Ground and excited state properties of polyamine chains bearing two terminal naphthalene units

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

[a] *Departamento de Química (CQC), Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3004-535 Coimbra, Portugal. E-mail: sseixas@ci.uc.pt*
[b] *Departament de Química Inorgànica, Facultat de Química, Universitat de València, Spain C/Dr. Moliner 50, 46100 Burjassot (València), Spain. E-mail: enrique.garcia-es@uv.es*
[c] *Departamento de Química, Centro de Química Fina e Biotecnologia, Universidade Nova de Lisboa, Quinta da Torre 2825 Monte de Caparica, Portugal. E-mail: fjp@dq.fct.unl.pt*
[d] *Departamento de Química Orgánica, Facultat de Farmacia, Universitat de València, Spain. Avda. Vicent Andrés Estellés s/n. 46100 Burjassot (València), Spain*

Received (in Cambridge, UK) 23rd November 2001, Accepted 25th February 2002
First published as an Advance Article on the web 25th March 2002

A series of compounds bearing two naphthalene units linked through methylene groups to both ends of different open-chain polyamines has been investigated. The fluorescence emission studies show the presence of an excimer species whose formation depends on the protonation state and length of the polyamine chains and implies the existence of a bending movement in the excited state allowing the two naphthalene units to approach and interact. This interpretation was clearly proven by time-resolved fluorescence with the appearance of double exponential decays with a rise time observed at the excimer emission wavelength. For comparison purposes one bis-chromophoric compound containing a rigid chain, and two mono-chromophoric analogs bearing a single terminal naphthalene unit were studied. Their emission spectra show a unique band and the fluorescence decays, are single exponential at pH values where just one species is present in the ground state, showing that in these cases no excimer or exciplex species is formed. The kinetics of excimer formation was used to evaluate the influence of the length and the pH in the flexibility of the polyamine chain.

Introduction

Polyamine compounds are water-soluble ambivalent receptors capable of coordinating metal ions when a sufficient number of deprotonated amino groups are available or, alternatively, coordinating anionic species if the number of protonated amino groups is sufficiently high. A way to monitor and potentially improve the performance of these receptors is to promote the attachment of fluorescent units capable of signalling the binding of the substrate. Numerous examples of similar chemosensors, suitable for coordinating metal cations or anions, have been reported in the literature through the past years.[1]

Very recently we have advanced knowledge of the ground and excited-state behaviour of systems containing open-chain polyamines bearing two terminal anthracene (or naphthalene) units.[2] Similarly to the analogue compounds containing only one fluorophore, these systems exhibit strong dependence of their fluorescence emission upon protonation and coordination to metals (*e.g.* Cu^{2+}, Zn^{2+}). One of the most amazing features of the chemistry of these receptors is the possibility of performing reversible movements in the excited state. Such movements can be easily detected by the appearance of a red shifted and non-structured emission band, identified as an excimer emission. Similar systems, whose shape and dynamic properties can be controlled by external stimuli, are a topic of increasing interest, in particular, those for which continuous movements can be induced while energy is being consumed (molecular machines). Indeed, many biological systems can be considered as more or less complex molecular machines operated by different chemical or physical stimuli, the ATP synthase being a paradigm of such complex machinery.[3] More recently, some stimulating examples of simple molecular-level systems have shown the possibility of constructing elementary components, capable of being assembled in a bottom-up approach, to build up more complex systems, and consequently obtain more sophisticated functions.[4–7] Polyamine receptors have also been the chemical basis of elementary systems, capable of performing simple movements controlled by external inputs (pH, temperature, light, redox potential, metal ions).[8–12]

In this work we present a more complete picture of the effect of chain dimension and protonation degree on the kinetics of excimer formation with polyamines bearing two terminal naphthalene chromophores. To do so, we have developed receptors **L** to **L4** (Scheme 1) containing naphthalene fluorophores at both ends. For comparison purposes **L7**, possessing a more rigid chain, and **L5** to **L6**, containing a single terminal naphthalene unit were also synthesised. Our aim is to study the effect of the chain dimension and pH on the kinetics of excimer formation and to use the changes in the rate constants as a probe of the chain flexibility.

