Coordination Chemistry Reviews
208 (2000) 17–32

COORDINATION CHEMISTRY REVIEWS

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Recent developments in transition metal ion detection by luminescent chemosensors

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Received 12 November 1999; accepted 15 December 1999

Contents

Abstract

Chemosensors find wide applications in many disciplines such as biochemistry, clinical and medical sciences, cell biology, analytical chemistry and environmental sciences. Aiming to develop new chemosensors for future applications, we have synthesised and studied many different species. We present here the latest luminescent chemosensors for transition metal ions studied in our laboratory. In the various systems active units and receptors are different as are the target ions: Zn^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Ag^{+} and Cu^{2+}. In solution a good

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PII: S0010-8545(00)00252-6

selectivity and affinity was observed and the binding is signalled in all cases by pronounced changes in the photophysical properties such as emission wavelength and intensity, and excited state lifetime of the inserted luminophore. The mechanism for signal transduction depends strongly on the chosen receptor and luminophore moieties, and has been investigated in detail by means of steady state and time resolved spectroscopy.

Keywords: Luminescence; Chemosensors; Transition metal ions; Molecular recognition; Supramolecular chemistry

1. Introduction

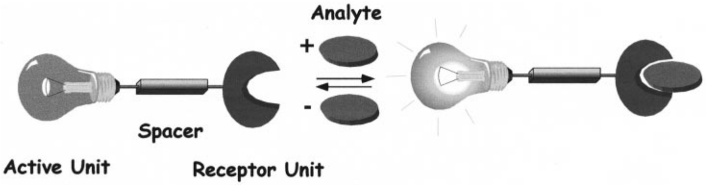
Chemosensors are molecules of abiotic origin that are able to bind selectively and reversibly the analyte of interest with a concomitant change in the property of the system, such as redox potentials and/or absorption or luminescence spectra [1–7]. The need for chemosensors nowadays is very evident, many efforts are devoted to their synthesis and study by many scientists in many different fields and a huge number of papers have been published [5].

To obtain the detection of the target analyte, two different processes are needed: molecular recognition and signal transduction. This means that chemosensors have to be built by components able to perform these functions. It is usually possible to schematise them as constituted by three fundamental units: a receptor (able to selectively bind the analyte), an active unit (that changes one or more of its properties upon analyte complexation), and the spacer that connects and tunes the interaction between them (Scheme 1).

Their properties open very interesting and attractive possibilities; in fact they enable one to perform real-space and real-time measurements using sensor molecules immobilised on surfaces (huge improvements have been introduced by the development of optical fibres) or free in solution.

Chemosensors find wide applications in many disciplines such as biochemistry, clinical and medical sciences, cell biology, analytical chemistry and environmental sciences.

Among the many kinds of chemosensors, fluorescence-based ones present many advantages: sensitivity (single molecule detection is possible), low cost, ease in application, versatility, and subnanometer spatial resolution with submillisecond



Scheme 1.

temporal resolution [1,2,5]. Moreover, many opportunities exist for modulating the photophysical properties of a luminophore, such as the introduction of proton-, energy- and electron-transfer processes, the presence of heavy-atom effects, changes in electronic density, and destabilisation of non emissive $n\pi^*$ excited states [7]. Due to the huge number of possible applications for chemosensors, the number of analytes of interest is practically infinite. In particular, we are studying the detection of metal ions, with a special interest for transition metal ions. These ions represent an environmental concern when present in uncontrolled amounts, and at the same time they are essential elements in biological systems when present in trace amounts.

In this short review we present some systems that we have investigated recently and that appear to be good candidates for application. They were projected and synthesised taking advantage of different luminophores and receptors; moreover the mechanisms involved in signal transduction were also studied and reported here.

2. Experimental

2.1. Materials

The solvents used were methanol and ethanol UVASOL from Merck Co. without further purification. Water was Millipore grade. Metal ion salts were ACS grade from Fluka and used without further purification. The crown ethers were available from earlier work.

2.2. Instrumentation

Absorption spectra were recorded with a Perkin–Elmer lambda 16 spectrophotometer. Corrected emission and excitation spectra and phosphorescence lifetimes were obtained with a Perkin–Elmer LS 50 spectrofluorimeter. The fluorescence lifetimes (uncertainty $\pm 5\%$) were obtained with an Edinburgh single-photon counting apparatus. Luminescence quantum yields (uncertainty $\pm 15\%$) were determined using quinine sulfate in 1 N H_2SO_4 aqueous solution ($\Phi = 0.546$) [8] and $Ru(bpy)_3^{2+}$ in aerated water solution ($\Phi = 0.028$) [9] as references. In order to allow a comparison of emission intensities, corrections for instrumental response, inner filter effects, and phototube sensitivity were performed [10].

