Journal of Fluorescence (2019) 29:569–575
https://doi.org/10.1007/s10895-019-02372-6

ORIGINAL ARTICLE

A New Spiropyran-Based Sensor for Colorimetric and Fluorescent Detection of Divalent Cu^{2+} and Hg^{2+} Ions and Trivalent Ce^{3+}, Cr^{3+} and Al^{3+} Ions

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Received: 10 June 2018 / Accepted: 20 March 2019 / Published online: 27 March 2019

Abstract
A new spiropyran derivative acts as colorimetric and fluorescent sensor for metal ions. Addition of Cu^{2+}, Al^{3+}, Cr^{3+} and Ce^{3+} to the sensor solution brings about marked increase in the absorption intensities while addition of other metal ions (Na^+, K^+, Li^+, Sr^{2+}, Hg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} and Ag^+) fails to cause substantial change in the UV–Vis spectra. The sensor can be used for detection of Hg^{2+}, Cu^{2+}, Ce^{3+}, Cr^{3+} and Al^{3+} ions by the naked eye and by fluorescence enhancement. The detection limit of Cu^{2+} and Hg^{2+} ions by the sensor is estimated to be 10 and 14 µM, respectively. Job's plot analysis on the sensor–Cu^{2+} complexation reveals the formation of a 2:1 stoichiometric complex between the sensor and Cu^{2+} ion.

Keywords Spiropyran · Fluorescent sensor · Colorimetric · Cu^{2+} and Hg^{2+} · Al^{3+} · Cr^{3+} and Ce^{3+}

Introduction

Owing to the significant role of Cu^{2+} ions in both biological and environmental systems and the potential damages to humans caused by excessively high Cu^{2+} concentration, selective and sensitive detection of Cu^{2+} is crucial. Fluorescent and/or colorimetric sensors are superb in this respect and have been widely applied to probing of Cu^{2+} ions [1–11]. On the other hand, as one of the most toxic elements even at low concentrations, mercury may threat the safety of humankind and environment. Thus highly selective and sensitive sensors for fluorescent detection of Hg^{2+} ions have been developed [12–19]. Compared with the one-to-one sensors the multi-ion systems, namely, the single-molecule chemosensors which can detect two or more interest ions simultaneously, seem to be more attractive. This novel concept of a single chemosensor for multiple analytes allows for a rapid and simple detection process and is cost effective. Some dual-function fluorescent chemosensors for Cu^{2+} and Hg^{2+} have been developed [20–24]. Several fluorescent chemosensors can even detect more than two metal ions simultaneously such as Cu^{2+}, Fe^{3+} and Cr^{3+} [25], Cu^{2+}, Zn^{2+} and Al^{3+} [26], and Hg^{2+}, Cr^{3+} and Ag^+ [27]. However, multifunctional chemosensors that can be utilized for simultaneous detection of divalent Cu^{2+} and Hg^{2+} ions and trivalent metal ions such as Al^{3+}, Cr^{3+} and Ce^{3+} ions have not been reported up to now. Such sensors may find their wide application to the detection of heavy metals and transitional metals in industrial waste water. We recently found that a colorimetric chemosensor based on a spirobenzopyran-appended polysiloxane exhibited multiple responses and could be used for selective sensing of Hg^{2+}, Ag^+, Fe^{3+} and pH [28]. In continuation to our study on fluorescent chemosensors for selective and sensitive multi-ion detection, herein we present the synthesis and recognition properties of a new spirobenzopyran-based chemosensor for

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Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10895-019-02372-6) contains supplementary material, which is available to authorized users.

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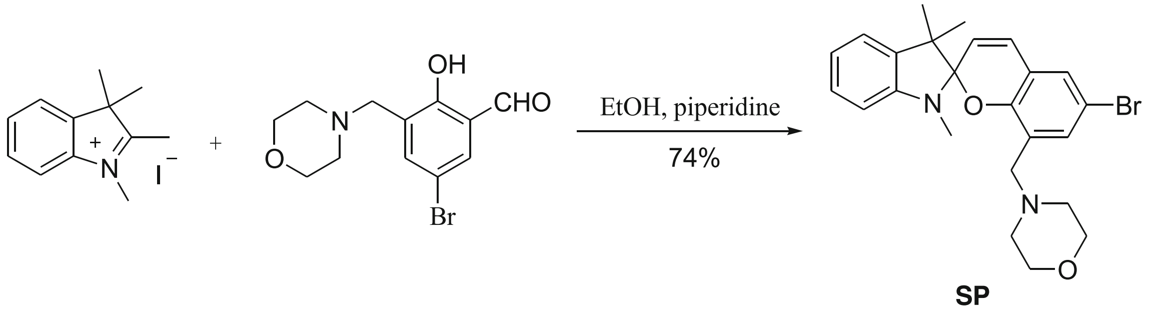


