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Structurally modified 1,10-phenanthroline based fluorophores for specific sensing of Ni^{2+} and Cu^{2+} ions

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We report two fluorophores with open coordination sites for specific sensing of Ni^{2+} and Cu^{2+} ions *via* a simple synthetic route. The fluorescence activity was completely quenched on coordination of the metal ions with the phenanthroline ring present in the fluorophore as is clearly evident from the photophysical studies.

Much attention has been focused in recent years on the development of new chemical sensors for the recognition of heavy metal ions as well as anionic species.[1] Metal ions play a vital role in a wide range of chemical and biological processes, yet some of them are potentially toxic. It is indeed important to detect metal ions for applications in waste management and environmental toxicology.[2] Metal ions such as Ni^{2+} and Cu^{2+} fall under the category of essential trace elements as they are indispensable for life. However, at higher concentration they damage the central nervous system and affect blood composition as well as the kidneys, liver, lungs and other vital parts of the human body. Hence, there has been an increasing interest in the field of sensors to monitor these metals selectively in the environment. The response from these sensors may be either through optical, electrical or magnetic resonance signals.[3]

Even though a number of techniques such as atomic absorption spectroscopy, inductively-coupled plasma mass spectrometry and inductively-coupled plasma atomic emission spectroscopy are available to detect these metal ions in food samples and industrial effluent, they still involve tedious procedures for sample treatment and are also expensive.[4] Optical signals based on changes in absorbance or fluorescence is the most frequently exploited technique because of the simplicity of the experimental methods.

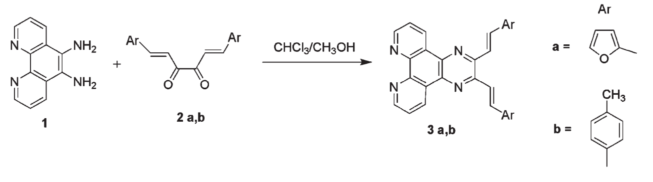
Luminescent chemosensors for recognizing environmentally significant ionic species are currently a challenging research topic. Among the various metal ion sensor molecules, fluorescent sensors have the additional advantage of finding application in trace ion analysis and imaging, since change in color immediately reveal the presence of a given analyte, which makes it valuable for application in the field of chemistry, biology, medicine, *etc.*[5] Fluorescence emission-based sensors also have very high sensitivity.[6]

In general, the sensing of cations such as Ni^{2+} and Cu^{2+} in aqueous solution requires a strong affinity for cations in the solvent as well as the ability to convert the cation recognition into a fluorescent or colorimetric signal.[7] Most of the fluorescent chemosensors for cations are composed of a cation recognition site (ionophore) with a fluorogenic site (fluorophore) which converts the recognition of the cation by the ionophore into an optical signal.[8]

1,10-Phenanthroline moieties are emerging as fluorescent sensors for the detection of metal ions.[9] Spectral shifts occur in the phenanthroline moiety after the ligation of the metal ion on the open coordination site, which in turn changes its color.[10] Sensors based on the phenanthroline moiety can be prepared by reacting with various aryl groups, thus resulting in fluorescent properties of the compound containing both the ionophore and fluorophore. The interaction with metal ions may be through coordinate bonding of the nitrogen atom in the phenanthroline ring.

In this paper, we report two excellent fluorophores with open coordination sites for the selective detection of Ni^{2+} and Cu^{2+}. The fluorophores **3a** and **3b** were prepared by employing a very simple synthetic route of condensation of diamine with a diketone as depicted in Scheme 1.† The reactants were prepared according to the literature.[11,12]

Surprisingly, both the compounds had excellent fluorescence visible to the human eye in solution. The compounds after purification from column chromatography were analysed for their photophysical properties. To evaluate the selectivity of the fluorophores **3a** and **3b** towards the analyte, their fluorescence behavior upon addition of various transition and heavy metal ions such as Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} have been examined.



