Switching from intramolecular energy transfer to intramolecular electron transfer by the action of pH and Zn^{2+} co-ordination

M. Teresa Albelda [a], Pilar Díaz [a], Enrique García-España [a,1], João C. Lima [b], Carlos Lodeiro [b], J. Seixas de Melo [c], A. Jorge Parola [b], Fernando Pina [b,*], Conxa Soriano [d]

[a] *Departament de Química Inorgànica, Facultat de Química, Universitat de València, Spain*
[b] *Departamento de Química, Centro de Química Fina e Biotecnologia, Universidade Nova de Lisboa, Quinta da Torre, 2825-114, Monte de Caparica, Portugal*
[c] *Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, Portugal*
[d] *Departament de Química Inorgànica, Facultat de Farmacia, Universitat de València, Spain*

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Abstract

Intramolecular electron (eT) and energy transfer (ET) have shown to occur in a covalently linked donor–acceptor (CLDA) system consisting of a naphthalene donor covalently linked through a polyamine chain connector to an anthracene acceptor; the connector has been chosen in order to switch ON or OFF the energy flux as a function of its protonation state as well as by co-ordination to Zn^{2+}. The largest energy transfer efficiency ($\eta = 0.61$) occurs for the fully protonated form (pH < 2), while at pH > 9 (eT) from the lone pairs of the nitrogens to the excited fluorophore takes place, leading to complete quenching of the emission. On the other hand at neutral and basic pH values, co-ordination of Zn^{2+} prevents the eT quenching allowing the ET process to occur. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Covalently linked donor–acceptor systems (CLDA) have been the subject of large attention because of their important implications in several chemical fields, such as electron and energy transfer (ET) theory, biological electron transfer (eT), and photochemical molecular devices [1,2]. In particular both through space and through bond ET were reported in systems containing naphtalene and anthracene [3–5]. The connector, *c*, cannot be considered as a simple innocent component and its role has been questioned, for example, in the *through bond/through space* classical discussion [1–5]. In this work we have designed

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* Corresponding author. Fax: +351-212948550.
  E-mail addresses: enrique.garcia-es@uv.es (E. García-España), fjp@dq.fct.unl.pt (F. Pina).
[1] Also corresponding author. Address: Dr. Moliner 50, 46100 Burjassot (València), Spain. Fax: +34-96-3864322.

an energy transfer CLDA system consisting of a naphthalene donor (D) linked through a poly-amine chain (c) to an anthracene acceptor (A). The connector was chosen in order to play a precise role in the system: to switch ON/OFF the ET flux.

2. Experimental

2.1. Synthesis

Compound L (Scheme 1) was prepared by re-action of L1 (0.275 g, 3.56 mmol) [6] with an-thracene-9-carbaldehyde in 50 ml of ethanol to give the imine. Then, $NaBH_4$ (0.202 g, 5.30 mmol) was added and the mixture was stirred at room temperature for 24 h. The ethanol was removed at reduced pressure. The resulting residue was treated with water and the amine extracted with CH_2Cl_2 (3×30 ml). The organic phase was washed with water dried with anhydrous sodium sulphate and the solvent evaporated to yield the free amine, which was dissolved in ethanol and precipitated as a hydrochloride salt. Yield, 32%, mp, 200–204 °C, NMR (D_2O): δ_H, 3.28–3.50 (m, 12H), 4.69 (s, 2H), 5.04 (s, 2H), 7.39–7.55 (m, 8H), 7.86–7.94 (m, 5H), 8.03 (d, $J = 8$ Hz, 2H), 8.40 (s, 1H); δ_C, 43.4, 43.4, 43.8, 43.8, 43.9, 44.1, 48.8, 48.8, 122.7, 122.8,

125.9, 127.0, 127.8, 128.2, 129.4, 129.9, 131.1, 131.2.

2.2. Potentiometry

Protonation and Zn^{2+} complex formation con-stants were calculated by pH-metric titrations carried out in 0.15 mol dm^{-3} NaCl at 298.1 ± 0.1 K. The program HYPERQUAD [7] was used to fit the experimental data.