Scheme 1 Synthesis of the sensor **SP**

fluorescent detection of Cu^{2+} and Hg^{2+} and colorimetric sensing of trivalent Al^{3+}, Cr^{3+} and Ce^{3+} ions.

Experimental

Materials and Reagents

All reagents and solvents used in the experiments were of analytical grade without further purification unless otherwise noted. Deionized water was used in all experiments. The metal stock solutions were prepared from the salts of $CoCl_2·6H_2O$, $AlCl_3$, $CrCl_3$, $Zn(OAc)_2$, $AgNO_3$, $Hg(OAc)_2$, $NiCl_2·6H_2O$, $CuSO_4$, LiBr, NaCl, KBr, $SrCl_2$, and $CeCl_3·5H_2O$. *N*-(2-hydroxy-3-formyl-5-bromobenzyl)morpholine and *N*-methyl-2,3,3-trimethylindolenium iodide were synthesized according to literature methods [29, 30].

Instruments and Measurements

^1H NMR and ^{13}C NMR spectra were measured on Bruker ACF-500 spectrometer by using TMS as an internal standard. IR spectra (KBr-disc) were recorded on Bruker Tensor 27 spectrophotometer. Mass spectra were measured on a MS Agilent 1100 Series LC/MSD Trap mass spectrometer (ESI-MS) and a Mariner ESI-TOF spectrometer (HR-MS). UV–Vis spectra were obtained using a Shimadzu UV-2300 spectrophotometer. Fluorescence spectra were measured on Perkin LS-55 fluorescence spectrophotometer. The stock solution of **SP** (2 mM) was prepared by dissolving **SP** in ethanol. The stock solution of various metal ions was prepared by dissolving the corresponding metal salts in deionized water. The test solution was prepared by mixing the desired metal ion solution (1 mL) with the stock solution of **SP** (1 mL). The measurements of fluorescence spectra were carried out at an excitation wavelength of 348 nm

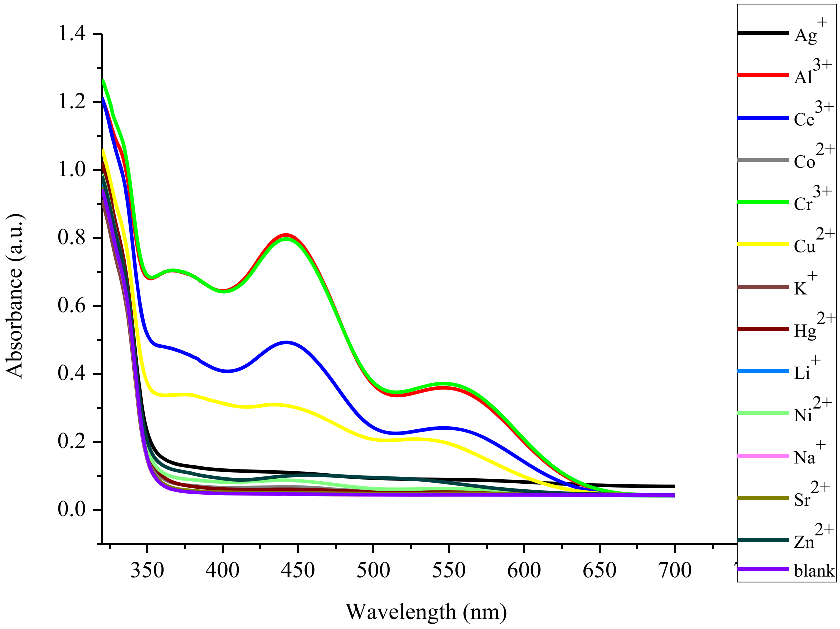


Fig. 1 UV–Vis spectra of **SP** solution (2.0 mM in ethanol) before and after addition of different metal ions (Na^+, K^+, Li^+, Sr^{2+}, Cr^{3+}, Hg^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Co^{2+}, Ni^{2+}, Ce^{3+} and Ag^+, 2.0 mM in deionized water)