Scheme 1

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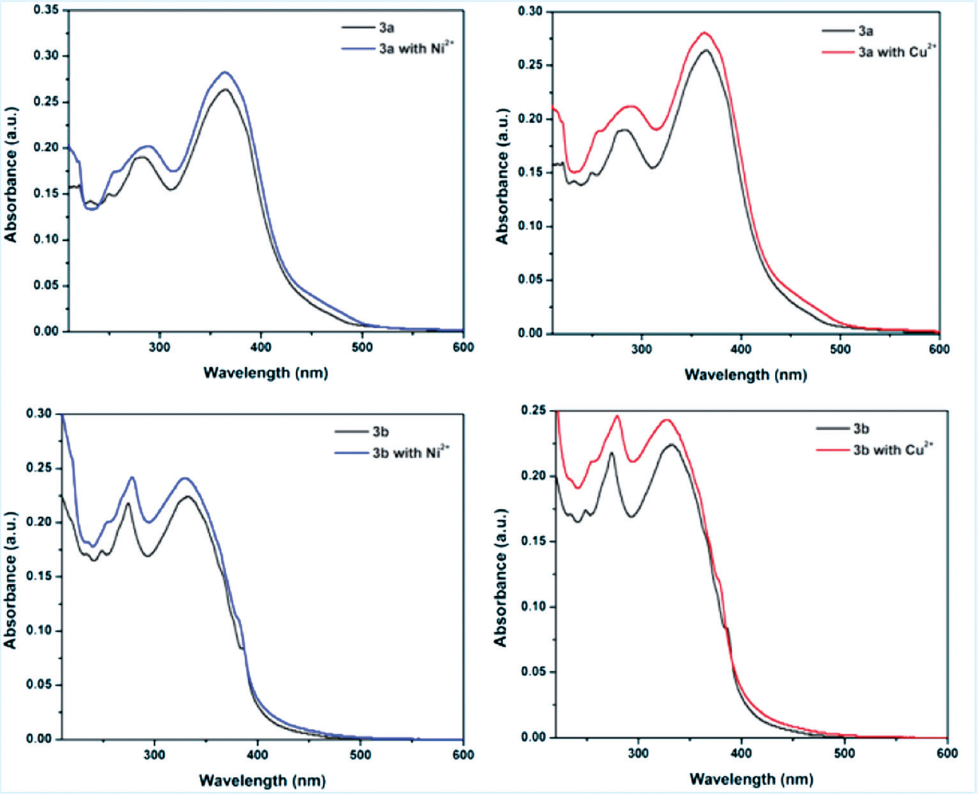

Fig. 1 Absorption spectra of **3a** with Ni^{2+} (top left), **3a** with Cu^{2+} (top right), **3b** with Ni^{2+} (bottom left) and **3b** with Cu^{2+} (bottom right).

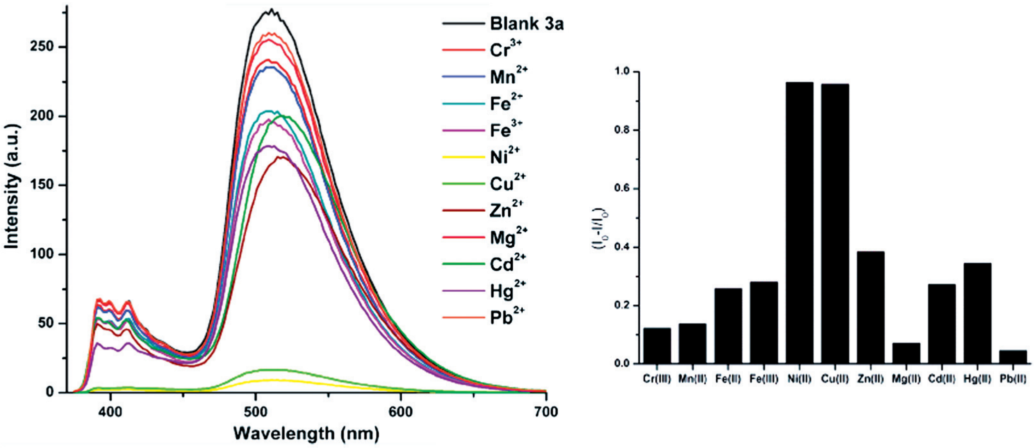

Fig. 2 Fluorescence response of **3a** to various metal ions in methanol. Bars represent fluorescence quenching ratio $(I_0 - I)/I_0$ of various metal ions.