Transient absorption experiments were performed as described in Ref. [11].

2.3. Metal binding studies

UV and emission spectra were run on 3 ml of a solution of the chemosensor. Aliquots (10 μl) of salt solution were then added with a micro syringe and spectra recorded. The intensity, read at the maximum of the adduct band, was fitted to $I_{corr} = \varphi_{cr}C_{cr} + \varphi_{cm}C_{cm}$, where C_{cr} and C_{cm} are the concentrations of uncomplexed and complexed chemosensor, respectively, and φ_{cr} and φ_{cm} are the proportionality constant between the corrected emission intensity (in arbitrary units) and the concentration of the uncomplexed and complexed chemosensor, respectively [12]. C_{cm} satisfies the usual binding expression in Eq. (1) where M_{tot} is the total concentration of added metal ion.

$$C_{\mathrm{cm}}^2 - ((C_{\mathrm{cm}} + C_{\mathrm{cr}}) + M_{\mathrm{tot}} + 1/K)C_{\mathrm{cm}} + M_{\mathrm{tot}}(C_{\mathrm{cm}} + C_{\mathrm{cr}}) = 0 \tag{1}$$

Values for the equilibrium constant, K were then obtained by simulation of the data with both K and φ_{cm} as adjustable parameters.

3. Results and discussion

3.1. A tripodal ligand bearing dansyl groups

The luminescent properties of dansyl group are very well known and have been used widely in order to obtain fluorescent sensors and labels [13–22], especially in the field of biochemistry for the detection of peptides and amino acids. We have borrowed this previous knowledge to design and synthesise [23] the ligand tris[5-(dimethylamino)-*N*-(2-aminoethyl)-1-naphthalenesulphonamide] (**1**), a new tripodal ligand incorporating the dansyl chromophore. We studied the luminescence properties of this ligand and its metal complexes, and we compared them with those of dansylethylenediamine metal complexes (**2**) in order to provide a more in-depth understanding of the behaviour of such a widely used chromophoric group.

The absorption spectra of the two ligands were very similar in shape but that of **1** was three times more intense, as expected because of the presence of three chromophoric groups. Dansylamide and its derivatives show typically intense and large luminescence bands in the 400–600 nm region. These bands are very sensitive to the polarity of the solvent and have a considerable charge-transfer character, caused by the mixing of the ^1L_a and ^1L_b states of naphthalene with a charge-transfer state arising from the promotion of a lone-pair electron on the amino group into an antibonding orbital of the naphthalene ring [24].

The constancy of the photophysical behaviour in compounds **1** and **2** shows that intramolecular interactions between the three chromophores in **1** are negligible.

Various amounts of many metal ions were added to solutions of **1** and **2** over a wide pH window (3–11) to test their efficiency as receptors.

Addition of Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Eu^{2+}, Mn^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, Cr^{2+} and Ni^{2+} did not lead to any change in the absorption and emission spectra of the dansyl derivatives **1** and **2** in all the pH ranges examined.

Strong changes in the luminescence properties of **1** were indeed observed upon addition of Cu^{2+}, Co^{2+}, Zn^{2+}, and Cd^{2+} at pH 9.5 (Fig. 1). Smaller but non-negligible changes could also be observed in the same conditions in the absorption bands. Only the addition of Cu^{2+} affected absorption and luminescence spectra of compound **2** in the pH window examined.

Upon addition of Ag^+ and Hg^{2+} metal ions, a blue shift of the fluorescence band of **1** could be observed; unfortunately precipitation problems prevented complete complexation and therefore further investigation.

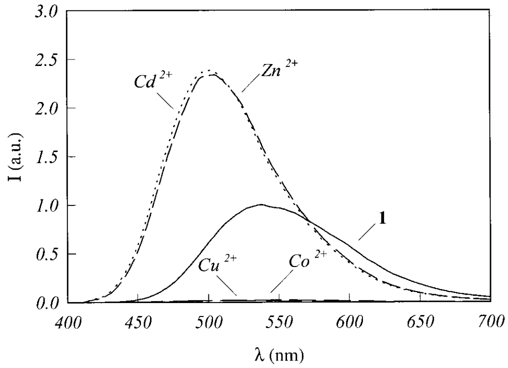


Fig. 1. Fluorescence spectra at room temperature ($\lambda_{exc} = 340$ nm) of **1** and of its complexes with Cu^{2+}, Co^{2+}, Cd^{2+}, and Zn^{2+}(acetonitrile:water (1:1, v:v), pH 9.5).