Fig. 2 Color changes in **SP** solution 10 min after addition of different metal ions (Na^+, K^+, Li^+, Sr^{2+}, Cr^{3+}, Hg^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Co^{2+}, Ni^{2+}, Ce^{3+} and Ag^+)

while the emission spectra were recorded in a range of 365–750 nm and the slit width was 8 nm.

Synthesis of the Sensor SP

N-Methyl-2,3,3-trimethylindolenium iodide (1.01 g, 6.2 mmol) in absolute ethanol (35 mL) was heated to reflux under N_2 atmosphere. Piperidine (0.5 mL, 0.43 g, 5.1 mmol) was added to the above solution. Then *N*-(2-hydroxy-3-formyl-5-bromobenzyl) morpholine (1.43 g, 5.1 mmol) dissolved in absolute ethanol (10 mL) was injected to the reaction mixture. The mixture was refluxed for 8 h. After reaction the solvent was removed by rotary evaporation and the crude product was purified by column chromatography with petroleum ether and ethyl acetate (20:1, *v*/v) as eluent to afford sensor **SP** as a yellow solid (1.65 g, 74%). Mp 136–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (s, 3H), 1.23 (s, 3H), 2.17 (s, 4H, NCH_2), 2.60 (s, 3H), 3.13 (s, 2H), 3.51 (s, 4H, OCH_2), 5.69 (d, J = 12.0 Hz, 1H, CH=CH), 6.65 (d, J = 12.0 Hz, 1H, CH=CH), 6.72–6.77 (m, 2H, Ar-H), 6.98–6.99 (m, 1H, Ar-H), 7.05–7.09 (m, 2H, Ar-H), 7.23–7.25 (m, 1H, Ar-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.25 (CH_3), 25.72 (CH_3), 29.11 (CH_3), 31.58 (NCH_2), 33.99 (NCH_2), 51.29 (NCH_2), 53.19 (OCH_2), 56.55 (OCH_2), 67.10, 104.73, 106.89, 111.37, 119.28, 120.13, 120.46, 121.34, 127.47, 128.16, 128.67, 133.05, 136.70, 148.05, 151.49. IR (KBr): ν 2965, 2850, 1620, 1596, 1509, 1460, 1395, 1300, 1284, 1212, 1147, 1069, 983, 898, 842, 786, 612 cm^{-1}. LR-MS: m/z 455.1 (M^+), 457.1 ($M^+ + 2$). HR-MS: m/z 455.1328; calcd. For $C_{24}H_{27}BrN_2O_2$ 455.1334.

Results and Discussion

Synthesis and Characterization of the Sensor SP

The novel spirobenzopyran-based sensor **SP** was synthesized as showed in Scheme 1. Condensation between the morpholinylmethyl salicylaldehyde compound and *N*-methyl-2,3,3-trimethylindolenium iodide in the presence of piperidine followed by cyclization in ethanol afforded sensor **SP** in 74% yield. The chemical structure of **SP** was fully characterized by ^{1}H NMR (Fig. S1), ^{13}C NMR (Fig. S2), mass spectrum (Fig. S3), and IR spectrum (Fig. S4). In the ^{1}H NMR spectrum the signals from the H atoms on the gem-dimethyl groups appeared at 1.10 and 1.23 ppm, respectively. Hydrogens on the N-CH_3 showed a chemical shift of 2.60 ppm. Signals from the morpholinyl group appeared at 2.17 and 3.51 ppm. The values 5.69 and 6.65 ppm were ascribed to the vinylene group and the coupling constant was 12.0 Hz. The peak from the molecular ion appeared at 455.1 in the mass spectrum. The peak at 457.1 with approximately the same intensity with that of the peak at 455.1 was induced by the isotope ^{81}Br. Overall the data in the spectra were in good accordance with the structure.

