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A differential receptor for selective and quantitative multi-ion analysis for Co^{2+} and Ni^{2+}/Cu^{2+}

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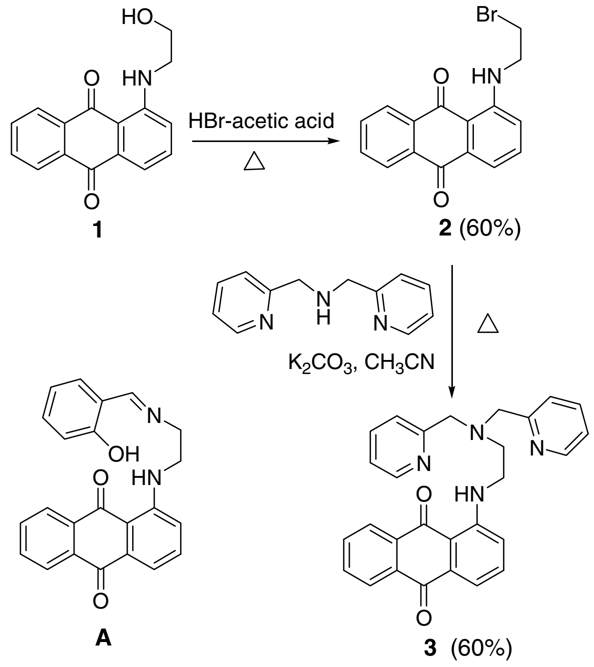
ABSTRACT

The differential mode of complexation of chromogenic sensor **3** with Co^{2+} versus Ni^{2+} (or Cu^{2+}) at pH 4.0 in water leads to new absorption bands at λ_{max} 620 nm in the case of Co^{2+}, at λ_{max} 380 and 460 nm for Ni^{2+} and at λ_{max} 460 nm for Cu^{2+}. These differential responses allow sensor **3** to be used for the selective and quantitative estimation of Co^{2+} and Ni^{2+} or Co^{2+} and Cu^{2+} from their mixtures.

Highly selective cation or anion sensing is important in many areas of technology, including environmental, biological, clinical and waste management applications.[1] Various concepts in metal ion sensing have been installed to enhance sensitivity, selectivity and the dynamic working range.[1,2] However, equipping the chromophores with more than one chemically addressable group still poses a major challenge. Such dual-responsive chromophores can find applications as 'molecular logic gates' and ion-pair indicators, in co-operative recognition of two different analytes or for the analysis of a single analyte with enhanced sensitivity and selectivity due to co-operative forces.[3]

More recently, the paradigm shift from selective to differential receptors has provided opportunities for single molecular-based simultaneous estimation of more than one analyte by single detection method,[4] or alternatively, by using an array of detection methods.[5] The availability of mathematical analysis systems[6] such as PCA (Principal component analysis), HCT (hierarchical cluster theory) and ANNs (Artificial neural network) has further facilitated the direct multiple estimations.

Recently,[4a] we have reported that differential complexation of chemosensor **A** (Scheme 1) with two distinctly ionisable (OH and NH) groups leads to two different bathochromic shifted absorption bands (also associated with different colours) on addition of Cu^{2+} or Ni^{2+}. This enabled simultaneous estimation of Cu^{2+} and Ni^{2+} from their mixtures.



Scheme 1.

In continuation of our work,[4a,7] we have designed a new anthracene-9,10-dione based chromogenic sensor **3** (red, λ_{max} 510 nm) which possesses three amine nitrogens with distinctly different pK_a values, that is, alkyl amine pK_a 8.4; pyridyl amine pK_a 4.4 and aryl amine pK_a <2.5, MeOH–H_2O (4:1) (Supplementary data, Fig. S1). Due to pH dependent availability of various amine nitrogens for coordination with metal ions, the chemosensor **3** shows pH dependent colour changes with selected metal ions. Chemosensor **3** at pH 4.0 (sodium acetate–acetic acid buffer) undergoes characteristic colour changes only on addition of Co^{2+} (blue, λ_{max} 620 nm), Ni^{2+} (yellowish pink, λ_{max} 380, 460 and 510 nm) and Cu^{2+} (yellow, λ_{max} 460 nm) (Fig. 1), whereas other metal ions do not affect the absorbance spectrum of **3**. This situation allows both

