Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Bernardo, M. Alexandra , Alves, Sérgio , Pina, Fernando , De Melo, J. Seixas , Albelda, M. Teresa , Garcia-España, Enrique , Llinares, José Miguel , Soriano, Conxa and Luis, Santiago V.(2001) 'Polyamine Linear Chains Bearing Two Identical Terminal Aromatic Units. Evidence for a Photo Induced Bending Movement', Supramolecular Chemistry, 13: 3, 435 — 445
To link to this Article: DOI: 10.1080/10610270108029459
URL: http://dx.doi.org/10.1080/10610270108029459

SUPRAMOLECULAR CHEMISTRY, Vol. 13, pp. 435–445
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Polyamine Linear Chains Bearing Two Identical Terminal Aromatic Units. Evidence for a Photo Induced Bending Movement*

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(Received 23 June 2000)

Several chemosensors bearing a fluorescent unit at both ends of a linear polyamine chain were synthesised. The protonation as well as the association constants with Cu^{2+} and Zn^{2+} were determined by potentiometry in 0.15 mol dm^{-3} NaCl at 298.1 K. In the case of 1,16-bis(1-naphthylmethyl)-1,4,7,10,13,16-hexaazadecane hexahydrochloride (L1), formation of an excimer emission in aqueous acidic solutions was observed. The system was characterized by steady state fluorescence emission and by time resolved fluorescence. In the ground state the molecule is expected to adopt a more or less linear conformation, while in the excited state a bending movement of the chain must occur in order to allow the excimer emission. The system can be viewed as an elementary machine driven by light.

Keywords: Excimer; Polyamine; Molecular machines; Chemosensors

INTRODUCTION

Polyamine molecules have shown to be one of the most versatile kind of receptors [1]. These compound can, as a function of their protonation degree, coordinate both metal ions (preferentially transition and postransition metal ions) or anionic species like halides, carboxylates, phosphates, anionic complexes, *etc.* [1–5]. The

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coordination of the first kind of substrates will occur through the lone pairs of non-protonated nitrogen atoms while co-ordination to anions will be driven, in a large percentage, by coulombic interactions between positively protonated nitrogens and the anionic species. The versatility of these compounds has allowed the preparation of very selective receptors for given substrates of different kind. This chemistry has awaken a lot of interest in the last decades being the research group of Prof. Paoletti at the University of Florence one of the leaders in the field [6].

One of the novel tendencies within this chemistry is associating a receptor unit to a signaling unit so that the recognition event can be advertised by the generation of a physical signal [1–5]. Luminescence is an adequate property for signaling and sensing because, among other characteristics, displays high sensibility of detection and it is easily measurable using unsophisticated equipment. In recent years our groups have been involved in the synthesis, coordination chemistry and photochemical characterization of different series of chemosensors containing a single hydrocarbon aromatic group as the signaling unit and a polyamine fragment as the receptor unit. These molecules were capable not only of sensing metal ions but also anions [4]. Metal ion sensing proceeds through chelation enhanced fluorescence effects (CHEF) in metal ions with complete sub-shells like Zn^{2+} or Cd^{2+}, or through chelation enhanced quenching effects (CHEQ) in metal ions like Cu^{2+} or Ni^{2+} with uncompleted *d* level [2]. ATP sensing occurs through a CHEQ effect prompted by stacking of the aromatic units of the partners [4c]. These systems can also constitute prototypes for the design of liquid logic gates [3].

Herewith we report on the synthesis of the hexadentate ligands L1–L2 which are made up by assembling together a pentaethylenehexaamine unit and two aromatic rings linked to the terminal nitrogens through a methylenic spacer (Chart 1). We explore their acid-base behaviour,

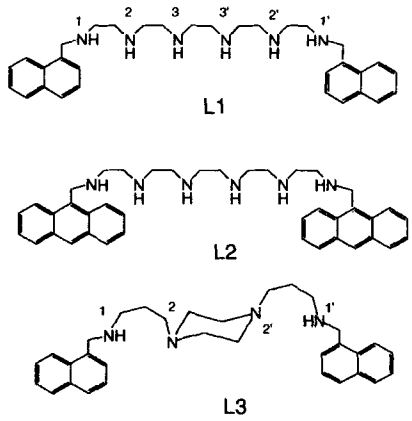


CHART 1

complexation to Co^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} and how some of these situations affect the luminescence of the systems. By means of comparison, we also include some aspects of the chemistry of the related receptor N,N′-bis(N-1-naphthylaminopropylpiperazine (L3).

