Single molecular colorimetric probe for simultaneous estimation of Cu^{2+} and Ni^{2+}†

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The different optical responses in chromogenic sensor 2 stimulated by addition of Cu^{2+} (red to blue) and Ni^{2+} (red to green) allow simultaneous estimation of Cu^{2+} and Ni^{2+}.

The area of molecular optical sensors has been developed to a significant maturity where receptors with good degree of selectivity towards target analyte can be designed and synthesized.[1] However, the concept of single molecular sensor for multiple analytes makes the situation complicated for simultaneous quantitative analysis of more than one analytes.[2] More recently, the paradigm shift from selective to differential receptors has provided opportunities for single molecular based simultaneous estimation of several similar analytes by single detection method[3] or alternatively by using an array of detection methods.[4] The availability of mathematical analysis systems[5] such as PCA, PLS, ANNs *etc.* has further facilitated the direct multiple estimations.

However, the differential response of analytes at different wavelengths eases out the situation where two different wavelengths (absorption/emission) allow the multiple estimations without much requirement of complicated mathematical systems. Here, each chemical input is recognised within a single molecule, forming ideally distinct chemical state with corresponding characteristic signals.

As a part of our study on developing molecular sensing switches,[6,7] we now demonstrate an 1-aminoanthracene-9,10-dione based chromogenic sensor **2** (red, λ_{max} 500 nm) that allows the sensing of multiple analytes with differently red-shifted spectral responses and characteristic colour changes only on addition of Cu^{2+} (blue, λ_{max} 600 nm) and Ni^{2+} (green, λ_{max} 750 nm) (Fig. 1), whereas other metal ions do not affect the absorbance spectra of receptor **2** and its complexes with Ni^{2+} and Cu^{2+}.

1-(2-Aminoethylamino)anthracene-9,10-dione (**1**)[8] on stirring with salicylaldehyde in ethanol resulted in the formation of the diamine-salicylaldehyde based Schiff base **2** (ethanol), (Scheme 1) (Expt 1a, ESI†).

The chemosensing properties are in general highly dependent on the pH of the system. Therefore, the influence of pH on both the receptor **2** and its complexes with Cu^{2+} and Ni^{2+} was evaluated in DMSO : H_2O (1 : 1, v/v). The absorbance of **2** at λ_{max} 500 nm remained by and large unaffected between pH 2–12 (Figures S1–S3†). Significantly, on lowering the pH from 12, the absorption band at λ_{max} 385 nm gradually decreased till pH 7.0 and on further lowering the pH, no change in spectrum was observed. This change in absorbance at λ_{max} 385 nm did not lead to any visible colour change in **2**. The decrease in absorbance at 385 nm between pH 12.0–7.0 points to protonation of the phenoxide ion to phenol, and on further lowering of the pH protonation at the imine nitrogen and anthraquineone oxygen takes place. The $\log\beta_{LH}$, $\log\beta_{LH2}$ and $\log\beta_{LH3}$ respectively are 9.98, 18.82 and 24.24.

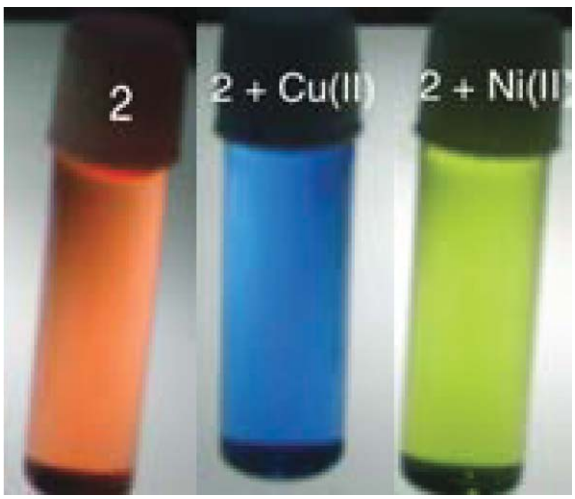
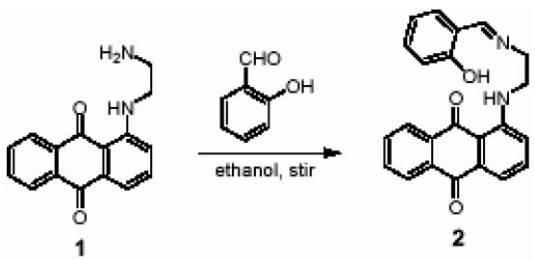


Fig. 1 Visual features observed in CH_3OH : H_2O (4 : 1, pH 7.0) solutions of **2** and their metal solutions.



Scheme 1

Figs. 2a and 2b show the absorbance spectra of receptor **2** under physiological conditions (50 μM; pH 7.0 ± 0.1; 10 mM HEPES; CH_3OH : H_2O, 4 : 1) for different Cu^{2+} and Ni^{2+} concentrations. On addition of Cu^{2+}, receptor **2** shows ~100 nm red shift from λ_{max} 500 nm to 600 nm which induces a colour change from red to blue. However, on addition of Ni^{2+}, a red shift ~250 nm from

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† Electronic supplementary information (ESI) available: The procedure for synthesis of and spectral data for **2** and the **2**–Ni^{2+} complex, selected absorption plots, species distribution plots showing the formation of different species and logβ values for the formation of these species are given. See DOI: 10.1039/b703529b

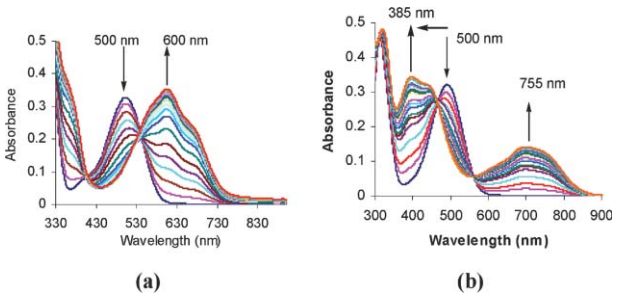

Fig. 2 Absorbance spectra of receptor **2** (50 μM) on addition of different concentrations of (a) Cu^{2+} and (b) Ni^{2+}.

