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Rhodamine-labelled new architecture for dual sensing of Co^{2+} and Hg^{2+} ions

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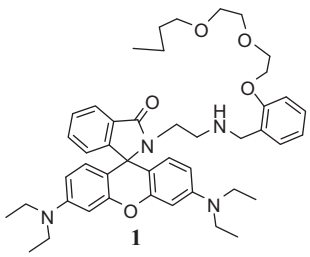
ABSTRACT

A new rhodamine-based chemosensor **1** has been designed and synthesized. The receptor selectively recognizes Co^{2+} and Hg^{2+} ions in CH_3CN/water (4:1, v/v; 10 μM tris HCl buffer, pH 6.8) by showing different extents of change in emission. The disappearance of colour of mercury-ensemble of **1** followed by appearance of distinct bluish colour under UV illumination upon addition of L-cysteine distinguishes Hg^{2+} from Co^{2+} ions. The receptor shows in vitro detection of both the ions in human cervical cancer (HeLa) cells.

The design and synthesis of optical chemosensors for the selective recognition of metal ions are of interest. In particular the development of fluorescent sensor for transition metal ions such as Hg^{2+} and Co^{2+}, due to their biological and environmental importance is challenging. Among the different heavy metal ions, mercury ion (Hg^{2+}) is dangerous as it can accumulate in the human body and causes a wide variety of diseases even in a low concentration, such as prenatal brain damage, serious cognitive disorders and Minamata disease.[1] Similarly, Co^{2+} ions play an important role. It is well known that Co^{2+} is the main composition of Vitamin B_{12}.[2] Animals deprived of cobalt show retarded growth; anaemia, loss of appetite and decreased lactation.[3] In large doses cobalt and its salts can be toxic. Occupational exposure (>0.05 mg/m^3) causes irritant and allergic effects.[3b] In excess it is associated with acute pneumonitis, dermatitis, asthma, cancer of the lung and sinus, adverse effects on blood and kidneys along with other disorders of the respiratory and central nervous systems.[3c] Selective monitoring of Co^{2+} in industrial, environmental and food samples is, therefore, needed. The chemosensors without rhodamine-labelled for sensing of this particular metal ion are known in the literature.[4–7]

In continuation of our work on the sensing of cations[8] and anions[9] of biological significance, we report in this communication a new rhodamine–based compound **1**, which recognizes both Co^{2+} and Hg^{2+} ions by exhibiting emission characteristics in semi-aqueous system [CH_3CN/water (4:1, v/v; 10 μM tris HCl buffer; pH 6.8)]. The present design in this account represents an example where Co^{2+} and Hg^{2+} ions are simultaneously detected in semiaqueous system both colorimetrically and fluorometrically. The disappearance of the colour of the mercury-ensemble of **1** in the presence of L-cysteine distinguishes it from Co^{2+} ions. It is established that rhodamine B and its derivatives (RhB) show good photo stability and high fluorescence quantum yield. Due to their interesting phenomenon they act as productive chemosensors towards metal ions by switching in between the spirocyclic form (which is colourless and non-fluorescent) and the ring-opened amide form which is pink and strongly fluorescent.[10,11] In the literature, although a number of rhodamine-labelled receptors are known for sensing of different metal ions, the simultaneous detection of both Co^{2+} and Hg^{2+} ions by rhodamine-labelled receptor module is indeed absent. However, in the present case, receptor **1** performs as a dual probe for sensing of Co^{2+} and Hg^{2+} ions exhibiting both colorimetric and fluorometric responses in CH_3CN–water (4:1, v/v; 10 μM tris HCl buffer; pH 6.8).