EXPERIMENTAL

Synthesis of the Receptors

1,16-Bis(1-Naphthylmethyl)-1,4,7,10,13, 16-hexaazadecane Hexahydrochloride (L2 · 6HCl)

Pentaethylenehexaamine (1.78 g, 4.3 mmol) and naphthylaldehyde (1.79 g, 8.6 mmol) were stirred overnight in 75 ml of EtOH. Sodium borohydride (0.33 g, 8.3 mmol) were then added and the resulting solution stirred for 6 h. The ethanol was removed at reduced pressure. The resulting residue was treated with water and the difunctionalised amine repeatedly extracted with dichloromethane (3 × 30 mL). The organic phase was dried with anhydrous sodium sulfate and the solvent evaporated to yield the free amine, which was dissolved in ethanol and precipitated as its hydrochloride salt. (Yield 49%). mp 170–175°C, δ_H: 7.82–7.73 (m, 7H), 7.42–7.26 (m, 7H), 4.45 (s, 4H), 3.37–3.2 (m, 20 H). δ_C: 134.3, 131.5,

130.4, 129.8, 128.3, 127.5, 126.5, 126.3, 123.3, 49.4, 45.4, 44.4, 44.2, 43.6. Anal. Calcd. For $C_{32}H_{50}Cl_6N_6$: C, 52.54; H, 6.89; N, 11.49. Found: C, 52.0; H, 7.00; N, 11.2.

1,16-Bis(9-Anthrylmethyl)-1,4,7,10,13,16-hexaazadecane Hexahydrochloride (L2 · 6HCl)

The experimental procedure was analogous to that used for preparation of L1 by reacting 9-anthracenecarbaldehyde and pentaethylenehexaamine (Yield 29%). mp 168–173°C. δ_H: 8.20 (s, 2H), 7.86 (d, 8H), 7.45 (d, 8H), 4.50 (s, 4H), 2.91–3.50 (m, 20H). δ_C: 131.7, 131.2, 130.5, 128.9, 126.6, 123.5, 52.9, 50.2, 44.6, 41.2. Anal. Calcd. For $C_{40}H_{54}Cl_6N_6$: C, 57.71; H, 6.54; N, 10.11. Found: C, 55.6; H, 7.0; N, 10.2

N,N'-Bis(N-1-naphthylaminopropyl) piperazine Tetrahydrobromide (L3 · 4HBr)

In a round bottom flask were introduced 1,4-bis(3-aminopropyl)piperazine (2.0 g, 10 mmol) and 1-naphthylaldehyde (2.1 g, 20 mmol) and dissolved in 100 mL of CH_3CN. The resulting solution was further stirred for 1 h. The solvent was removed at reduced pressure to obtain quantitatively the imine as an oil. Reduction was carried out by adding $NaBH_4$ (2:1 molar ratio) to a solution of the imine dissolved in a 1:1 v/v mixture of CH_2Cl_2/EtOH. The compound was finally isolated as its hydrobromide salt. (Yield: 75%). mp: 247–251°C. δ_H: 7.97–8.08 (m, 6H), 7.67–7.54 (m, 8H), 4.52 (s, 4H), 3.44 (s, 8H), 3.27–3.16 (m, 8H), 2.30–2.10 (m, 4H). δ_C = 134.3, 131.3, 130.3, 129.8, 128.2, 127.4, 126.9, 126.3, 123.2, 54.3, 49.9, 48.8, 45.1, 21.5. Anal. Calcd. For $C_{32}H_{44}N_4Br_4$; C, 47.8; H, 5.5; N, 7.0. Found: C, 48.1; H, 5.6; N, 7.1.

emf Measurements

The potentiometric titrations were carried out at 298.1 ± 0.1 K in 0.15 mol dm^{-3} NaCl. The experimental procedure (burette, potentiometer, cell, stirrer, microcomputer, *etc.*) has been fully described elsewhere [8]. The acquisition of the emf data was performed with the computer program PASAT [9]. The reference electrode was an Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as an hydrogen-ion concentration probe by titration of previously standardized amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by the Gran's method [10], which gives the standard potential, $E^{0\prime}$, and the ionic product of water (pK_w = 13.73(1)). The concentrations of the different metal ions employed were determined gravimetrically by standard methods. NaCl was used as the supporting electrolyte instead of the most usual $NaClO_4$ due to the higher solubility of the receptors in this medium.

