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Photoactive chemosensors. Part 1: A 9,10-anthraquinone and 2-aminothiophenol based Cu(II) selective chemosensor

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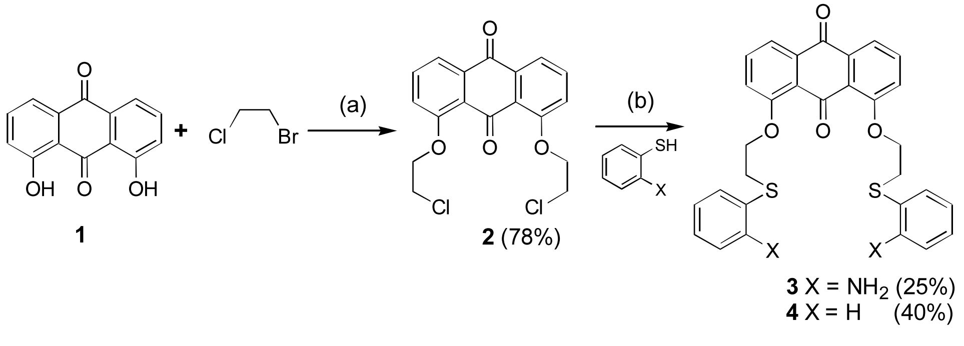
Abstract—The title chemosensor can estimate 20–300 μM Cu(II) ions spectrophotometrically even in the presence of 10 mM Ni(II), Cd(II), Zn(II), Ag(I) and Pb(II) and 1 mM Hg(II) ions. © 2002 Elsevier Science Ltd. All rights reserved.

The development of new molecular systems for the optical detection of alkali, alkaline earth and transition metal ions has attained prime importance for biological and environmental applications.[1,2] In azurin, a blue copper protein,[3c] the Cu(II) binding site consists of two histidine, one cysteine, one methionine and a weakly bonded carbonyl oxygen. However, synthetic Cu(II) ionophores, in general possess, diamide–diamine,[4,5] triamine,[6] hydrazide,[7] hydroxamic acid or *O*-acylhydroxylamine[8,9] based motifs and only in one case tetrathia 14-crown-4[10] has a thioether, been used. Conspicuously, in order to achieve Cu(II) selective ionophores, the potential of mixed ligating sites (S, N, O), as prevalent in nature (in azurins and other Cu-blue proteins[3]), remains untapped. In the present work, we have designed an ionophore which possesses 2×S, 2× NH_2 and a carbonyl as the potential ligating sites and which has been found to detect 20–300 μM Cu(II) by absorption spectroscopy even in the presence of 10 mM Ni(II), Cd(II), Zn(II), Ag(I) and Pb(II) and 1 mM Hg(II) ions (Scheme 1).

1,8-Dihydroxyanthraquinone (**1**) undergoes alkylation with 1-bromo-2-chloroethane under phase transfer catalysed conditions to provide 1,8-(2-chloroethoxy)-anthraquinone (**2**)[11] (78%). This undergoes nucleophilic substitution with 2-aminothiophenol and thiophenol to provide **3**[12] (25%), and **4**[12] (40%), respectively.

The UV–vis spectrum of **3** in CH_3CN: H_2O (4:1) shows λ_{max} at 380.5, 305.5, 251.5 and 208.5 nm. The absorption spectrum of **3** does not show absorption after 520 nm. On addition of Cu(II) nitrate (1 equiv.), a remarkable increase in absorption in the region 520–800 nm is observed which increases with an increase in concentration of Cu(II) and attains a plateau at 7 equiv. of Cu(II) nitrate (Fig. 1). Visibly, a significant change in colour from light yellow (receptor **3**) to brown is also



Scheme 1. (a) K_2CO_3, DMF, tetrabutylammonium HSO_4, 18-C-6, 80°C, 48 h; (b) K_2CO_3, DMF, TBA–HSO_4, 12 h.