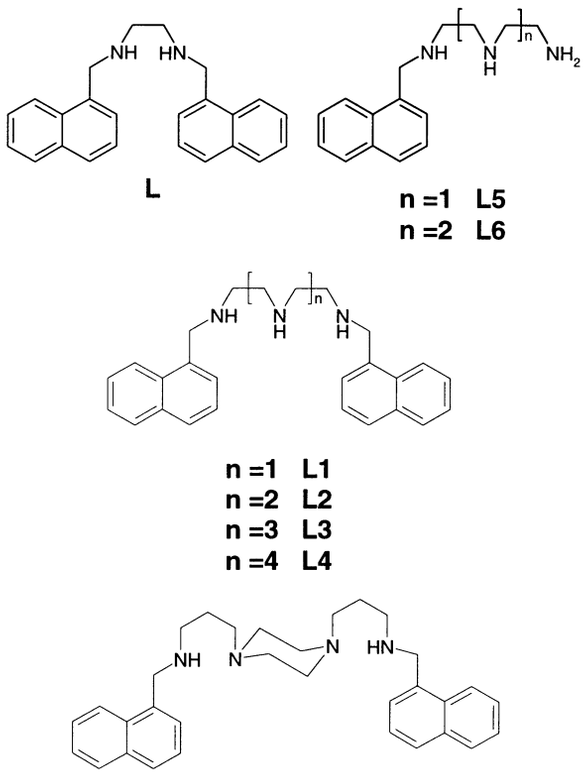
Experimental

Synthesis

The synthesis of receptors **L**–**L4** has been accomplished following the procedure reported in ref. 2*b*.

***N*-Naphthalen-1-ylmethyl-*N′*-{2-[(naphthalen-1-ylmethyl)amino]ethyl}ethane-1,2-diamine trihydrochloride (L1·3HCl).** Diethylenetriamine (0.88 g, 8.6 mmol) and naphthalene-1-carbaldehyde (2.59 g, 16.6 mmol) were stirred

DOI: 10.1039/b110769k



Scheme 1

for 72 h in 75 ml of EtOH. Sodium borohydride (0.66 g, 17.2 mmol) was then added and the resulting solution stirred overnight. 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. 86% yield; mp 201–204 °C; solvent D_2O, δ_H (ppm): 3.29 (t, J = 6 Hz, 4H), 3.40 (t, J = 6 Hz, 4H), 4.65 (s, 4H), 7.43–7.58 (m, 8H), 7.89–7.98 (m, 6H); δ_C (ppm): 43.6, 43.8, 48.7, 122.7, 125.9, 126.3, 127.1, 127.8, 129.5, 129.9, 131.1, 131.1, 131.7, 133.9. Anal. Calcd. for $C_{26}H_{32}Cl_3N_3$: C 63.35, H 6.54, N 8.52. Found: C 63.7, H 6.1, N 8.6%.

***N*,*N*′-Bis(naphthalen-1-ylmethyl)ethane-1,2-diamine dihydrochloride (L·2HCl).** 71% yield; mp 238–241 °C; solvent D_2O, δ_H (ppm): 3.37 (s, 4H), 4.65 (s, 4H), 7.41 (t, J = 8 Hz, 2H), 7.48 (d, J = 8 Hz, 2H), 7.50–7.60 m (4H), 7.91 (d, J = 8 Hz, 4H); δ_C (ppm): 42.9, 48.7, 122.4, 122.7, 126.0, 126.1, 126.9, 127.7, 129.4, 129.8, 131.0, 133.7.

***N*-Naphthalen-1-ylmethyl-*N*′-(2-{2-[(naphthalen-1-ylmethyl)-amino]ethylamino}ethyl)ethane-1,2-diamine tetrahydrochloride (L2·4HCl).** 75% yield; mp 228–231 °C; solvent D_2O, δ_H (ppm): 3.34 (s, 4H), 3.37 (t, J = 6 Hz, 4H), 3.46 (t, J= 6 Hz, 4H), 4.65 (s, 4H), 7.44–7.58 (m, 8H), 7.87–7.99 (m, 6H); δ_C (ppm): 43.2, 43.9, 43.8, 48.9, 122.8, 125.9, 126.2, 127.1, 127.9, 129.5, 131.1, 131.1, 133.9. Anal. Calcd. for $C_{28}H_{38}C_{14}N_4$: C 58.75, H 6.69, N 9.79. Found: C 58.9, H 6.7, N 9.8%.

