

A novel fluorescent chemosensor exhibiting exciplex emission. An example of an elementary molecular machine driven by pH and by light

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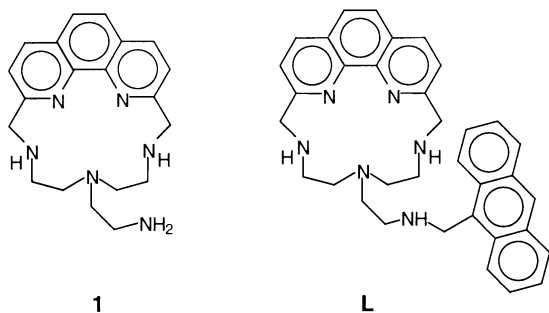
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Coordination/detachment of a pendent functionality in the Zn(II) complex with a macrocyclic ligand L gives rise to on/off switching of exciplex emission, defining an elementary molecular machine whose movements are driven by both pH and light.

Chemical systems capable of performing controlled movements at the molecular level are a topic of great interest. In particular great attention is paid to molecular systems whose movements can be controlled by external inputs (pH, temperature, light, redox potential, metal ions).^{1–6}

In the present work we describe a Zn(II) complex behaving as an elementary molecular machine driven by pH and light. The mechanical function of this machine consists in the movement of a ligand moiety determined by pH-controlled coordination–detachment of a donor atom leading to the formation of an exciplex emitter. The ligand used, **L**, was obtained by reaction



of anthracene-9-carbaldehyde (EtOH, room temperature, 48 h) with the macrocyclic precursor **1**, followed by reduction *in situ* of the resulting imine with NaBH₄, according to a reported procedure.⁷ **1** was synthesized by condensation of 2,9-bis-(bromomethyl)-1,10-phenanthroline with tris(2-tosylaminoethyl)amine by using the Richman and Atkins procedure.⁸

The absorption spectrum of the free ligand presents the characteristic band of the anthracene moiety ($\lambda_{\text{max}} = 352$ nm), and is only slightly dependent on the pH. The most intense absorption band occurs at 252 nm, a region where both the first singlet of phenanthroline, and the second singlet of anthracene absorb. However, the fluorescence emission exciting at 352 or 252 nm is the same, as expected from the Kasha–Vavilov's rule.⁹

The most interesting feature of the fluorescence emission concerns its dramatic dependence on the protonation state of the compound.[†] A total quenching of the emission is observed for the species **L**, **HL**⁺ and **H₂L**²⁺, while the **H₃L**³⁺ form exhibits an intense emission. As observed for many other similar molecules possessing the anthracene fluorophore attached to a polyamine chain, the quenching effect can be explained by an electron transfer process from unprotonated amine groups to the excited anthracene.^{10,11} On the other hand protonation of amines rises

their oxidation potential to >2.5 V changing the photoinduced electron transfer reaction from exoergic to endoergic, thus precluding the quenching effect.¹² ¹H NMR titrations performed at different pH values showed that in **H₃L**³⁺ all three benzylic nitrogens are protonated. Only the N2 amine remains unprotonated, although, according to the emission spectra, this would not be an efficient site for photo-induced electron transfer quenching, probably because of involvement in hydrogen bonding to adjacent protonated nitrogens. The species **H₂L**²⁺, **HL**⁺ and **L** have two, three and four unprotonated nitrogens, respectively, accounting for the observed quenching effect.

