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Subodh Kumar[a]; Navneet Kaur[a]
[a] Department of Chemistry, Guru Nanak Dev University, Amritsar, India

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Nature of 1-(2-aminoethylamino)-anthracene-9, 10-diones - Cu(II) Interactions Responsible for Striking Colour Changes

SUBODH KUMAR* and NAVNEET KAUR

Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, India

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Chromogenic sensors 2 on addition of Cu(II) undergo deprotonation at aryl NH to give remarkable colour change from red (λ_{max} 492 nm) to blue (λ_{max} 600 nm). This selective NH deprotonation enables 2 for both naked eye and spectrophotometric determination of Cu(II) even in the presence of other metal ions.

The development of receptors which undergo colour change [1,2] on addition of an analyte – an anion [2–15], cation [16–25] or neutral molecule [26–31] have attained great significance due to their possible applications in the development of new methodologies for both their quantitative and qualitative estimations. In such receptors, bathochromic or hypsochromic shift of absorption spectra or visual colour change is affected by the respective increase or decrease in electron densities on the chromophore moiety arising due to its interaction with analyte.

In recent years, the anion induced polarization/deprotonation (in extreme cases) of OH in case of appropriately substituted phenols [32–35] and NH in case of appropriately substituted anilides and aryl ureas [36–41] has been conspicuously used for developing chromogenic anion sensors. In general, these investigations have been made in non-aqueous aprotic solvents and the presence of water adversely affects the anion induced colour change due to ease in protonation of the anionic form of chromophore which by and large exists in naked form.

In case of chromogenic sensors for metal ions, similar deprotonation of the phenolic chromophores has been quite generously used for developing alkali and alkaline earth metal ion sensors [42–46] but probably due to less acidic nature of NH, its deprotonation in the design of chromogenic metal ion sensors has been scarcely investigated [47]. Since, in case of metal ion sensors, the anion thus formed on deprotonation of NH is more stabilized by cation–anion electrostatic interactions than in case of anion sensors, it is expected to provide wider scope in developing metal ion sensors.

1-Aminoanthracene-9,10-dione based anion sensors due to facilitated NH deprotonation in the presence of additional electron-deficient centre are known to undergo colour changes on addition of anions [48–51] but their applications in development of cation sensors are not available. Now, we report that 1-aminoanthracene-9,10-dione based receptors **2** possessing appropriately placed electron-rich binding site, on addition of Cu(II) undergo distinct visual colour change from red to blue and bathochromic shift of λ_{max} from 492 nm to 600 nm. These colour changes are not affected by the presence of alkali, alkaline earth and other transition metal ions like Ni(II), Co(II), Cd(II), Zn(II) etc. The combination of pH and UV–Vis titrations of receptors **2** and their Cu(II) complexes conspicuously delineate the NH deprotonation of 1-aminoanthraquinone moiety responsible for these colour changes.

The receptors **2** have been synthesized [52] (Scheme 1) by nucleophilic substitution of 1-chloroanthracene-9,10-diones (**1**) with excess of respective diamine in acetonitrile in the presence of K_2CO_3 (base).

The affinity of receptors **2** for a series of transition metal ions, alkali and alkaline earth metal ions has been investigated at pH 7.0 ± 0.1 (10 mM HEPES in CH_3OH:H_2O 1:1). The solutions of receptors **2** (100 μM) on addition of Cu(II) (100 μM) show a remarkable colour change from red (λ_{max} 492 nm) to blue (λ_{max} 600 nm).The addition of other metal ions does not show any visible colour change even with

*Corresponding author. E-mail: subodh_gndu@yahoo.co.in

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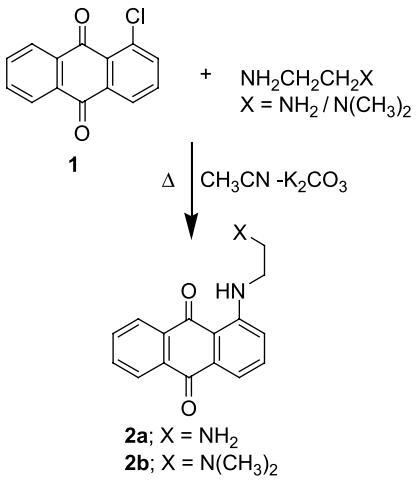


SCHEME 1 Synthesis of chemosensors **2**

large excess of metal ions viz. Ni(II), Cd(II), Co(II), Zn(II), Ag(I), Fe(II), Pb(II), Li(I), Na(I), K(I), Mg(II), Ca(II), Sr(II) and Ba(II). Therefore, receptors **2** show highly selective visual detection of Cu(II) in the presence of other metal ions such as alkali, alkaline earth and transition metal ions. This Cu(II) selectivity could be attributed to the highest Lewis acid character of Cu(II) amongst dipositive cations in parallal with Irving-Williams series of stability of dipositive metal ion complexes [53].