All these changes for **1** (Fig. 2) and **2** are very sensitive to the pH conditions: almost negligible at pH values lower than four, they reach a plateau at higher pH values. This behaviour is fully reversible; superimposable titration profiles have been obtained starting from pH 11 and 3 and adding HCl or NaOH, respectively, each profile being characteristic for the ligand and the metal ion involved in complexation.

It has been experimentally proven that at pH 6.5 the tripodal ligand complexes only Cu^{2+} ions with a stoichiometry 1:1, with no interference by the other ions.

For **2** there is evidence for a 1:2 (metal:ligand) complex, although a 1:1 stoichiometry at higher metal concentrations cannot be ruled out [18].

Addition of one equivalent of Cu^{2+} ions to a 1×10^{-4} M neutral water:acetonitrile (1:1, v:v) solution of **1** or **2** caused a strong decrease in the fluorescence intensity and lifetime of the ligands. The quenching observed for **1** has

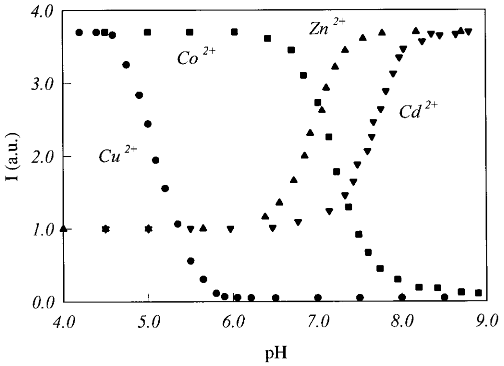


Fig. 2. Fluorescence intensity versus pH ($\lambda_{exc} = 340$ nm) for solutions containing equimolar amounts (8×10^{-5} M) of **1** and (i) Cu^{2+} ions ($\lambda_{em} = 540$ nm, ●); (ii) Co^{2+} ions ($\lambda_{em} = 540$ nm, ■); (iii) Zn^{2+} ions ($\lambda_{em} = 500$ nm, ▲); and (iv) Cd^{2+} ions ($\lambda_{em} = 500$ nm, ▼).

been explained, as already reported for other dansyl derivatives, as being due to the complex formation by the amino group, followed by abstraction of the sulfonamide hydrogen [16,17,25]. The addition of an equimolar amount of base with respect to the ligand leads to the observation of a plateau and this is a further evidence for this mechanism. A similar complexation–deprotonation mechanism can also be invoked for **1**, but in this case, the pattern shown by the fluorescence spectra indicates clearly that almost complete quenching is reached after the addition of two equivalents of base with the formation of a neutral complex obtained with the deprotonation of only two dansyl moieties. The further deprotonation of the third side arm, indicated by changes in the absorption spectra, is obtained only in a second step at $\mathrm{pH} > 7.5$ with the addition of the third equivalent of base.

In principle, the quenching effect after the formation of the complex can be ascribed for both ligands to either a dansyl to metal energy transfer (ET) or a metal to dansyl electron transfer (eT) mechanism. However the estimated quenching rate constant at 77 K has a high value (about 10^{10} s^{-1}) suggesting at least a contribution from the ET mechanism [26].

On adding Co^{2+} ions to a solution of **2** no changes in absorption and fluorescence spectra were observed. However, at pH values higher than 7, quenching of the fluorescence intensity of **1** was observed. To explain the different behaviour of the two ligands, a co-operative effect of the three arms of the ligand **1** has to be again invoked. Titration experiments revealed a 1:1 (ligand:metal) stoichiometry of the complex and a simultaneous deprotonation of all three dansyl moieties. The possible quenching mechanisms are the same as proposed above, and again the high value of the quenching rate constant at 77 K suggests a contribution of the energy transfer mechanism.

On the other hand, addition of Zn^{2+} and Cd^{2+} ions to basic water–acetonitrile solutions of **1** caused a noticeable blue shift of their fluorescence bands, with a concomitant increase in the quantum yield and lifetime. The formation of complexes follows the same mechanism explained above, the stoichiometry revealed is again 1:1, and a simultaneous deprotonation of all three dansyl groups of **1** takes place, as already observed for the Co^{2+} ions. In these cases, the deprotonation–complexation process increases the electronic density on the naphthalene ring, moving the amine-to-naphthalene charge transfer state present in the dansyl chromophore towards higher energy. With these metal ions we did not observe any quenching process. This was expected since Zn^{2+} and Cd^{2+} are d^{10} ions and their complexation does not usually introduce low energy metal-centred or charge-separate excited states in the molecule, so that ET and eT processes can not occur.