The computer program HYPERQUAD [11], was used to calculate the protonation and stability constants. The titration curves for each system (*ca.* 100 experimental points corresponding to at least three measurements, pH range investigated 2–10, concentration of metals and L ranging from 1×10^{-3} to 5×10^{-3} mol dm^{-3}) were treated either as a single set or as separated curves without significant variations in the values of the stability constants. Finally, the sets of data were merged together and treated simultaneously to give the final stability constants.

NMR Measurements

The ^1H and ^{13}C NMR spectra were recorded on Varian UNITY 300 and UNITY 400 spectrometers, operating at 299.95 and 399.95 MHz for ^1H and at 75.43 and 100.58 MHz for ^{13}C. The spectra were obtained at room temperature in D_2O or $CDCl_3$ solutions. For the ^{13}C NMR spectra dioxane was used as a reference standard (δ = 67.4 ppm) and for the ^1H spectra the solvent signal. Probe temperature was regulated by a variable temperature accessory.

Adjustments to the desired pH were made using drops of DCl or NaOD solutions. The pH was calculated from the measured pD values using the correlation, pH = pD − 0.4 [12].

Spectrophotometric and Spectrofluorimetric Measurements

Absorption spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer and fluorescence emission on a SPEX F111 Fluorolog spectrofluorimeter. $HClO_4$ and NaOH were used to adjust the pH values that were measured on a Metrohm 713 pH meter.

Fluorescence lifetimes were measured with an apparatus using a IBH 5000 coaxial flashlamp filled with H_2 as excitation source, Philips XP2020Q photomultiplier, with wavelength selected with Jobin-Ivon H20 monochromator and Canberra instruments time-to-amplitude converter and multichannel analyser. Alternate measurements (1000 counts per cycle at the maximum) of the pulse profile at 281 nm and the sample emission were performed until $1-2\times10^4$ counts at the maximum were reached. The fluorescence decays were analysed using the method of modulating functions of Striker with automatic correction for the photomultiplier "wavelength shift" [13].

RESULTS AND DISCUSSION

Protonation

Table I gathers the stepwise protonation constants of polyamines L1 − L3. Ligands L1 − L2 present a similar pattern in their acid-base behavior in aqueous solution. The two ligands show a group of relatively high constants for their three first protonation steps ($\log K_{HL}$ − $\log K_{H_3L}$ ($\Delta(\log K_{HL}/K_{H_3L}) = 1.75$ for L1 and 1.44 for L2), and show a more significant reduction in basicity upon fourth (for instance for L1, $\Delta(\log K_{H_3L}/K_{H_4L} = 1.47$) and particularly fifth protonation ($\Delta(\log K_{H_4L}/K_{H_5L} = 2.24$) and sixth protonation ($\Delta(\log K_{H_5L}/K_{H_6L} = 2.35$). The sixth protonation step of L2 falls below two logarithm units and the potentiometric studies do not permit an accurate quantification. As a general rule it can be stated that the presence of aromatic groups tends to lower the overall basicity of the amines [4, 14]. In this sense, the cumulative stability constants we have found for the full protonation of the parent open-chain polyamine 1,4,7,10,13,16-hexaazahexadecane (penten) is $\log\beta_6 = 42.9$ ($6H^+ + L = H_6L^{6+}$). The observed trends can be easily explained taking into account that protons would bind these receptors in those nitrogen atoms which produce least repulsion between positive charges. While the three first protonations can take place in non adjacent nitrogen atoms, fourth protonation must occur adjacent to an already protonated amine and that would be the reason of the larger decrease in basicity at this stage [14].

