



Fluorescent Chemosensors Based upon Macrocyclic Polyamines Containing Aromatic Sectors

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Abstract

The basicity and the coordination properties of several polyamine macrocycles containing phenanthroline or dipyridine moieties as integral part of the cyclic framework are reported. The ligands behave as fluorescent chemosensors for both H^+ and metal ions. The use of such ligands in the preparation of simple molecular machines, of chemosensors for metallohexacyanide anions, and of catalysts for photoinduced redox reactions is also described. The paper is a brief review of recent works performed by the authors.

Introduction

An attractive method to detect the presence in solution of non-fluorescing species is the use of fluorescent receptors, whose emission properties are affected by interaction with the target compound [1]. In order to obtain a quantification of the fluorescence emission signal upon substrate-receptor interaction it is necessary that either chelation enhancement of fluorescence (CHEF) or chelation enhancement of quenching (CHEQ) effects are observed.

The binding sites of these chemosensors can be either integrated into the fluorophore structure (intrinsic chemosensors) or connected to the fluorophore through a spacer (conjugate chemosensors). Also receptors showing mixed intrinsic-conjugate characteristics have been developed. Of particular interest are fluorescent chemosensors capable of functioning in aqueous solution, since most of the chemosensors that function efficiently in less polar solvents do not give adequate responses in water either due to low solubility limits or to weak binding to the target species. A successful method to obtain efficient water-soluble chemosensors consists in the assembling of a fluorophore with a polyamine ligand. In particular, tight association with substrate species is often achieved when the polyamine moieties of such receptors have a macrocyclic arrangement. In the last few years we have synthesized a number of similar molecules (Chart 1), and employed them as fluorescent chemosensors or photosensitizers [2–8]. Other macrocyclic ligands with similar characteristics have been studied by different groups [9–19].

In this paper we present a brief review of some results recently obtained on the topic in our laboratory.

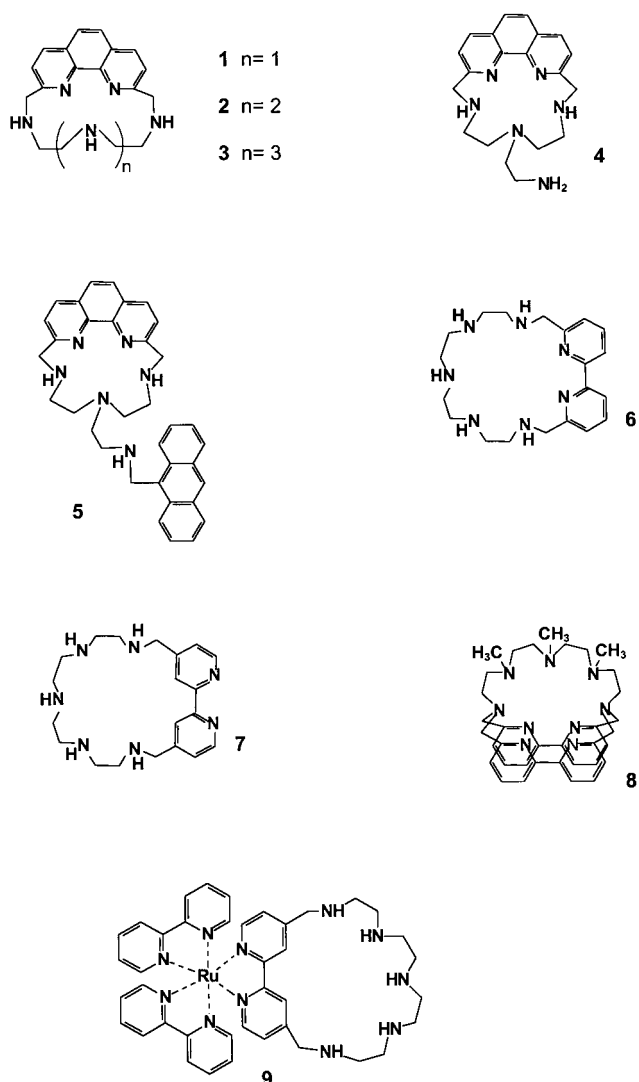


Chart 1.