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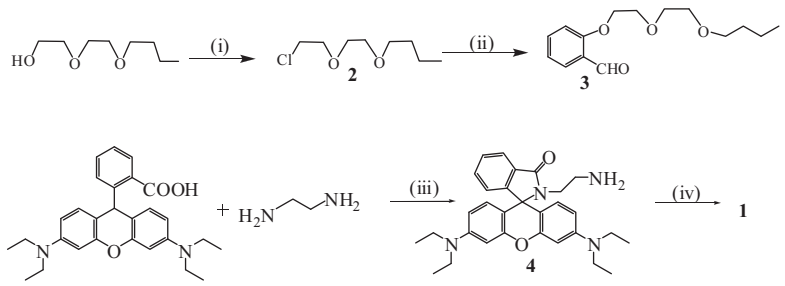

Scheme 1. Reagents and conditions: (i) $SOCl_2$, pyridine, dry $CHCl_3$, reflux, 10 h, 95%; (ii) salicylaldehyde, K_2CO_3, EtOH, reflux, 6 h, 62%; (iii) EtOH, reflux, 9 h, 87%; (iv) a. **3**, dry MeOH, reflux, 10 h; b. $NaBH_4$, dry MeOH, reflux, 12 h, 68%.

The receptor **1** was synthesized according to Scheme 1. Initially the diethylene glycol monobutyl ether was converted to chloride **2** on reaction with $SOCl_2$ in $CHCl_3$. Salicylaldehyde was next reacted with **2** in the presence of K_2CO_3 under refluxing condition to give the intermediate **3**. The aldehyde **3** was next refluxed with the amine **4**[12] in dry CH_3OH to give the Schiff's base which on reduction with $NaBH_4$ introduced the desired compound **1** in appreciable yield. All the compounds were characterized by ^1H NMR, ^{13}C, FTIR and mass analysis.

The metal ion binding properties of **1** towards the metal ions such as Hg^{2+}, Co^{2+}, Cd^{2+}, Fe^{3+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Ag^{+}, Pb^{2+}, Al^{3+}, Cr^{3+} and Sn^{4+} (taken as their perchlorate salts except Al^{3+}, Cr^{3+} and Sn^{4+}) were investigated in CH_3CN/H_2O solution ($CH_3CN:H_2O$ = 4:1, v/v; 10 μM tris HCl buffer, pH 6.8). The solution of **1** without cations, is nearly non fluorescent. However, on excitation at 490 nm, a nonstructured emission at 580 nm underwent an insignificant change upon contact with all the metal ions except Hg^{2+} and Co^{2+} ions (Supplementary data). Figure 1 shows the change in fluorescence ratio $[(I - I_0)/I_0]$ of **1** at 580 nm in the presence of 20 equiv amounts of the different metal ions.

It is evident from Figure 1 that the receptor is much selective to Co^{2+} ions. Other metal ions except Hg^{2+} weakly perturbed the emission of **1** at this wavelength. On progression of titration of **1** with the metal ions, it is observed that only in the presence of Co^{2+} and Hg^{2+} ions a new peak at 580 nm appears with a significant intensity. Figure 2a shows the emission titration spectra with Co^{2+} ions and also the associated change in colour under illumination of UV light. Figure 2b, under identical condition, is the emission titration spectra obtained from the gradual addition of $Hg(ClO_4)_2$ solution to the solution of **1** ($c = 2.25 \times 10^{-4}$ M) in CH_3CN/H_2O (4:1, v/v; 10 μM tris HCl buffer; pH 6.8). Other ions failed to develop the peak at 580 nm (Supplementary data). Thus these two ions (Co^{2+} and Hg^{2+}) are easily distinguishable from the rest of the ions by examining the peak at 580 nm (Supplementary data).