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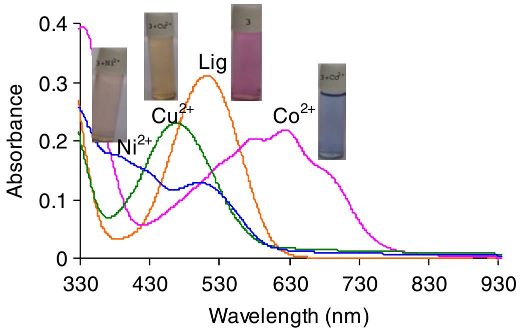

Figure 1. Differently shifted spectral responses and visual colour changes of sensor **3** on addition of Co^{2+}, Cu^{2+} and Ni^{2+}.

qualitative (naked eye colour change) and quantitative (spectrophotometer) analysis of two analytes, that is, Co^{2+} and Cu^{2+} or Co^{2+} and Ni^{2+} from their mixtures. Unlike conventional array-based systems,[5] the present approach involves direct correlation of absorbances at designated wavelengths with respect to the concentration of metal ions. This constitutes the first example of a single molecular multianalyte optical sensor for simultaneous analysis of Co^{2+} and Cu^{2+}/Ni^{2+} in water.

1-(2-Hydroxyethylamino)-anthracene-9,10-dione (**1**) on bromination with HBr-acetic acid (33%) gave **2** (60%) as a red solid, mp 155 °C, M^+ *m/z* 329, 331 (1:1). Nucleophilic substitution of **2** with di-(2-picolyl)amine gave **3** (60%) as a red solid, mp 135 °C, M^+ *m/z* 448 (Scheme 1).[8]

A solution of **3** (50 μM) (CH_3OH–H_2O 4:1, 10 mM HEPES, pH 7.0 ± 0.1), on addition of solutions of Co^{2+}, Ni^{2+} and Cu^{2+}, showed a visible colour change from red to blue and their UV–vis spectra exhibited differently red shifted absorption bands (Supplementary data, Figs. S2–S4). The addition of other metal ions K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+}, Ag^+, Pb^{2+}, etc., even at 0.01 M concentrations caused negligible responses to the absorbance of sensor **3**. The combination of pH and UV–vis titrations of 1:1 solutions of **3** with Co^{2+}, Ni^{2+}, Cu^{2+} could rationalise a diagnostic pattern for their simultaneous estimation. A 1:1 solution of **3** and Co^{2+} (methanol–water: 4:1) on moving from pH 12 to 2 remained blue in colour and showed only small changes in absorbance and λ_{max} values in this pH range (Supplementary data, Fig. S5). The 1:1 solutions of **3** with Cu^{2+} and Ni^{2+} remained blue between pH 12 and 6, but on further lowering the pH, the blue colour slowly faded with the appearance of a yellow/pinkish-yellow colour at pH 4 which persisted even at pH 2 (Supplementary data, Figs. S6 and S7). These results clearly pointed to the differential colour changes of **3** with Co^{2+}, Ni^{2+} and Cu^{2+} at pH $\leqslant 4$.

A solution of **3** (50 μM) in sodium acetate–acetic acid buffer (pH 4.0) on addition of Co^{2+}, Ni^{2+} and Cu^{2+} gave respective blue (λ_{max} 620 nm), yellowish pink (λ_{max} 380, 460 and 510 nm) and yellow (λ_{max} 460 nm) colours (Fig. 2) (Supplementary data, Fig. S8). The spectral fitting of the titration data of **3** against Co^{2+}, Ni^{2+} and Cu^{2+} shows the formation of 1:1 (**3**–M^{2+}) complexes with $\log \beta$ values of 6.75 ± 0.35, 5.86 ± 0.35 and 7.10 ± 0.72. The linear increase in absorbances between 5 and 50 μM metal ion concentrations allows their individual quantitative estimations. Significantly, the addition of other metal ions, viz. K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+}, Ag^+ and Pb^{2+} (0.01 M) to a solution of **3** (at pH 4.0) causes insignificant changes in the absorbance spectrum of **3** (Supplementary data, Fig. S9).

Therefore, at pH 4, in titrations of **3** with Co^{2+}, Ni^{2+} and Cu^{2+}, the appearance of a new absorption at 580–700 nm in the case of Co^{2+} and the lack of any absorbance due to Ni^{2+} and Cu^{2+} complexes in this region enables the estimation of Co^{2+} (~620 nm). Further, the appearance of an isosbestic point at 416 nm in the case of the titration of **3** with Co^{2+} and the increase in absorbance at 416 nm in the case of titrations with Cu^{2+} and Ni^{2+} enables the estimation of Cu^{2+} and Ni^{2+} (at 416 nm) in the presence of Co^{2+}.