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Phenanthroline fluorophores

Phenanthroline-containing chemosensors have received much attention in recent years, since this aromatic group, which behaves as an intrinsic chemosensor for H^+ and metal cations, contains two amine groups that can act cooperatively in the binding of metals, its fluorescence emission properties being highly sensitive to the interaction with these species. We have recently studied the three macrocyclic conjugate chemosensor **1–3** containing a phenanthroline unit as integral part of the cyclic framework [2, 3].

The shape and position of the fluorescence emission bands of these molecules are identical to those of phenanthroline, but the intensity of the emission increases with decreasing pH decreasing again in very acidic solutions, as shown for **3** in Figure 1. Quenching of the emission in similar compounds takes place through an electron transfer mechanism involving the lone pairs of the amine nitrogens in benzylic position and the excited fluorophore. When such benzylic nitrogens are protonated the quenching mechanism is inactive and the molecule emits. Potentiometric and 1H and ^{13}C NMR measurements display that, while the amine groups of these compounds are easily protonated above pH 2, the phenanthroline nitrogens, characterized by lower basicity, do not participate directly in protonation, although, as shown by NMR studies, they are involved, at some extent, in the stabilization of the protonated species via intramolecular hydrogen bonding. As expected such involvement increases with decreasing pH, i.e., with increasing ligand protonation. Rather surprisingly, the observed decrease of the emission at very low pH corresponds to the formation of the fully protonated ligands (referring to aliphatic nitrogens) which are not the most emissive forms. Such loss of emission intensity can be explained by considering the possibility of inversion between the strongly emissive $\pi\pi^*$ state of phenanthroline and the poorly emissive $n\pi^*$ one. Interaction of phenanthroline nitrogen atoms with H^+ can stabilize the $n\pi^*$ state with respect to the $\pi\pi^*$ state, leading to inversion of the states and decrease of the fluorescence emission intensity. Upon detachment of one proton from the fully protonated receptors (referring to aliphatic nitrogens) the hydrogen bond interaction of phenanthroline nitrogens with the ammonium groups is weakened and the intensity of the emission is consequently enhanced. At higher pH values when the first benzylic nitrogen becomes not involved in protonation, the electron transfer mechanism can operate and the emission is completely quenched. This occurs with the formation of the species $H1^+$, $H2^{2+}$, and $H3^{3+}$ (Figure 1).

As shown in Figure 2 for **3**, upon complexation with Zn(II) the quenching of the fluorescence emission occurring at higher pH values is displaced toward the acidic zone, determining the conditions for detection of Zn(II) in solution. This behavior is due to the fact that in the ZnL^{2+} ($L = 1-3$) complex at least one of the amine groups in benzylic position is not involved in metal ion coordination, and hence is available for the quenching mechanism. Such structural characteristics can be ascribed to the rigidity of the phenanthroline group, that leads to a marked stiffening of the

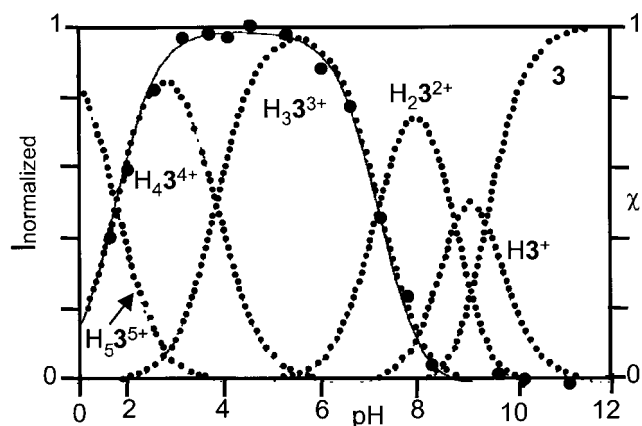


Figure 1. Fluorescence emission titration curve and mole fraction distribution curves of protonated species for ligand **3** in water.