On addition of 10 μM Cu(II) to solution of receptors **2**, the emergence of a new peak at λ_{max} 600 nm along with a visual change in colour of the resulting solution was observed. The intensity of absorbance at λ_{max} 600 nm increased gradually with the increase in concentration of Cu(II) upto 100 μM and then a plateau was achieved. However, concomitant decrease in absorbance at λ_{max} 492 nm with the addition of Cu(II) was observed. This results in isosbestic point at 530 nm (Fig. 1).

The spectral fittings of the spectral data (Fig. 2) obtained by the titration of **2a** (100 μM) with Cu(II) at pH = 7.0 ± 0.1 shows the formation of ML ($\log \beta_{ML}$ 5.6 ± 0.1) and ML_2 ($\log \beta_{ML_2}$ 10.1 ± 0.3) (where M = Cu and L = **2a**) species as described in Eq. (1). The distribution of these species depends on the concentration of Cu(II) added. At 5×10^{-5} M Cu(II), CuL_2, CuL and L are present in ~ 25% amounts and on increasing concentration of Cu(II), the percentage of CuL increases upto ~ 90% at 3×10^{-4} M Cu(II) concentration. Similarly, the chromogenic receptor **2b** with Cu(II) shows the formation of ML_2 and ML species (Eq. (2)). However, **2b** shows relatively higher $\log \beta_{ML}$ and $\log \beta_{ML2}$ values than that observed for **2a**.

$$2a \underset{\log \beta_{ML_2}=10.13}{\overset{Cu(II)}{\rightleftharpoons}} Cu(II)\cdot 2a_2 \underset{\log \beta_{ML}=5.61}{\overset{Cu(II)}{\rightleftharpoons}} Cu(II)\cdot 2a \quad (1)$$

$$2b \underset{\log \beta_{ML_2}=13.74}{\overset{Cu(II)}{\rightleftharpoons}} Cu(II)\cdot 2b_2 \underset{\log \beta_{ML}=7.50}{\overset{Cu(II)}{\rightleftharpoons}} Cu(II)\cdot 2b \quad (2)$$

The insight into the various species formed during titration of receptors **2** with Cu(II) has been obtained by using combination of pH and UV–Vis titrations of these receptors and their complexes with Cu(II). Sensors **2** (λ_{max} 492 nm) on increase in pH from 7.4 to 12 show small red shift by 15 ± 2 nm which remains unaffected in acidic solution (pH 1–7). More significantly, the absorbance at λ_{max} 492 nm remains by and large unaffected between pH 1–12. The spectral fitting of these spectra obtained by titration of receptors **2** with acid or base shows that at pH < 7, **2** remain in protonated form ($\log \beta_{\mathbf{2a}H} = 8.66 \pm 0.09$; $\log \beta_{\mathbf{2b}H} = 7.12 \pm 0.06$).

UV–Vis spectrum of **2a**.Cu(II) complex shows the presence of two strong absorption bands; centered at 492 nm (λ_{max} of **2a**) and at 600 nm (due to complex formation). On lowering the pH from 6, the absorbance at λ_{max} 492 nm due to receptors **2** or its protonated species gradually increased. In the basic medium, the absorbance of the complexed species **2a**.Cu(II) is increased. Between pH 6.8–7.8, the

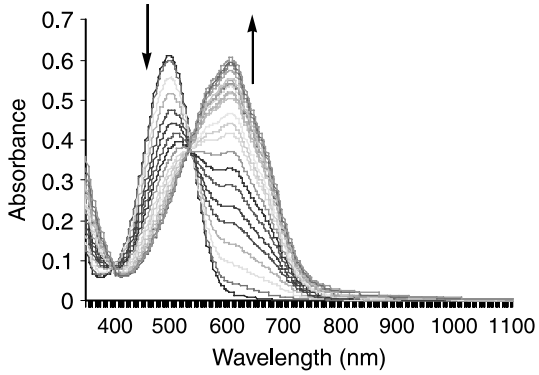


FIGURE 1 Changes in the UV-Vis spectraof **2a** (100 μM) at pH 7.0 upon titration with Cu(II).

