

Luminescent Chemosensors Based on Anthracene or Dioxyxanthone Derivatives

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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. They find wide applications in lots of disciplines and our work is directed to develop new species for future applications. We present here the latest luminescent chemosensors studied in our laboratory. The chosen luminophore moieties are anthracene and dioxyxanthone derivatives that have been differently connected with receptor units such as crown ethers and thioethers. In solution a good selectivity and affinity was observed for different ions such as Na⁺, K⁺, Cs⁺, Ba²⁺, Sr²⁺, Ca²⁺ and Ag⁺. The binding is signaled in all cases by pronounced changes in the photophysical properties of the luminophore present in the structure of the chemosensor.

KEY WORDS: Luminescent chemosensors; crown ethers; thioethers; silver; alkaline-earth metal ions.

INTRODUCTION

One of the outstanding fields in modern scientific research is without any doubt the study of sensing molecules, that is, of chemosensors [1–4]. Due to the almost-infinite number of possible target molecules and to the many different techniques suitable for their study, chemosensors can and do find use in many disciplines such as clinical and medical sciences, cell biology, analytical chemistry, and environmental sciences [1–6]. Aiming to develop new fluorescent chemosensors for biological and environmental applications, we have designed and studied new chemical species able to reversibly bind metal ions.

Of the many different kinds of chemosensors, fluorescence-based ones are a very interesting category for future practical applications, thanks to the sensitivity (single molecule detection is possible), versatility, and low

costs typical of fluorescence measurements [1]. Furthermore, many possibilities exist for modulating the photophysical properties of a luminophore and this opens many opportunities in designing efficient luminescent chemosensors allowing many different ways of tailoring good chromophores with some receptor units [1,2].

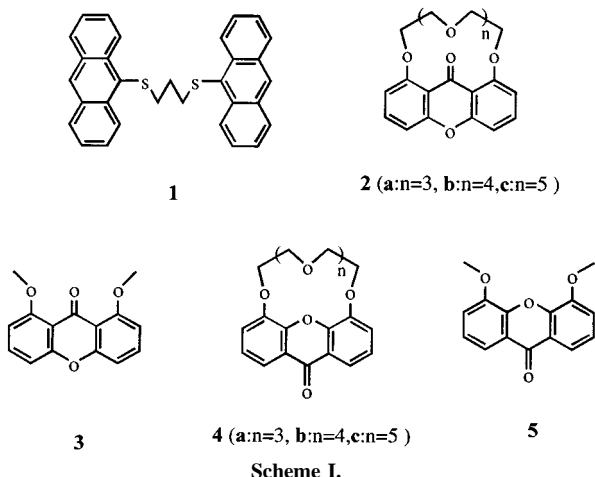
In our search, we make use of a large variety of luminophores and receptors [7–9], and the mechanisms involved in signal transduction are always different, depending upon their nature. We report here in detail photophysical studies on two of these systems based on anthracene or dioxyxanthone chromophores (see Scheme I) and able to detect metal ions.

A THIA-ANTHRACENE CHEMOSENSOR

Anthracene and its derivatives constitute a very well-known class of fluorophores with very interesting photophysical properties. They are extensively used in designing luminescent chemosensors and switches and, recently, the possibility of these aromatic units to give π – π stack-

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ing and π -cation or π -H interactions has been successfully investigated [10,11].

We are particularly interested in the investigation of thiocrowns and thioethers since sulfur atoms possess very good coordination properties toward soft metal ions. Here we present a study on an anthracene podand (**1**) consisting of two anthryl groups connected by a $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}-$ spacer, a species that we have designed pursuing the aim of the formation of thia-anthracene receptors. The desired compound was prepared, following reactions commonly used in the synthesis of thiocrown ethers and thiocryptand receptors [12,13], in one step and in a 99% yield. The complexation properties of this compound were investigated using UV-VIS and fluorescence titration techniques and the results are reported hereafter.

