



Visible Colourimetric and Ratiometric Fluorescent Chemosensors for Cu(II) and Ni(II) Ions

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New fluorescent and colourimetric chemosensors based on copper(II) and nickel(II) coordination of *bis*-O,O-bidentate Schiff base ligands are reported. Its high selectivity towards the complexation with copper(II) and nickel(II) over other metals were demonstrated by UV, fluorescence, colour change in visible range and ^1H NMR spectra.

Keywords: Schiff base, Metal ions, Complexation, UV, Fluorescence, Chemosensor.

INTRODUCTION

Fluorescent and ratiometric sensors for the detection and measurement of copper and nickel ions has been actively investigated, as these metal ions are significant environmental pollutant and are essential trace element in biological system [1]. A colourimetric and ratiometric fluorescent chemosensor combines the sensitivity of fluorescence with the convenience and aesthetic appeal of a colourimetric assay [2]. Colour changes, as signaling an event detected by the naked eye, are widely used owing to the low cost or lack of equipment required. A number of chemosensors for metal ions have been reported to be capable of correlating metal ions concentration with changes in spectroscopic characteristics [3]. Many of these chemosensors are based on the interactions of metal ion with the π -electron system of a chromophore or fluorophore in the host-guest chemistry, resulting upon complexation.

Although many interesting results have been reported in recent years regarding colourimetric and ratiometric fluorescent chemosensors for Cu(II) and Ni(II) [4], there are still abundant aspects that need to be conveniently addressed in this field. Especially reports of highly selective chemosensor for target metal ions are still limited. The perceived colour change is useful not only for the ratiometric method of detection but also for rapid visual sensing.

Method for the construction of copper(II) coordinated supra molecular architectures of *bis*-N,O-bidentate Schiff base ligands has also been reported earlier [5-7].

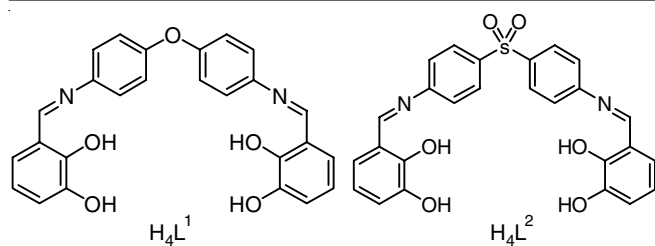
It is reported that *bis*-3-hydroxy derivatives of Salen can bind *d*- and *f*-metal ions to their inner N_2O_2 and outer O_4 sites, respectively. It was also reported that some of these hexadentate Schiff bases can simultaneously coordinate *d*-ions in both

compartments [8-10]. Ligands derived from 3-hydroxysalicylaldehyde and several simple diamines have been used to prepare some N_2O_2 mononuclear and $\text{N}_2\text{O}_2 + \text{O}_4$ binuclear complexes. The latter mostly contain Cu(II), Ni(II) or Fe(III) in the inner chamber and Mn(II), Co(II) or Fe(III) in outer compartment. A few binuclear complexes of Cu(II) and Zn(II) are with Zn ion coordinated in the outer O_4 compartment [11].

In this paper, we have reported that, Cu(II) and Ni(II) can also coordinate in the outer O_4 compartment without forming any binuclear complexes. Our system can act as fluorescent chemosensor as it is able to bind metal in organic medium and change its emission in ratiometric fashion. This system displays dual emission, which makes it 'internally calibrated' for the study of the association with metal by means of steady state fluorescence spectroscopy. Schiff bases "Salen" coordinates metal ions through imine nitrogen and phenolic oxygen atoms. But our Schiff bases, H_4L^1 and H_4L^2 , contain two oxygen and one nitrogen donor in each half of the molecule for bonding, so there will be a competition between these two sites. The disappearance of two peaks for two -OH groups in proton NMR spectra of the ligands after the addition of metal ions proves that -OH groups are taking part in binding.

EXPERIMENTAL

The Schiff bases H_4L^1 and H_4L^2 were synthesized by the usual condensation of *bis*-(4-aminophenyl) ether and *bis*-(4-aminophenyl) sulphone (0.5 mol) with 2,3-dihydroxy benzaldehyde (1 mol) in methanol. Red (H_4L^1) and yellow (H_4L^2) coloured solid precipitate obtained were collected by filtration. Here we have shown that these two ligand can bind Cu(II) and Ni(II) ions in bidentate fashion to each metal ions showing change in colour in the visible range.



