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Colourimetric detection of Hg^{2+} by a chromogenic reagent based on methyl orange and open-chain polyazaoxaalkanes

Felix Sancenón, Ramón Martínez-Máñez* and Juan Soto

Departamento de Química, Universidad Politécnica de Valencia, Camino de Vera s/n, 46071 Valencia, Spain

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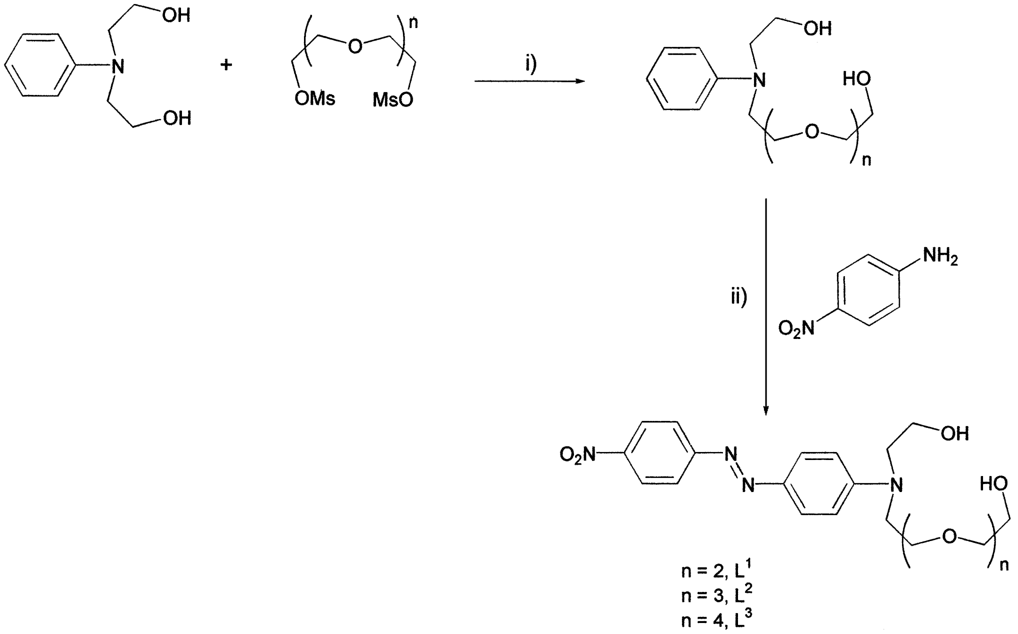
Abstract—The receptors $\mathbf{L}^1$, $\mathbf{L}^2$ and $\mathbf{L}^3$ containing pendant aza–oxa binding sites have been synthesised and their UV–vis spectrum studied in the presence of alkali, alkali–earth and transition metal ions in dioxane. The dye $\mathbf{L}^3$ changes its colour selectively upon Hg^{2+} addition. © 2001 Elsevier Science Ltd. All rights reserved.

The development of sensing receptors based on supramolecular and host–guest chemistry has become attractive not only for chemists but also for researchers in other academic fields, and remarkable progress has recently been made in this area.[1] New sensing receptors can be developed by the combination in the same molecule of two blocks; groups able to give coordination processes with target receptors and signalling subunits that can display selective changes in macroscopically observable features such as electrochemical shifts[2], emission[3] or colour upon guest binding.[4] New developments in this field are of importance because the resulting receptors may be applied for the development of practical devices for the selective sensing of target substrates.



Scheme 1. (i) NaH, CH_3CN, Δ; (ii) aqueous HCl, $NaNO_2$.

Keywords: chromogenic reagents; mercury detection; iron detection; aza–oxa binding sites.

* Corresponding author: Tel.: 34-963877343, fax: 34-963877349; e-mail: rmaez@qim.upv.es

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Sensing receptors for heavy toxic metal ions are of interest in areas such as environmental chemistry, where the development of highly selective analytical tools is of importance. Metal-ion detection by coordination with molecules containing electrochemical or fluorescent signalling subunits have recently been developed but the use of those receptors would need large and expensive analytical equipment.[5] An alternative is to design molecules able to selectively capture target-metal cations combined with colour changes.[6] Colour reactions are popular criteria for the identification and quantitative determination of substances and are the basis for some easy-to-use applications as DIP-sticks assays or suitable for optical fibre applications.

Here we report the synthesis of dyes bearing binding sites that show high metal ion specific colour changes. The synthesis of **L**^{1}, **L**^{2} and **L**^{3} began with the condensation of *N*-phenyldiethanolamine in the presence of sodium hydride with the corresponding dimesylated polyehyleneglycol in acetonitrile as solvent.[7] The obtained benzo polyazaoxaalkane compounds were diazoated with *p*-nitroaniline and sodium nitrite in aqueous 5% hydrochloric acid[8] (Scheme 1). The ligands were obtained as orange solids in ca. 70% yield. ^{1}H, ^{13}C NMR and mass spectra were in agreement with the proposed structures.[9]

The nitrate or perchlorate salts of the cations Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Al^{3+}, Sb^{3+} were added to solutions of **L**^{1}, **L**^{2} and **L**^{3}, in trying to find selective colour changes. Solutions of receptors in dioxane were prepared in a 10^{-4} M concentration. All measurements were carried out using ligand:metal 1:1 molar ratios.