The absorption spectrum of **1** (in dichloromethane:methanol, 8:2, v/v) presents the typical pattern of the anthracene units contained in the molecule, showing a structured band in the 330- to 400-nm region and an intense band at 257 nm. The observation that no alteration of the chromophore absorption property can be pointed out allows us to state that almost no interaction between the two anthracene moieties takes place in the ground state. On the contrary, the fluorescence spectrum differs greatly from that of simple anthracene (Fig. 1), revealing the presence of a broader band superimposed on the typical structured band of the isolated fluorophore and slightly shifted toward longer wavelengths. The assumption of the existence of a double emission due to different luminescent excited states finds confirmation in the time-resolved experiments. From the analysis of the decay of the fluorescence signal, in fact, it resulted that a double-exponential model was needed to interpolate correctly the experimental data, giving two distinct lifetime values (5.5 and 0.8 ns).

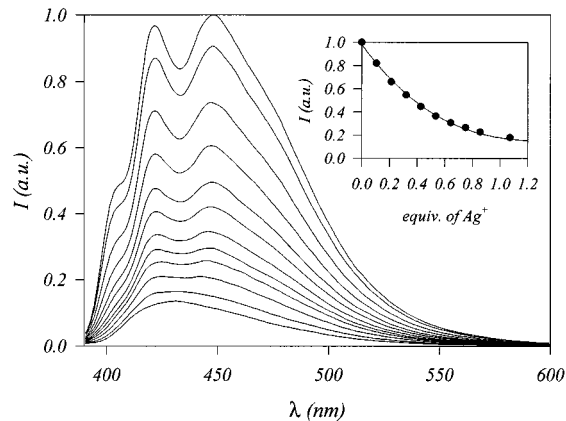


Fig. 1. Fluorescence spectra of **1** in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (8:2) in the presence of increasing amounts of silver ions. *Inset:* Dependence of the fluorescence intensity at $\lambda_{\text{em}} = 450$ nm upon the amount of added silver ions.

The attribution of the two lifetimes is made possible by the examination of the luminescence decays in different wavelength ranges. In particular, collecting only the light emitted in the tail of the spectrum, namely, over 500 nm, a single-exponential decay was detected, with a lifetime close to 0.8 ns. Since the slower-term contribution increases toward lower wavelengths, it can be stated that 5.5 ns is the lifetime of the excited state whose radiative deactivation originates the higher-energy structured anthracene-type fluorescence band.

It is worth noting that the above-described photophysical properties are not altered by changing the concentration in the range between 1×10^{-6} and 10^{-4} M. This observation clearly indicates that an intramolecular process has to be responsible for the double luminescence. It has also been seen that the shape of the luminescence band clearly depends on the polarity of the solvent; in particular, the contribution of the nonstructured component in $\text{MeOH}/\text{CH}_2\text{Cl}_2$ mixtures increases for higher methanol fractions, that is, increasing the polarity of the mixture itself. Finally, no differences were observed between excitation spectra recorded at different emission wavelengths, all being superimposable on the absorption spectrum. All the experimental observations reported above lead us to look at the formation of an intramolecular excimer between the two anthracene moieties of **1** as responsible for the appearance of the broader, red shifted fluorescence band [14].

In the presence of silver ions (perchlorate or trifluoroacetate salts), the above-described fluorescence spectrum of **1** undergoes remarkable changes. Titration experiments showed that a gradual increase in the concentration of silver ions causes a progressive decrease in the structured luminescence band, while the other, broader

band ends by prevailing (Fig. 1). It is worth noting that a 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 comes together with a decrease in intensity of the other band.

Time-resolved experiments performed during titration show that in luminescence decay the contribution of the slower term progressively disappears, and after the addition of more than one equivalent of silver ions, a satisfying data fit can be reached with a single-exponential decay model, yielding a lifetime of 0.6 ns.

The absorption spectrum undergoes significant changes upon complexation: a slight red shift of the lower-energy bands takes place together with a broadening of the same band. The coordination of the metal ion imposes a much more rigid structure to the ligand, and in such a geometry the two anthracene moieties are presumably much closer than in the free ligand. This makes their interaction much easier in both the ground and the excited state. The distortion of the absorption spectrum can be seen as confirmation of such an increased interaction between the two chromophoric units in the ground state. In the excited state, this change in the geometry makes the formation of the excimer more efficient, and as a consequence, it could be the favorite deactivation path of the *S_1 excited state of the anthracene.