Colour change from yellow to deep green and yellow to red was observed when Cu(II) and Ni(II) ion solutions were added to H_4L^1 respectively. Similarly the change from pale yellow to green and pale yellow to orange were observed when Cu(II) and Ni(II) ion were added to H_4L^2 in acetonitrile solution. Addition of other metal ions such as Li(I), Na(I), K(I), Mg(II), Ca(II), Fe(III), Cd(II), Ag(I) and Pb(II) produced insignificant changes in both absorption and fluorescent spectra of both H_4L^1 and H_4L^2 . This means that H_4L^1 and H_4L^2 have an outstandingly high selectivity for Cu(II) and Ni(II). So H_4L^1 and H_4L^2 could be contemplated as “naked eye” chemosensor for Cu(II) and Ni(II) ion.

Bis[4-[(2,3-dihydroxy)methylideneamino]phenyl]ether (H_4L^1): Bis-(4-aminophenyl)ether (1 g, 2.27 mmol) was added gradually to a methanol (100 mL) solution of 2,3-dihydroxy benzaldehyde (0.63 g, 4.54 mmol) and the solution was stirred for 0.5 h. The red shining precipitate was collected by filtration. m.p. 175 °C; IR (KBr, $\nu_{\max}$, cm^{-1}): 3430, 1623, 1463, 1360, 1270, 1231; ^1H NMR (200 MHz, CDCl_3): 13.18 (2H, br s), 9.21 (2H, s), 8.93 (2H, s), 7.5 (4H, d, $J = 8.8$), 7.06–7.16 (6H, m), 6.91–7.0 (2H, m), 6.78–6.81 (2H, m); Mass (ES^+): m/z 441 ($M^+ + 1$); Elemental analysis calcd. for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_5$: C 70.90, H 4.54, N 6.36 %, found C 70.54, H 4.75, N 6.25 %.

Bis[4-[(2,3-dihydroxy)methylideneamino]phenyl]sulfone (H_4L^2): Bis-(4-aminophenyl)sulfone (1 g, 2.04 mmol) was added gradually to a methanol (100 mL) solution of 2,3-dihydroxy benzaldehyde (0.13 g, 4.09 mmol) and the solution was stirred for 1 h at 50 °C and the yellow precipitate was collected by filtration. m.p. 251 °C; IR (KBr, $\nu_{\max}$, cm^{-1}): 3434, 1620, 1570, 1460; ^1H NMR (200 MHz, $\text{DMSO}-d_6$): 10.69 (2H, br s), 9.96 (2H, s), 8.37 (2H, s), 7.16–7.71 (6H, m), 6.98–7.05 (6H, m), 6.81 (t, 2H, $J = 7.5$); Mass (ES^+): m/z 489 ($M^+ + 1$); Elemental analysis calcd. for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_6\text{S}$: C 63.93, H 4.13, N 5.73 %, found C 63.88, H 4.23, N 5.55 %.

Cu(II) complex of H_4L^1 : Aqueous solution (50 mL) of Cu(II) acetate hydrate (0.34 g, 1.7 mmol) was added to the acetonitrile solution (50 mL) of H_4L^1 (0.37 g, 0.85 mmol) in 2:1 molar ratio, stirred for 0.5 h at room temperature. After that a brown coloured precipitate was formed and collected by filtration and washed thoroughly with water to remove excess Cu(II) acetate. IR (KBr, $\nu_{\max}$, cm^{-1}): 1620, 1570, 1460; ^1H NMR (200 MHz, CDCl_3): 8.93 (2H, s), 7.49 (4H, d, $J = 8.2$), 7.06–7.15 (4H, m), 6.90–6.99 (4H, m), 6.78–6.90 (2H, m); Mass (ES^+): m/z 437.19, 564.44, 565.31 (M^+); Elemental analysis calcd. for $\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_5\text{Cu}_2 \cdot 4\text{H}_2\text{O}$: C 49.13, H 3.78, N 4.40 %, found C 49.02, H 3.69, N 4.54 %.