The UV–vis spectra of **L**^{1}, **L**^{2} and **L**^{3} show intense bands in the UV zone and a band centred at 460 nm in visible region responsible for their yellow–orange colour. The intense band in the ultraviolet zone is due to electronic transitions on the benzene rings, whereas the visible band is attributed to charge transfer between the donor and the acceptor part of the molecule.[10] When **L**^{3} interacts with Hg^{2+} the visible band suffers a bathochromic shift changing the colour of the solution from yellow–orange to red. When **L**^{1}, **L**^{2} or **L**^{3} react with Fe^{3+} the visible band disappears and the colour of the solution changes to pale yellow. Fig. 1 shows the UV–vis spectra of **L**^{3} and **L**^{3} in the presence of Hg^{2+}, Ba^{2+} and Fe^{3+} in dioxane.

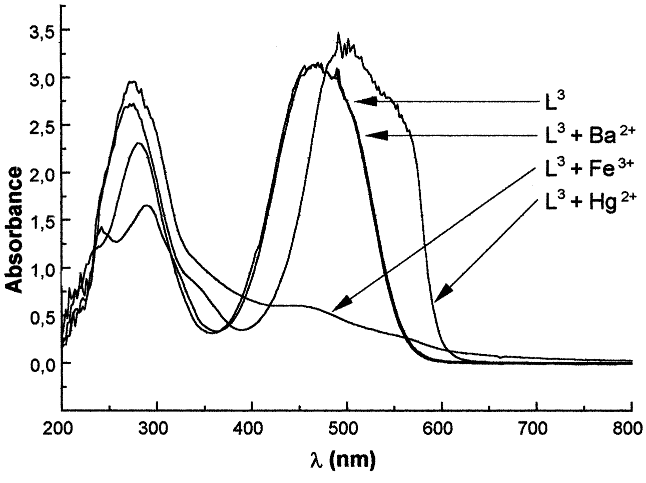

Figure 1. UV–vis spectrum of **L**^{3} and **L**^{3} in the presence of Hg^{2+}, Ba^{2+} and Fe^{3+} in dioxane.

It is noticeable that only Hg^{2+} from near 20 metal ions is able to produce a bathochromic shift on **L**^{3} indicating that the colour variation is highly specific for Hg^{2+}. Hg^{2+} only modifies the colour of **L**^{3} but not that of **L**^{1} or **L**^{2} showing the importance of the size of the aza–oxa open chain. ^{1}H NMR studies on **L**^{3} in the presence of Hg^{2+} showed a remarkable shift of signals of both the aza–oxa binding site and the aromatic ring attached to the aza–oxa open chain. Free receptor shows signals for the protons of the aza–oxa group in the 3.5–3.8 ppm range and three groups of resonances centred at δ 6.9, 7.9 and 8.3 ppm attributed to the aromatic protons which are respectively nearer to the amino, the azo and the nitro groups. In the presence of Hg^{2+} the protons of the aza–oxa binding site are in the 3.5–4.1 range and the signal at 6.9 ppm has been shifted to δ 7.4. These shifts suggest a strong interaction of the Hg^{2+} cation with the aza–oxa chain. This contrasts with the ^{1}H NMR of **L**^{3} in the presence of other metal ions such as Zn^{2+} for which only a slight shift of the signals of the protons of the aza–oxa binding site was found, suggesting a lower degree of metal–ligand interaction. Fe^{3+} also produces a considerable alteration of the absorption spectrum of the ligands; its presence induces the disappearance of the visible band (see Fig. 1). This effect is the same for **L**^{1}, **L**^{2} and **L**^{3} and this total elimination of the charge transfer visible band that is independent of the aza–oxa binding site chain might suggest a strong coordination of the metal ion with the azo group or may be produced as a result of a redox reaction.

In conclusion, the chromogenic aza–oxa derivative **L**^{3} shows an extraordinary selectivity for Hg^{2+} over nearly 20 other common metal ions. Additionally Fe^{3+} also produces a selective elimination of the visible absorption band. These two features can provide the occasion of using these or related ligands as new chromogenic reagents for the sensing of target toxic heavy metal ions.

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   Receptor $\mathbf{L}^2$: ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.50–3.90 (m, 20H), 6.75 (d, 2H, $J=7.5$ Hz), 7.90 (dd, 4H, $J=7.5$ Hz), 8.28 (d, 2H, $J=7.5$ Hz). ^{13}C NMR (300 MHz, CDCl$_3$): δ 51.97, 55.65, 60.54, 68.52, 70.24, 70.44, 70.51, 112.08, 122.62, 124.67, 126.00, 143.94, 147.45, 151.72, 156.50. *m*/*z*: calcd 462, experimental 431 (M$-$NO$^+$).

   Receptor $\mathbf{L}^3$: ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.50–3.90 (m, 24H), 6.78 (d, 2H, $J=7.5$ Hz), 7.89 (dd, 4H, $J=7.5$ Hz), 8.30 (d, 2H, $J=7.5$ Hz). ^{13}C NMR (300 MHz, CDCl$_3$): δ 51.97, 55.63, 60.51, 68.42, 70.28, 70.44, 112.08, 122.62, 124.67, 126.03, 143.70, 143.70, 147.31, 151.57, 156.49. *m*/*z*: calcd 506, experimental 475 (M$-$NO$^+$).
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