The assumption of the formation of the excimer well explains the disappearance of the structured fluorescence band but it does not account for the experimentally observed general decrease in the luminescence intensity. Since the lifetime of the excimeric excited state seems not to be influenced by complexation, one has to assume that a further nonradiative process is responsible for the faster deactivation of the anthracene singlet excited state. An electron transfer process involving the silver ions is thermodynamically possible and could explain the quenching of the fluorescence [15]. Moreover, other possible interpretations such as the occurrence of an energy transfer process from the anthracene to the metal-centered excited states must be ruled out, since the d^{10} silver ions do not have a low-energy metal-centered state.

A deeper investigation indicated that the association process takes place in two steps, and when a solution of silver ions is added to **1**, there is the formation, first, of $[Ag^+ \cdot 1_2]$ and, then, of $[Ag^+ \cdot 1]$. To fit the titration curve, we supposed that these two species present substantially the same photophysical properties because no experimental evidence supported a different interpretation. Taking this statement into account, the association constants for the two consecutive equilibria can be estimated to be $K_1 = 2 \times 10^5 M^{-1}$ and $K_2 = 8 \times 10^4 M^{-1}$.

A large number of metal ions usually show a good affinity toward sulfur-containing compounds; to investigate the possibility that compound **1** could complex some of them, titration experiments with Hg^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , and Co^{2+} were also performed, but no changes in the spectroscopic properties of **1** were observed in any case. Such behavior could be explained in two ways, either that these species do not complex **1** or that the chromophoric unit does not undergo any change upon their complexation. To clarify this point we performed competition experiments. The addition of the above-listed metal ions to an equimolar solution of **1** and Ag^+ did not lead to any recovery of the fluorescence, showing that they do not interfere in any way with silver complex formation.

The present study demonstrates how such a simple chemical receptor as **1** possesses very interesting complexation properties and it encourages further studies directed toward the incorporation of anthracene unit into more complex structures such as, for example, thia-crown ethers. This effort could lead to the realization of species able to recognize other target ions with an even higher efficiency.

CROWN ETHER–DIOXYXANTHONE CHEMOSENSORS

The structure of xanthone (xanthen-9-one) and its photophysical properties suggest that its incorporation into crown ethers and related structures would yield ionophores with a number of desirable features. An appropriate synthesis can yield macrocycles with either oxygen in a position to participate in binding to guest species and this might modify both the binding properties of the crowns and the response to ion binding of the fluorophore [16–19].

We studied two families of compounds, **2a–2c** and **4a–4c**, and, for a better understanding of their properties, the two model molecules **3** and **5**. These parent chromophores present very different photophysical properties. The most evident one is the difference in fluorescence intensity: 1,8-dioxyxanthone derivatives show only a very weak fluorescence intensity, while all the 4,5-dioxyxanthone derivatives are strongly fluorescent even at room temperature.

1,8-Dioxyxanthone Derivatives

The absorption spectra in methanol solution of 1,8-dioxyxanthone derivatives **2a–2c** ($\lambda_{max} = 305$ and $\epsilon_{max} = 12,000 M^{-1} cm^{-1}$) and their very weak fluores-

cence spectra ($\lambda_{\max} = 439 \text{ nm}$, $\Phi_{\text{em}} < 10^{-4}$) are very similar to those obtained for the model compound **3**. The low fluorescence quantum yield of 1,8-dioxoxanthone derivatives and related crowns can be explained in terms of ground-state conformations (found by X-ray crystal structures and already published [16]) containing a non-planar xanthone chromophore whose first excited state is a nonemitting $n-\pi^*$ state.

Upon the addition of Ca^{2+} , Sr^{2+} , and Ba^{2+} metal ions, but not Mg^{2+} or alkali metal ions, to a **2a–2c** crown ether solution, changes in the absorption bands could be observed, while the fluorescence strongly increased in intensity (see Fig. 2 for changes in the fluorescence profile upon titration of **2c** with Ba^{2+}). Experimental data show that the peak position, the luminescence quantum yield, and the excited-state lifetime depend slightly on the crown ether and on the added metal ion, and the excitation spectra undergo parallel changes with respect to the ones observed for the absorption spectra.