An analogous hypsochromic shift with a concomitant increase of the luminescence intensity is also observed for dansyl derivatives upon raising the energy of this excited state using low polar solvents [24].

Finally, among the latter ions, **1** shows a remarkable affinity and selectivity towards the Cu^{2+} ions, as can be seen from the titration experiment performed in the presence of the other possible interfering metal ions at nearly physiological pH. (Fig. 3) Furthermore the pH window in which complete quenching occurs is quite large compared with that of other chemosensors for Cu^{2+} [27].

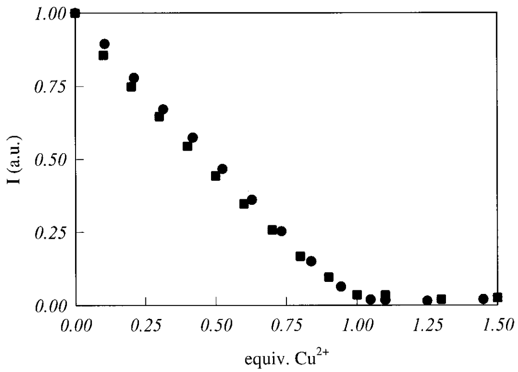


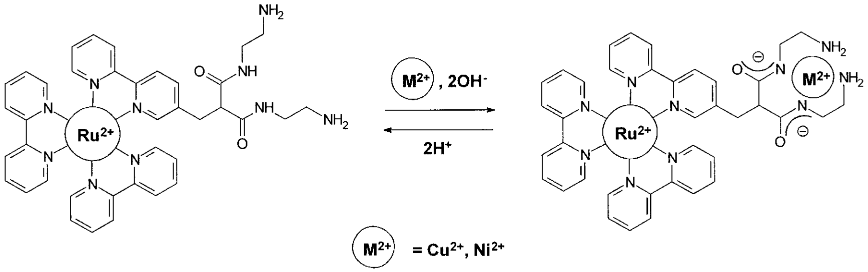
Fig. 3. Dependence of the fluorescence intensity ($\lambda_{exc} = 340$ nm, $\lambda_{em} = 540$ nm) of a solution (i) containing **1** (8×10^{-5} M) at pH 9.5 (circles); and (ii) containing **1** (8×10^{-5}M), Zn^{2+}, Co^{2+}, and Cd^{2+} (1.6×10^{-4}M) at pH 6.5 (squares) upon addition of Cu^{2+}.

These characteristics showed by **1** towards the Cu^{2+} ions at pH > 4, suggests a possible use of this ligand as luminescent chemosensor for this ion.

3.2. A $[Ru(bipy)_3]^{2+}$ based chemosensor

Dioxo-tetraamines (and in particular dioxo-2,3,2-tet≡1,4,8,11-tetraazaundecane-5,7-dione), an already well known category of ligands, can be employed successfully as receptor units for the synthesis of chemosensors to be used to signal the presence of Ni^{2+} and Cu^{2+} in aqueous solution [26]. Dioxo-tetraamine fragments can bind only Ni^{2+} and Cu^{2+} efficiently and selectively, among the series of divalent transition metal cations belonging to the first transition row, moreover they allow one to select between Ni^{2+} and Cu^{2+} since the complexation process (Scheme 2) is pH-dependent and takes place at remarkably different pH values for the two cations.

In view of the possible analytical use of systems of this kind in natural and biologically relevant environments (i.e. water as a medium, at a neutral or slightly



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Scheme 2.

basic pH) a hydrophilic luminescent chemosensor was designed to obtain a water-soluble sensor, selective for Cu^{2+} and Ni^{2+}. This new species presents the dioxo-2,3,2-tet binding unit appended to the highly fluorescent, water soluble $[Ru(bipy)_3]^{2+}$ unit (bipy = 2,2′-bipyridine) (see Ref. [28] for synthetic details). The two-component system **3** can be dissolved in water with concentrations ranging up to 10^{-2} M.