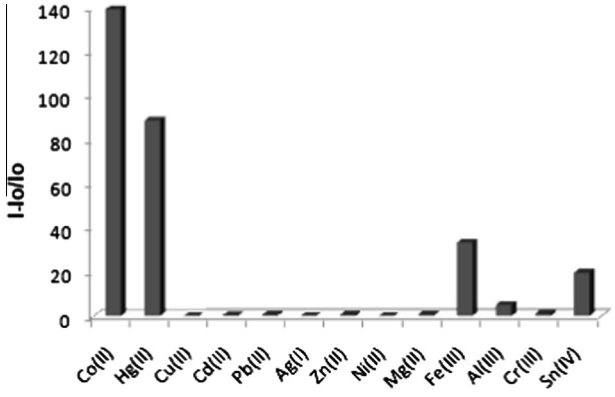

Figure 1. Change in fluorescence ratio of **1** ($c = 2.25 \times 10^{-4}$ M) at 580 nm upon addition of 20 equiv amounts of cations (taken as perchlorate salt; $Al_2(SO_4)_3$, $Cr(NO_3)_3$ and $SnCl_4$ were considered for Al^{3+}, Cr^{3+} and Sn^{4+}).

The pronounced OFF–ON type of Co^{2+}—selectivity was further established from the fluorescence at 580 nm. The Co^{2+} ion binding induced change in emission of **1** in the presence and absence of 15 equiv amounts of other metal ions was evaluated (Supplementary data, Fig. 3S) and the interference of the metal ions considered in the present study, is established to be negligible. The stoichiometries[13] of the complexes of **1** with both Co^{2+} and Hg^{2+} ions were established to be 1:1 and the binding constant values (K_a)[14] were found to be $(8.95 \pm 0.89) \times 10^4\ M^{-1}$ and $(6.02 \pm 1.9) \times 10^4\ M^{-1}$ for Co^{2+} and Hg^{2+}, respectively (Supplementary data). The values are close in magnitude and a small increase in K_a for Co^{2+} is attributed to its better fitting at the binding core of **1** (Fig. 3a). Due to a minor change in emission we were unable to determine the binding constant values for other metal ions.

To support the binding structure, we recorded the FTIR and ^1H NMR of **1** in the presence and absence of the equiv. amount of the mercury and cobalt salts. The amide carbonyl stretching of the spirolactam part in FTIR appeared at 1678 cm^{-1} and reduced to a lower wave number 1671 and 1675 cm^{-1} in the presence of Hg^{2+} and Co^{2+} ions, respectively. In ^1H NMR, the signals of **1** both in the aromatic and aliphatic regions became broad in the presence of Co^{2+} and Hg^{2+} ions (Fig. 3b). In the presence of Co^{2+} and Hg^{2+} ions the signals for the different types of assigned protons underwent a chemical shift change (see the caption of Fig. 3b). It is clear from the spectral change that both Hg^{2+} and Co^{2+} are complexed in the cavity involving the amide ion and poly ether chain.

The ring opening in **1** to form the metal chelated species of type **1A** was confirmed by ^{13}C NMR (Supplementary data). The gradual disappearance of the signal at 67.6 ppm for the tertiary carbon of the spirolactam ring of **1** (labelled as '**I**'; Fig. 3a) intimated the opening of the spirolactam ring. Careful analysis of ^{13}C NMR reveals that the open form is in equilibrium with the cyclic structure. As shown in Fig. 4a, without Co^{2+} ion, **1** scarcely shows absorption at 555 nm, indicating that **1** exists in spirolactam form. Addition of Co^{2+} (Fig. 4a) and also Hg^{2+} (Fig. 4b) separately to the solution of **1** ($c = 2.25 \times 10^{-4}$ M) in CH_3CN/H_2O (4:1, v/v; 10 μM tris HCl buffer; pH 6.8) brought about a strong absorption at 555 nm along with clear colour change from colourless to pink, as is normally noticed for rhodamine—based probes. The appearance of pink colour is attributed to the opening of the spirolactam rings and creation of the delocalized xanthene moieties. This was not observed when the titrations were conducted with other metal ions (Supplementary data). In case of Fe^{3+} weak absorption at 555 nm along with faint pink colour of the solution was noticed (Supplementary data). The stoichiometries[13] of both Co- and Hg complexes in the ground state and in excited state, are observed to be 1:1 (supporting information). To check the reversibility in the complexation, fluorescence and absorption spectra of cobalt and mercury complexes of **1** in CH_3CN/H_2O (4:1, v/v; 10 μM tris HCl buffer; pH 6.8) were observed upon addition of KI and Na_2EDTA solution. Addition of KI and Na_2EDTA solution reduced both emission and absorption. The pink colour