Ni(II) complex of H_4L^2 : Aqueous solution (50 mL) of Ni(II) acetate hydrate (0.34 g, 1.8 mmol) was added to the acetonitrile solution (50 mL) of H_4L^1 (0.44 g, 0.9 mmol) in

2:1 molar ratio, stirred for 0.5 h at room temperature. After that a reddish brown coloured precipitate was formed and collected by filtration and washed thoroughly with water to remove excess Ni(II) acetate. IR (KBr, $\nu_{\max}$, cm^{-1}): 1625, 1575, 1460 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3): δ 9.60 (s, 2H), 6.15–7.01 (m, 7H), 7.21–8.01 (m, 7H); Mass (MALDI): m/z 624 ($M^+ + \text{Na}$); Elemental analysis calcd. for $\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_6\text{SNi}_2 \cdot 8\text{H}_2\text{O}$: C 41.86, H 4.29, N 3.75 %, found C 41.69, H 4.11, N 3.81 %.

RESULTS AND DISCUSSION

Upon addition of Cu(II) acetate solution to the H_4L^1 solution, the ligand π - π^* band at 339 nm decreases and a new band at 427 nm (Fig. 1a) due to bond-pair coordination of oxygen lone pair with Cu(II), which induces a colour change from yellow to green due to d - d transition. A mole ratio plot using the change in absorbance at 343 and 422 nm clearly demonstrated the formation of 1:2 complex (Fig. 2a). Addition of Ni(II) ion to the H_4L^1 solution the ligand π - π^* band at 346 nm decreases and a new band at 409 nm (Fig. 1b) due to the same reason, induce a colour change from yellow to red. A mole ratio plot using the change in absorbance at 340 and 408 nm clearly demonstrated the formation of 1:2 complex (Fig. 2b).

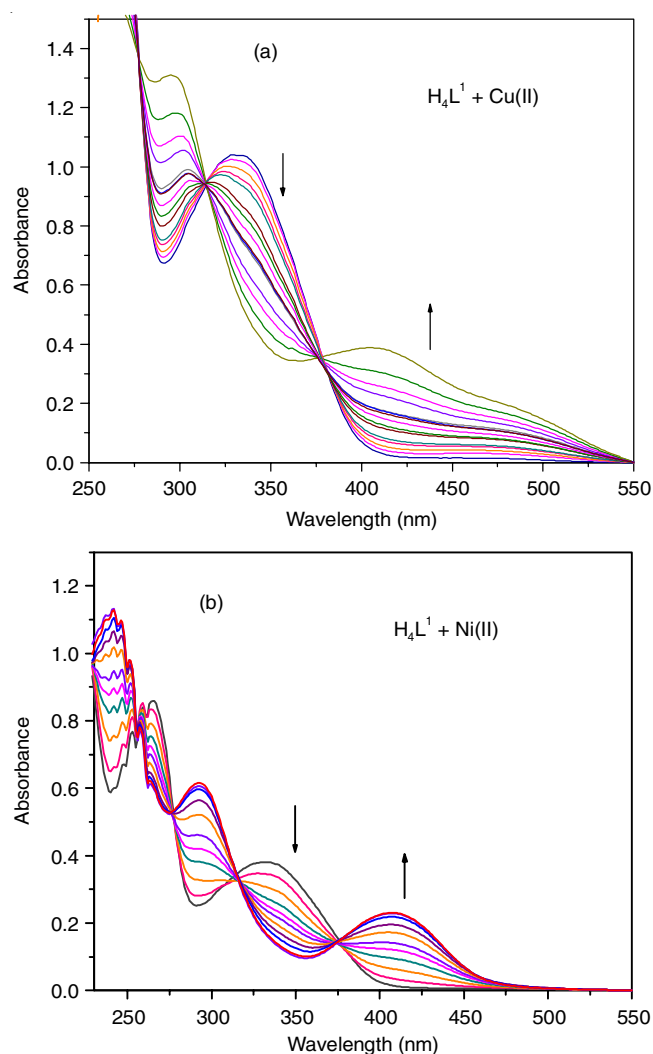


Fig. 1. Uncorrected UV absorption spectra of H_4L^1 (1.5×10^{-4}) in acetonitrile solution in the presence of Cu(II) and Ni(II) at concentration ranging from 0–50 μM . a) H_4L^1 with Cu(II), b) H_4L^1 with Ni(II)