Sensing Behavior of the Sensor SP

UV–Vis spectra of **SP** before and after addition of different metal ions (Na^+, K^+, Li^+, Sr^{2+}, Cr^{3+}, Hg^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Co^{2+}, Ni^{2+}, Ce^{3+} and Ag^+) were measured and showed in Fig. 1. Solution of the sensor **SP** in aqueous ethanol showed

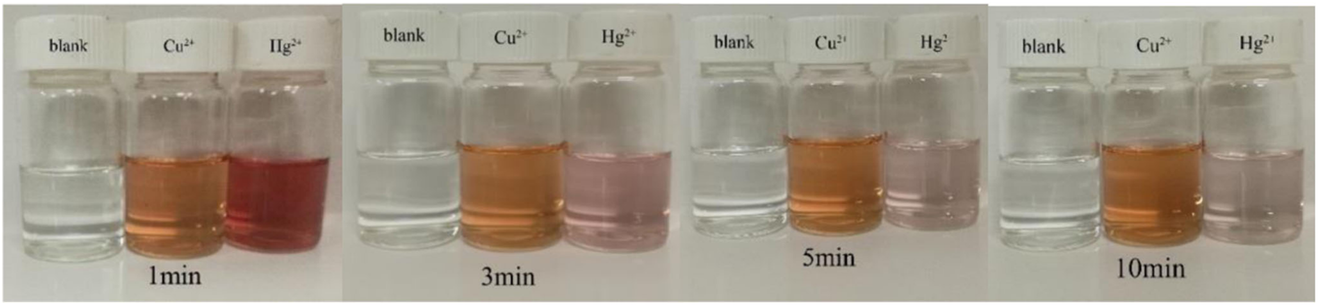


Fig. 3 Color change in **SP** solution 1, 3, 5 and 10 min after addition of Cu^{2+} or Hg^{2+}

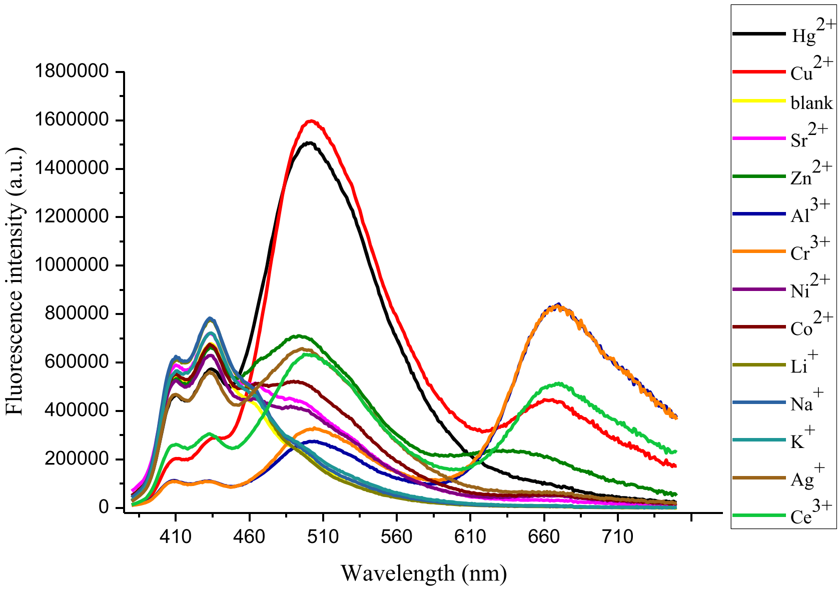


Fig. 4 Fluorescence emission spectra ($\lambda_{ex} = 348$ nm) of **SP** (2×10^{-4} M in EtOH) and **SP** with different metal ions (K^+, Cu^{2+}, Zn^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, Al^{3+}, Ag^+, Na^+, Li^+, Sr^{2+} and Ce^{3+}, 2.0×10^{-4} M)