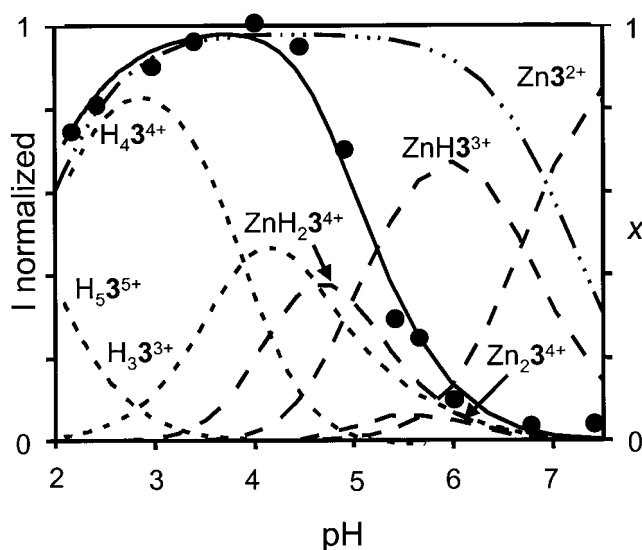


Figure 2. Steady state fluorescence emission curves of **3** in the absence (---) of Zn(II) and in the presence (●) of Zn(II) (metal to ligand 1:1 molar ratio), and species distribution curves in water.

cyclic ligands and, therefore, precludes the simultaneous participation of all the amine nitrogens in the coordination. Furthermore, phenanthroline has electron-withdrawing properties, which reduce the basicity and the donor ability of the amine groups in benzylic position. As a matter of fact, in the solid state the benzylic nitrogens are only weakly involved in metal coordination, as shown by the crystal structure of the $Zn1(H_2O)^{2+}$ cation [2]. In acidic solution complex protonation causes, in the case of **2** and **3**, the involvement of both benzylic nitrogens in either protonation or metal ion coordination, allowing the fluorescence emission to take place. This occurs with the diprotonated complex of **3** (Figure 2) and the monoprotonated complex of **2** [3]. The Zn(II) complex with **1**, not forming protonated species, is always quenched [2].

Receptor **1** was modified to obtain a new receptor able to signal more efficiently the presence in solution of metal ions, such as Zn(II). The modification, performed through a completely new synthetic route not involving the preparation of **1**, was made by preparing the intermediate molecule **4** which was successively functionalized on the pendent arm

by attaching an anthracene group, to obtain **5** [4]. The new ligand **5** was expected to assume a folded conformation, upon metal ion coordination, leading to π -stacking interaction between the two aromatic moieties. Indeed the crystal structure of the tetraprotonated form of the precursor **4** displayed a correct folded conformation (Figure 3) even in absence of coordinated metal ions [20]. Receptor **5** is not very soluble in water; for this reason an acetonitrile-water (1:1, v/v) mixture was employed for the solution studies [4]. **5** forms stable Zn(II) complexes with $\text{ZnH}_2\mathbf{5}^{4+}$, $\text{ZnH}\mathbf{5}^{3+}$, $\text{Zn}\mathbf{5}^{2+}$, $\text{Zn}\mathbf{5}(\text{OH})^+$, and $\text{Zn}\mathbf{5}(\text{OH})_2$ stoichiometry. ^1H NMR spectra recorded at different pH values showed that deprotonation of the $\text{ZnH}_2\mathbf{5}^{4+}$ complex to give $\text{ZnH}\mathbf{5}^{3+}$ takes place at the nitrogen of the pendant arm and coordination of this donor atoms to the metal ion enables the two aromatic moieties to interact *via* π stacking. The fluorescence emission spectra of the Zn(II) complexes with **5** ($\lambda_{\text{max}} = 418$ nm) are quite similar to those of the protonated ligand. As shown in Figure 4, all complexes are not emissive except $\text{ZnH}_2\mathbf{5}^{4+}$ which still exhibits an intense emission with a maximum at 418 nm. The most interesting feature of this system, however, is the formation of a non-structured and red shifted emission band (Figure 4), occurring for all complexes with the exception of $\text{Zn}\mathbf{5}(\text{OH})_2$. This exciplex type emission was ascribed to an intramolecular π -stacking complex in the excited state, involving phenanthroline and anthracene. On the other hand, the ^1H NMR spectra showed that the π -stacking complex is already formed in the ground state for the species $\text{ZnH}\mathbf{5}^{3+}$, $\text{Zn}\mathbf{5}^{2+}$ and $\text{Zn}\mathbf{5}(\text{OH})^+$, but not for $\text{ZnH}_2\mathbf{5}^{4+}$ and $\text{Zn}\mathbf{5}(\text{OH})_2$. As a consequence, for $\text{ZnH}_2\mathbf{5}^{4+}$ the π -stacking exists only during the excited state lifetime. As shown by both NMR and photochemical measurements, the π -stacking interaction disappears at more basic pH values where detachment of the amine nitrogen of the pendent arm from Zn(II) is expected to occur upon coordination of the second OH^- ion. Hence, **5** is able to perform an elegant sensing of Zn(II) ion, forming a complex which behaves as an elementary molecular machine driven by both pH and light (Figure 5).