***N*-Naphthalen-1-ylmethyl-*N*′-[2-(2-{2-[(naphthalen-1-yl-methyl)amino]ethylamino}ethylamino)ethyl]ethane-1,2-diamine pentahydrochloride (L3·5HCl).** 56% yield; mp 215–218 °C; solvent D_2O, δ_H (ppm): 3.38–3.56 (m, 16H), 4.70 (s, 4H), 7.48–7.66 (m, 8H), 7.94–8.06 (m, 6H); δ_C (ppm): 42.8, 43.5, 43.6, 44.5, 48.6, 122.4, 125.6, 125.6, 125.9, 126.7, 127.5, 129.1, 129.6, 130.8, 133.6. Anal. Calcd. for $C_{30}H_{44}C_{15}N_5$: C 55.57, H 6.80, N 10.74. Found: C 55.8, H 6.8, N 10.9%.

***N*-Naphthalen-1-ylmethyl-*N*′-{2-[2-(2-{2-[(naphthalen-1-yl-methyl)amino]ethylamino}ethylamino)ethylamino]ethyl}ethane-1,2-diamine hexahydrochloride (L4·6HCl).** 49 % yield; mp 170–175 °C; solvent D_2O, δ_H (ppm): 3.37–3.2 (m, 20H), 4.45 (s, 4H), 7.42–7.26 (m, 8H), 7.82–7.73 (m, 6H); δ_C (ppm): 43.6, 44.2, 44.4, 45.4, 49.4, 123.3, 126.3, 126.5, 127.5, 128.3, 129.8, 130.4, 131.5, 134.3. Anal. Calcd. for $C_{32}H_{50}Cl_6N_6$: C 52.54, H 6.9, N 11.5. Found: C 52.0, H 7.0, N 11.2%.

***N*-{2-[(Naphthalen-1-ylmethyl)amino]ethyl}ethane-1,2-diamine trihydrochloride (L5·3HCl).** A five-fold excess of diethylenetriamine (3.10 g, 30 mmol) and naphthalene-1-carbaldehyde (0.94 g, 6 mmol) were stirred for 48 h in 75 mL of EtOH. Sodium borohydride (1 g, 26.0 mmol) was added and the mixture stirred at room temperature for 24 h. The solvent was removed at reduced pressure, the resulting residue treated with water and the functionalised amine repeatedly extracted with dichloromethane (3 × 30 mL). The organic phase was washed with water and dried over anhydrous sodium sulfate and the solvent evaporated to yield the free amine, which was dissolved in ethanol and precipitated as its hydrochloride salt. 98% yield; mp 198–201 °C; solvent D_2O, δ_H (ppm): 3.29 (t, J = 6 Hz, 2H), 3.36 (t, J = 6 Hz, 2H), 3.45 (t, J = 4 Hz, 2H), 3.49 (t, J = 4 Hz, 2H), 4.7 (s, 2H), 7.3–7.6 (m, 4H), 7.89–7.99 (m, 3H); δ_C (ppm): 35.5, 43.0, 43.7, 44.8, 48.9, 122.7, 125.84, 126.2, 127.0, 127.8, 129.4, 129.9, 130.5, 131.0, 133.8. Anal. Calcd. for $C_{15}H_{24}N_3Cl_3$: C 51.08, H 6.86, N 11.91. Found: C 51.2, H 7.1, N 12.0%.

***N*-(2-{2-[(Naphthalen-1-ylmethyl)amino]ethylamino}-ethyl)ethane-1,2-diamine tetrahydrochloride. (L6·4HCl).** 95 % yield; mp 247–250 °C; solvent D_2O, δ_H (ppm): 3.25–3.28 (m, 2H), 3.29–3.47 (m, 10H), 4.72 (s, 2H), 7.47–7.59 (m, 4H), 7.92–8.01(m, 3H); δ_C (ppm): 35.6, 43.2, 43.7, 43.9, 44.9, 49.0, 112.8, 125.9, 127.1, 127.9, 129.5, 130.0, 131.2. Anal. Calcd. for $C_{17}H_{30}N_4Cl_4$: C 47.24, H 7.00, N 12.96. Found: C 48.1, H 7.5, N 13.1%.

Naphthalen-1-ylmethyl[3-(4-{3-[(naphthalen-1-ylmethyl)-amino]propyl}piperazin-1-yl)propyl]amine tetrahydrochloride (L7·4HCl). The synthesis of this receptor has been accomplished following the procedure reported in ref. 2*a*.