2.3. Spectrophotometric and spectrofluorimetric measurements

All solutions were prepared in 0.15 mol dm^{-3} NaCl. HCl and NaOH were used to adjust the pH values that were measured on a Metrohm 713 pH meter. Absorption spectra were recorded on a Perkin–Elmer Lambda 6 spectrophotometer and fluorescence emission on a Jobin Yvon-Spex Flu-orolog 3.22 spectrofluorimeter. The fluorescence decays were obtained at pH = 1.41 (in 0.15 mol dm^{-3} NaCl), with excitation at 280 nm and the emission collected at 330 and 450 nm using the equipment described elsewhere [8]. All measurements were made in the presence of oxy-gen to reproduce the conditions where steady-state fluorescence data were obtained. The fluorescence
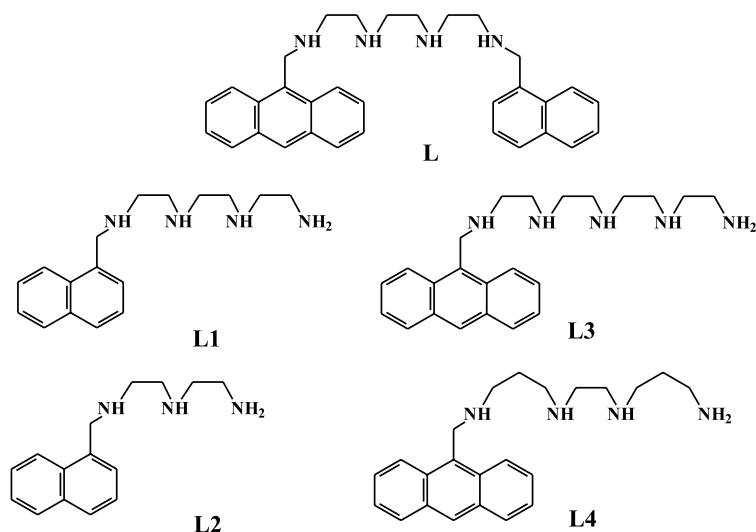
Scheme 1.

decays were analysed using the method of modulating functions implemented by Striker with automatic correction for the photomultiplier 'wavelength shift' [9].

3. Results and Discussion

In the previous work carried out with the related mono-chromophoric compounds L3 and L4 we have shown that the absorption and the fluorescence emission of the fully protonated forms are practically independent of the polyamine chain length [6]. In this sense, we have checked that compounds L1 and L2 containing a single naphthalene fragment present the same behaviour.

An interesting feature of compound L is the fact that the absorption spectrum of its fully protonated form is practically coincident with the sum of the absorption spectra of the mono-naphthalene (L1 or L2) and the mono-anthracene (L3 or L4) analogues, Fig. 1A. Accordingly, the first transition of compound L appearing in the range $300 < \lambda < 400$ nm can be readily assigned to the absorption of the anthracene unit, whilst the second one at $250 < \lambda < 300$ nm to that of the naphthalene moiety. As shown in Fig. 1A, it is possible to selectively excite the anthracene unit, for example, at 360 nm. On the other hand, the naphthalene moiety can be excited to an extent of 91% of the total absorbed light at 280 nm. The fluorescence emission obtained upon excitation at 280 nm, Fig. 1B, decreases with increasing pH. Identical pattern was observed for the anthracene unit emission upon selective excitation at 360 nm. This type of pH dependence has been previously found for mono- or bis-chromophoric systems containing benzene, naphthalene or anthracene units attached to polyamine chains, and was attributed to an eT quenching mechanism involving the lone pairs of the amines and the excited fluorophore [10–12]. In the case of the fully protonated forms, this process is prevented by the protonation of the amine groups.

However, the most interesting feature of the L system is the clear evidence for occurrence of an ET process from naphthalene to anthracene, as observed in the emission spectra of Fig 1B and in the normalised excitation spectrum of L, in Fig. 1A, trace 5. An ET efficiency $\eta = 0.61$ can be calculated from this excitation spectrum and from the absorption spectrum of L (trace 1), after correcting for the absorption of the anthracene fluorophore (9% at 280 nm): $\eta = (1 - I_{280}/A_{280})/\alpha_{280}^N$, where I_{280} is the intensity of the normalised excitation spectrum, A_{280} is the absorbance and α_{280}^N is the fraction of light absorbed by the naphtalene moiety, fully protonated form of L at 280 nm. From the fluorescence emission quantum yield of the naphthalene fluorophore in L ($\Phi_D = 0.069$, fully protonated form) and that of the analogue L1
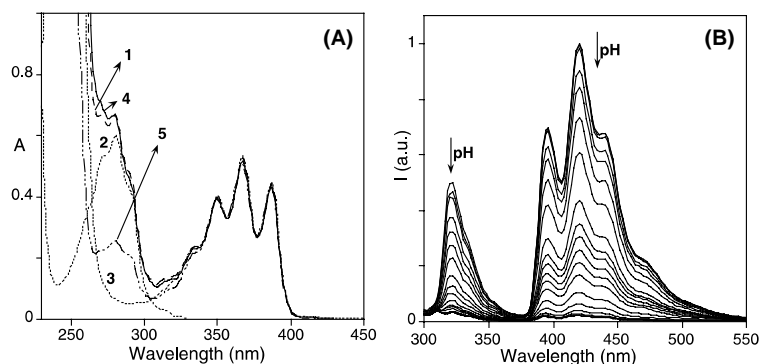

