fig. 6),  $\sim$ 510 nm band was gradually decreased and simultaneously blue-shifted to appear at 450 nm. Similarly, absorption titration experiment was carried out with Ag<sup>+</sup> ion. Upon increasing the concentration of Ag<sup>+</sup> ion (0–2 equiv) to the solution of complex **2**, the  $\sim$ 510 nm band blue shifted to appear at  $\sim$ 465 nm upon 0.5 equiv addition of Ag<sup>+</sup> and further increase in the Ag<sup>+</sup> ion concentration, no significant modulation in the absorption spectra were observed except a gradual enhancement in the absorbance



**Fig. 6** Absorption titration spectra of complex **2** (30  $\mu\text{M}$ ) with increasing concentration of  $\text{Hg}^{2+}$  (2–30  $\mu\text{M}$ ) in aqueous-acetonitrile (1:1, v/v). *Inset* shows the Benesi–Hildebrand graph

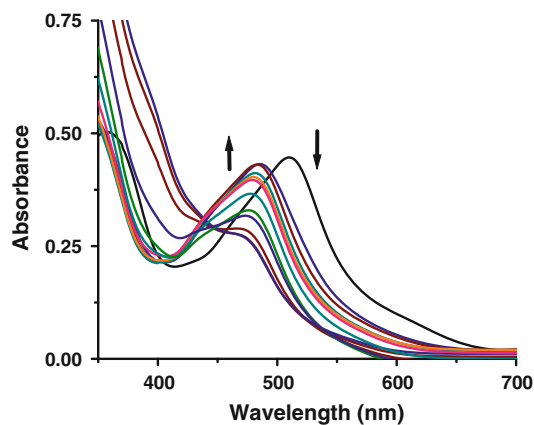
of  $\sim 465$  nm band (Fig. 7 and S1). Concomitantly, orange color of the complex solution changed to yellow (Fig. 5).

The colorimetric selective sensing of the complex **2** with soft metal cations in aqueous-acetonitrile were also monitored using UV–Vis absorption titration experiments and corresponding binding constants were calculated. The absorption titrations of **2** with  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  ions were separately performed by monitoring the changes in absorption spectrum of **2** (30  $\mu\text{M}$ ) in aqueous-acetonitrile. The concentration of **2** was kept constant at 30  $\mu\text{M}$  while the concentrations of  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  were varied within 2–30  $\mu\text{M}$ . The absorption due to  $\text{Hg}^{2+}$  or  $\text{Ag}^+$  ions was eliminated initially by keeping their equal quantities separately in the complexes **2** and reference solution. From the absorption data, the intrinsic binding constant  $K_b$  was determined from a graph obtained by plotting  $[\text{guest}]/(\epsilon_a - \epsilon_f)$  vs.  $[\text{guest}]$  using Eq. (1) [23] and Benesi–Hildebrand method [24].

$$[\text{guest}]/(\epsilon_a - \epsilon_f) = [\text{guest}]/(\epsilon_b - \epsilon_f) + [K_b(\epsilon_b - \epsilon_f)]^{-1} \quad (1)$$

Where,  $[\text{guest}]$  is the concentration of  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  ions. The apparent absorption coefficients  $\epsilon_a$ ,  $\epsilon_f$  and  $\epsilon_b$  correspond to  $A_{\text{obsd}}/[\text{complexes } \mathbf{2}]$ , the extinction coefficient of free complexes **2** and extinction coefficient of **2** in fully bound form, respectively [23]. The value of  $K_b$  is calculated as the ratio of slope to the intercept and was found association constant ( $K_a = 6.2 \times 10^4 \text{ m}^{-1}$ ) for  $\text{Hg}^{2+}$  as compared to the value observed for  $\text{Ag}^+$  ions ( $K_a = 1.8 \times 10^4 \text{ m}^{-1}$ ).