This same reasoning may explain the protonation behavior of the open-chain polyamine reinforced with the piperazine ring. This compound presents two large constants and two much lower ones. The analysis of the variations of the ^1H NMR and ^{13}C NMR chemical shifts with the pH clearly denote that the first two protonations occur on the secondary nitrogen

TABLE I Protonation constants of the receptors L1 − L3 determined in 0.15 mol dm^{-3} NaCl at 298.1 ± 0.1 K

Reaction	L1	L2	L3
$L + H = HL$[a]	10.04(4)[b]	9.03(3)	8.9(1)
$HL + H = H_2L$	8.94(3)	8.22(2)	8.94(2)
$H_2L + H = H_3L$	8.29(3)	7.59(2)	6.46(4)
$H_3L + H = H_4L$	6.82(4)	6.07(3)	2.85(6)
$H_4L + H = H_5L$	4.58(4)	4.07(3)	
$H_5L + H = H_6L$	2.23(1)	< 2	
$\log\beta$[c]	40.9	37.0	27.1

[a] Charges omitted by clarity.
[b] Values in parentheses are standard deviations in the last significant figure.
[c] $\log\beta = \Sigma\log K_{H_iL}$.

atoms of the chain being the piperazinic ones involved in the last two protonation steps.

Stability Constants for the Formation of Co^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} Metal Complexes

In Tables II and III are collected the stability constants for the formation of Co^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} complexes of the receptors L1 and L2, respectively. Both receptors form just mononuclear complexes while binuclear ones have not been detected in any of these systems. The stability constants of the complexes of L1 are higher than those of L2 in accordance with its higher basicity and hydrophilicity [4]. The low values of stability constants obtained for the formation of $[ML]^{2+}$ complexes and the large values of the protonation constants, particularly for the first protonation equilibria $ML^{2+} + H^+ = HML^{3+}$, suggest an uncompleted participation of the nitrogen donors of L1 and L2 in the coordination to the different metal ions. For instance, the stability constant for the $[CuL]^{2+}$ complexes of the hexamine 1,4,7,10,13,16,19-hexaazahexadecane ($\log K_{CuL} = 22.40$) or the pentaamine 1,4,7,10,15-pentaazatridecane ($\log K_{CuL} = 22.8$) [15] are clearly higher than those found in our case. Even the monofunctionalized tetraamine N-(3-aminopropyl)-N′-3-anthracen-9-ylmethylaminopropylethane-1,2-diamine [4d], containing a single anthracene fragment presents a slightly larger constant ($\log K_{CuL} = 19.45$) than L1 and L2, that can be partly ascribed to a better alternation of 5- and 6-membered chelate rings. The crystal structure revealed in this last case a 4-coordination for the Cu^{2+} ions. All this analysis suggest

TABLE II Stability constants for the interaction of L1 with the metal ions Co^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} determined in 0.15 mol dm^{-3} NaCl at 298.1 ± 0.1 K

Reaction	Co^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
M + L = ML	7.85(3)	17.13(6)	9.48(6)	8.41(5)
M + L + H = MHL	17.42(3)	25.73(5)	18.59(4)	18.71(3)
M + L + 2H = MH_2L	24.92(1)	31.75(3)	25.70(2)	25.39(3)
M + L + 3H = MH_3L		35.58(4)		
ML + H = MHL	9.6	8.6	8.3	9.1
MHL + H = MH_2L	7.5	6.0	7.1	6.8
MH_2L + H = MH_3L		3.8		

Charges omitted by clarity; Values in parentheses are standard deviations in the last significant figure.

TABLE III Stability constants for the interaction of L2 with the Metal Ions Co^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} determined in 0.15 mol dm^{-3} NaCl at 298.1 ± 0.1 K

Reaction	Co^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
M + L = ML	7.63(9)	17.4(1)	10.28(5)	9.21(7)
M + L + H = MHL	16.18(7)	24.98(6)	17.62(4)	17.25(6)
M + L + 2H = MH_2L	23.12(2)	29.54(4)	23.89(3)	23.18(4)
M + L + H_2O = ML(OH) + H	−2.9(1)	7.4(1)	1.12(8)	−1.30(7)
ML + H = MHL	8.6	7.6	7.3	8.0
MHL + H = MH_2L	6.9	4.6	6.3	5.9
ML + OH = ML(OH)	3.2	3.7	4.6	3.2

Charges omitted by clarity; Values in parentheses are standard deviations in the last significant figure.

coordination number four as the most likely for the Cu^{2+} complexes of L1 and L2. Similar conclusions can be extended to the other metal ions considered.

FLUORESCENCE EMISSION STUDIES

Free Ligands

The absorption spectra of compounds L1 to L3 are similar to those exhibited by the respective aromatic chromophore units and are slightly dependent on the protonation state of the chain, indicating a small interaction between these two moieties.