Fig. 1. (A) Absorption spectra of compounds L (1), L1 (2) and L3 (3) 1.0×10^{-4} mol dm^{-3} in NaCl 0.15 mol dm^{-3} (fully protonated forms), sum of 2 and 3 (4) and excitation spectrum ($\lambda_{em} = 420$ nm) of L normalised to the absorption of the anthracene unit (5). (B) Fluorescence emission spectra of compound L 1.02×10^{-5} mol dm^{-3} in NaCl 0.15 mol dm^{-3}, from pH 1.64 (top spectrum) to pH 12 (bottom spectrum).
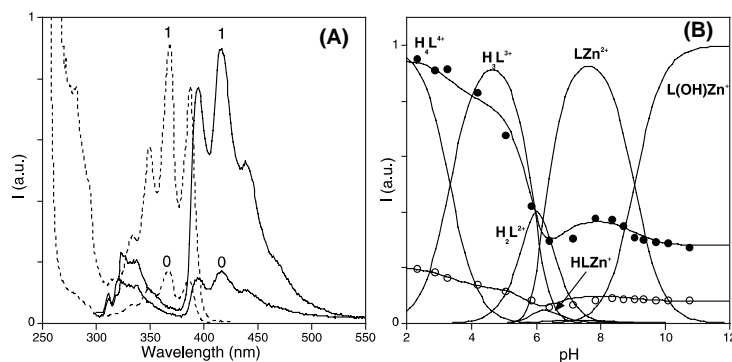
Fig. 2. (A) Fluorescence emission ($\lambda_{exc} = 280$ nm, solid line) and excitation (dotted line) of free L 1.02×10^{-5} mol dm^{-3} in NaCl 0.15 mol dm^{-3} (0), and L in the presence of an equimolar amount of Zn^{2+} (1) at pH = 8.5. (B) Fluorescence emission titration curves for $\lambda_{exc} = 360$ nm and $\lambda_{em} = 420$ nm ($\bullet$), $\lambda_{exc} = 280$ nm and $\lambda_{em} = 420$ nm ($\circ$).

($\Phi = 0.18$, fully protonated form) an ET efficiency $\eta = 0.62$ is also obtained.

The fluorescence emission at pH = 8.5, upon excitation at 280 nm, as well as the excitation spectra collected at 440 nm, in the absence and in the presence of equimolar quantities of Zn^{2+} are represented in Fig. 2A.

This figure clearly shows a chelation enhancement of the fluorescence (CHEF) promoted by Zn^{2+} which, like protons, prevents the eT quenching process [6,10–12]. Co-ordination to Zn^{2+} leads to the formation of a ZnL^{2+} complex, which is the major species in solution in the 6–9 pH range (Table 1, Fig. 2B). The stability constants and comparison with related systems suggest the involvement of all four nitrogen donors in

Table 1
Logarithms of the protonation constants for the receptor L and stability constants for the interaction of L with Zn^{2+} determinated in NaCl 0.15 mol dm^{-3} at 298.1 ± 0.1 K

Reaction	L	Zn^{2+}
H + L $\leftrightarrow$ HL[a]	8.81(3)[b]	–
H + HL $\leftrightarrow$ H$_2$L	7.97(3)	–
H + H$_2$L $\leftrightarrow$ H$_3$L	5.96(5)	–
H + H$_3$L $\leftrightarrow$ H$_4$L	3.33(5)	–
M + L $\leftrightarrow$ ML	–	9.59(3)
H + ML $\leftrightarrow$ MHL	–	5.2(1)
OH + ML $\leftrightarrow$ ML(OH)	–	4.09(6)

[a] Charges omitted for clarity.
[b] Values in parentheses are standard deviations in the last significant figure.

the co-ordination to the metal ion. The decrease in the fluorescence emission observed for pH > 9 can be attributed to the formation of the hydroxylated ZnL(OH)$^+$ species. This behaviour is a common feature in this kind of systems [6,10–13]. The fluorescence emission titration curves of L:Zn^{2+} (1:1) exciting in anthracene ($\lambda_{exc} = 330$ nm, $\lambda_{em} = 420$ nm) and naphthalene ($\lambda_{exc} = 280$ nm, $\lambda_{em} = 420$ nm), presented also in Fig. 2B show that introduction of Zn^{2+} allows the ET process ($\eta = 0.63$, pH = 8.5) to take place even at moderately basic pH values.