The binding of  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  ions was further compared by monitoring fluorescence changes in **2** with and without  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  ions. In contrast to colorimetric detection and UV–Vis spectroscopic results, fluorescence spectral titration gave response exclusively for  $\text{Ag}^+$  ions only. Upon addition of  $\text{Ag}^+$  ions, the emission band of



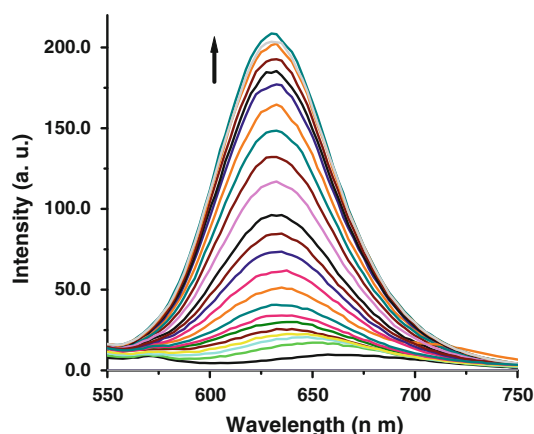
**Fig. 7** Absorption titration spectra of complex **2** (30  $\mu\text{M}$ ) with increasing concentration of  $\text{Ag}^+$  (2–30  $\mu\text{M}$ ) in aqueous-acetonitrile (1:1, v/v)

complex **2** was blue-shifted to  $\lambda_{\text{em}}$  630 nm with concomitant tenfold enhancement in its luminescence intensity (Fig. 8). Thus, shift of about 40 nm in maximum emission wavelength and the enhancement of the luminescence by addition of one equivalent of  $\text{Ag}^+$  ions indicated that there is no interference from **2** in the detection of  $\text{Ag}^+$  ions hence it also suggested the formation of an excimer [16]. The fluorescence enhancement could be attributed to cation- $\pi$  electron interactions of electron rich aromatic rings and free  $-\text{NCS}$  fragment present in the complex **2** which in turn suppress the photo induced electron transfer from nitrogen ligands. Although the size difference between  $\text{Ag}^+$  and  $\text{Hg}^{2+}$  is solution is suppose to be small [25] yet the relative large size of  $\text{Ag}^+$  can also be one of the factors to observe enhanced fluorescence. Additionally, both compound **2** and its complex, **2**+ $\text{Ag}^+$  exhibited fluorescence quenching.

The stability constant  $K_s$  is determined from the change in peak position or fluorescence intensity resulting from the titration of dilute solutions (30  $\mu\text{M}$ ) of the fluorophoric systems against guest solutions. The linear fit of the fluorescence intensity data at a particular wavelength for 1:1 complexation was obtained [26] by applying the following Eq. (2).

$$IF^0/(IF - IF^0) = [a/(b - a)][(1/K_s[M]) + 1] \quad (2)$$

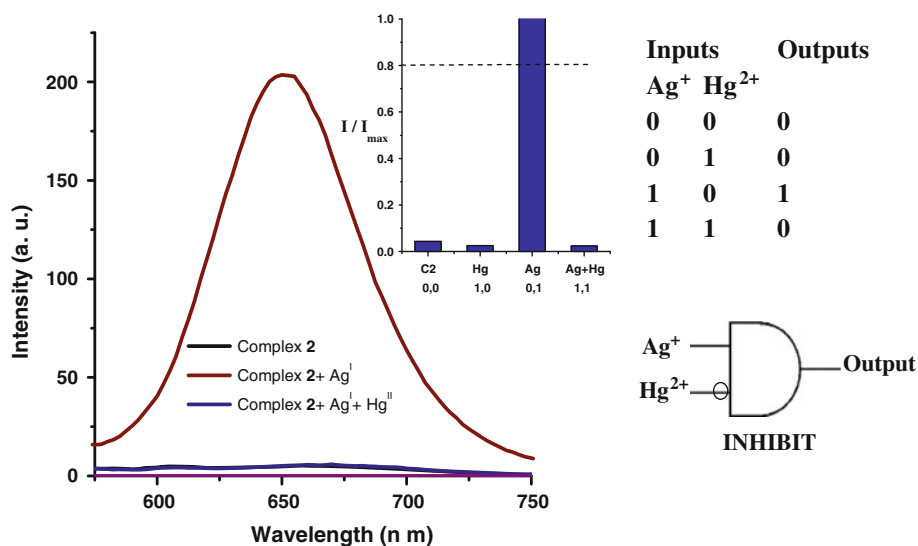
Where,  $IF^0$  and  $IF$  are the fluorescence intensities of the free **2** and **2**-guest complex, respectively;  $[M]$  is the concentration of the guest added for complexation. The  $K_s$  is obtained as intercept/slope ratio from the plot of  $IF^0/(IF - IF^0)$  against  $[M]^{-1}$ . The change in the emission spectral data at a particular wavelength fitted into the above equation results in determination of  $K_s$ . The stability constant calculated for binding of  $\text{Ag}^+$  is found to be  $1.3 \times 10^4 \text{ M}^{-1}$  indicating a strong overall binding resulting into tenfold enhancement in fluorescence intensity.