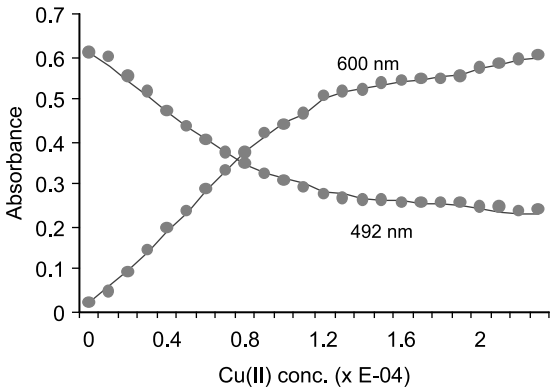


FIGURE 2 The curve fitting of UV-Vis spectral data of 2a (100 μM in MeOH- H_2O 1:1) at 492 and 600 nm on addition of $Cu(NO_3)_2$. (○) experimental points, (--) fitted line.

absorbance of **2a**.Cu(II) complex remains stable (within ± 2%) (Fig. 3).

The evaluation of spectral data obtained from this combination of pH and UV–Vis titration of **2a**–Cu(II) (1:1) solution shows that **2a** during complexation with Cu(II) undergoes deprotonation to form **2a**H^-·Cu(II) between pH 6–8 which on increasing pH is converted to **2a**H^-·Cu(II)·OH^- complex (Fig. 4, Eq. (3)).

$$\mathrm{Cu(II)} + \mathbf{2a} \underset{\log\beta_1=0.4}{\overset{-H^+}{\rightleftharpoons}} \mathrm{Cu(II)\cdot 2aH^-} \underset{\log\beta_2=7.7}{\overset{-H^+}{\rightleftharpoons}} \mathrm{Cu(II)\cdot 2aH^-OH^-} \quad (3)$$

$$\mathrm{Cu(II)} + \mathbf{2b} \underset{\log\beta_1=0.19}{\overset{-H^+}{\rightleftharpoons}} \mathrm{Cu(II)\cdot 2bH^-} \underset{\log\beta_2=9.37}{\overset{-H^+}{\rightleftharpoons}} \mathrm{Cu(II)\cdot 2bH^-OH^-} \quad (4)$$

Similarly, **2b** forms MLH_{-1} (0.17 ± 0.03) and $MLH^{-1}OH^-$ (9.37 ± 0.07) species (Eq. (4)). Therefore, both receptors **2a** and **2b** on addition of Cu(II) at pH 7 undergo deprotonation at aryl NH, which is responsible for colour change from red to blue and bathochromic λ_{max} shift from 492 nm to 600 nm (108 nm shift). Similar, bathochromic shift (130 nm) has been earlier shown to arise due to NH deprotonation in case of ureas [36,37]. The Cu(II) mediated deprotonation of aryl amine NH between pH 4–12 resulting in bathochromic shift both in absorption and emission spectra of naphthalimide based receptor has been recently reported [47].

The formation of anionic species responsible for colour change in receptors **2** on addition of Cu(II) is further supported by the appearance of blue colour and bathochromic shift on using polar solvents viz. CH_3OH or DMSO and lack of bathochromic shift in

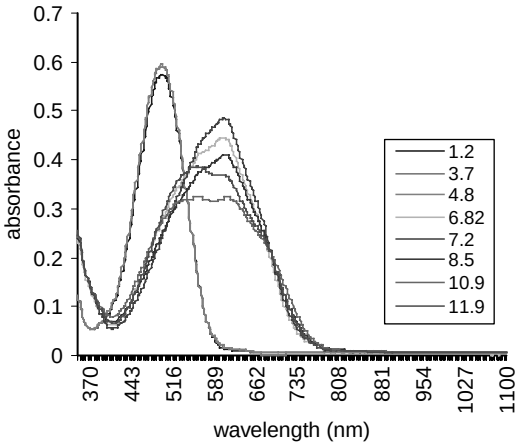


FIGURE 3 Changes in the UV-Vis spectra of **2a - Cu(II)** complex upon titration with diluted acid and base

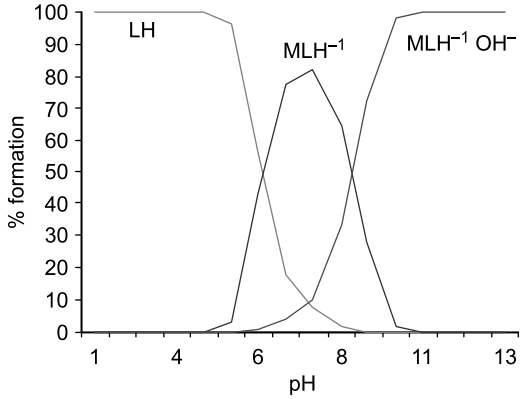
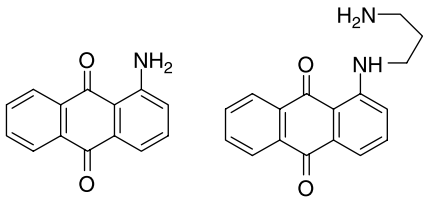


FIGURE 4 Species distribution diagram as a function of pH for a system containing 100 μM Cu(II) and 100 μM **2a**.