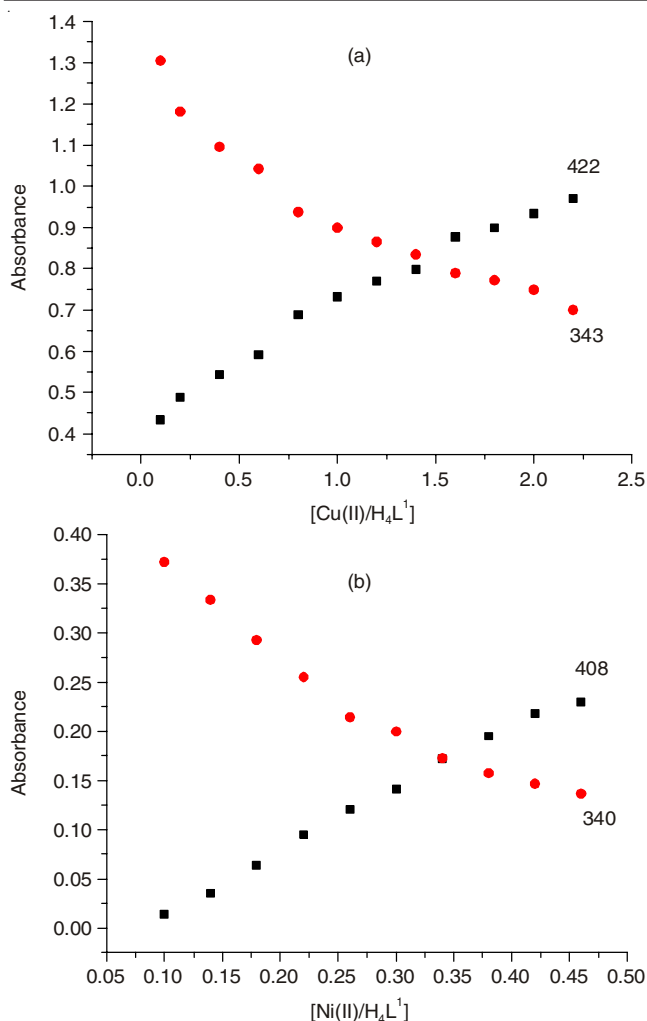


Fig. 2. (a) Molar ratio plot of H_4L^1 and Cu(II) using the change in absorbance at 340 and 408 nm, clearly demonstrate the formation of the Cu(II): H_4L^1 = 2:1 molar ratio as judged by observing the clear inflection point at $[Cu(II)/H_4L^1] = 2$; (b) Molar ratio plot of H_4L^1 and Ni(II) using the change in absorbance at 340 and 408 nm, clearly demonstrate the formation of the Ni(II): H_4L^1 = 2:1 molar ratio as judged by observing the clear inflection point at $[Ni(II)/H_4L^1] = 2$

Upon addition of Cu(II) acetate solution to the H_4L^2 solution, the ligand $\pi-\pi^*$ band at 342 nm decreases and a new band at 422 nm due to bond-pair coordination of oxygen with Cu(II), inducing a colour change from pale yellow to green (Fig. 3a). Upon addition of Ni(II) ion to the H_4L^2 solution, the ligand $\pi-\pi^*$ band at 339 nm decreases and a new band at 413 nm due to the same reason (Fig. 3b).

So proposed mode of complexation of H_4L^1 and H_4L^2 with Cu(II) and Ni(II) is as follows (Fig. 4). This is also supported by both mass spectroscopy and CHN analysis.

The fluorescence of H_4L^1 and H_4L^2 were recorded in freshly distilled acetonitrile as solvent. The addition of Cu(II) solution to the H_4L^1 shows decrease in intensity at 393 nm (Fig. 5a) after addition of 1 equiv of Cu(II). As expected, when more than 1 equiv of Cu(II) was added a red-shifted fluorescence emission band was found centered at 286 nm. Similarly on addition of Ni(II) solution there was a decrease in fluorescence intensity at 394 nm and an increase at 287 nm (Fig. 5b). Same phenomenon was repeated in case of H_4L^2 when Cu^{2+} and Ni^{2+} added individually to it (Fig. 5c and 5d).