**Fig. 8** Emission titration spectra of complex **2** (30  $\mu\text{M}$ ) with increasing concentration of  $\text{Ag}^+$  (2–30  $\mu\text{M}$ ) in aqueous-acetonitrile (1:1, v/v)

Thus, complex **2** is able to distinguish  $\text{Ag}^+$  ions using fluorescence measurement from a mixture of other toxic cations. But owing to stronger binding of  $\text{Hg}^{2+}$  ions with complex **2**, it was thought to study fluorescence on–off behavior of complex **2** with  $\text{Ag}^+$  and  $\text{Hg}^{2+}$ . As anticipated, binding of  $\text{Ag}^+$  brings out a tenfold enhancement in emission intensity of complex **2** but addition of  $\text{Hg}^{2+}$  in the same solution quenches the emission intensity to normal (Fig. 9). This clearly suggested about the probability of  $\text{Ag}^+$  ion displacement from  $\text{2} + \text{Ag}^+$  and fluorescence quenching due to high spin orbit coupling [27] exerted by  $\text{Hg}^{2+}$  ions. It may happen due to greater affinity of complex **2** towards  $\text{Hg}^{2+}$  ions in comparison to  $\text{Ag}^+$  ions. Therefore, the output signal obtained at 630 nm, it has been observed that in the presence or absence of both the input signals ( $\text{Ag}^+ = \text{Hg}^{2+}$ : 1 or  $\text{Ag}^+ = \text{Hg}^{2+}$ : 0) no output signal is obtained, whereas, in the presence of the  $\text{Ag}^+$  ion as only input signal ( $\text{Ag}^+$ : 1,  $\text{Hg}^{2+}$ : 0) enhanced output

**Fig. 9** Bar diagram representation of the output (relative fluorescence) for  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  ions at  $\sim 630$  nm of the INHIBIT logic gate, logic scheme and truth table



fluorescence signal is observed but upon reversing the sequence ( $\text{Ag}^+$ : 0,  $\text{Hg}^{2+}$ : 1), resulted no output signal. Thus, the logic circuit incorporating the truth table constituted the two input based an INHIBIT logic gate that demonstrated a noncommutative behavior that is, one of the inputs may disable the whole system.

## Experimental

### Materials and method

Ruthenium(III)chloride, 2,2'-bipyridine, copper(II) dinitrate hexahydrate and ammonium thiocyanate were purchased from Sigma Aldrich Chem. Co. and were used as received without further purification. All the solvents were purchased from E. Merck and were freshly distilled prior to their use. The  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Cu}(\text{bpy})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  were prepared and characterized using reported procedure [19]. Elemental analyses were carried out on a Carbo-Erba elemental analyzer 1108. IR spectra were recorded as KBr pellets on a JASCO FT-IR 5300 spectrometer. UV/visible and luminescence measurements were made in the range of 200–800 nm on a JASCO V-630 spectrometer and Perkin Elmer LS-45 Luminescence spectrometer, respectively. Cyclic voltammetric measurements were performed on a CHI 620c Electrochemical Analyzer using glassy carbon as working electrode, a platinum wire auxiliary electrode, and  $\text{Ag}/\text{Ag}^+$  reference electrode in a standard three-electrode configuration. Tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte, and concentration of the solutions of complexes in DMSO was maintained as  $10^{-3}$  M. ESR spectra were recorded at 273 and 77 K on a Varian E-line Century Series ESR spectrometer equipped with a dual cavity and operating at X-band of 100 kHz modulation

frequency. Tetracyanoethylene was used as the field marker ( $g = 2.00277$ ).