The fluorescence emission spectra of compounds L1 to L3 and the emission titration curves superimposed to the mole fraction distribution of the several protonated species in solution are reported in Figure 1. As can be seen in this Figure, the pH dependent fluorescence emission spectra of these compounds is quenched with decreasing of the protonation degree of the polyamine chain. This phenomenon has been widely observed in similar compounds and is attributed to a photoinduced electron transfer process from the lone pairs of the amine to the excited aromatic unit [1–4]. The largest fluorescence emission intensity occurs for the fully protonated form. In this species, protonation of the nitrogens raises the oxidation potential of the amine *ca.* 2.5 eV [3a], changing the photoinduced electron transfer reaction from exergonic to endergonic, thus precluding the quenching effect [16]. In accordance to previous results carried out with the analogue compounds bearing only one anthracene unit, the quenching effect is effective only upon removing a certain number of protons (depending on the dimension of the chain), in particular the proton attached to nitrogen 2 [4d]. In the case of the H_3L^{3+} form of compound L2 the protons seem to be located in both anthrylic nitrogens and in one of the central nitrogens, thus leaving nitrogens 2 and 2′ free to quench the emission. Concerning compound L3 it is clear from the NMR data that the largest quenching effect occurs upon

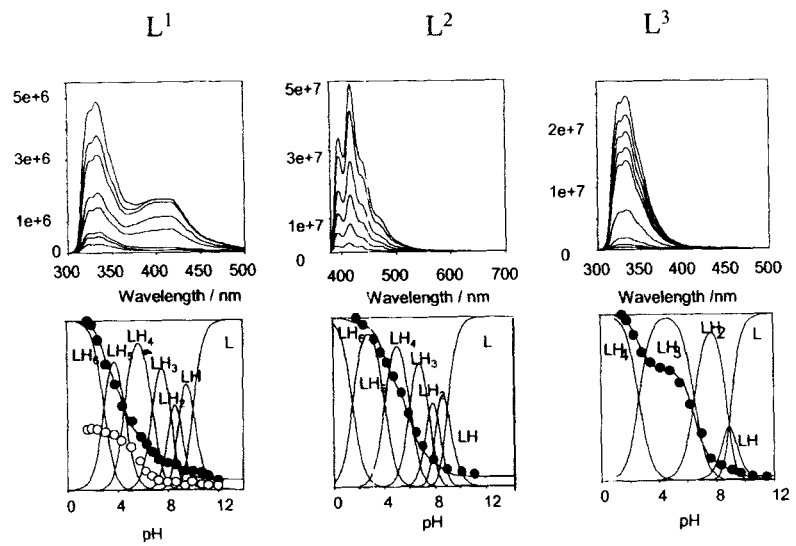


FIGURE 1 top – Fluorescence emission curves of L1 to L3 as a function of pH at the excitation wavelength of 287 nm, 373 nm, 287 nm, respectively; down – Fluorescence emission titration curves of L1 ($\lambda_{exc} = 287$; λ_{em}(monomer) = 334 nm; λ_{em}(excimer) = 418 nm), L2 ($\lambda_{exc} = 373$; $\lambda_{em} = 418$), and L3 ($\lambda_{exc} = 287$ nm; $\lambda_{em} = 334$ nm), superimposed to the respective mole fraction distribution of the different species present in solution.

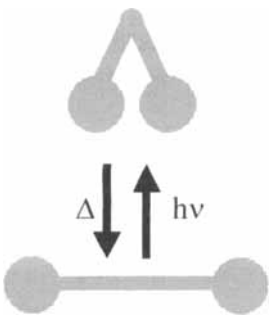
removing the two protons from the piperazinic nitrogens.

The behaviour of compound L1 is more complex due to the competition between the emissions from the monomer and the excimer, see below.

The most interesting feature of this figure is the formation of a new red shifted band, that occurs simultaneously with the characteristic naphthalene emission in the case of the compound L1. This type of bands has been observed whenever emissive excimers or exciplexes are formed [17]. Such a band is not observed when the mobility of the polyamine chain is reduced by the presence of a piperazine unit, as is the case of the analogous compound, L3, Figure 1.

In order to distinguish between intramolecular and intermolecular excimers, we recorded the fluorescence emission spectra of L1 at different concentrations ranging from 2×10^{-6} M to 5×10^{-5} M and pH = 3.0. In this concentration range, the ratio between the emission maximum of the monomer (334 nm) and excimer (418 nm) is maintained constant. This result supports the formation of an intramolecular excimer involving the two naphthalene units of the same molecule (see Scheme 1). Moreover, the excitation spectrum of L1 is not dependent on the emission wavelength.