We attribute the dramatic increase in the fluorescence intensity to the stabilization of a planar form of the xanthone moiety by complexation; in fact, planarity in this case leads to a lowering in energy of the emitting $\pi-\pi^*$ state, which becomes the lowest excited state. Metal ion complexation introduces a double-positive charge near the oxygen chetonic atom of the xanthone skeleton and this can stabilize the planar conformer, which presents a negative charge on that atom and a positive one on the etheric oxygen in 10 position. This behavior is typical for all the complexes with the crowns **2a–2c**; furthermore, all of them show, in degassed solutions, a delayed fluorescence, with a lifetime in the range of 10–60 μs , which is 10^4 times longer than that of the prompt fluorescence. This delayed fluorescence can be

accounted for by the presence of an equilibrium between the fluorescent singlet excited state and a lower-lying and longer-living triplet state. In all cases an identical band shape was observed for prompt and delayed fluorescence, and this rules out the possibility of an involvement of different luminescent excited states. The presence of molecular oxygen is most probably the responsible for the fast deactivation of the triplet excited state in aerated solution, and this is in line with other experimental data on analogous delayed fluorescence for other aromatic ketones as benzophenone [20].

The large increase in the fluorescence band upon the addition of alkaline earth metal ions demonstrates that the crown ethers **2a–2c** have an effective off/on response to the complexation of these species. This kind of response is one of the most desirable properties that a luminescent sensor can have, as is already well known, since it allows the operator to obtain the best measuring conditions in terms of sensibility and precision due to the low signal-to-noise ratio. Furthermore, **2c** shows good selectivity toward Ba^{2+} ions ($K_{\text{ass}} = 8.9 \times 10^4 \text{ M}^{-1}$, $K_{\text{Ba}}/K_{\text{Sr}} = 80$), so that this crown ether can work as a sensor for Ba^{2+} in the presence of alkaline and alkaline-earth metal ions such as Na^+ , K^+ , Cs^+ , Mg^{2+} (1000 times excess), Sr^{2+} (10 times excess), and Ca^{2+} (100 times excess), although the Ba^{2+} complex has the lowest quantum yield.

4,5-Dioxoxanthone Derivatives

The absorption spectra in methanol solution of the 4,5-dioxoxanthone crowns **4a–4c** and model compound **5** are very similar ($\lambda_{\max} = 355$ and $\epsilon_{\max} = 5700 \text{ M}^{-1} \text{ cm}^{-1}$) and all of them are very fluorescent ($\lambda_{\max} = 437 \text{ nm}$, $\Phi_{\text{em}} = 0.3$). On the contrary to what was observed for 1,8-dioxoxanthone derivatives, molecular modeling shows that the most stable conformation of 4,5-diethoxoxanthone and its crown derivatives incorporates a planar xanthone array [19]. The possibility to accommodate a planar conformation leads to the stabilization of the $\pi-\pi^*$ state, which is responsible for such an intense fluorescence band.

On the contrary to what was observed for 1,8-dioxoxanthone derivatives, both fluorescence spectra and conductivity did not change on the addition of earth alkali metal ions and this suggests values for the association constants lower than 100 M^{-1} .

As far as the crowns **4a–4c** are concerned, strong effects were instead observed on fluorescence spectra upon the addition of sodium, potassium, or cesium bromide, while the effects on the absorbance spectra in methanolic solutions were very small. The intensity of the

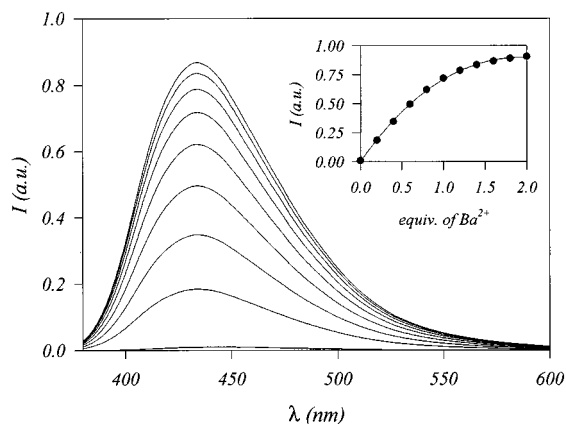


Fig. 2. Fluorescence spectra of **2c** in MeOH in the presence of increasing amounts of barium ions. *Inset:* Dependence of the fluorescence intensity at $\lambda_{\text{em}} = 435 \text{ nm}$ upon the amount of added barium ions.