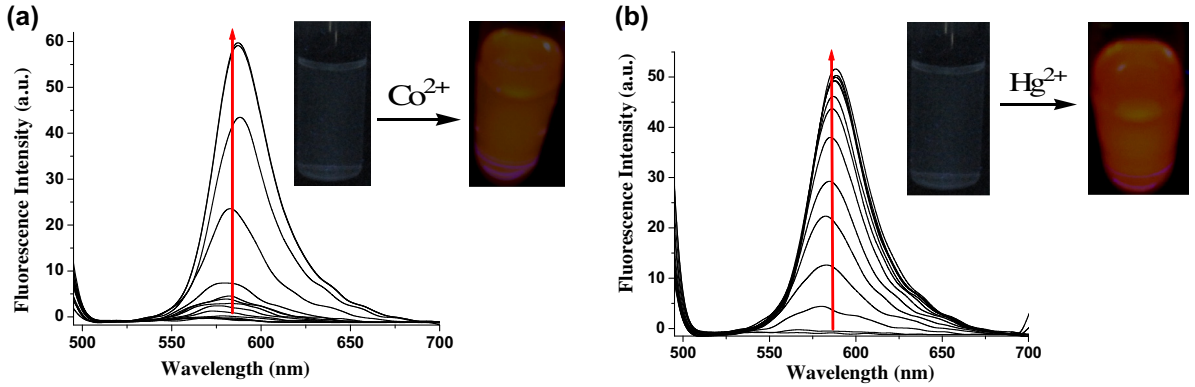

Figure 2. Fluorescence titration spectra of **1** ($c = 2.25 \times 10^{-4}$ M) in CH_3CN/water (4:1, v/v; 10 μM tris HCl buffer, pH 6.8) upon addition of (a) Co^{2+}, (b) Hg^{2+}; inset: colour change of the receptor solution under illumination of UV light.

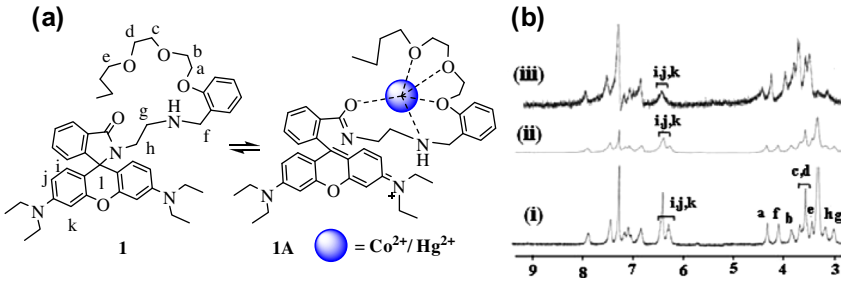

Figure 3. (a) Suggested modes of interaction of **1** with Co^{2+}/Hg^{2+} ions in solution; (b) partial ^1H NMR (400 MHz) of (i) **1** (6.2×10^{-3} M); with 1 equiv amount of (ii) $Co(ClO_4)_2$ [$\Delta\delta$ for $a = -0.02$, $b = -0.02$, c, $d = -0.02$ to -0.03, $f = 0.15$, $g = 0.12$, $h = 0.16$] and (iii) $Hg(ClO_4)_2$ [$\Delta\delta$ for $a = 0.07$, $b = 0.25$, c, $d = 0.12$ to 0.14, $f = 0.12$, $g = 0.13$, $h = 0.22$] in $CDCl_3$.