Fluorescence studies were carried out for compounds **3a** and **3b** and both the emission spectra were mirror images of the absorption spectra of the respective compounds. The fluorescence spectra of **3a** and **3b** show strong emission of the phenanthroline moiety at 513 nm and 503 nm respectively.

On addition of metal ions, the phenanthroline moiety is expected to bind to a certain analyte, in turn altering the photophysical properties. Fluorescence of the fluorophores in the presence of various metal ions was initially studied in a 1 : 1 stoichiometric ratio. The fluorescence intensity was found to decrease on addition of different metal ions. The extent of quenching depended upon the binding interaction of the metal ion with the receptor molecule. Addition of metal ions other than Cu^{2+} and Ni^{2+} led to very little change in the intensity of emission of compound **3a** at 513 nm.

The excitation energy was found to be 365 nm and 295 nm for **3a** and **3b** respectively. The excitation energy of the two fluorophores did not show any change in the presence of the two metal ions. These results are also in line with the absorption spectra of the fluorophores in the presence of the two metal ions (Fig. 1).

The absorption spectra of **3a** and **3b** with Ni^{2+} and Cu^{2+} is given in Fig. 1. In both the cases, addition of Cu^{2+} or Ni^{2+} did not lead to any shift in the position of the absorption peaks of

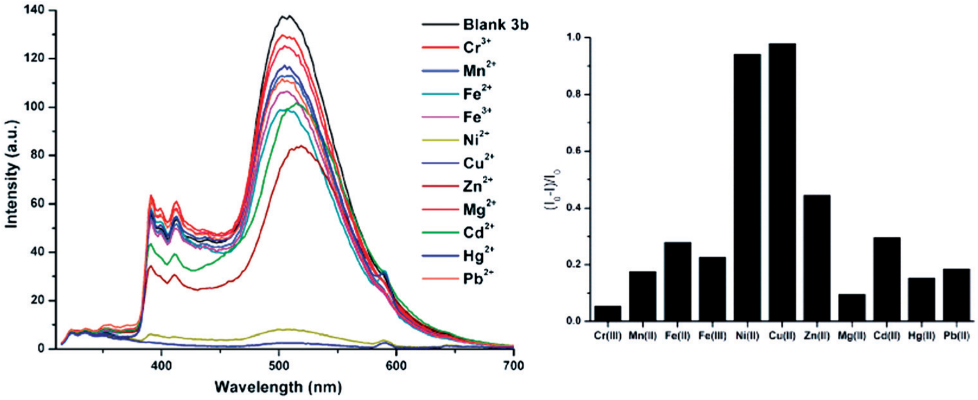

Fig. 3 Fluorescence response of **3b** to various metal ions in methanol. Bars represent fluorescence quenching ratio $(I_0 - I)/I_0$ of various metal ions.

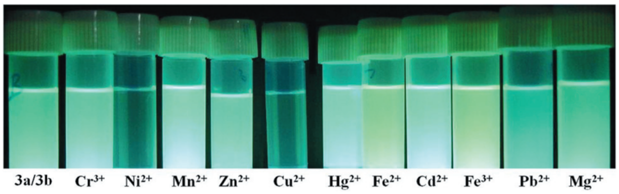

Fig. 4 Image under UV light of **3a**/**3b** to various metal ions in methanol.

fluorophores. Addition of these two metal ions also did not lead to appearance of any new peak in the visible region of the absorption spectra. Addition of metal ions other than Cu^{2+} or Ni^{2+} also did not result in any change in the energy of the fluorophore absorption. The intensity of the fluorophore absorption peak however, increased in the presence of Cu^{2+}/Ni^{2+}.

On the other hand, a significant change was observed in the intensity of emission of compound **3a** in the presence of Ni^{2+} and Cu^{2+}. A complete quenching of the emission band at 513 nm, which is characteristic of the phenanthroline ring was observed in the presence of Ni^{2+}/Cu^{2+} (Fig. 2).