CH_3CN. The addition of Cu(II) to solution of **2a** in CH_3CN shows hypsochromic shift from 492 nm to 480 nm and points towards the different mode of complexation of **2** in CH_3CN than in cases of DMSO or methanol as solvent.

In order to rationalize the role of β-amino unit in Cu(II) induced deprotonation of aryl NH in receptors **2**, the complexation behaviour of **3**, lacking an additional binding site and **4** possessing an additional NH_2 binding site linked through a longer carbon spacer, towards Cu(II) was investigated. The lack of colour change in case of **3** and **4**, on addition of Cu(II), points to both the presence of an additional binding site (chelate effect) and its appropriate placement for achieving deprotonation at NH of 1-aminoanthracene-9,10-dione moiety. These results are in analogy with the well known bite size effect, where Cu(II) and other transition metal ions show considerable decrease in stability with receptors possessing 1,3-diaminopropane unit in comparison to receptors possessing ethylene diamine unit [54].



Thus chromogenic 1-aminoanthracene-9,10-dione moiety, which has been earlier used for colourimetric estimation of anions, in the presence of additional electron-rich unit in receptor **2** undergoes deprotonation at aryl NH to achieve visual and spectrophotometric Cu(II) (cation) estimation.

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[52] ***1-(2-aminoethylamino)anthracene-9,10-dione (2a):*** 75%; red solid; m.p. 278°C ($CHCl_3$); FAB Mass 267(M^++1); ^{1}H NMR ($CDCl_3$): δ 1.53 (bs, 2H, NH_2, exchanges with D_2O), 3.12 (t, J=6.0 Hz, 2H, CH_2), 3.47 (q, J=6.0 Hz, 2H, CH_2, converts to triplet on D_2O exchange), 7.13 (d, J=8.0 Hz, 1H, ArH), 7.54–7.66 (m, 2H, ArH), 7.73–7.80 (m, 2H, ArH), 8.25–8.34 (m, 2H, ArH), 9.97 (bs,1H, NH, exchanges with D_2O); ^{13}C NMR (normal/DEPT-135) ($CDCl_3$): δ 39.87 (− ve, CH_2), 42.13 (− ve, CH_2), 115.62 (ab, ArC), 121.24 (+ve, ArCH), 121.68 (+ve, ArCH), 127.37 (+ve, ArCH), 127.96 (+ve, ArCH), 132.61 (ab, ArC), 133.79 (ab, ArC), 134.72 (ab, ArC), 135.35 (+ve, ArCH), 135.93 (+ve, ArCH), 137.40 (+ve, ArCH), 148.62 (ab, ArC), 185.22 (ab, CO), 187.07 (ab, CO). (Found C, 71.91; H, 5.30; N, 10.74%. $C_{16}H_{14}N_2O_2$ requires C, 72.16; H. 5.30, N, 10.52%.) **1-(2-dimethylamino)anthracene-9,10-dione (2b):** 70%; red solid; m.p. 270°C ($CHCl_3$); FAB Mass 295 (M^++1); ^{1}H NMR ($CDCl_3$): δ 2.35 (s, 6H, 2 × CH_3),), 2.68 (t, J=6.6 Hz, 2H, CH_2), 3.43 (q, J=6.3 Hz, 2H, CH_2, converts to triplet on D_2O exchange), 7.05 (d, J=8.4 Hz, 1H, ArH 8.23 (d, J=7.8 Hz, 1H, ArH), 8.31 (d, J=7.2 Hz, 2H, ArH), 9.81 (bs, 1H, NH, exchanges with D_2O); ^{13}C NMR (normal/DEPT-135) ($CDCl_3$): δ 40.93 (− ve, CH_2), 45.52 (+ve, CH_3), 57.96 (− ve, CH_2), 113.05 (ab, ArC), 115.54 (+ve, ArCH), 117.77 (+ve, ArCH), 126.54 (+ve, ArCH), 126.69 (+ve, ArCH), 132.87 (+ve, ArCH), 132.9 (ab, ArC), 133.72 (+ve, ArCH), 133.8 (ab, ArC), 134.61 (ab, ArC), 135.13 (+ve, ArCH), 151.57 (ab, ArC), 182.93 (ab, CO), 184.14 (ab,CO). (Found C, 73.72; H, 6.39; N, 9.31%. $C_{18}H_{18}N_2O_2$ requires C, 73.45; H, 6.16; N. 9.52%)
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