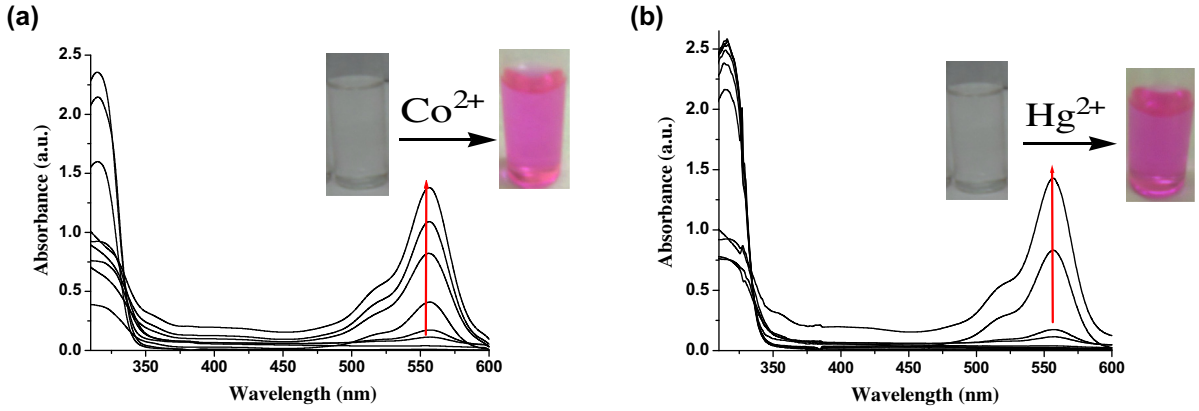

Figure 4. Absorption titration spectra of **1** ($c = 2.25 \times 10^{-4}$ M) in CH_3CN/H_2O (4:1, v/v; 10 μM tris HCl buffer; pH 6.8) upon addition of (a) Co^{2+}, (b) Hg^{2+}.

of both the solutions vanished, indicating the reversibility in the complex formation (Supplementary data).

Further, to differentiate the Hg^{2+} and Co^{2+} complexes of receptor **1** from each other, we carried out an experiment adding L-cysteine. Addition of L-cysteine to the solution of Hg^{2+} and Co^{2+} complexes of **1** brought different results in colour as well as in fluorescence. On addition of L-cysteine, fluorescence intensities of **1**-Hg^{2+} and **1**-Co^{2+} (Supplementary data) complexes were decreased almost to the same extent. This was also true in UV–vis spectra (Fig. 5). But in case of Co^{2+}-**1** complex, the colour of the solution in the presence of L-cysteine was not fully discharged. In this regard, addition of L-cysteine diminished entirely the absorption intensity of **1**-Hg^{2+} complex at 555 nm (Fig. 5a) whereas in case of **1**-Co^{2+} complex L-cysteine reduced the intensity at 555 nm to a small extent (Fig. 5b). In the presence of L-cysteine, the deep pink colour of **1**-Hg^{2+} complex became faint and under illumination of UV light gave blue fluorescence (Supplementary data, Fig. 8S). In case of **1**-Co^{2+} complex, the pink colour changed to slight wine colour on gradual addition of L-cysteine. It is mentionable that homocysteine, glutathione and non thiol-containing α-amino acid (e.g., L-valine) were unable to distinguish the Hg^{2+} and Co^{2+} complexes (Supplementary data, Fig. 9S).

In an effort to understand the detection limit for Co^{2+} and Hg^{2+} ions by sensor **1**, fluorescence spectra of **1** were recorded in the presence of respective ions of different concentrations (Supplementary data, Fig. 10S). Analysis of the results gives the detection limit 10^{-4} to 10^{-5} M.[15] Visually both Co^{2+} and Hg^{2+} ions can be detected successfully up to 1×10^{-3} M.