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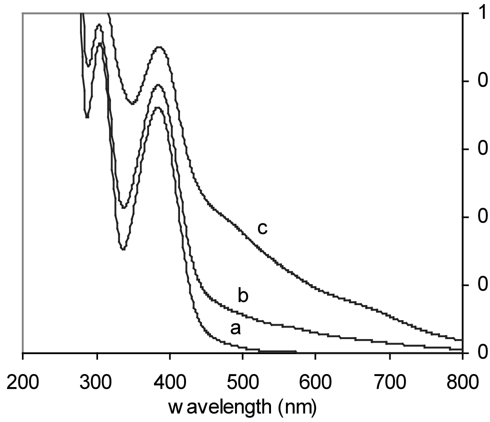

Figure 1. The UV–vis spectra of (a) **3** (100 μM), (b) **3**+Cu (II) (100 μM), (c) **3**+Cu (II) excess.

observed. The addition of Ni(II), Cd(II), Zn(II), Ag(I), Pb(II) and Hg(II) cations does not affect the absorption spectrum of **3**. Therefore, **3** shows an increase in absorption only on addition of Cu(II) and remains unaffected with other metal ions such as Ni(II), Cd(II), Zn(II), Ag(I), Pb(II) and Hg(II).

The titration[13] of **3** (10^{-4} M) with copper nitrate shows a gradual increase in absorption between 20 and 600 μM Cu(II) after which a plateau is achieved (Fig. 2). There is a linear change in absorption from 20 to 300 μM Cu(II) but after this, the rate of increase in the absorption decreases. Titration of **3** with copper nitrate in the presence of 10 mM Cd(II), Ni(II), Zn(II), Ag(I) and Pb(II) nitrates and 1 mM Hg(II) acetate[14] does not affect the absorption as observed in the case of Cu(II) only (Fig. 3). Therefore, these metal ions do not interfere in the estimation of Cu(II). The chromophore **4** lacking the NH_2 group does not show any change in its absorption spectrum on addition of copper nitrate.

Therefore, **3** can be used for the estimation of 20–300 μM Cu(II) in the presence of Ni(II), Cd(II), Zn(II), Ag(I), Pb(II) and Hg(II). Investigations on the mode of complexation of **3** with Cu(II) and the development of fluorescent receptors based on this model are under investigation.

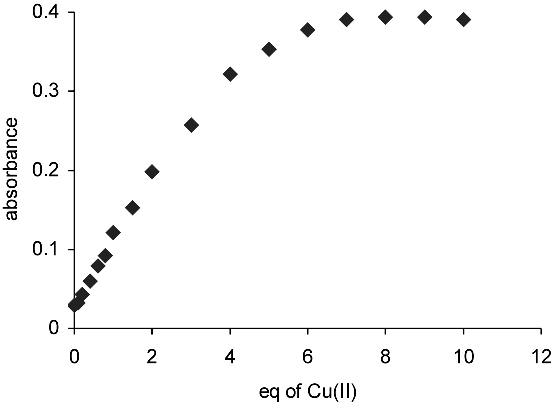

Figure 2. Titration of Cu(II) against **3** (100 μM) in $CH_3CN:H_2O$ (4:1)

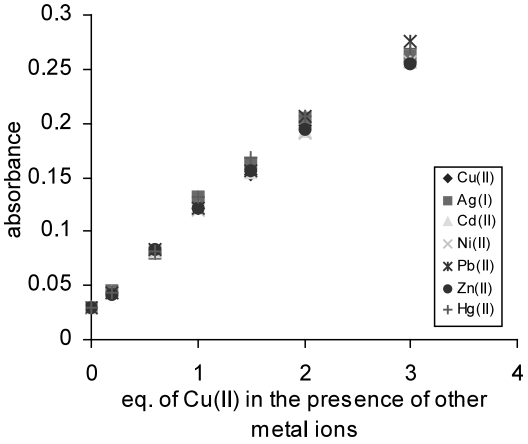

Figure 3. Estimation of Cu(II) in the presence of Cd(II), Ni(II), Zn(II), Ag(I), Pb(II) (10 mM) and Hg(II) (1 mM).