Potentiometric measurements performed in water–MeCN (1 : 1, v/v) solutions, containing Zn(II) and **L** in 1 : 1 molar ratios, showed the formation of stable complexes ([ZnL]²⁺, [ZnHL]³⁺, [ZnH₂L]⁴⁺, [ZnL(OH)]⁺, [ZnL(OH)₂]) over the entire pH region investigated.[†] The formation of these Zn(II) complexes has also been followed by recording ¹H NMR spectra at different pH values, indicating that deprotonation of [ZnH₂L]⁴⁺ to form [ZnHL]³⁺ (pH 3–5) takes place at the amine nitrogen of the pendant arm. At the same time, remarkable shifts for the signals of anthracene and phenanthroline protons evidence the formation of a π -stacking interaction between the two aromatic moieties in the [ZnHL]³⁺ complex. In other words, metal coordination by the deprotonated amine group of the pendant arm enables the two aromatic moieties to interact *via* π -stacking. Such stacking interaction is maintained in the [ZnL]²⁺ and [ZnL(OH)]⁺ species, as shown by the fact that the spectra do not bear significant changes at neutral or slightly alkaline pH. By contrast, NMR data obtained in very alkaline media (pH 10–13), where [ZnL(OH)₂]²⁺ is formed, suggest that binding of the second OH[–] ion causes the detachment of the amine group of the pendant arm and consequent loss of the π -stacking interaction.

Like many other Zn(II) complexes bearing polyamine chains attached to a fluorophore, the fluorescence emission spectra of the Zn(II) complexes with **L** ($\lambda_{\text{max}} = 418$ nm) are quite similar to those of the protonated ligand (Fig. 1). This is explained by the fact that coordination of Zn(II) to the amine groups (like protonation) precludes the electron transfer quenching effect.^{10–12} On this basis, the quenching effect occurs only at pH values that permit the existence of nitrogens which are neither attached to the metal nor protonated (Fig. 1). This clearly occurs for all the complexes species except [ZnH₂L]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 (Fig. 1), occurring for all metal complexes with the exception of [ZnL(OH)₂]. The excitation spectrum at pH = 6.4, collected at 418 nm is coincident with the absorption spectrum. However the excitation spectrum collected at 600 nm is slightly red shifted, as expected from a ground state association. This exciplex type emission can thus be ascribed to an intramolecular

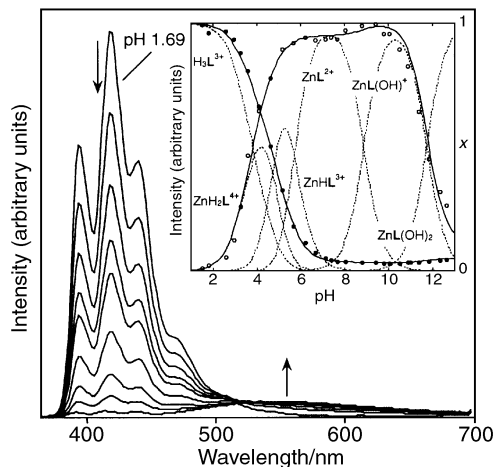


Fig. 1 Fluorescence emission spectra of the Zn(II)-L (1 : 1) system in 0.15 M NaCl MeCN-H₂O (1 : 1, v/v) at different pH values: 1.69; 3.73; 4.4; 4.87; 5.1; 5.57; 6.05; 6.55; 10.37 ($\lambda_{exc} = 352$ nm). Inset: fluorimetric titration of the same system: (●) emission followed at 418 nm, (○) exciplex emission followed at 600 nm. Species distribution curves (inset) represent mol fractions.

π -stacking complex in the excited state, involving phenanthroline and anthracene. As described above, the π -stacking complex is already formed in the ground state for the species [ZnHL]³⁺, [ZnL]²⁺ and [ZnL(OH)]⁺, but not for [ZnH₂L]⁴⁺ and [ZnL(OH)₂]. As a consequence, for [ZnH₂L]⁴⁺ the π -stacking complex must be formed during the excited state lifetime. The π stacking complex in the ground state and the exciplex emission from the excited state can be explained as a consequence of coordination of the nitrogen of the pendent arm to the metal, since this leads to a geometry where phenanthroline and anthracene are forced to stay close to each other in a sandwich-like mode. This structure is maintained upon coordination of a single OH⁻ ion to the metal, probably because the binding occurs at the opposite side of the pendent arm, while the exciplex emission, as well as the π -stacking complex, disappear at more basic pH values, in agreement with the detachment of the amine nitrogen of the pendent arm caused by coordination of the second OH⁻ ion.