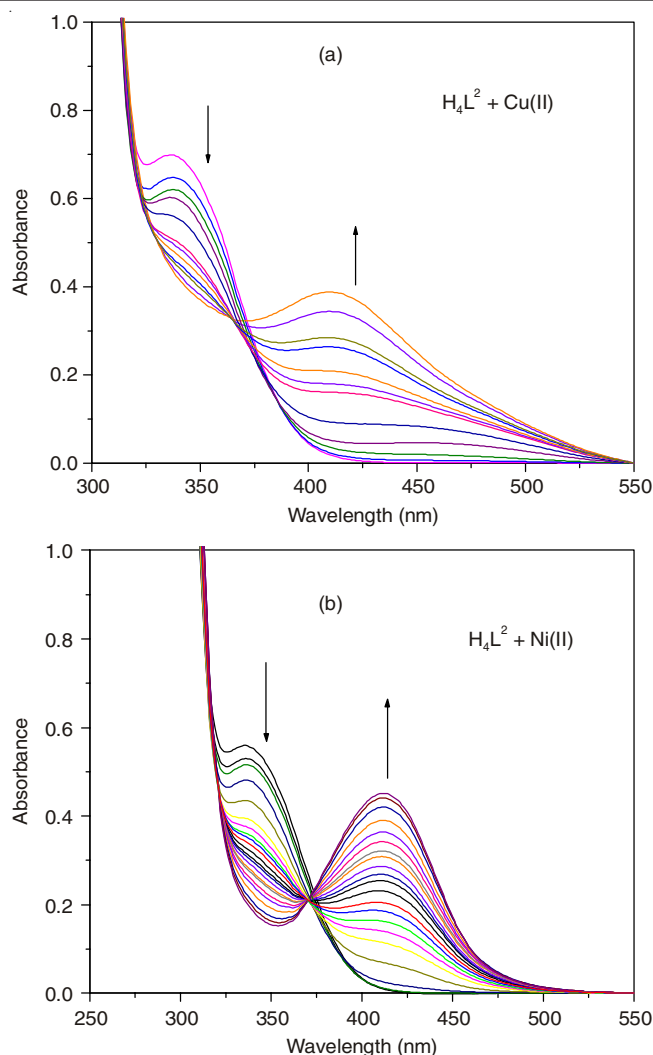


Fig. 3. Uncorrected UV absorption spectra of H_4L^1 (1.5×10^{-4}) in acetonitrile solution in the presence of Cu(II) and Ni(II) at concentration ranging from 0-50 μM ; (a) H_4L^2 with Cu(II), (b) H_4L^2 with Ni(II)