Emf measurements

The potentiometric titrations were carried out at 298.1 ± 0.1 K in NaCl 0.15 mol dm^{-3}. The experimental procedure (burette, potentiometer, cell, stirrer, microcomputer, *etc.*) has been fully described elsewhere.[13] The acquisition of the emf data was performed with the computer program PASAT.[14] 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 standardised amounts of HCl with CO_2-free NaOH solutions and by determining the equivalence point by Gran's method,[15] which gives the standard potential, $E^{\circ\prime}$, 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 slightly higher solubility of the receptors in this medium.

The computer program HYPERQUAD,[16] 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 2–11) were treated either as a single set or as separated curves without significant variations in the values of the stability constants.

Table 1 Stepwise protonation constants for **L1**–**L7** determined at 298.0 ± 0.1 K in NaCl 0.15 mol dm^{-3}

Reaction [a]	L1	L2	L3	L4 [c]	L5	L6	L7 [c]
$H + L \rightleftharpoons HL$	8.38(2) [b]	9.12(2)	9.32(1)	10.04(4)	9.80(1)	9.67 (1)	8.90 (1)
$H + HL \rightleftharpoons H_2L$	7.81(1)	8.22(2)	8.58(1)	8.94(3)	8.23(1)	8.74 (1)	8.94 (2)
$H + H_2L \rightleftharpoons H_3L$	3.81(3)	6.01(3)	7.39(2)	8.29(3)	3.94(2)	6.26 (3)	6.46 (4)
$H + H_3L \rightleftharpoons H_4L$	—	3.18(3)	4.77(3)	6.82(4)	—	3.25 (3)	2.85 (6)
$H + H_4L \rightleftharpoons H_5L$	—	—	2.68(3)	4.58(4)	—	—	—
$H + H_5L \rightleftharpoons H_6L$	—	—	—	2.23(1)	—	—	—
Log β	19.99	26.53	32.74	40.90	21.96	27.92	27.15

[a] Charges omitted for clarity. [b] Numbers in parentheses are standard deviations in the last significant figure. [c] Taken from ref. 2*a*.

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 1,4-dioxane was used as a reference standard (δ = 67.4 ppm) and for the ^1H spectra the solvent signal was used. A variable temperature accessory regulated probe temperature. Adjustments to the desired pH values 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.[17]

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 by the time correlated single photon counting technique (TCSPC) as described elswhere.[2a] The fluorescence decays were analysed using the method of modulating functions implemented by Striker *et al.* with automatic correction for the photomultiplier "wavelength shift".[18] All measurements were made in the presence of oxygen to reproduce the conditions where steady state fluorescence data were obtained.

Results and discussion

Acid–base behaviour

Table 1 reports the stepwise protonation constants of ligands **L1**–**L7** determined by potentiometry at 298.1 K in 0.15 mol dm^{-3} NaCl. The corresponding constants previously reported for **L4** and **L7** have also been included for comparison. In the case of **L**, the protonation constants were measured by steady state fluorescence emission due to low solubility.

Firstly we would like to emphasize that, as already observed with similar systems,[1c] there is a reduction in the basicity of the polyamines substituted at their ends with aromatic groups in comparison to the related polyamines, either without aromatic substituents or with methylbenzene fragments linked at both terminal nitrogens of the chain.[19] This reduction can be attributed in large part to the hydrophobicity afforded by the aromatic groups. It is interesting to observe that a plot of the cumulative basicity constants *vs.* the number of atoms in the bridge gives rise to a linear representation lying below the obtained trend for the related polyamines with terminal methylbenzene groups as a result of the higher hydrophobicity of the naphthalene groups.

The stepwise sequence of protonation constants for the different ligands follows the expected trends in order to achieve a minimum electrostatic repulsion between charged sites.[20] Ligands containing an odd number of nitrogen atoms display two groups of constants; the values of the constants of the first group being much higher than those of the second group. On the other hand, the polyamines with an even number of nitrogens present a first group of high constants, an intermediate one and another group of much lower constants. For instance, for **L2**, containing four nitrogen atoms, the difference between log K_{HL} and log K_{H_2L} is just 0.9 logarithmic units, that between log K_{H_2L} and log K_{H_3L} is 2.21 and that between log K_{H_3L} and log K_{H_4L} is 2.83.