Dipyridine fluorophores

Another intrinsic chemosensor used to built receptor molecules is dipyridine. In a recent study [5] we have employed dipyridine to obtain the two isomeric ligands **6** and **7** differing for the arrangement of donor atoms. In **6** all ligand nitrogens converge towards the interior of the macrocyclic cavity, while in **7** the dipyridine nitrogens are orientated outside the cavity, giving rise to a receptor with two distinct, divergent binding sites. The dipyridine nitrogens of these ligands are involved in protonation in moderately acidic solution. This characteristics allow the use of absorption spectra for the analysis of both protonation and coordination properties of these ligands. In fact protonation of the dipyridine nitrogens can be easily monitored by means of spectrophotometric measurements, following the appearance of a typical band at 304 nm. The absorbance reaches a maximum when both dipyridine nitrogens are protonated

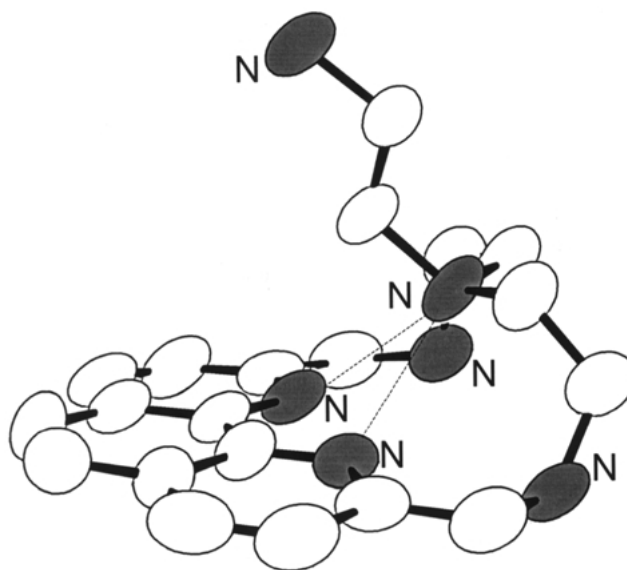


Figure 3. Crystal structure of the $\text{H}_4\mathbf{4}^+$ cation with indication of intramolecular hydrogen bonds.

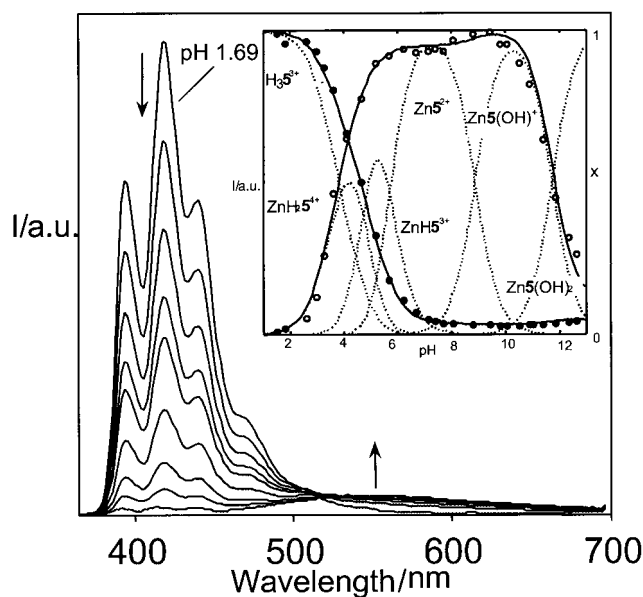


Figure 4. Fluorescence emission spectra of the Zn(II)/**5** system (acetonitrile-water 1:1, v/v) at different pH values: 1.69, 3.73, 4.4, 4.87, 5.1, 5.57, 6.05, 6.55, 10.37 ($\lambda_{\text{exc}} = 352$ nm). Inset: fluorimetric titrations of the same system (emission followed at 418 nm (●—), exciplex emission followed at 600 nm (○—)) and molar fraction curves of the species formed.