two weak absorption bands at around 450 and 550 nm, respectively. Addition of Cr^{3+}, Cu^{2+}, Al^{3+} and Ce^{3+} brought about marked increase in the absorption intensities of the two bands while addition of other metal ions failed to cause substantial change in the spectra. UV–Vis spectrum of **SP**/Al^{3+} almost overlapped with that of **SP**/Cr^{3+} and exhibited the strongest absorption intensities. These changes in the UV–Vis spectral absorption were also reflected in the color changes of **SP** solution upon addition of different metal ions. As showed in Fig. 2, colorless **SP** solution turned brown after addition of Ce^{3+} or Cu^{2+} while addition of Cr^{3+} or Al^{3+} caused color change to purple. Addition of Hg^{2+} induced red color at first (in one minute) but the red solution faded gradually and turned nearly colorless in 10 min, as showed in Fig. 3. Addition of other metal ions (Na^+, K^+, Li^+, Sr^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} and Ag^+) to **SP** solution did not bring about distinct color change. Therefore sensor **SP** was capable of colorimetric detection of Ce^{3+}, Cu^{2+}, Hg^{2+}, Al^{3+} and Cr^{3+} ions.

Fluorescence emission spectra of **SP** solution (2×10^{-4} M in EtOH) before and after addition of different metal ions (K^+, Cu^{2+}, Zn^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, Al^{3+}, Ag^+, Na^+, Li^+, Sr^{2+} and Ce^{3+}, from 2.0×10^{-4} M of KCl, $CuCl_2$, $ZnCl_2$, $HgCl_2$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $Cr(NO_3)_3$, $Al(NO_3)_3$, $AgNO_3$, NaCl, LiCl, $SrCl_2$ and $Ce(NO_3)_3$ aqueous solution, respectively) were measured at $\lambda_{ex} = 348$ nm and showed in Fig. 4. The fluorescence spectrum of **SP** revealed only a weak emission band at around 510 nm upon excitation at 348 nm. Addition of Cu^{2+} ion induced drastic enhancement in the intensity of the fluorescence emission band at 510 nm and a strong fluorescence emission peak at around 675 nm. Addition of Hg^{2+} ion

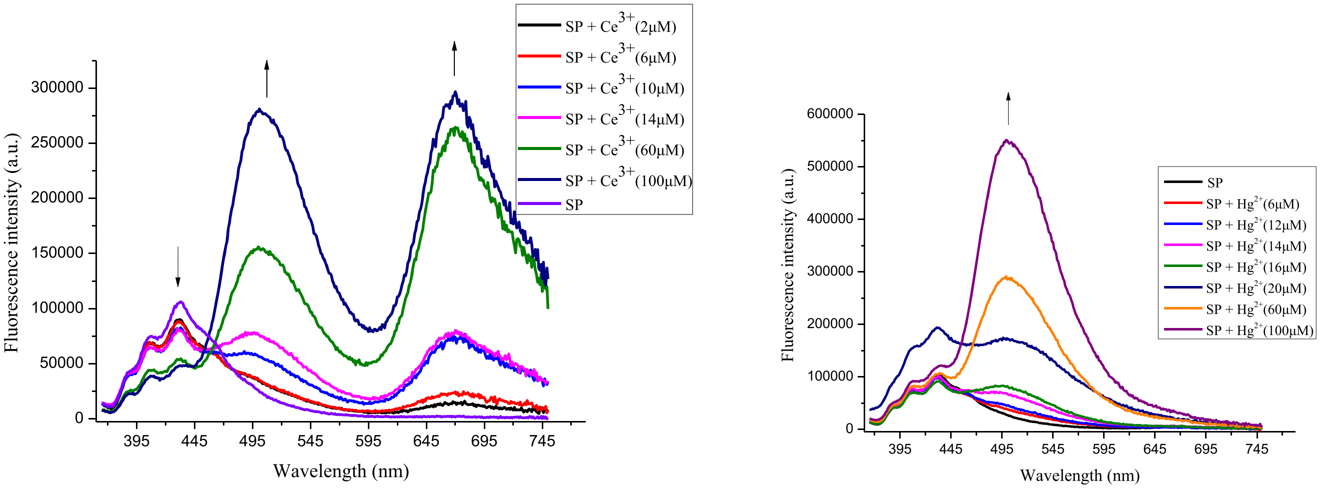
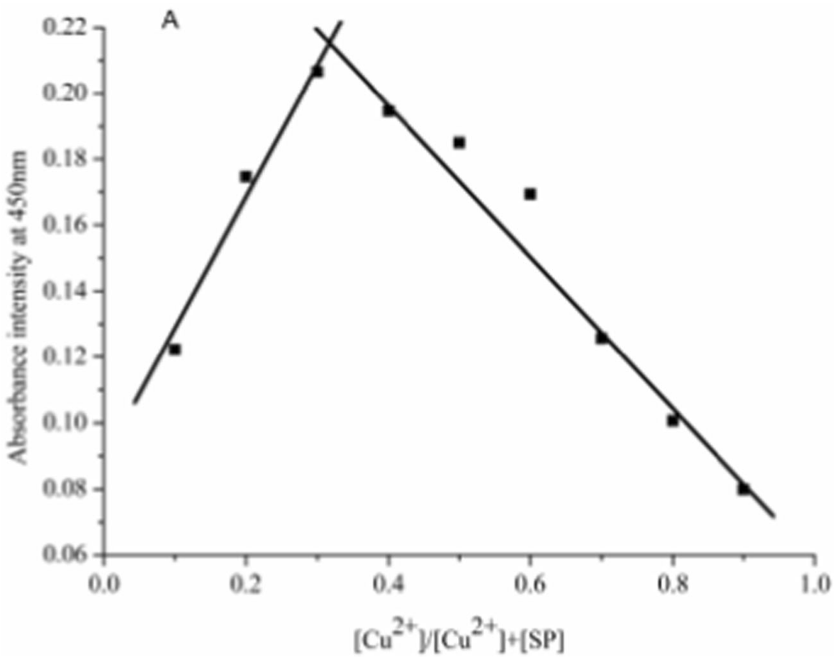