Absorption and fluorescence emission spectroscopy

In recent years we have used a precise procedure to investigate the fluorescence emission of compounds bearing aromatic fluorescent probes attached to a polyamine chain.[2,19,21] Representation of the fluorescence emission titration curves conjointly with the mole fraction distribution of the differently protonated species (obtained by potentiometry) can be further used to calculate the relative fluorescence emission quantum yields of all the emissive species. More information regarding the location of the protons at each protonation stage can be obtained by ^1H and/or ^{13}C NMR titration, allowing identification of the nitrogens responsible for fluorescence emission quenching.

The general pattern for the electronic absorption of the present family of compounds is identical to the one reported for similar polyamines possessing a single fluorescent unit at the end of the chain.[22] The absorption spectrum of these compounds is very similar to naphthalene itself and the dependence on the pH of the solution is negligible.[2] This behaviour suggests lack of interaction in the ground state between the amines and the two naphthalene units. Moreover the absorption spectrum is practically independent of the dimension of the polyamine chain, and the mole absorption coefficients of the bis-chromophoric compounds **L** to **L4** and **L7** are twice the value of the mono-chromophoric analogs **L5** and **L6**.

In contrast, as shown in Fig. 1, the fluorescence emission intensity is largely dependent on the protonation state of the compound, because deprotonation of the amines allows them to quench the excited fluorophore by electron transfer.[1c] However, the most interesting feature of the emission spectra of the present systems, exemplified in Fig. 1 for **L** and **L1**, is the appearance of a red shifted, non-structured band which can be attributed to the emission of an excimer. This structureless band does not occur with the compounds containing one single terminal naphthalene unit (**L5** and **L6**), or in the previously reported[2a] receptor **L7** possessing a rigid skeleton between the two naphthalene chromophores (Fig. 1). The absence of the red shifted band in these systems excludes the possibility of an emission from a charge transfer state involving the deprotonated amine and the naphthalene unit.[23]

We have previously reported the observation of an identical excimer emission band for the largest member of the family, **L4**,[2a] as well as for **L1**[2b] and observed that the fluorescence decays can be fitted with a sum of two exponentials, displaying the same decay times at both monomer and excimer emission wavelengths. Moreover, the short decay time at the excimer