Acknowledgements

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11. (**2**): (78%); mp 315°C; MS *m*/*z* 364 (M^+), 366, 368; ^1H NMR ($CDCl_3$): δ 3.77 (t, $J=6.2$ Hz, 4H, $2\times CH_2$), 4.39 (t, $J=6.2$ Hz, 4H, $2\times CH_2$), 7.34 (dd, $J_1=8.0$ Hz, $J_2=1.0$

Hz, 2H, 2×ArH), 7.63 (t, $J=8.0$ Hz, 2H, 2×ArH) 7.89 (dd, $J_1=8.0$ Hz, $J_2=1.0$ Hz, 2H, 2×ArH); ^{13}C NMR ($CDCl_3$) (normal/DEPT-135): δ 41.32 (–ve, CH_2), 70.52 (–ve, CH_2), 120.66 (+ve, CH), 121.70 (+ve, CH), 125.46 (ab, C), 133.86 (+ve, CH), 135.01 (ab, C), 158.17 (ab, C), 183.18 (ab, C).

12. (**3**): (25%); mp 340°C; MS *m*/*z* 542 (M^+); ^{1}H NMR ($CDCl_3$): δ 2.61 (bs, 4H, 2×NH_2), 3.22 (t, $J=6.6$ Hz, 4H, 2×SCH_2), 4.23 (t, $J=6.6$ Hz, 4H, 2×OCH_2), 6.59–6.69 (m, 4H, ArH), 7.06–7.18 (m, 4H, ArH), 7.41 (dd, $J_1=8$ Hz, $J_2=1$ Hz, 2H, ArH), 7.55 (t, $J=8$ Hz, 2H, ArH), 7.81 (d, $J=8$ Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) (normal/DEPT-135): δ 33.69 (–ve, CH_2), 67.93 (–ve, CH_2), 114.98 (+ve, CH), 116.00 (+ve, CH), 118.28 (+ve, CH), 119.53 (+ve, CH), 130.44 (+ve, CH), 133.70 (+ve, CH), 134.97 (ab, C), 136.76 (+ve, CH), 149.32 (ab, C), 163.18 (ab, C), 158.23 (ab, C), 181.10 (ab, C), 183.21 (ab, C); IR ν_{max} (cm^{-1}): 1587 (CO), 1672 (CO), 3355, 3367 (NH_2). (**4**): (40%); mp 280°C; MS *m*/*z* 512 (M^+); ^{1}H NMR ($CDCl_3$): δ 3.44 (t, $J=7.2$ Hz, 4H, 2×CH_2), 4.29 (t, $J=7.2$ Hz, 4H, 2×CH_2), 7.18–7.32 (m, 8H, ArH), 7.39–7.45 (m, 4H, ArH), 7.56 (t, $J=8.0$ Hz, 2H, ArH), 7.84 (dd, $J_1=8.0$ Hz, $J_2=1.0$ Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) (normal/DEPT-135): δ 32.44 (–ve, CH_2), 68.75 (–ve, CH_2), 119.73 (+ve, CH), 120.42 (+ve, CH),124.73 (ab, ArC), 126.61 (+ve, CH), 129.08 (+ve, CH), 129.93 (+ve, CH), 133.74 (+ve, CH),134.79 (ab, ArC), 135.08 (ab, ArC), 158.17 (ab, C), 182.11 (ab, C), 183.73 (ab, C); IR ν_{max} (cm^{-1}): 1583 (CO), 1669 (CO).
13. Titration experiment: Solutions containing **3** (10^{-4} M) and various concentrations of copper nitrate (10^{-5} M to 10^{-3} M) were prepared in CH_3CN:H_2O (4:1). For interference evaluation, the solutions containing **3** (10^{-4} M), one of the interfering metal ions [Ni(II), Cd(II), Zn(II), Ag(I), Pb(II) (10^{-2} M), Hg(II) (10^{-3} M), Na(I), K(I) (10^{-1} M)] and (2×10^{-5}, 6×10^{-5}, 10^{-4}, 15×10^{-4}, 20×10^{-4}, 30×10^{-4} M) of copper nitrate in CH_3CN:H_2O (4:1) were prepared. The solutions were kept at 25°C for 3 h and were shaken occasionally and their absorption spectra were recorded.
14. On using higher concentrations of Hg(II), precipitation occurs.