Complexation properties of **3** towards transition metal cations have been examined by observing the variation of its fluorescence intensity (I_f) and lifetime (τ) as a function of pH, in the presence of these cations. In the $2 < pH < 12$ range, in the absence of metal cations, the luminescence quantum yield (0.030) and lifetime (440 ns) of **3** in aerated water solutions are very similar to those observed for the $Ru(bpy)_3^{2+}$ chromophore under the same conditions. This indicates that the dioxo-2,3,2-tet fragment does not substantially perturb the excited state properties of the Ru moiety. On the other hand, when Ni^{2+} or Cu^{2+} (as their perchlorate or chloride salts) are added up to 1:1 molar ratio with respect to system **3**, the I_f versus pH plot shows a typical sigmoid profile (Fig. 4). These experimental results indicate that binding of the metal ion by the dioxo-2,3,2-tet fragment, takes place in the narrow pH range of the steeply descending portion of the sigmoid according to the equilibrium shown in Scheme 2.

As can be seen in Fig. 4, the complexation by **3** of Cu^{2+} begins at pH 5.8 and is complete at pH 6.8 under the titration conditions, while it begins at pH 7.5 and is complete at pH 8.5 for Ni^{2+}. Under the conditions corresponding to the descending portion of the sigmoid, the decay profile shows the appearance of a second component with a much shorter lifetime (11 and 15 ns for Ni^{2+} and Cu^{2+}, respectively), clearly indicating an intramolecular quenching process; this component becomes the only one present at higher pH values. From Eq. (2), intramolecular quenching rate constant values, k_q, of 6.4×10^7 s^{-1} for Cu^{2+} and 8.9×10^7 s^{-1} for Ni^{2+} can be calculated.

$$k_q = 1/\tau - 1/\tau^{\circ} \tag{2}$$

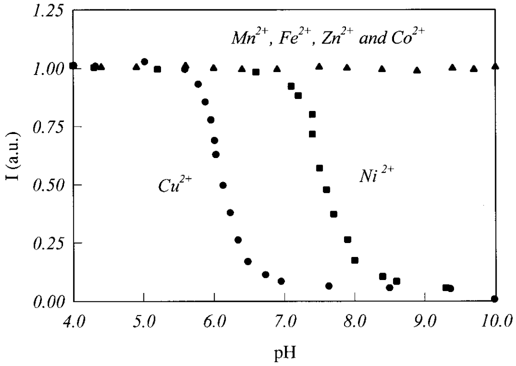

Fig. 4. pH dependence of the luminescence intensity at $\lambda_{em} = 610$ nm ($\lambda_{exc} = 450$ nm) in water for solutions containing **3** and equimolar amounts of the metal ions reported in the plot.

In principle eT and ET processes are both possible and, in order to discriminate between them, flash photolysis experiments were carried out. After the 532 nm excitation pulse, no evidence for the presence of Ru^{I} species could be detected, and the only transient absorbing species were due to the excited states of the Ru^{II} chromophore. Furthermore, steady state quenching experiments performed at 77 K showed that the quenching process was very fast (1.5×10^7 and 2.1×10^7 s^{-1} for Cu^{2+} and Ni^{2+}, respectively) also in frozen medium at low temperatures. These observations suggest that the ET transfer is the more suitable candidate in order to explain the luminescence quenching of **3**.

When complexation processes of Cu^{2+} and Ni^{2+} are complete, I_f is reduced to less than 5% of its maximum value. Titration experiments of Cu^{2+} and Ni^{2+} carried out in presence of other metal ions such as Mn^{2+}, Fe^{2+}, Zn^{2+} and Co^{2+} indicated that their interference is negligible in the pH range examined.

The selection of Cu^{2+} over Ni^{2+} can be obtained by choosing the correct working pH value. A solution of **3**, buffered at pH 7.0, shows no variation in I_f by the addition of Ni^{2+} (or other divalent first row transition metal cations), while the addition of increasing amounts of Cu^{2+} causes the expected fluorescence quenching that is complete after the addition of one equivalent of metal cation (i.e. ligand:metal molar ratio 1:1) (Fig. 5).

The observations reported above enables us to say that system **3** behaves as an ON–OFF sensor based on the ET mechanism for these two metal cations. Another very important observation is that the last titration experiment reported was performed using concentrations of **3** as low as 10^{-7} M, and this indicates that this species is a suitable sensor for copper cations even under analytically relevant conditions.