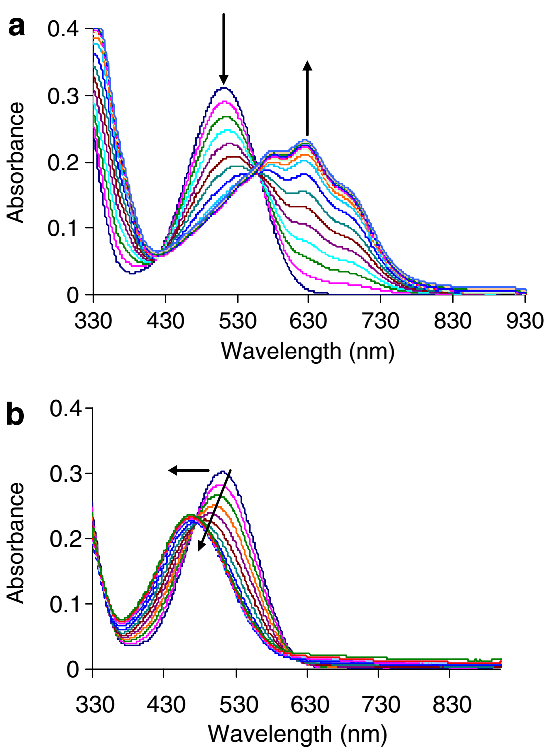

Figure 2. Responses of the absorption spectra of **3** (50 μM) (H_2O, acetic acid–sodium acetate, pH 4.0 ± 0.1) towards 2.5 μM incremental addition of (a) Co^{2+} and (b) Cu^{2+}.

The absorbance spectra of a solution of **3** and various mixtures of Co^{2+} and Ni^{2+} or Co^{2+} and Cu^{2+} show well-defined changes at λ_{max} 620 nm and at 416 nm arising, respectively, due to Co^{2+} and Ni^{2+}/Cu^{2+} (Supplementary data, Fig. S10).

The plots of concentration of Co^{2+}, Ni^{2+} and Cu^{2+} from their individual solutions and their comparison with those from mixtures of Co^{2+} and Ni^{2+} or Co^{2+} and Cu^{2+} show that absorbances arising due to the presence of 0.3×10^{-5} M–2.7×10^{-5} M Co^{2+} and Cu^{2+} or Co^{2+} and Ni^{2+} can be measured accurately from their mixtures within ±5% error (Fig. 3) (Supplementary data, Fig. S11) with the limiting condition that the total concentration of metal ions being analysed should not be more than 3.0×10^{-5} M.

The stimuli interaction induced blue[9] and red[9,10] shifts in a chromophore are marked with the respective decrease or increase in electron-donating abilities of the substituents participating in interactions and makes the basis for differential modes of complexation. At pH 7.0, the red shift in the case of Co^{2+}, Ni^{2+} and Cu^{2+} points to aryl NH deprotonation. However, under acidic conditions, that is, at pH 4.0, the blue shift in the case of Ni^{2+} and Cu^{2+} and red shift in Co^{2+} shows the differential mode of interaction of these metal ions towards sensor **3**. Here, aryl NH coordinates with Ni^{2+} and Cu^{2+} to cause hypsochromic shift, however, Co^{2+} coordination along with deprotonation results in increased electron-density and red shift of the spectral band. As single crystals of complexes of **3** with Co^{2+}, Ni^{2+}, Cu^{2+}, etc., could not be obtained, conclusive evidence in favour of mode of complexation cannot be given.

Thus, sensor **3** is the first example of a single molecular multianalyte optical sensor which can simultaneously analyse Co^{2+} and Cu^{2+}/Ni^{2+} in water (pH 4.0).