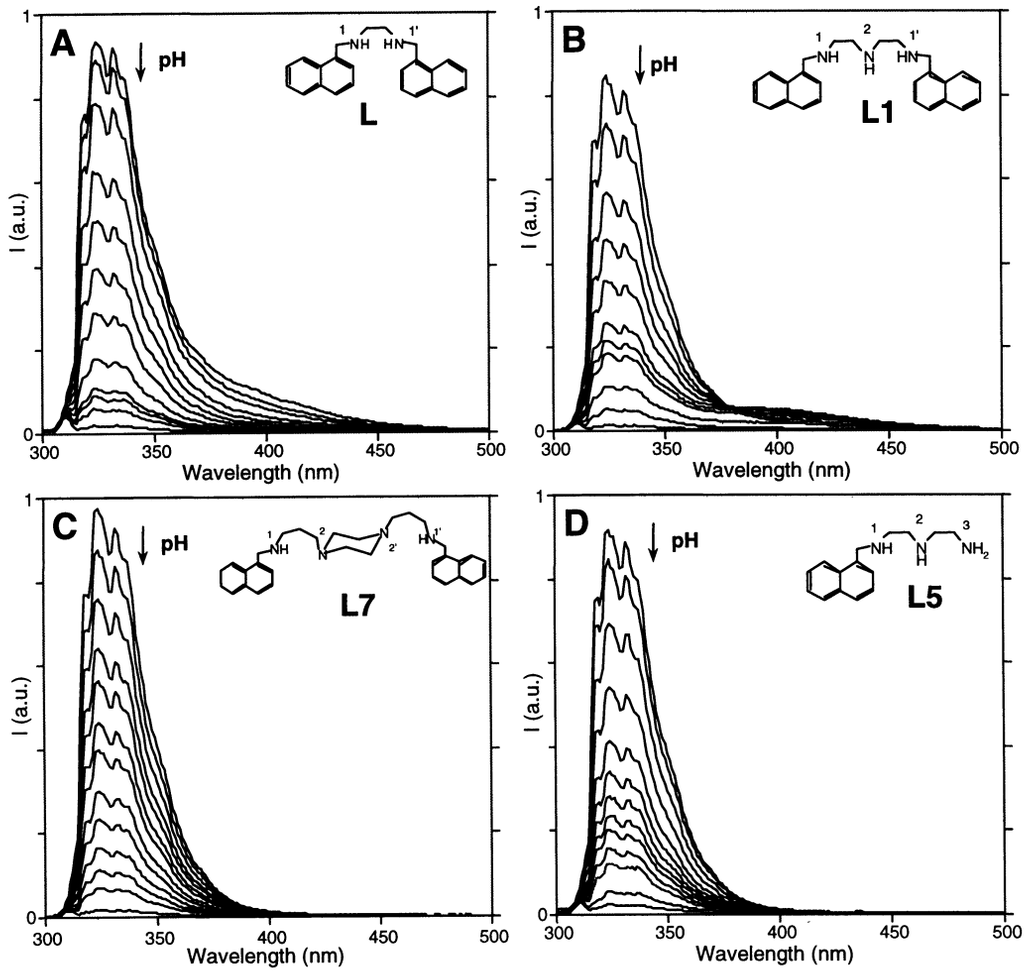


Fig. 1 Fluorescence emission spectra of componds **L**, **L1**, **L5** and **L7** at λ_{exc} = 280 nm, 25 °C, for the following pH values: **L**—1.4, 4.1, 5.2, 5.6, 5.95, 6.3, 6.6, 7.1, 8.5, 9.1, 9.75, 10.70. **L1**—1.8, 2.9, 3.4, 3.8, 4.2, 5.0, 5.8, 6.7, 7.8, 8.9, 10.5. **L5**—1.8, 3.05, 3.7, 4.3, 4.85, 5.5, 6.5, 7.4, 7.65, 8.2, 8.6, 10.1, 10.8. **L7**—1.7, 2.5, 4.4, 5.65, 6.0, 6.3, 6.5, 6.9, 7.2, 7.7, 8.6, 9.3, 10.6.

emission wavelength (418 nm) is associated with a negative pre-exponential, confirming that the excimer is formed in the excited state at the expense of the excited monomer.[2] Excimer formation implies an interaction at close distance between the two naphthalenes (π–π stacking) and consequently, the possibility of carrying out elemental, and reversible movements, driven by light absorption, can be considered.[2] In all cases (including the bis-chromophoric compounds), concentration effects on the shape of the fluorescence emission spectra were not observed, confirming the presence of intramolecular, and not intermolecular, excimer formation.

Useful information about these systems can be obtained from the titration curves, as reported in Fig. 2. According to a general pattern of behaviour found for this type of compound, the fully protonated form is the most emissive species because quenching by electron transfer, from protonated amines to the excited fluorophore, is not thermodynamically favourable.[1c,2] In **L** the first deprotonation occurs in one of the two equivalent naphthylic nitrogens, leading to an efficient (but not total) quenching effect. It is interesting to note that the fully protonated species exhibits excimer emission, explainable by the fact that, due to the small dimension of the chain, a simple rotation movement of the two naphthalene rings allows them to interact. In the case of **L**, the excimer emission band does not appear with the 418 nm maximum, but underneath the most intense monomer emission band. This is shown in Fig. 1, where the excimer emission can be clearly seen in the red-edge of the emission spectra. The attribution of this shoulder in the monomer emission band to the emissive excimer was unequivocally established by time-resolved fluorescence data, see below and ref. 2*b*. As regards the type of excimer structure formed, it seems clear that the compound **L** represents the sole exception, with the excimer emission appearing blue-shifted with respect to the excimer emission of the longer chains. In fact, in all the other compounds of the present series, the excimer emission band exhibits a clear maximum at 418 nm. In **L1** the fully protonated species does not show any excimer emission because of the increased distance between the two chromophores. However upon the first deprotonation, which occurs mainly from the central nitrogen, the chain acquires more flexibility allowing the formation of excimer. On the other hand, increase of the chain flexibility can also be obtained by an increase of its dimension, as proved by inspection of the excimer emission intensity in the case of the fully protonated forms of **L2**, **L3** and **L4**. In these compounds even at very acidic pH values, where the chain is fully protonated, the excimer emission can be clearly observed. In contrast, in the case of **L7**, which possesses a rigid chain, the excimer formation is completely hindered in the full pH range.