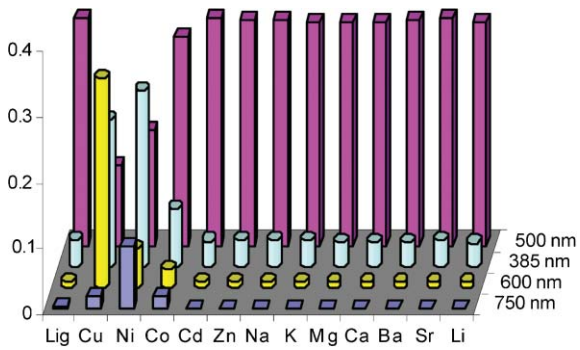

Fig. 3 Spectrophotometric responses of receptor **2** (50 μM) to selected metal ions (50 μM).

λ_{max} 500 nm to 750 nm with concomitant appearance of a new band at 385 nm is observed. This caused the colour change from red to green (Fig. 1). The plot of absorbances at λ_{max} 500 nm (due to **2**), λ_{max} 600 nm (due to the **2**–Cu^{2+} complex) and λ_{max} 750 nm (due to the **2**–Ni^{2+} complex) *vs.* conc. of Cu^{2+} and Ni^{2+} allows the estimation of individual Cu^{2+} and Ni^{2+} concentrations (Figures S4–S5†). Significantly, the dependence of absorption ratios of **2** on addition of metal ions shows that disturbance in the absorption spectrum of **2** is insignificant due to the other metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}*etc* (Fig. 3) except in cases of Cu^{2+} and Ni^{2+}.

The combination of pH and UV-vis titration of 1 : 1 solution of **2** and Cu^{2+} suggests deprotonation of the aryl amine NH and shows the formation of $MLH_{-1}(OH^-)$, MLH_{-1} and MLH with logβ values of −3.49, 5.86 and 18.98 respectively (Figure S6†). Similarly, a 1 : 1 mixture of **2**–Ni^{2+} solution on pH titration shows the formation of only MLH_{-1} and $MLH_{-1}(OH^-)$ and points to the formation of neutral complex of **2** with Ni^{2+} (Figure S7†). The formation of this neutral complex is also supported by ^1H, ^{13}C NMR, FAB Mass spectral data and elemental analysis of **2**–Ni^{2+} complex (Expt. 1b, ESI†).

The similar association constants (Table 1, ESI†) of **2** with Cu^{2+} and Ni^{2+} and different absorbance domains of **2**–M^{2+} complexes provide opportunities for simultaneous observation of their effects in absorbance spectra obtained by addition of varied mixtures of Cu^{2+} and Ni^{2+} to solution of **2** (50 μM; pH 7.0 ± 0.1; 10 mM HEPES; MeOH : H_2O, 4 : 1) (Figure S8†). The calculations of concentrations Ni^{2+} and Cu^{2+} are based on the only absorbance due to Ni^{2+} in 740–790 nm region and its equal additive effects in 620–650 nm, the region used for measurement of Cu^{2+}. The

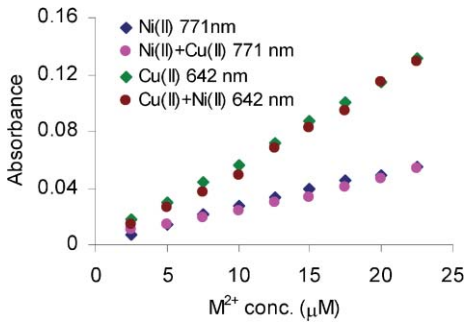

Fig. 4 Calibration curve of Cu^{2+} and $Ni^{2+}$and determination of Cu^{2+} and Ni^{2+} from Ni^{2+} and Cu^{2+} mixtures.

absorbance at 770 nm for Ni^{2+} and 642 nm for Cu^{2+} estimation has been chosen (the contribution of absorbance due to Ni^{2+} at 642 nm is equal to the one at 770 nm). The absorbance at 770 nm is directly proportional to the concentration of Ni^{2+}. The absorbance A_{Cu2+} 642 nm is calculated by subtraction of Ni^{2+} contribution using equation A_{Cu2+} 642 nm = A_o642 nm − A_o770 nm. Here, A_o642 nm and A_o770 nm denote the observed absorbances at corresponding wavelengths.

These calculations show that absorbances arising due to the presence of 2–25 μM Cu^{2+} and Ni^{2+} can be measured accurately from their mixtures within ±5% error (Fig. 4) with the limiting condition that total metal ion concentration should not be more than 25 μM.

Therefore, the different optical responses in sensor **2** towards Cu^{2+} and Ni^{2+} allow their simultaneous estimation from their mixtures.

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