In a similar manner, the emission band of **3b** at 503 nm was completely quenched only on addition of Ni^{2+} and Cu^{2+}; whereas no marked changes were seen in the emission band of **3b** in the presence of other metal ions, except for a slight change in intensity. Even though Zn^{2+}, Fe^{3+} and Cd^{2+} ions quenched the fluorescence emission of both the fluorophores, the quenching effect of Ni^{2+} and Cu^{2+} was much more than that observed with Zn^{2+}, Fe^{3+} and Cd^{2+} as can be seen from the bar graph shown in Fig. 3. Pictorial representation of the response of fluorophores with metal ions is shown in Fig. 4.

Fluorescence titration experiments were carried out to investigate the complexation of Ni^{2+}/Cu^{2+} with the fluorophores **3a** and **3b** (Fig. 5 and 6). Both the fluorophores showed a considerable decrease in fluorescence intensity on increasing the metal ion concentration and a complete quenching of fluorescence band was observed at 1 : 1 equivalents of the fluorophore to metal ion. From the Job's plot, 1 : 1 stoichiometry of the metal ion to fluorophore was confirmed. The fluorophore **3a** was able to detect 0.4 ppm of Ni^{2+} and 0.35 ppm of Cu^{2+} with a quenching efficiency of 80% and in the case of **3b**, the detection limits were 0.2 ppm and 0.4 ppm for Cu^{2+} and Ni^{2+} respectively. From the Stern–Volmer relationship, the binding constant of fluorophores with the metal ions were calculated and the values were found to be 8.96×10^6 M and 2.51×10^7 M for **3a** with Cu^{2+} and Ni^{2+} respectively. The values for **3b** with Cu^{2+} and Ni^{2+} were 8.13×10^6 M and 3.75×10^6 M respectively.

From the photophysical studies, it is observed that most of the metal ions can bind to the phenanthroline moiety in the ligand, yet a complete quenching was observed only in the case of Ni^{2+} and Cu^{2+} in a 1 : 1 ratio of metal to ligand. In order to further understand the behaviour of these metal ions with the fluorophores, DFT calculations have been carried out. As Ni^{2+} and

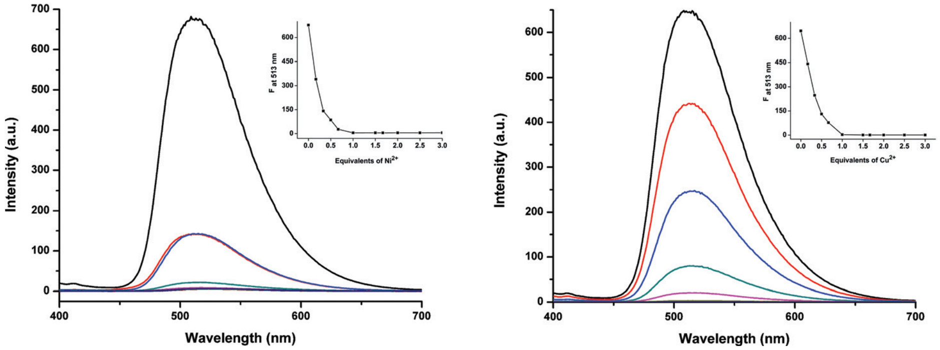

Fig. 5 Fluorescence titration experiment of **3a** with various concentrations of Ni^{2+} and Cu^{2+} ions. Inset represents the respective Job's plot.