Further experimental evidence for the excimer formation was obtained with time resolved fluorescence data. Using the time correlated single photon counting technique we were able to observe a single exponential decay for L3, with a lifetime of 29.5 ns at pH = 2, and a double-exponential fluorescence decay for L1, (see Fig. 2). This behaviour means that two kinetic coupled species are involved in the first singlet excited state. In intramolecular excimer formation, these excited state species consist of a monomer (N^*) and an excimer (E^*).



SCHEME 1

The kinetics of intramolecular excimer formation can be described by Scheme 2. In this scheme, N^* represents the excited monomer of the bichromophoric system L1, in which just one of the two naphthalene units is excited; $N^* \ldots N$ and E^* represents the intramolecular excimer $^1(L1)^*$; k_1 and k_{-1} are the first-order rate constants of intramolecular excimer formation and dissociation, respectively. The reciprocal lifetimes $1/\tau_N$ (monomer) and $1/\tau_E$ (excimer) are also presented. The fact that the ratio I_{E^*}/I_{N^*} increases at low pH values (see Fig. 1), indicates that while the partially protonated forms (namely H_5L^{5+} and H_4L^{4+}) have a significant quenching effect in the monomer, they exhibit a much reduced effect in the case of the excimer, see Figure 1. A plausible explanation for this behaviour, may be found in the different energies of the excited monomer and excimer. In fact, ΔG^0 for the excited state electron transfer process (ESPT) depends on $-\Delta E_{0-0}$, the energy of the 0–0 absorption band of S_1, which is higher in the monomer than in the excimer (the excimer is red shifted in comparison with the monomer). In other words, ΔG^0 for the ESPT process is expected to be less negative for the excimer than for the monomer.

The same excited monomer-excimer kinetics also occurs in methanol as exemplified in Figure 2. It is to be stressed that in Figure 2 the rise-time, *i.e.*, the negative pre-exponential at $\lambda_{em} = 410$ nm (where the excimer emits) clearly shows that the excimer is only formed in the excited state at exclusive expenses of the excited monomer.

Using the data in Figure 2, Scheme 2 leads to a system of two linear differential equations,

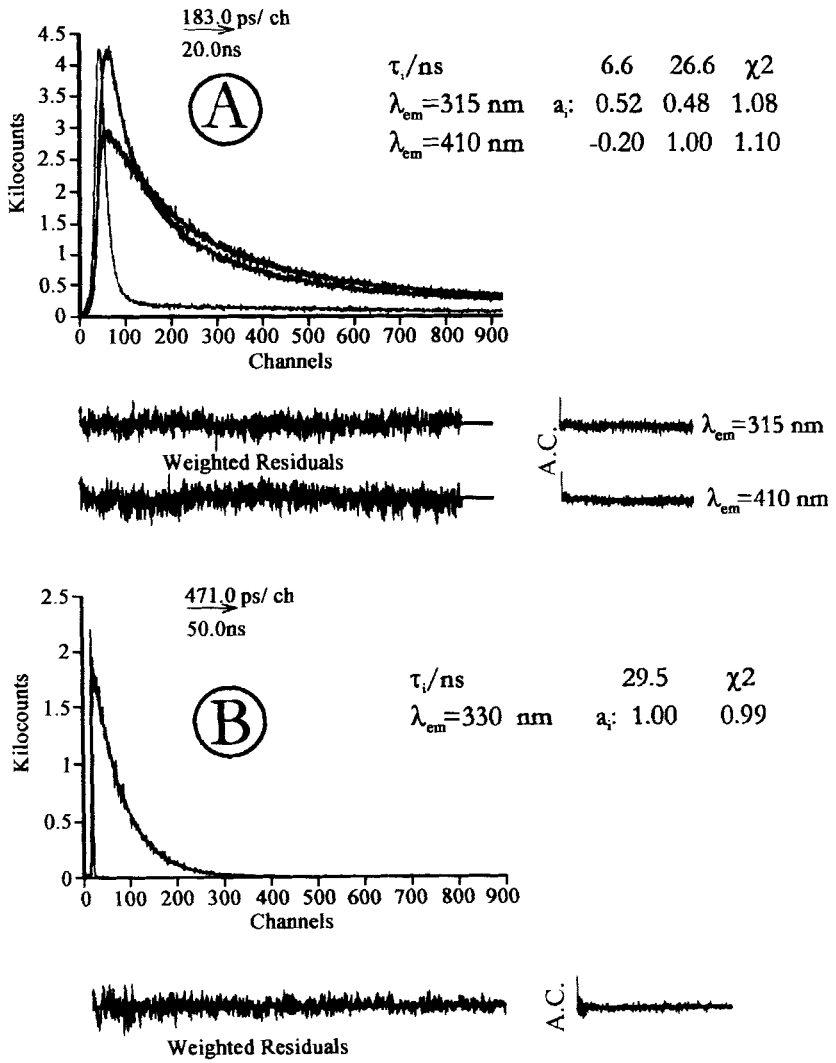
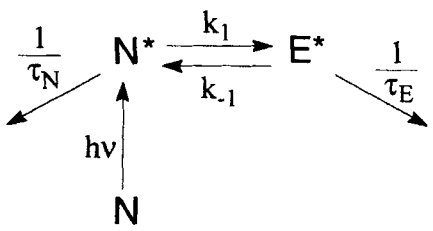