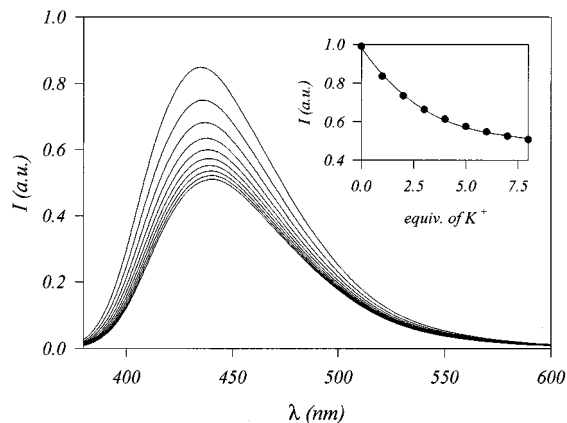
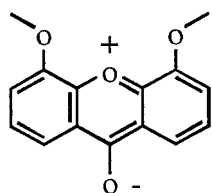


Fig. 3. Fluorescence spectra of **4b** in MeOH in the presence of increasing amounts of potassium ions. *Inset:* Dependence of the fluorescence intensity at $\lambda_{em} = 440$ nm upon the amount of added potassium ions.

fluorescence band showed strong quenching upon complexation (see Fig 3 for changes in the fluorescence profile upon titration of **4b** with K^+), accompanied by a reduction in fluorescence lifetime. The values for association constants extracted from the curves (insets in figures) were in excellent agreement with data obtained by conductivity measurements and they are one order of magnitude lower than those calculated for 1,8-dioxyxanthone derivatives. [21]

The decrease in fluorescence intensity of the crown ethers upon complexation can be attributed to the coordination of the metal ion at the ether oxygen, which would destabilize the planar conformation. Complexation stabilizes a conformation (see Scheme II) bearing a positive charge on the side of the crown ether cavity, which promotes the folding of the xanthone moiety. This folding causes an enhancement in energy of the $\pi-\pi^*$ emitting state so that the nonemitting $n-\pi^*$ excited state becomes the lowest in energy, yielding the observed luminescence quenching. The effect of metal ion binding on the chromophore is thus exactly the opposite of what was observed in the 1,8-dioxyxanthone-based crowns. For this family of metal ion complexes no delayed luminescence was observed in deaerated solutions, indicating that in 4, 5-dioxyxanthone derivatives the energy gap between the



Scheme II.

fluorescent lowest singlet state and the lower-lying triplet state is higher and cannot be overcome even at room temperature.

The two families of crown ethers reported here can be seen as an series of chemical sensors with partial specificity to the different alkaline and alkaline earth metal ions. Moreover, the presence of the delayed fluorescence observed for the metal ion complexes with **2a–2c** has some importance from an application viewpoint since it could allow us, using time-resolved spectroscopy, to increase the signal-to-noise ratio during analyte detection [22].

EXPERIMENTAL

Materials

The solvents used were methanol and dichloromethane UVASOL from Merck Co. without further purification. Metal ion salts were ACS grade from Fluka and used without further purification.

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 a 1 N H_2SO_4 aqueous solution ($\Phi = 0.546$) [23] as a reference. To allow comparison of emission intensities, corrections for instrumental response, inner filter effects, and phototube sensitivity were performed. [24]

CONCLUSIONS

All the species presented here have shown such photophysical properties to be good candidates for practical applications. The thia-anthracene chemosensor constitutes a very encouraging starting point for developing a series of related ones with different affinities for other target ions, while the dioxyxanthone-based chemosensors represent two families of chemical sensors with partial specificity toward the different alkaline and alkaline-earth metal ions.

All these findings suggest the possible use of these species for the construction of an electronic tongue which

could, in principle, determine simultaneously the concentration of many metal ions as a function of time; in this particular case, the metal ions would be Na^+ , K^+ , Cs^+ , Ba^{2+} , Sr^{2+} , and Ca^{2+} .

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