Time-resolved fluorescence data were obtained for the fully protonated form of L in order to get more insight on the dynamic aspects of the ET process. Fluorescence decays were obtained upon excitation at 280 nm, and monitored at $\lambda_{em} = 330$ nm, where the fluorescence emission is essentially due to the naphthalene unit, and at $\lambda_{em} = 450$ nm, where only anthracene emits. The decays at both wavelengths are properly fitted with sums of two exponentials with only one decay time common at both wavelengths, Table 2.

The 23.3 ns decay time at 330 nm is identical to the lifetime of the parent compound L1 (23.4 ns, in the same conditions) and must unequivocally be associated to a conformer that is unable to transfer energy. The shortest lifetime component ($\tau_1 = 1.1$ ns) appears with an associated negative pre-exponential factor at 450 nm allowing its assignment to an ET process occurring in a second type of conformers. The 11.3 ns decay time that appears

Table 2
Decay times (τ) and normalized pre-exponential factors (a) for L in NaCl 0.15 mol dm^{-3}, pH $= 1.41$, undegassed solutions

λ (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1	a_2	a_3
	1.1	11.3	23.3			
330				0.63	–	0.37
450				−0.61	1.00	–

only at 450 nm is identical to the lifetime of the parent compound L3 (11.3 ns, in the same conditions) and is assigned to the anthracene moiety of L in the absence of back ET. These data are consistent with the presence of two populations of conformers: one unable to transfer energy (37%, Table 2) and the other (63%, Table 2) transferring energy with almost unit efficiency. In fact the ET of these last conformers, calculated from the decay times using Eqs. (1) and (2), is $\eta = 0.95$.

$$1/\tau_1 = 1/\tau_{L1} + k_{ET}, \tag{1}$$

$$\eta = k_{ET}/(k_{ET} + 1/\tau_{L1}). \tag{2}$$

Within the framework of Förster's theory [14,15], conformers that are unable to transfer energy must have orthogonal transition moments. On the other hand, for conformers with parallel transition moments, an efficiency of 0.91 is predicted, using Eq. (3).

$$\eta = R_0^6/(R_0^6 + R^6). \tag{3}$$

The interchromophoric distance ($R = 19$ Å) in the fully protonated form of L was calculated from molecular modelling with HYPERCHEM3 from HYPERCUBE software, and the Förster's critical distance ($R_0 = 28$ Å) was calculated according to Eq. (4) [14,15] with an overlap integral $J(\lambda) = 3 \times 10^{13}$ M^{-1} cm^{-1} nm^4, $n(H_2O) = 1.4$, $\Phi_D \equiv \Phi_{L1} = 0.18$ and the geometric factor $k^2 = 4$.

$$R_0 \ (\text{Å}) = 0.211[k^2 n^{-4} \Phi_D J(\lambda)]^{1/6}. \tag{4}$$

The experimental value is thus in close agreement with the theoretical one. The 0.62 ET efficiency observed in steady state measurements seems to arise exclusively from the 63% of conformers able to transfer energy with almost unit efficiency.
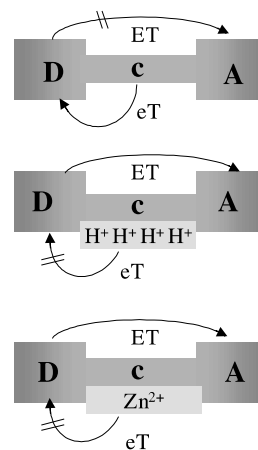
Scheme 2.

4. Conclusions

The photochemical behaviour of the CLDA system here presented is summarised in Scheme 2. In the absence of metal ions or protons, the system is deactivated due to an eT process involving the excited donor (system OFF). Protonation at a sufficient extent or co-ordination to Zn^{2+}, blocks the eT and turns on the ET process from the naphthalene unit (D) to the anthracene one (A) (system ON).

Acknowledgements

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