FIGURE 2 Fluorescence decays of (A) L1 in methanol obtained with global analysis and (B) L3 in water at pH = 2.0, at temperature 293 K, obtained at $\lambda_{exc} = 281$ nm. Autocorrelation functions (A.C.) are shown as inserts and weighted residuals (W.R.) are plotted below the decays. The decay times (τ), pre-exponential factors (a_i) and (χ^2) at different emission wavelengths are also shown.



SCHEME 2

shown in matricial form, Eq. (1), translating the time evolution concentration dependence of N* and E*:

$$\frac{d}{dt}\begin{bmatrix} N^* \\ E^* \end{bmatrix} = \begin{bmatrix} -((1/\tau_N)+k_1) & k_{-1} \\ k_1 & ((1/\tau_E)+k_{-1}) \end{bmatrix} \cdot \begin{bmatrix} N^* \\ E^* \end{bmatrix} \quad (1)$$

For such a system the concentrations of N^* and E^* follow a well-known double exponential decay law [17]

$$\begin{bmatrix} N^*(t) \\ E^*(t) \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \cdot \begin{bmatrix} e^{-\lambda_1 t} \\ e^{\lambda_2 t} \end{bmatrix} \quad (2)$$

where the reciprocals of the shorter ($\lambda_2 = 1/\tau_2$) and the longer ($\lambda_1 = 1/\tau_1$) decay times are related to the rate constants in Scheme 2 by Eq. (3):

$$2\lambda_{2,1} = \{(X+Y)\} \pm \left[(X-Y)^2 + 4k_1k_{-1}\right]^{1/2} \quad (3)$$

with

$$X = \frac{1}{\tau_N} + k_1; \quad Y = \frac{1}{\tau_E} + k_{-1} \quad (4)$$

Using Eqs. (2)-(4) with the decay times obtained in water at pH = 2, $\tau_2 = 7.9$ ns and $\tau_1 = 25.3$ ns, which are slightly different than the ones obtained in methanol (reported in Fig. 2), and with the ratio of the pre-exponential factors in the monomer:

$$A = \frac{a_{12}}{a_{11}} = \frac{X-\lambda_1}{\lambda_2 - X} = 0.93 \quad (5)$$

and with $\tau_N = 29.5$ ns (fluorescence lifetime of the unquenched parent compound, L3), and $\tau_E = 16.7$ ns, obtained by the internal convolution procedure [18], we have obtained the following rate constants: $k_1 = 0.05\ ns^{-1}$ and $k_{-1} = 0.03\ ns^{-1}$. These data clearly show that the process is not diffusion controlled. The low values for both rate constants are not unexpected since the strong rigidity of the protonated nitrogen-methylenic bridge requires a high interconversion barrier to be overcome in order to form the excimer species. The lack of excimer formation in the case of L2, is not unexpected because the anthracene unit, in contrast with naphthalene, is not so efficient in the formation of excimers due to its low fluorescence emission lifetime in liquid solutions at room temperature [16].