The potential biological application of the sensor **1** was evaluated for in vitro detection of Co^{2+} and Hg^{2+} ions in human cervical

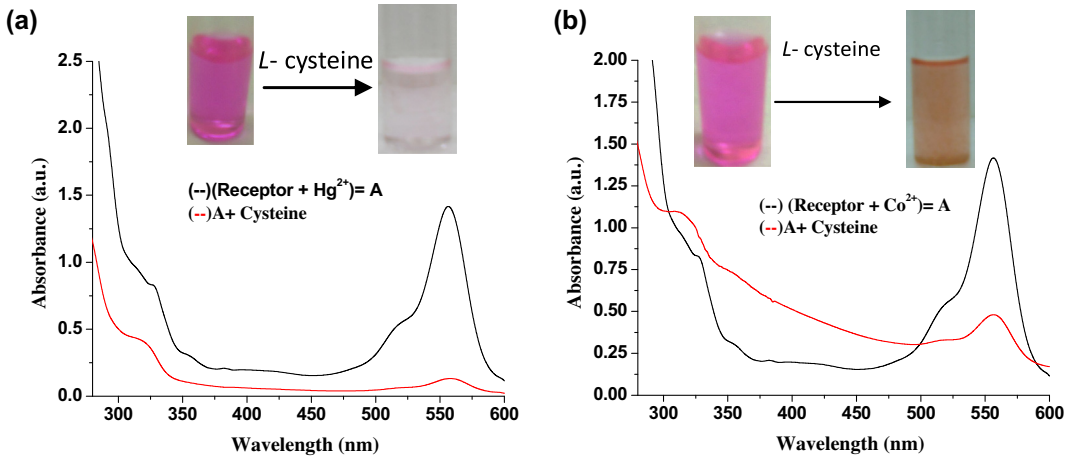

Figure 5. Change in absorbance of (a) **1**-Hg^{2+}; (b) 1-Co^{2+} complex in CH_3CN–H_2O (4:1, v/v; 10 μM tris HCl buffer; pH 6.8) upon addition of L-cysteine ($c = 1.5 \times 10^{-3}$ M); Inset: colour change upon addition of L-cysteine.

cancer (HeLa) cells. The HeLa cells were incubated with 5 μl of sensor **1** (10 μM in CH_3CN/H_2O (4:1, v/v)) in DMEM (Dulbecco modified eagles medium) medium (without FBS) for 30 min at 37 °C and washed with phosphate buffered saline (PBS) buffer (pH 7.4) to remove excess of sensor **1**. DMEM medium (without FBS) was again added to the cells. The cells were next treated with 5 μl of $Co(ClO_4)_2$ (30 μM) and incubated again for 30 min at 37 °C. A control set of cells which was devoid of Co^{2+} ion was kept. Similar experiment was done for $Hg(ClO_4)_2$. The addition of sensor **1** to the cells did not show any cytotoxicity (Supplementary data) as evident from the morphology of the cells (Fig. 6). In this context, Figure 6a and b represents the bright field images of the cells before and after treatment of the cells with **1**, respectively. Cells incubated with **1** without Hg^{2+} and Co^{2+} (Fig. 6c) did not show any fluorescence property. It was also true when cells were incubated with Co^{2+} and Hg^{2+} ions without receptor **1** (Fig. 6d and e). On the contrary, cells incubated with the receptor **1** and then with Hg^{2+} ions showed the occurrence of red fluorescence (Fig. 6f). Again cells incubated with the receptor **1** and then with Co^{2+} ions showed the occurrence of red fluorescence (Fig. 6g). These facts indicate the permeability of the receptor inside the cells and the binding of Hg^{2+} and Co^{2+} ions with the receptor.

The KI-adding experiments as experimental evidence to support the reversibility in structural change was also applied in human cervical cancer (Hela) cells. Red coloured cells obtained from the incubation of the receptor followed by treatment with Co^{2+}/Hg^{2+} became invisible in fluorescence upon addition of KI (30 μM) (Supplementary data). A similar result was also obtained in the case of Hg^{2+} complex.