Time-resolved fluorescence measurements collected at 419 and 550 nm reveal that, independently of the pH value considered, the decays are always fitted with sums of two or three exponentials. The fluorescence decay of the parent compound, 9-(methylaminomethyl)anthracene, measured at pH = 2 is however single exponential with a lifetime of 10.5 ns. Within the pH range studied (1.6–12.0), two lifetimes with values of 2–2.9 and 5.2–10.5 ns are observed. For lower pH values the contribution of the shorter lifetime is largely predominant at 419 nm (99%), but not so much at 550 nm (70%). As the pH increases the contribution of the second lifetime increases with a concomitant decrease of the shorter component. A third lifetime, attributed to the emissive exciplex species of 21–25 ns, begins to appear at pH = 5. For pH = 8.7 the contribution of this new species is predominant at $\lambda_{em} = 550$ nm (45% of the overall decay) but almost negligible at $\lambda_{em} = 419$ nm. This means that the back reaction from the exciplex to the monomer(s) is almost non-existent. Although always present for pH > 5, the emission contribution of the exciplex seems to reach a maximum at pH ca. 8, slowly decreasing at higher pH values.

We interpret the existence of the two first lifetimes to the presence of two opened structures (monomers) in equilibrium, one clearly ascribable to the free [H₃L]³⁺ species and the other probably to the [ZnH₂L]⁴⁺ complex. In conjunction with steady-state data it is clear that these two monomer species emit in the same region and can only be distinguished by time-resolved fluorescence. In cases where exciplex emission occurs, no negative pre-exponential, i.e. a rise-time, is observed as a result of two factors: the first is related to previous findings that

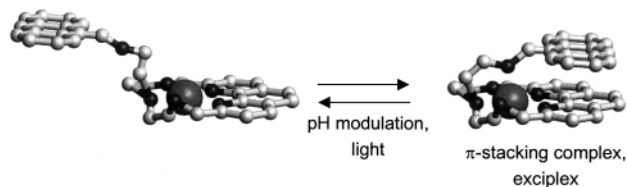


Fig. 2 Modulated formation of the π -stacking complex (exciplex).

a pre-formed exciplex is already present in the ground-state, and the second is a consequence of the fact that the fluorescence emission of the monomer(s) extends to the emission region where the exciplex emits.

The system here reported exhibits a significant advantage, in comparison with other similar compounds, because coordination of the pendent arm to the metal can be easily monitored by the appearance of the exciplex emission. The system defines an elementary molecular machine whose movements are driven by pH, and also by light around pH 4 (Fig. 2). Additionally, it can operate in acidic media switching from the species H₃L³⁺ to [ZnH₂L]⁴⁺ or in alkaline media between [ZnL(OH)]⁺ and [ZnL(OH)₂].

Interestingly the exciplex emission occurs not only in MeCN-water mixtures but also in pure water, in contrast with other exciplexes or excimers reported in literature which are only stable in non-polar solvents.⁹

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Notes and references

† Ligand protonation and Zn(II) complexation constants were determined by potentiometric titration performed in 0.10 mol dm⁻³ NMe₄Cl water-MeCN (1 : 1, v/v) solutions at 298.1 ± 0.1 K. Calculated values are: log K^{HL} = 9.0(1), log K^{H₂L} = 8.3(1), log K^{H₃L} = 6.1(2), log K^{ML} = 14.0(1), log K^{MHL} = 5.8(1), log K^{MH₂L} = 4.6(1), log K^{MLOH} = 6.1(1), log K^{MLOH₂} = 4.3(1) (K^{A/B} = [AB]/[A][B]).

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