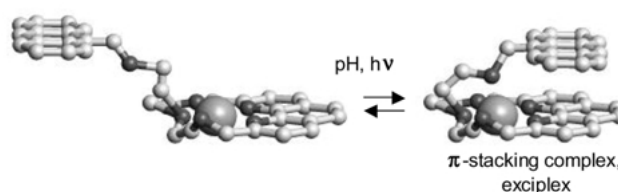


Figure 5. The Zn(II)/**5** system: an elementary molecular machine driven by pH and by light.

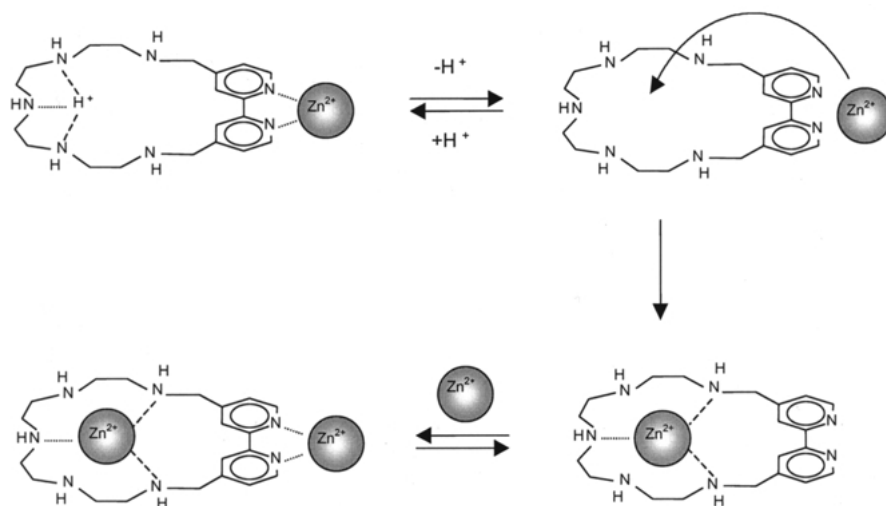


Figure 6. Schematic representation of the different coordination modes occurring in the formation of Zn(II) complexes with **7**.

and falls down with their deprotonation. For **6** and **7**, the absorption spectra offered a clearer information regarding proton location than NMR measurements, in particular in presence of metal ion coordination. Both **6** and **7** are able to form mono- and binuclear complexes with Zn(II). **6** displays a greater tendency to form mononuclear species, since it can use a greater number of donor atoms to bind the metal ion, while **7** displays a greater tendency to bind the second metal ion, due to the presence in its structure of two separated binding sites which bring the two metal ions far apart from each other reducing the electrostatic repulsion. The presence of two distinct binding sites is, most likely, also at the origin of the marked tendency of the Zn^{7+} complex to bear stepwise protonation up to the formation of the tetraprotonated species. An interesting feature of this system is the effect of protonation in determining the metal coordination environment. According to both stability constants and absorption data, the Zn(II) ion is bound outside the cavity in the $\text{ZnH}_4\text{7}^{6+}$ complex; when the acidic protons are removed, the Zn(II) ion remains coordinated outside the cavity until the last proton is removed; then complexation takes place inside the cavity and external binding of a second metal ion may occur, as schematised in Figure 6.

Recently we have reported the synthesis of a new cryptand ligand **8** containing two dipyrindine chromophores [6, 7]. The principal difference from previous dipyrindine-containing cryptands is the presence in **8** of a polyamine chain connecting the two heteroaromatic units. This polyamine moiety was inserted in the ligand in the attempt to make more accessible the binding cavity, reducing the characteristic kinetic inertness presented by cryptands in complexation reactions. Furthermore, this polyamine chain containing three amine groups was expected to allow pH modulation of the chemical and photophysical ligand properties. Indeed complexation of alkali (Li^+ , Na^+ , K^+) and alkaline-earth (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) metal ion by the cryptand takes place through fast reaction allowing us to determine the stability constants of the relevant complexes in aqueous solutions. Noteworthy, **8** displays a good binding ability towards