Fig. 5 Changes in fluorescence emission spectra ($\lambda_{ex} = 348$ nm) of **SP** (2.0×10^{-4} M) upon addition of different concentrations of Cu^{2+} (2, 6, 10, 14, 60 and 100 μM) or Hg^{2+} ion (6, 12, 14, 16, 20, 60 and 100 μM)

Fig. 6 Job's analysis of **SP**–Cu^{2+} complex ([**SP**] + [Cu^{2+}] = 2.0 × 10^{-4} M)

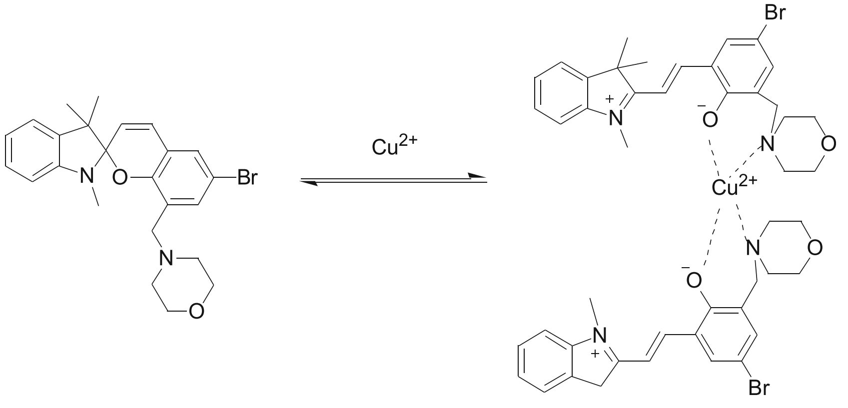


also induced drastic enhancement in the intensity of the fluorescence emission band at 510 nm but no strong fluorescence emission peak at around 675 nm was observed. Addition of Al^{3+} or Cr^{3+} ion induced a very strong fluorescence emission band at 675 nm. Addition of Ce^{3+} ion induced moderate enhancement in the intensity of the fluorescence emission band at 510 nm and a strong fluorescence emission peak at around 675 nm. Addition of other metal ions (Na^+, K^+, Li^+, Sr^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Ag^+) to **SP** did not cause distinct change in the fluorescence emission spectra. Thus **SP** can be used as a fluorescence turn-on sensor for selective detection of Cu^{2+}, Hg^{2+}, Al^{3+}, Cr^{3+} and Ce^{3+} ions.