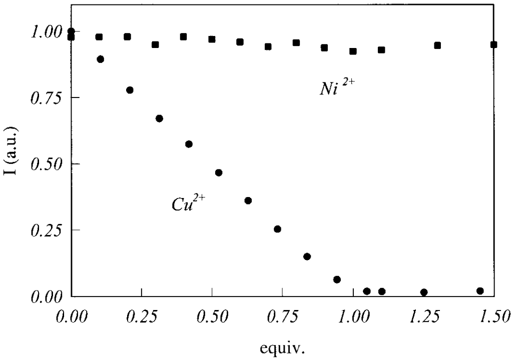

Fig. 5. Dependence of the luminescence intensity ($\lambda_{exc} = 450$ nm, $\lambda_{em} = 610$ nm) of a solution containing **3**, buffered at pH 7.0, upon addition of increasing amounts of Cu^{2+} (circles) or Ni^{2+} (squares).

3.3. A thia-antracene chemosensor

Anthracene and its derivatives have been attracting the attention of scientists for a long time for their particularly interesting photophysical properties. These highly fluorescent units are used widely in designing luminescent chemosensors and switches based on photoinduced electron transfer processes [5].

Recently, the possibility of this aromatic units to give π-stacking and π-cation or π–H interactions has been investigated [29] and it has been shown, for example, that diamino anthracene derivatives intercalate CT-DNA with high affinity [30].

The chemical structure of anthracene based chemosensors or labels can contain many different receptor units, such as aliphatic or aromatic amino groups, that determine the recognition properties of the whole system [5]. In this context we have studied the formation of thia-anthracene receptors that lead to the synthesis of an anthracene podand **4** consisting of two anthryl groups connected by a $SCH_2CH_2CH_2S$ spacer. The desired compound was prepared as described previously [31]. The complexation properties of this compound were investigated using UV–vis and fluorescence titration techniques and the results are reported.

Absorption and emission spectra of **4** were performed in dichloromethane: methanol (8:2, v/v) solutions. The absorption spectrum presents the typical pattern of the anthracene chromophore, with a structured band in the 330–400 nm region and an intense band at 257 nm (Fig. 6).

The fluorescence spectrum (Fig. 7), on the contrary, shows a pattern that can be seen as the superimposition of the expected structured band of the anthracene moiety and a much broader band shifted towards longer wavelengths.

The existence of two different luminescent excited states is also evident from the time decay profile that can be fitted only with a two exponential equation yielding two different lifetimes, i.e. 5.5 and 0.8 ns. The analysis of the pre-exponential terms obtained from the fitting of the excited state decay at different emission wavelengths shows that the longer term can be attributed to the higher-energy, structured band, while the shorter one can be attributed to the broader band.

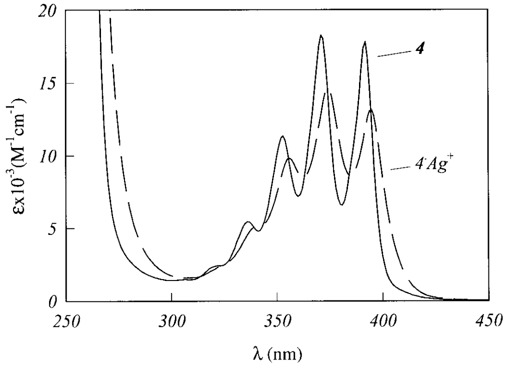

Fig. 6. Absorption spectra in dichloromethane:methanol (8:2, v:v) of **4** and of its complex with Ag^+.

Absorption and fluorescence spectra and excited state lifetimes are not concentration dependent in the range between 10^{-6} and 10^{-4} M but the luminescence changes on changing the polarity of the solvent; in particular the contribution of the non-structured component at longer wavelength increases on going from pure dichloromethane to pure methanol.

Excitation spectra recorded at different emission wavelength are all superimposable on the absorption spectrum showing that the interaction that causes the two different luminescent excited states has almost negligible effects on the ground state. A possible explanation could be the formation of an intramolecular excimer between the two anthracene moieties of **4**, which would be responsible for the broader, red shifted fluorescence band. Similar behaviour has already been observed with a crown ether containing two 9,10-dimethoxy anthracene moieties [32].

The complexation properties, and eventually selectivity, toward cations of **4** were investigated adding increasing amounts of various metal ions such as Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, and Co^{2+}, to a solution of this species; no changes of the photophysical properties were observed.

However the addition of silver ions as perchlorate or trifluoroacetate salts to a dichloromethane:methanol (8:2, v/v) solution of **4** caused monitorable changes in the absorption spectrum (Fig. 6) and even more pronounced modifications in the fluorescence pattern (Fig. 7) even if other metal ions are present.