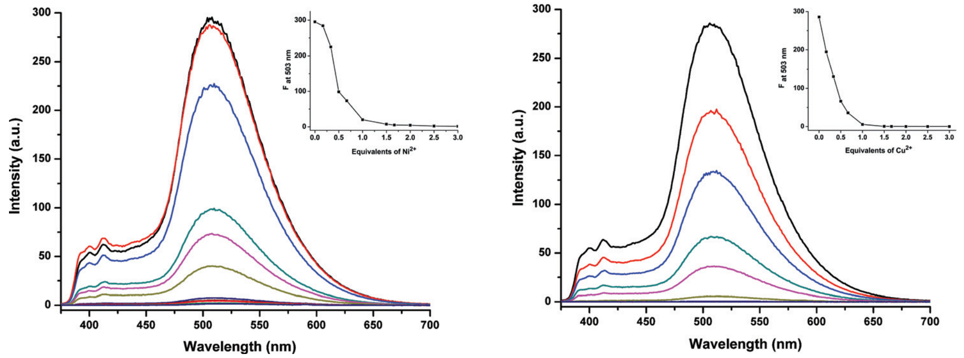

Fig. 6 Fluorescence titration experiment of **3b** with various concentrations of Ni^{2+} and Cu^{2+} ions. Inset represents the respective Job's plot.

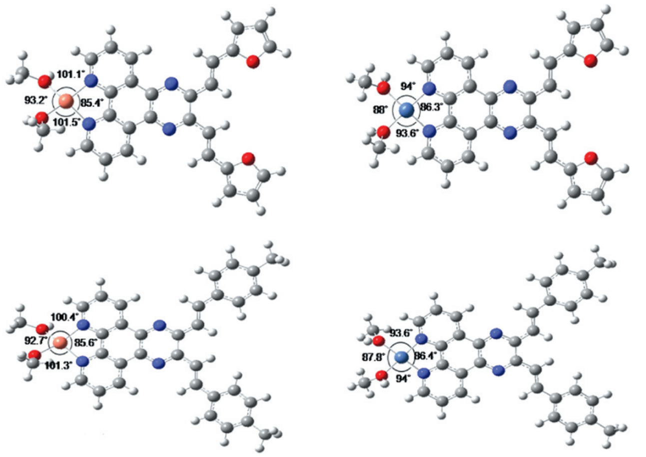

Fig. 7 Optimised structures of **3a** with Cu^{2+} (top left), **3a** with Ni^{2+} (top right), **3b** with Cu^{2+} (bottom left) and **3b** with Ni^{2+} (bottom right).

Cu^{2+} are known for their 4-coordination complexes, the input structures were designed in a way to have bidentate coordination with the fluorophores, whereas the other two coordination sites are occupied by the solvent molecule (Fig. 7). The structural optimisation was done using the Gaussian 03 package adopting the B3LYP method with 6-31G as the basis set.[13,14]

It can be seen from the optimised structures that Ni^{2+} and Cu^{2+} adopts distorted square planar symmetry and tetrahedral symmetry respectively, which is due to the angle strain around the five membered ring structure formed by the coordination of the metal ion with the ligand.

In order to understand the absorption spectral behaviour of the fluorophores on addition of Ni^{2+}/Cu^{2+} ions, TD-DFT calculations[15,16] were carried out for the first 35 excitations lying in the region of 350–800 nm. Electron density of the HOMO of both fluorophores **3a** and **3b** lies on the electron-donating part of the ligand and for the LUMO, the electron density lies on the electron-withdrawing part. From the energy level diagram (Fig. 8), it can be seen that addition of the metal ions leads to the stabilization of the HOMO and LUMO of the fluorophores. The contour plots of the HOMO after the addition of metal ions shows that the electron density is over the electron-donating part of the fluorophore as in the case of free fluorophore. However, the electron density of the LUMO was situated over the metal ion, leading to the quenching of the fluorescence.