In conclusion, we have shown that the rhodamine-labelled receptor **1** is capable of detecting Co^{2+} and Hg^{2+} ions simultaneously in aq. CH_3CN by exhibiting different extents of change in emission. The present example will be a new addendum in the literature on rhodamine labelled receptors for simultaneous detection of Co^{2+} and Hg^{2+} ions. Simultaneous involvement of amide parts of the rhodamines with the polyether chain favour the strong chelation of Co^{2+} and Hg^{2+} ions over the other cations examined. Inspite of almost identical behaviour in fluorescence of receptor **1** towards Hg^{2+} and Co^{2+}, the disappearance of the colour of the mercury- ensemble in the presence of L-cysteine distinguishes it from Co^{2+} ions. Moreover, the chemosensor **1** is found to be

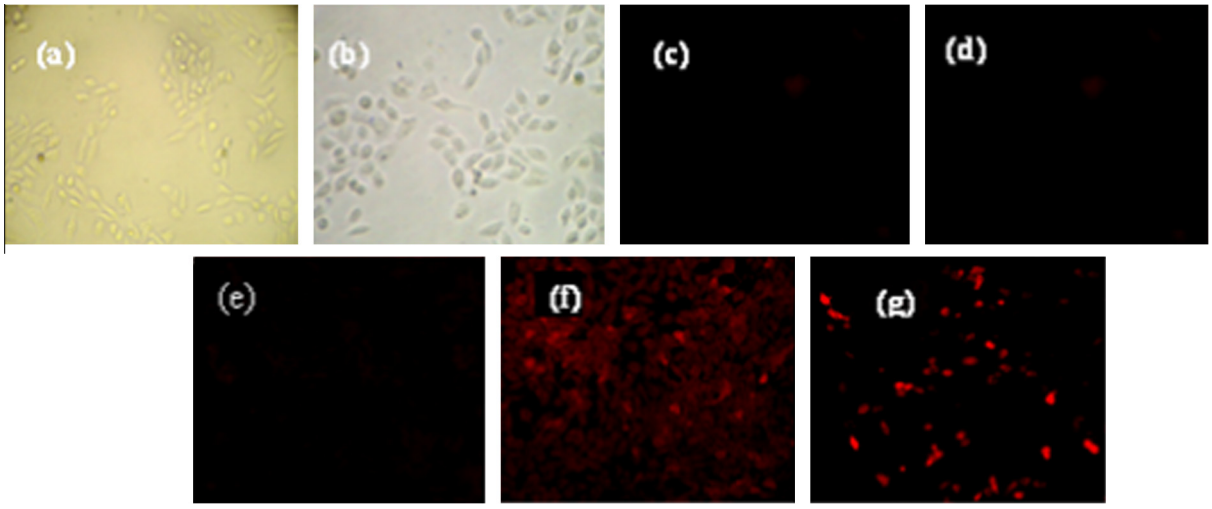

Figure 6. Fluorescence and bright field images of HeLa cells: (a) bright field image of normal cells; (b) bright field image of cells treated with receptor **1** (10 μM) for 1 h at 37 °C; (c) fluorescence image of cells treated with **1** (10 μM) for 1 h at 37 °C; (d) fluorescence image of cells treated with $Co(ClO_4)_2$ (30.0 μM) for 1 h at 37 °C; (e) fluorescence image of cells treated with $Hg(ClO_4)_2$ (30 μM) for 1 h at 37 °C; (f) red fluorescence images of cells upon treatment with receptor **1** (10 μM) and then $Hg(ClO_4)_2$ (30 μM) for 1 h at 37 °C; (g) red fluorescence images of cells upon treatment with **1** (10 μM) and then $Co(ClO_4)_2$ (30.0 μM) for 1 h at 37 °C. $\lambda_{ex} = 510$ nm.

efficient in reporting the presence of both Co^{2+} and Hg^{2+} ions inside the cell.

Acknowledgments

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Supplementary data

Supplementary data (Figures showing the change in fluorescence and UV–vis titrations of receptor **1** with the metal ions, binding constant curves, Job plots, sensitivity of **1** towards Hg^{2+} and Co^{2+} ions, reversibility in complexation, detection limit, MTT assay, ^{13}C NMR spectral changes of **1** with the addition of Co^{2+}, experimental procedure, ^{1}H, ^{13}C NMR spectra and mass spectra are available.) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.09.062.

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