Changes in fluorescence emission spectra ($\lambda_{ex} = 348$ nm) of **SP** (2.0 × 10^{-4} M) upon addition of different concentrations of Cu^{2+} (2, 6, 10, 14, 60 and 100 μM) or Hg^{2+} ion (6, 12, 14, 16, 20, 60 and 100 μM) were measured and showed in Fig. 5. It can be found that the intensity of the fluorescence emission band at both 510 and 675 nm increases with increase in the concentration of added Cu^{2+} ion. The fluorescence intensity only increases a little when the concentration of Cu^{2+} ion is below 10 μM. A distinct enhancement in the fluorescence intensity was observed when the concentration of Cu^{2+} ion is 10 μM. Similarly, increase in the intensity of the fluorescence emission band at 510 nm with increase in the concentration of added Hg^{2+} ion is observed. When the concentration of Hg^{2+} ion increases to 12 μM, merely a little increase in the fluorescence intensity is found. Further increase in the concentration of Hg^{2+} ion to 14 μM results in a sharp enhancement in the fluorescence intensity. Therefore the detection limit of Cu^{2+} and Hg^{2+} ions by **SP** is estimated to be 10 and 14 μM, respectively.

From the above sensing behavior of **SP** towards Cu^{2+}, Hg^{2+}, Ce^{3+}, Cr^{3+} and Al^{3+} ions it can be concluded that **SP** serves as a selective chemosensor for detection of Cu^{2+}, Hg^{2+} and Ce^{3+} ions and for simultaneous detection of Cr^{3+} and Al^{3+} ions by colorimetric and fluorogenic mode.

Scheme 2 Proposed sensing mechanism of **SP** towards Cu^{2+} ion



It is known that spiropyran derivatives can be utilized for probing metal ions through complex formation between spiropyran and metal ion [8–11, 31–33]. The spectroscopic determination of the complexes' composition can be achieved by means of the isomolar solutions technique (Job method). In this work the Job's plot was drawn with the total concentration of **SP** and Cu^{2+} being 20 mM. The plot of the Job analysis of the spiropyran–Cu^{2+} complex is showed in Fig. 6. It is visible that the maximum absorbance intensity appears at around 0.33 M fraction which indicates the formation of a 2:1 stoichiometric complex between **SP** and Cu^{2+} ion, in good accordance with the previously reported results [10].

Based on the complexation stoichiometric ratio, a possible coordination mode for **SP** with Cu^{2+} ion is proposed as showed in Scheme 2. The sensor **SP** undergoes a ring-opening process in the presence of Cu^{2+} ion then the ring-opening merocyanine complexes with Cu^{2+} ion in a 2:1 binding ratio, to produce brown color and strong fluorescence.

Conclusions

A new colorimetric and fluorescent chemosensor **SP** for multiple metal ions detection has been developed based on the metal-coordination tunable photochromism of a spiropyran. Addition of Cu^{2+}, Al^{3+}, Cr^{3+} and Ce^{3+} to the sensor solution brings about marked increase in the absorption intensities in the UV–Vis spectra. Addition of Hg^{2+} to the sensor solution induces red color at first but the red solution fades gradually and turns colorless in 10 min. Colorless **SP** solution turns brown upon addition of Ce^{3+} or Cu^{2+} while addition of Cr^{3+} or Al^{3+} causes color change to purple. Thus Hg^{2+}, Cu^{2+}, Ce^{3+}, Cr^{3+} and Al^{3+} ions can be identified by the naked eye and UV–Vis spectrum. On the other hand, **SP** can be used as a fluorescence turn-on chemosensor for selective detection of Cu^{2+}, Hg^{2+}, Al^{3+}, Cr^{3+} and Ce^{3+} ions. Addition of Cu^{2+} ion to **SP** solution induces a strong fluorescence emission peak at around 675 nm and drastic enhancement in the intensity of the fluorescence emission band at 510 nm. Addition of Hg^{2+} ion also induced drastic enhancement in the intensity of the fluorescence emission at 510 nm but no strong fluorescence emission appears at 675 nm. Addition of Al^{3+} or Cr^{3+} ion leads to a very strong fluorescence band at 675 nm while addition of Ce^{3+} ion induces a strong fluorescence peak at around 675 nm and moderate enhancement in the fluorescence emission at 510 nm. Addition of other metal ions (Na^+, K^+, Li^+, Sr^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Ag^+) to **SP** solution fails to cause distinct change in the fluorescence emission spectra. The detection limit of Cu^{2+} and Hg^{2+} ions by **SP** is estimated to be 10 and 14 μM, respectively. Job's plot reveals the formation of a 2:1 stoichiometric complex between **SP** and Cu^{2+} ion.

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