In particular, upon addition of increasing amounts of Ag^+ ions, the fluorescence band decreases in intensity and loses its structure. It is worth noticing that weakening of the luminescence occurs even when only the lower energy section of the spectrum, namely over 500 nm, is examined, indicating that the disappearance of the structured band is concomitant with a decrease in intensity of the other band. Complexation also effects the excited state decay profile: after addition of more than one equivalent of silver ions, the profile can be fitted with one exponential term, indicating the presence of only one, quite short (0.6 ns), excited state lifetime.

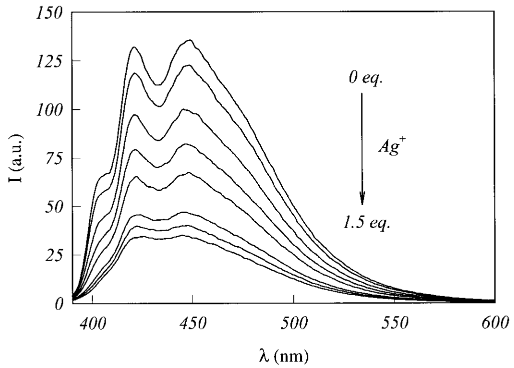

Fig. 7. Fluorescence spectra in dichloromethane:methanol (8:2, v:v) of **4** ($\lambda_{exc} = 383$ nm) upon addition of increasing amounts of Ag^+.

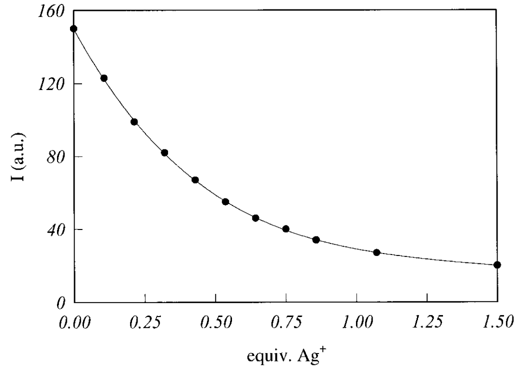

Fig. 8. Fluorescence intensity of **4** ($\lambda_{exc} = 383$ nm) at $\lambda_{em} = 450$ nm versus equivalents of Ag^+ added.

On the other hand the titration profile (Fig. 8) can be fitted only with the assumption that two consecutive equilibria 3 and 4 exist, and that the fluorescence properties of **4** are the same in $[Ag\cdot\mathbf{4}]^+$ and $[Ag\cdot(\mathbf{4})_2]^+$.

$$Ag^+ + \mathbf{4} \leftrightarrows [Ag\cdot\mathbf{4}]^+ \tag{3}$$

$$[Ag\cdot\mathbf{4}]^+ + \mathbf{4} \leftrightarrows [Ag\cdot(\mathbf{4})_2]^+ \tag{4}$$

Association constants calculated for the experimental conditions used were found to be 2×10^5 and 8×10^4 M^{-1} for equilibria 3 and 4, respectively.

The observed variation of the shape in the fluorescence spectrum could be explained by the occurrence of conformational changes upon complexation that forces the two anthracene fragments in complexed **4** to lie in closer contact with respect to the free **4**. This could account for the presence of only a short-lived, non-structured band, after the addition of one equivalent of silver ions, very similar to the excimer component of the free **4**. These conformational changes, causing a stronger intramolecular interaction in the ground state, could also explain the observed changes in the absorption spectrum.

The assumption of the formation of the excimer, however, does not account for the experimentally observed general decrease of the luminescence intensity. The lifetime of the excimeric excited state seems not to be influenced by complexation; therefore one has to assume that a further non radiative process is responsible for a faster deactivation of the anthracene singlet excited state. Two processes could explain the quenching of the fluorescence [15], the most likely is an electron transfer process involving silver ions which is possible thermodynamically. The other one is an energy transfer process from the anthracene to the metal centred excited states but this must be ruled out, since the d^{10} silver ions do not have low energy metal centred states.

Complexation studies performed on model compound **4** demonstrate that even such a simple chemical receptor possesses very interesting complexation properties and this encourages further studies that will concentrate on the incorporation of anthracene unit into thia-crown ethers. This would change and enlarge the spectra of the possible target ions.

3.4. An 8-hydroxyquinoline based chemosensor

Compound **5** was synthesised and studied within a series of related species that take advantage of the easily tuneable selectivity of crown ethers towards different metal ions to obtain new luminescent chemosensors [33]. 8-Hydroxyquinoline groups were used as the chelating fluorophores in this series of derivatised macrocycles since they show fluorescence modulation when complexed to certain metal ions [34].