### Synthesis of complex 1

A methanolic solution (10.0 mL) of ammonium thiocyanate (0.152 g, 2.0 mmol) was added dropwise to a methanolic solution (10.0 mL) of  $\text{Cu}(\text{bpy})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (0.361 g, 1.0 mmol). The mixture was stirred at room temperature for 2 h. A green coloured precipitate thus obtained was filtered out, washed with methanol and dried in vacuo. The complex was crystallized in DMF and methanol. Yield: 75 %. Mp > 250 °C. Elemental analysis calcd (%) for  $\text{C}_{12}\text{H}_8\text{N}_4\text{S}_2\text{Cu}$ : C, 42.85; H, 2.38; N, 16.66. Found: C, 42.98; H, 2.59; N, 16.25. IR (KBr pellet,  $\text{cm}^{-1}$ ): 1604 ( $\nu_{\text{bpy}}$ ), 2081 ( $\nu_{\text{NCS}}$ ). FAB-MS: ( $m/z$ ): 336  $[\text{M}]^+$ , UV-Vis (DMSO,  $10^{-4}$  M):  $\lambda_{\text{max}}(\text{nm})$  ( $\epsilon_{\text{max}} \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) 375 (3.11), 680 (0.113).

### Synthesis of complex 2

A methanolic solution (10.0 mL) of  $\text{AgNO}_3$  (0.169 g, 1.0 mmol) was added to a methanolic solution (10 mL) of  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  (0.260 g, 0.5 mmol) and the mixture was stirred overnight. The white precipitate thus obtained was filtered through Celite and filtrate was used for further reaction. The filtrate was added to a solution of  $\text{Cu}(\text{bpy})(\text{NCS})_2$  (0.169 g, 0.5 mmol) in DMF (5.0 mL). The content was refluxed under a nitrogen atmosphere for 6 h. After cooling at room temperature, an aqueous solution of  $\text{NH}_4\text{PF}_6$  was added slowly to it and the resulting solution was then cooled in a refrigerator. After 24 h, a dark colored solid appeared, which was filtered and washed several times with water and then dried in vacuo. The complex was further purified on alumina column using acetonitrile as eluent. Yield: 40 %, M. P. >250 °C, Elemental analysis calcd. (%) for  $\text{C}_{32}\text{H}_{23}\text{N}_9\text{O}_3\text{S}_2\text{PF}_6\text{CuRu}$ : C, 40.19; H, 2.53; N, 13.18. Found: C, 40.78; H, 2.87; N, 12.98; IR (KBr pellet,  $\text{cm}^{-1}$ ): 1600 ( $\nu_{\text{bpy}}$ ), 2071 & 2107 ( $\nu_{\text{NCS}}$ ), 843 ( $\nu_{\text{PF}}$ ). ESI-MS: ( $m/z$ ): 956  $[\text{M}]^+$ ; UV-Vis (DMSO,  $10^{-4}$  M):  $\lambda_{\text{max}}(\text{nm})$  ( $\epsilon_{\text{max}} \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) 360 (0.49), 510 (0.443).

### Conclusion

A hetero-bimetallic complex of composition  $[\text{Cu}(\text{bpy})(\text{NCS})(\mu\text{-NCS})\text{Ru}(\text{bpy})_2\text{NO}_3] \cdot \text{PF}_6$  gives chromogenic response on binding with  $\text{Hg}^{2+}$  and  $\text{Ag}^+$ . The response is more pronounced with  $\text{Hg}^{2+}$  nitrate as compared to  $\text{Ag}^+$  nitrate. However, complex displays an emission band at lower energy region which get enhanced tenfold upon addition of  $\text{Ag}^+$  ion but it is quenched upon addition of  $\text{Hg}^{2+}$  ion. It could be stronger binding of  $\text{Hg}^{2+}$  with

complex **2** which resulted into the displacement of  $\text{Ag}^+$  hence quenching the emission from complex **2**. Competitive binding experiments in presence of several other cations suggest that the complex can sense  $\text{Ag}^+$  ions in presence of ten times excess of other environmentally relevant cations with an exception of  $\text{Hg}^{2+}$  ions. Thus, complex under present investigation behaves as a fluorescence on-off sensor.

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