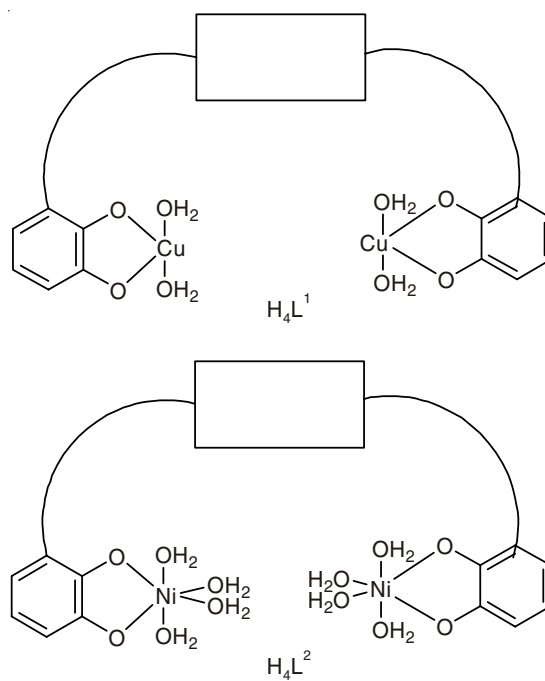


Fig. 4

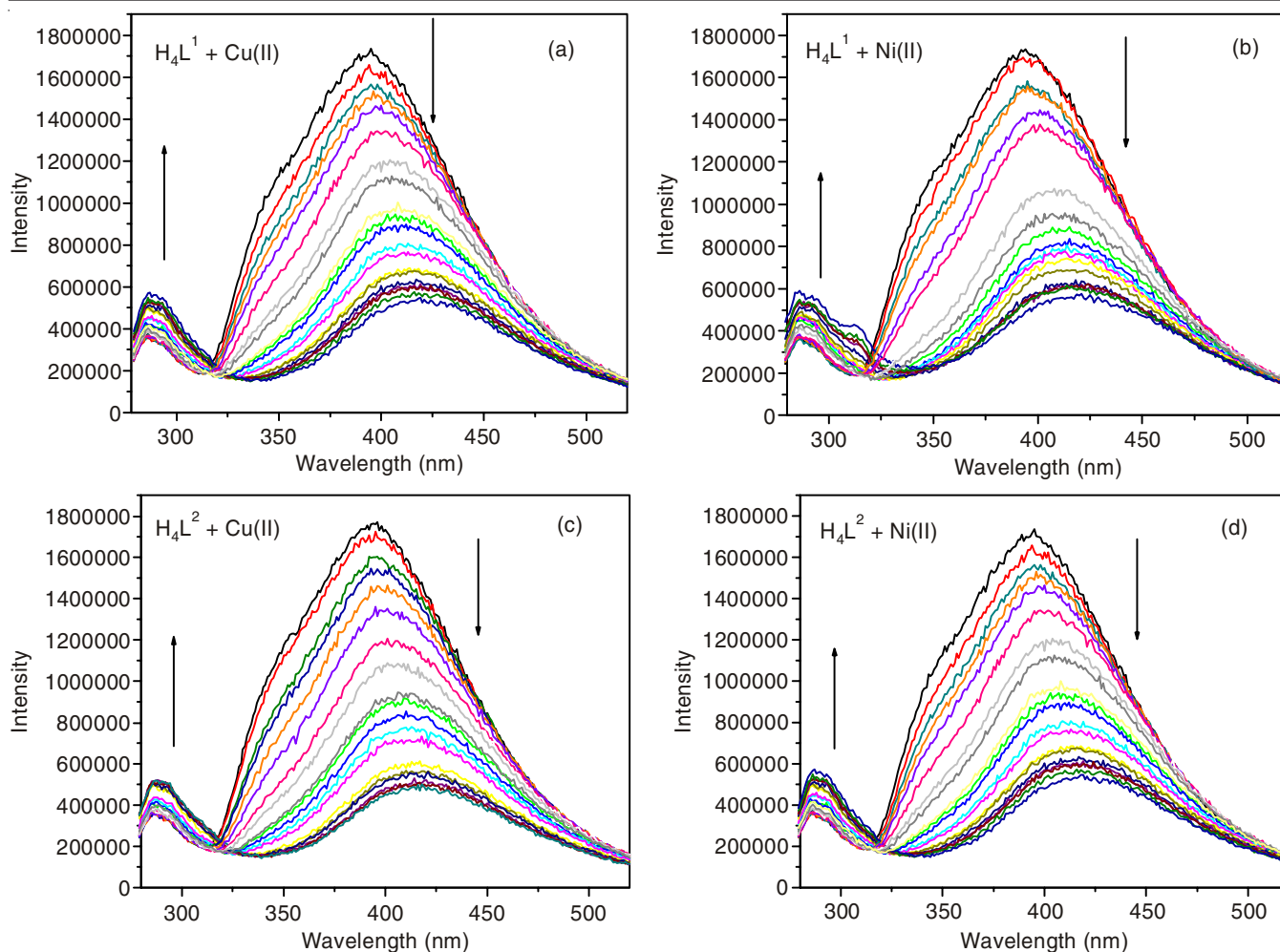


Fig. 5. Uncorrected emission spectra of H_4L^1 and H_4L^1 (1.5×10^{-4} M) in acetonitrile in the presence of Cu(II) and Ni(II) solutions at concentration ranging from 0–50 μ M. Excitation wavelength: 250 nm. (a) H_4L^1 with Cu(II), (b) H_4L^1 with Ni(II), (c) H_4L^2 with Cu(II), (d) H_4L^2 with Ni(II)

Conclusion

A new colourimetric chemosensors for Cu(II) and Ni(II) ions are developed, which give rise to large changes in UV, fluorescence and show change in colour in the visible range, providing a great advantage for the detection of those metal ions. The solution colour change and the change in fluorescence spectra attributed to the deprotonation of phenolic -OH conjugated to the imine attached to the phenyl ring. The design strategy and characteristics physical properties of those probes would help to extend the development of fluorescent and colourimetric probes for metal ions.

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