A very similar species bearing chloride groups instead of the nitro groups as substituents on the 8-hydroxyquinoline had already been studied in our laboratory and shown to be a very efficient luminescent chemosensor for Mg^{2+} ions [35]. Titrations of a solution of this species in MeOH–H_2O (1:1) with increasing amounts of magnesium ions exhibit an appreciable enhancement of the fluorescence band allowing quantitative detection of this metal ion in solution.

Preliminary studies [36] of **5** showed that it forms stable complexes with Hg^{2+} and Cd^{2+} ions. Absorption spectra in methanolic solutions upon Hg^{2+} and Cd^{2+} complexation show noticeable changes (Fig. 9), while an increase in the intensity of the emission spectra can be observed. The addition of alkali and alkali-earth metal ions does not cause any change of the luminescence band of **5**.

The uncomplexed macrocycle shows a very weak luminescence band centred at 490 nm. The very low quantum yield ($< 5 \times 10^{-5}$) is consistent with the luminescence properties of the parent neutral 8-hyroxyquinoline in protic solvents, where intra- and inter-molecular excited state proton transfer has been invoked to explain the high efficiency of the radiationless deactivation to the ground state [37].

Upon association with Hg^{2+} and excitation at 420 nm, the fluorescence intensity of **5** increases by a factor of six. The titration of a solution 1×10^{-5} M of **5** in methanol with Hg^{2+} was monitored via fluorescence (Fig. 10) and the association constant was estimated to be 1×10^{7} M^{-1}. The fluorescence intensity reached a maximum when one equivalent of the metal ions was added indicating that the stoichiometry of the complex is 1:1.

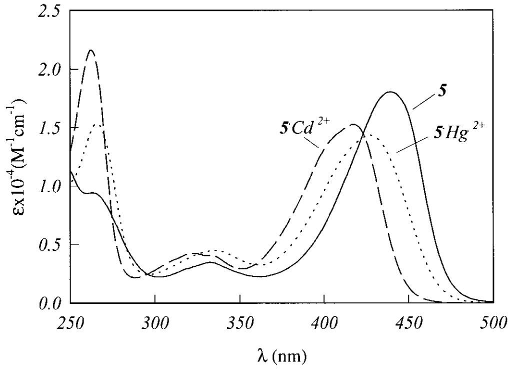

Fig. 9. Absorption spectra in methanol of **5** and of its complexes with Hg^{2+} and Cd^{2+}.

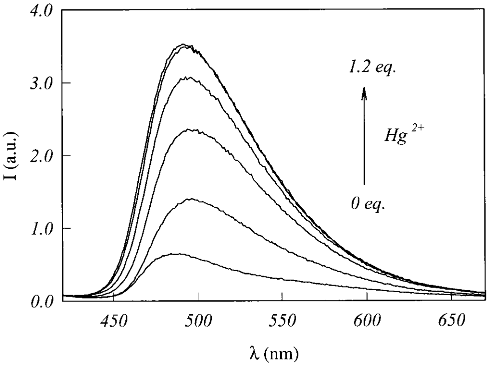

Fig. 10. Fluorescence spectra in methanol ($\lambda_{exc} = 420$ nm) of **5** upon addition of increasing amounts of Hg^{2+}.

The same experiments performed with Cd^{2+} ions again suggest a 1:1 stoichiometry, although in this case the association constant is estimated to be 3×10^5 M^{-1}.

The wavelengths of the maxima of the emission intensity are slightly different for the Hg^{2+}-**5**, Cd^{2+}-**5** complexes, and this could allow discrimination between them.

All these observations indicate that compound **5** has good selectivity toward Hg^{2+} ions. Keeping in mind the importance of Hg^{2+} ions as environmental pollutants, we think that these results are very interesting for future development and practical applications. From a synthetic point of view, further efforts are devoted to change the size of the crown and the substituents or their positions on the 8-hydroxyquinoline aiming to tune the magnitude of the affinity constant and the nature of the target ions.

4. Conclusions

The new chemical species reported here perform as sensors for different transition metal ions, such as Zn^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Ag^{+} and Cu^{2+}, providing pronounced changes in their photophysical properties, in some cases even under physiological pH conditions. The signal transduction mechanism depends strongly on the chosen receptor and luminophore moieties for the species presented here are dansyl group, ruthenium complexes, anthracene and hydroxyquinoline derivatives. Thanks to their interesting properties, these systems appear as very promising candidates for analytical applications.

Acknowledgements

We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Progetto Dispositivi Supramolecolari), Università di Bologna (Funds for Selected Topics) and CNR (Sensori Fluorescenti Supramolecolari) for financial support.

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