these metal ions, with a marked selectivity towards Na^+ , among alkali metals, and Ca^{2+} and Sr^{2+} among alkaline-earth metals. A peculiar characteristic of these complexes is the high tendency to form protonated species in solution. All complexes form mono- and diprotonated species, while even triprotonated ones are formed in the case of Na^+ , Ca^{2+} , and Ba^{2+} . The values of the complex protonation constants as well as the absorption spectra recorded on complex solutions at different pH values indicate that protonation occurs on the polyamine chain while dipyrindine groups are involved in metal coordination. The most interesting feature of this system, however, is the formation of an Eu(III) cryptate complex whose luminescence emission is modulate by complex protonation. Figure 7 displays the crystal structure of the $[\text{EuCl}_3\text{H}_2\text{8}]^{2+}$ complex cation showing the metal ion encapsulated into the ligand cavity, coordinated by the nitrogen atoms of the two dipyrindine groups, the two bridgehead nitrogens, and three chloride anions. Most likely the three coordinated chloride anions are replaced by water molecules in aqueous solution. Solutions of the complex in absence of chloride shows the characteristic visible emission of the metal with a maximum at 617 nm, upon excitation at 306 nm. Figure 8 reports the pH dependence of the luminescence emission at 617 nm along with the distribution curves of the species formed obtained by least square fitting of the emission curve. As shown in Figure 8, emission reaches a maximum around pH 8 decreasing both in more acidic and in more alkaline solutions. The luminescence decrease in acidic solution was ascribed to the coordination of water molecules replacing the amine nitrogens of the aliphatic chain detached from Eu(III) upon protonation, while quenching of the emission in alkaline solution was attributed to the formation of hydroxylated complexes (Figure 8). These features originate a novel pH-modulated *antenna effect*.

Considering the ability of ligand **7** to coordinate metal ion by the dipyrindine nitrogens outside the cavity, we thought to use this ligand to obtain a receptor (**9**) having a $\text{Ru}(\text{II})(\text{bpy})_3$ (bpy = bipyridine) unit and a polyamine binding unit, in order to make use of the emission and redox

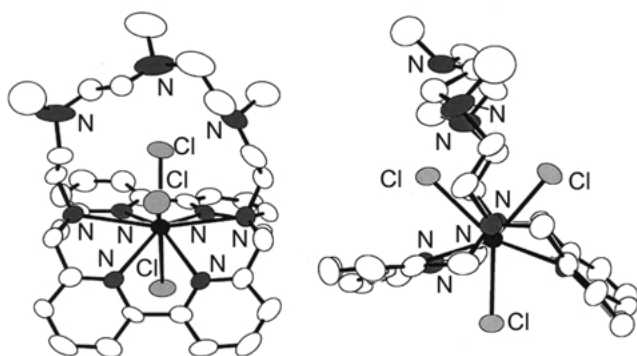


Figure 7. Different views of the crystal structure of the $[\text{EuCl}_3\text{H}_2\mathbf{8}]^{2+}$ cation.

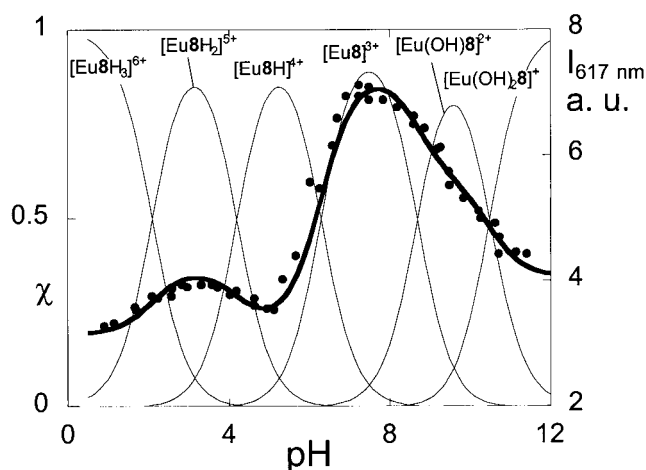


Figure 8. Luminescence emission (\bullet) of the Eu(III) complex with $\mathbf{8}$ ($\lambda_{\text{exc}} = 260 \text{ nm}$; $\lambda_{\text{em}} = 617 \text{ nm}$, $[\mathbf{8}] = [\text{Eu(III)}] = 5 \times 10^{-5} \text{ M}$, 300 K) and molar fraction of the Eu(III) complexes.