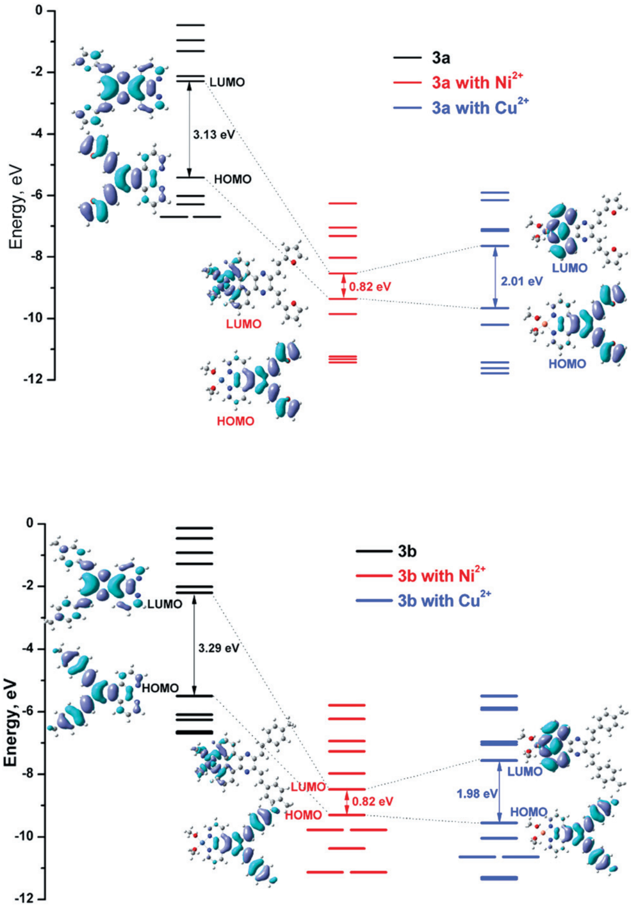

Fig. 8 Energy levels of various HOMO and LUMO's of **3a** (top) and **3b** (bottom) in the absence and the presence of Cu^{2+} and Ni^{2+} ions. Contour plots of the HOMO and LUMO are shown (isosurface cut-off value: 0.02).

In conclusion, we have reported two fluorophores which are prepared *via* condensation without involving tedious procedures. Both compounds involve only slight structural modification in the fluorogenic site and both of them specifically recognize Ni^{2+} and Cu^{2+}.

Notes and references

† **Synthesis of 3a (2,3-bis((*E*)-2-(furan-2-yl)vinyl)pyrazino[2,3-*f*]-[1,10]phenanthroline)**: To a methanolic solution of phendiamine (210 mg, 1 mmol), 1,6-di(furan-2-yl) hexa-1,5-diene-3,4-dione (242 mg, 1 mmol) in chloroform–methanol was added and refluxed for 5 hours. The completion of the reaction was monitored through thin layer chromatography. The solvent was removed in a rotary evaporator and the residue was purified through alumina gel chromatography using methanol–chloroform as the eluent (Yield = 72%). ^{1}H NMR (500 MHz, CD$_3$OD) δ (ppm) = 8.34 (d, J = 7.3 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.36 (d, J = 7.05 Hz, 2H), 6.84 (t, J = 7.5 Hz, 2H), 6.38 (d, J = 7.05 Hz, 2H), 6.25 (d, J = 14.9 Hz, 2H), 6.15 (t, J = 4.8 Hz, 2H), 5.84 (d, J = 14.9 Hz, 2H). MS (ESI) m/z = 417 [M$^+$].

Synthesis of 3b (2,3-bis(4-methylstyryl)pyrazino[2,3-*f*][1,10]phenanthroline): To a methanolic solution of phendiamine (210 mg, 1 mmol), 1,6-bis(4-methylphenyl)hexa-1,5-diene-3,4-dione (290 mg, 1 mmol) in chloroform–methanol was added and refluxed for 5 hours. The completion of the reaction was monitored through thin layer chromatography. The solvent was removed in a rotary evaporator and the residue was purified through alumina gel chromatography using methanol–chloroform as the eluent (Yield = 78%). ^{1}H NMR (500 MHz, CD$_3$OD) δ (ppm) = 7.59 (d, J = 8.6 Hz, 2H), 6.84 (t, J = 8.55 Hz, 2H), 6.78 (d, J = 8.05 Hz, 4H), 6.64 (d, J = 8.55 Hz, 2H), 6.59 (d, J = 8.05 Hz, 4H), 6.43 (d, J = 14.9 Hz, 2H), 6.0 (d, J = 14.9 Hz, 2H), 1.24 (s, 3H). MS (ESI) m/z = 465 [M$^+$].

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