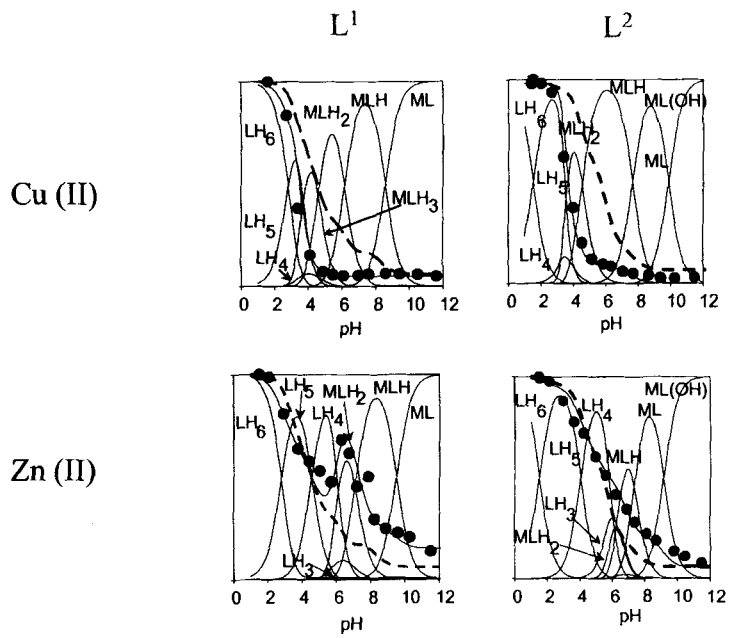


FIGURE 3 Fluorescence emission titration curves of L1 ($\lambda_{exc} = 287$ nm; $\lambda_{em} = 334$ nm) and L2 ($\lambda_{exc} = 373$ nm; $\lambda_{em} = 418$ nm) in the presence of Cu^{2+} and Zn^{2+}.

Metal Complexes

In Figure 3 the fluorescence emission spectra of the L1 and L2 complexes with two paradigmatic metals ions Cu^{2+} and Zn^{2+} are presented. In which concerns the Cu^{2+} complexes it can be observed a general quenching effect. Quenching of the fluorescence emission upon Cu^{2+} complexation is a very common effect, being attributed to the introduction by the metal of deactivation processes, such as energy transfer. In the case of L2 we detected a weak fluorescence emission from the species $[CuH_2L]^{4+}$. One possible explanation is the formation of a metal complex involving the 4 central nitrogens leaving the benzylic nitrogens protonated. This type of structure would take away the metal from the vicinity of both aromatic units reducing in this way the metal-ligand interaction by increasing the metal-flurophore distance. This reasoning can be confirmed by the recently described intense emission of the species $[CuH_3L]^{5+}$ in which L is the analogous of L2 containing only one terminal anthracene [4d].

In contrast with Cu^{2+} complexes it is known that polyammonium complexes of Zn^{2+} are in generally emissive species. This was once more confirmed by the emission spectra reported in Figure 2. The most emissive species is always $[ZnH_2L]^{4+}$. In this case, all the nitrogens atoms should be either involved in the binding with the metal or protonated, precluding any possibility of photo induced electron transfer. However as observed for the free ligand, the intensity of the emission is reduced by deprotonation of the nitrogens which become available to carry out a quenching effect, probably by the same type of mechanism, *i.e.*, photoinduced electron transfer.

PHOTO INDUCED BENDING MOVEMENT

Much interest has been recently paid to molecular systems capable of performing molecular movements under the action of external stimuli, because these type of studies is expected to contribute to a better knowledge of much complex machines operating in Nature [19–22].

In acidic aqueous media at least two kinds of forces contribute to establish the geometry of the receptors here considered: (a) charge repulsion of the protonated nitrogens of the chain forcing the structure to assume an extended conformation; (b) hydrophobicity of the aromatic units which favours a folded conformation facilitating their location at close distance.

In the ground state it seems that the first one prevails while in the excited state, the excimer emission reveals that the second one is dominant. As a consequence the molecule executes a bending movement whose effectiveness depends on pH, Scheme 1. This movement in the excited state disappears when the mobility of the chain is reduced by the presence of reinforcing piperazine groups, as is the case of compound L3, see ligand drawing (Chart 1).

Acknowledgements

We are indebted to the Fundação para a Ciência e Tecnologia (Portugal) and DGICYT Proj. no. PB 96-0796-CO2 (Spain) for financial support. One of us M. T. A. wishes to acknowledge Generalitat Valenciana for a Ph. D. grant.

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