properties of this core in signalling or photosensitising substrate species. $\mathbf{9}$ was obtained by a simple reaction involving $\mathbf{7}$ and $\text{Ru}(\text{bpy})_2\text{Xl}_2$ in ethyleneglycol. The crystal structure of $[\text{Ru}(\text{bpy})_2(\text{H}_3\mathbf{9})]^{5+}$, that is $\text{H}_3\mathbf{9}^{3+}$, is reported in Figure 9. Similar receptors based upon a $\text{Ru}(\text{II})(\text{bpy})_3$ unit were synthesised in previous works [21]. In general these compounds were insoluble in water, while our receptor is water soluble. Although $\mathbf{9}$ is able to bind up to five protons in aqueous solution the absorption spectrum of this compound in solution is almost independent of pH. Upon excitation of the complex in the metal to ligand charge transfer band centred at 470 nm, the complex emits in the visible region. The emission is pH dependent, decreasing with decreasing pH. A smooth quenching of the emission takes place with ligand protonation, as shown in Figure 10. In presence of $\text{Zn}(\text{II})$ several complexes are formed, but the fluorescence emission displays only a very small chelation enhancement of fluorescence. On the contrary, complexation of $\text{Cu}(\text{II})$ gives rise to a marked quenching of the emission (Figure 11). The quenching was ascribed to an energy transfer process from the excited $\text{Ru}(\text{bpy})_3$ unit to $\text{Cu}(\text{II})$. Indeed, the $\text{Cu}(\text{II})$ complexes generally have d-d transitions matching the excitation energy of the $\text{Ru}(\text{bpy})_3$ unit. Interestingly, the emission is restored at very high pH values (Figure 11). Formation of $\text{Cu}(\text{II})$ hydroxo complexes, determining the stripping of the

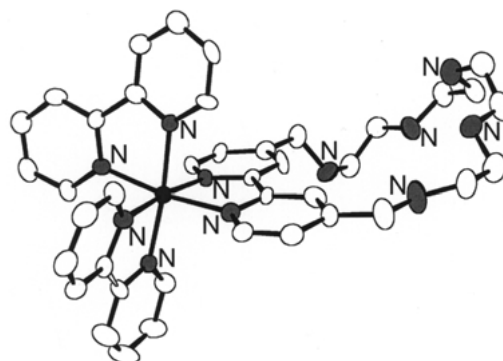


Figure 9. Crystal structure of the $[\text{Ru}(\text{bpy})_2(\text{H}_3\mathbf{9})]^{5+}$ cation.

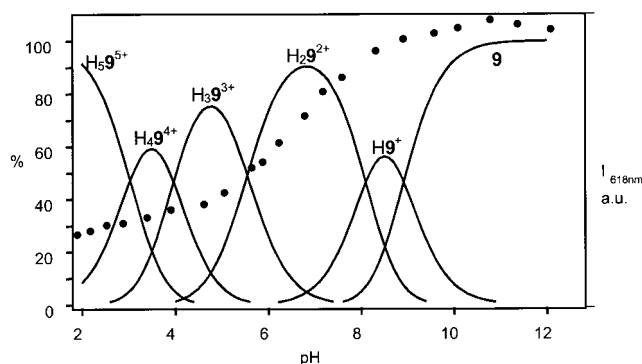


Figure 10. Emission titration curve (\bullet) of $\mathbf{9}$ obtained at $\lambda_{\text{em}} = 618 \text{ nm}$ and $\lambda_{\text{ex}} = 470 \text{ nm}$, and molar fraction of the protonated species.

metal ion from the macrocyclic cavity with the formation of a free ligand was suggested to justify such a revival of the emission. Support for this interpretation was provided by calculation on simulated distributions of species at equilibrium, and by the fact that the emission spectra obtained in alkaline media, in presence of $\text{Cu}(\text{II})$, are consistent with those obtained under the same conditions for compound $\mathbf{9}$ in absence of metal ion. Hence, $\mathbf{9}$ exhibits a modest detection ability for $\text{Zn}(\text{II})$ and a marked detection ability for $\text{Cu}(\text{II})$.

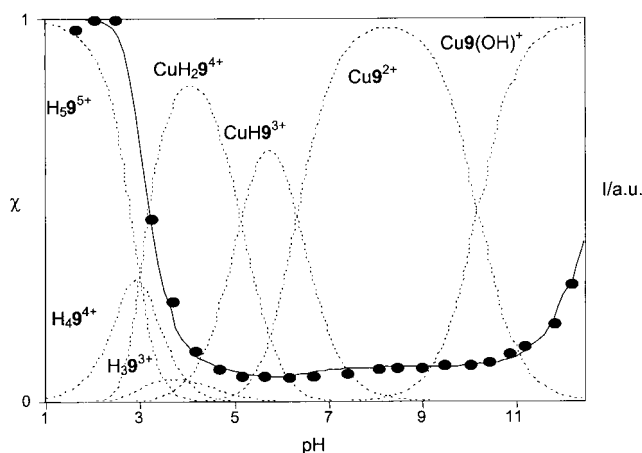


Figure 11. Emission titration curve (\bullet) of the $\text{Cu}(\text{II})/\mathbf{9}$ system obtained at $\lambda_{\text{em}} = 616 \text{ nm}$ and $\lambda_{\text{ex}} = 470 \text{ nm}$, and molar fraction distribution curves.