Time-resolved fluorescence

The fluorescence of these systems arises from the contribution of several emitting species. As a consequence of this, the resulting fluorescence decays are complex. However, at the pH values where a single form is present in the ground state (as predicted by the potentiometric titrations) the decays are simplified and become: (a) single exponential decays at the monomer emission wavelength if at that pH excimer emission is not observed (or in the case of mono-chromophoric

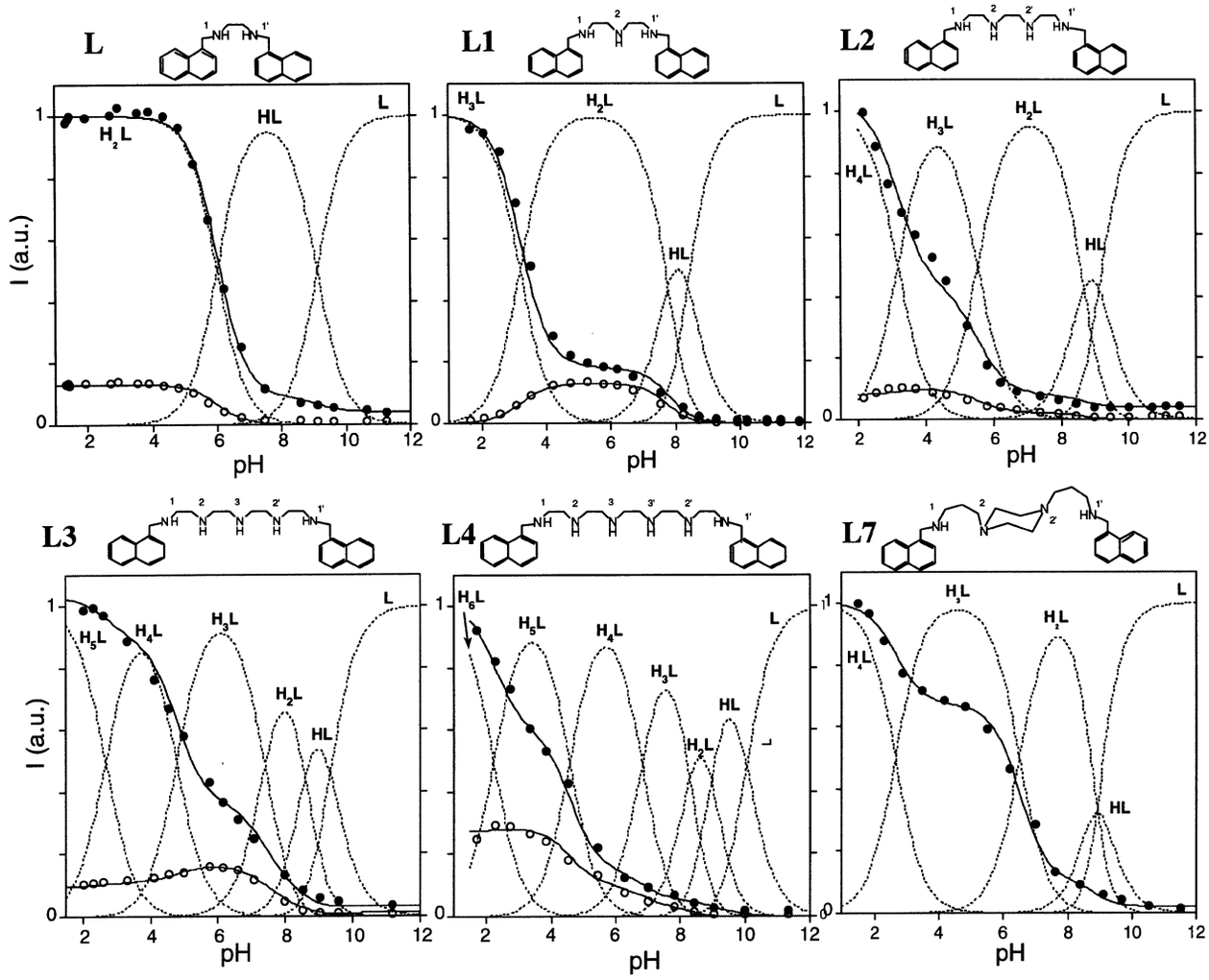
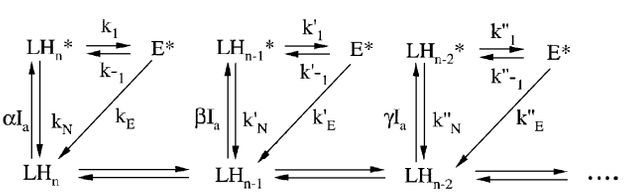


Fig. 2 Steady state fluorescence emission titration curves of **L** to **L4** and **L7** at λ_{exc} = 280 nm, λ_{em} = 334 nm and temperature of 25 °C.

compounds); (b) double exponential at both monomer and excimer emission wavelengths whenever at the chosen pH excimer emission is observed (see Fig. 3).