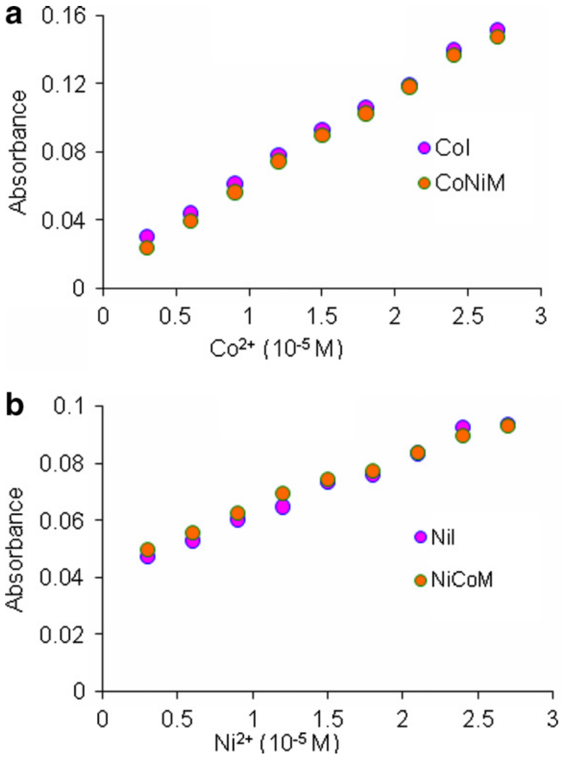

Figure 3. Comparison of the absorbance of **3** on addition of only Co^{2+} or Ni^{2+} with those of their mixtures, (a) Co^{2+} only and mixture of Co^{2+} and Ni^{2+}, (b) Ni^{2+} only and a mixture of Co^{2+} and Ni^{2+}.

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Supplementary data

Selected absorption plots for sensor **3**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.06.023.

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8. Compound **2**: (60%), red solid, mp 155 °C (CH_3CN); FAB mass M^+ m/z 329, 331 (1:1) (M^+); IR ν_{max} ($CHCl_3$) 1627, 1664 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$): δ 3.62 (t, J = 6.6 Hz, 2H, CH_2), 3.98 (q, J = 6.6 Hz, 2H, CH_2), 7.07 (d, J = 8.7 Hz, 1H, ArH), 7.56–7.67 (m, 2H, ArH), 7.72–7.83 (m, 2H, ArH), 8.23–8.32 (m, 2H, ArH), 9.99 (br s, 1H, NH); ^{13}C NMR (normal/DEPT-135) (75 MHz; $CDCl_3$): δ 42.3 (CH_2), 44.5 (CH_2), 113.7 (C), 116.3 (CH), 117.3 (CH), 126.7 (CH), 126.8 (CH), 132.9 (C), 133.2 (CH), 134.0 (CH), 134.8 (C), 134.8 (C), 135.4 (CH), 151.0 (C), 183.6 (C), 185.34 (C) (Found: C, 57.93; H, 3.98; N, 4.09. $C_{16}H_{12}BrNO_2$ requires C, 58.20; H, 3.66; N, 4.24.).
   Compound **3**: (60%); red solid; mp 135 °C (CH_2Cl_2); FAB mass M^+ m/z 448 (M^+); IR ν_{max} ($CHCl_3$) 1629, 1666, 3274, 3377 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$): δ 2.96 (t, J = 6.0 Hz, 2H, CH_2), 3.45 (q, J = 6.0 Hz, 2H, CH_2), 3.94 (s, 4H, 2 × CH_2), 6.94 (d, J = 8.7 Hz, 1H, ArH), 7.13 (t, J = 6.6 Hz, 2H, ArH), 7.47 (t, J = 7.5 Hz, 1H, ArH), 7.57 (d, J = 7.5 Hz, 1H, ArH), 7.64 (t, J = 7.5 Hz, 2H, ArH), 7.70–7.84 (m, 4H, ArH), 8.25 (d, J = 7.5 Hz, 1H, ArH), 8.36 (d, J = 7.5 Hz, 1H, ArH), 8.50 (d, J = 5.1 Hz, 2H, ArH), 9.95 (br s, 1H, NH, exchanges with D_2O); ^{13}C NMR (normal/DEPT-135) (75 MHz; $CDCl_3$): δ 40.4 (CH_2), 52.5 (CH_2), 60.6 (CH_2), 113.1 (C), 115.6 (CH), 118.0 (CH), 122.1 (CH), 123.4 (CH), 126.6 (CH), 126.7 (CH), 132.9 (CH), 133.0 (C), 133.9 (CH), 135.1 (CH), 136.6 (CH), 148.8 (CH), 151.3 (C), 159.0 (C), 183.9 (C), 184.6 (C) (Found: C, 74.76; H, 5.67; N, 12.65. $C_{28}H_{24}N_4O_2$ requires C, 74.98; H, 5.39; N, 12.49).
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