Photosensitized processes

It is well known that polyammonium cations are good receptors for anionic species in solution [22]. In particular very stable adducts are formed with $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$, principally due to the high negative charge of such anions. Hence, it was expected that also protonated species of **9** might be able to form similar adducts. The interest towards such systems stemmed from the fact that the emission of the parent compound $[\text{Ru}(\text{bpy})_3]^{2+}$ was known to be efficiently quenched by interaction with metallo-cyanide complexes [23], and thus $[\text{Ru}(\text{bpy})_3]^{2+}$ could be used as a sensor for this type of anions. Compound **9** contains the basic ruthenium sensing unit, but in addition possesses an extra binding polyamine receptor, that is expected to influence the overall process, improving the efficiency in anion sensing. Actually, the hexacyanide complexes of Fe(II) and Fe(III) form very stable pairs with the variously protonated forms of **9** and are more efficient than $[\text{Ru}(\text{bpy})_3]^{2+}$ in performing the quenching of the luminescent emission of **9** [8]. The quenching mechanism involves an electron transfer process taking place from Fe(II) complex to the excited $\text{Ru}(\text{bpy})_3$ unit and, vice versa, from the excited $\text{Ru}(\text{bpy})_3$ unit to the Fe(III) complex.

Considering such redox properties of the $\text{Ru}(\text{bpy})_3$ unit, it was thought to explore the activity of **9** in photocatalytic oxidation reactions. Good results were obtained by using **9** as a catalyst in the photoinduced oxidation of iodide to iodine by dioxygen [8]. Balzani *et al.*, in a earlier work, used the Co(III) sepulchrate complex as photosensitizer to promote this reaction [24]. Experimentally, when **9** complex is added to a I^- solution, even in small amounts with respect to I^- , at pH values around the neutrality or lower, and the solution is irradiated at 436 nm, formation of I_3^- is immediately observed by the appearance of the typical color of I_3^- in solution, which is due to the absorption band at 350 nm. It must be noted that the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex is not able to promote this reaction. As a matter of fact, the positive charge accumulated on the polyamine moiety upon protonation attracts the iodide anion (Figure 12) which can perform an electron transfer to the excited $\text{Ru}(\text{II})$ complex unit, forming a reduced dipyridine radical anion. The iodine atom then reacts with the iodide anions in solution producing I_3^- as a final product, by a sequence of well known reactions. On the other side, the dipyridine radical anion is reoxidized by dioxygen. Unfortunately, the system is not very efficient, mostly due to the fact that iodide is able to give a modest quenching (about 5%) of the excited state of the catalyst and to a competitive back reaction, consisting of an electron transfer from the dipyridine radical anion to the I_3^- , that decreases the net formation of photo-products.

Acknowledgements

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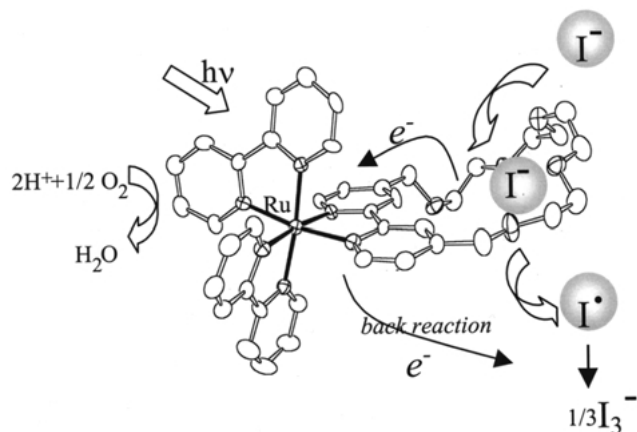


Figure 12. Photocatalytic activation of the iodide oxidation to iodine by O_2 promoted by protonated forms of **9**.

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