The general scheme accounting for the simultaneous presence of electron transfer quenching of the monomer and excimer formation for all bis-chromophoric compounds is depicted in Scheme 2.



Scheme 2

Here, k_N, k'_N and k''_N are the rate constants for deactivation of the monomer excited state in the absence of the process of excimer formation and they include the rate constant for electron transfer quenching whenever it is present, *e.g.*, $k'_N = 1/\tau_0 + k'_q$, where $\tau_0 = k_N^{-1}$ is the decay time in the absence of quenching (23.4 ns for the fully protonated form of the mono-chromophoric compounds) and k'_q is the electron transfer quenching rate constant for that particular form. The value of k_N, the decay rate constant for the fully protonated form, in the absence of excimer formation, is the same for all the compounds ($k_N = 4.27 \times 10^7$ s^{-1} in aerated solutions and $k_N = 3.13 \times 10^7$ s^{-1} in degassed solutions). The rate constants k'_N and k''_N, that include the electron transfer quenching rate constant, are experimentally accessible as they are the reciprocal decay times of the parent mono-chromophoric compound with the same degree of protonation and are presented in Table 2 for the compounds **L1** and **L2** (parents **L5** and **L6**). In the case of compounds **L3** and **L4** (for which there are no parent compounds) the constants k'_N and k''_N can be obtained from the exponential dependence of the electron transfer quenching rate constant with distance. †

Moreover if, as stated above, the pH values are chosen in order to maximize the fraction of a single species (a, β or $\gamma \cong 1$) the decays are fitted with sums of two exponentials and Scheme 2 simplifies to a Birks-type scheme involving only one of the ground state forms (LH_n, LH_{n-1} or LH_{n-2}) and the excimer decay rate constants (k_E, k'_E or k''_E), excimer formation rate constants (k_1, k'_1 or k''_1), and excimer dissociation rate constants (k_{-1}, k'_{-1} or k''_{-1}) can be calculated. The values of the calculated rate constants are also presented in Table 2.

Effect of the temperature

The temperature dependence of the steady-state fluorescence emission of the bis-chromophoric **L1** and its mono-chromophoric analogous compound, **L5**, is reported in Fig. 4. As expected, with both compounds, the fluorescence emission intensity increases with the decrease in the temperature. However, with the bis-chromophoric compound, this temperature

† Using the first and second deprotonations of compounds **L5**, **L6** and **L7**, a plot of the quenching constant against the distance, d, between the chromophore and the deprotonated amine gives an exponential dependence of the form $k_q = 3.4 \times 10^9 \times \exp(-0.45d/\text{Å})$.

Table 2 Calculated rate constants for excimer formation (k_1), excimer dissociation (k_{-1}) and excimer decay (k_E), and excimer binding energies (ΔH^*) and entropy (ΔS^*) for compounds **L**–**L4** and reciprocal decay times of the parent compounds **L5** and **L6** (k_N)

	Compound	pH	Charge	Parent	$k_N/10^7\ s^{-1}$	$k_1/10^7\ s^{-1}$	$k_{-1}/10^7\ s^{-1}$	$k_E/10^7\ s^{-1}$	ΔH^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}
1	**L**	2.2	2+		4.27	13.4	26.8	41.5	−34	−121
2	**L1**	5.5	2+	**L5**	12.3	9.35	8.68	3.31	−26	−89
3	**L2**	4.5	3+	**L6**	8.62	5.58	1.88	4.72	−15	−42
4	**L3**	1.7	5+		4.27	1.87	3.30	4.50	−6.0	−25
5		3.9	4+		5.62	4.69	5.04	4.35	−24	−83
6		6.1	3+		8.20	7.13	2.16	4.03	−28	−86
7	**L4**	2.0[a]	6+		3.13[a]	2.99	2.10	4.45	−7.0	−21
8		3.5	5+		4.71	11.0	1.42	4.13	−23	−61
9		5.6	4+		8.19	17.7	1.32	3.51	−43	−125

[a] Degassed solution.

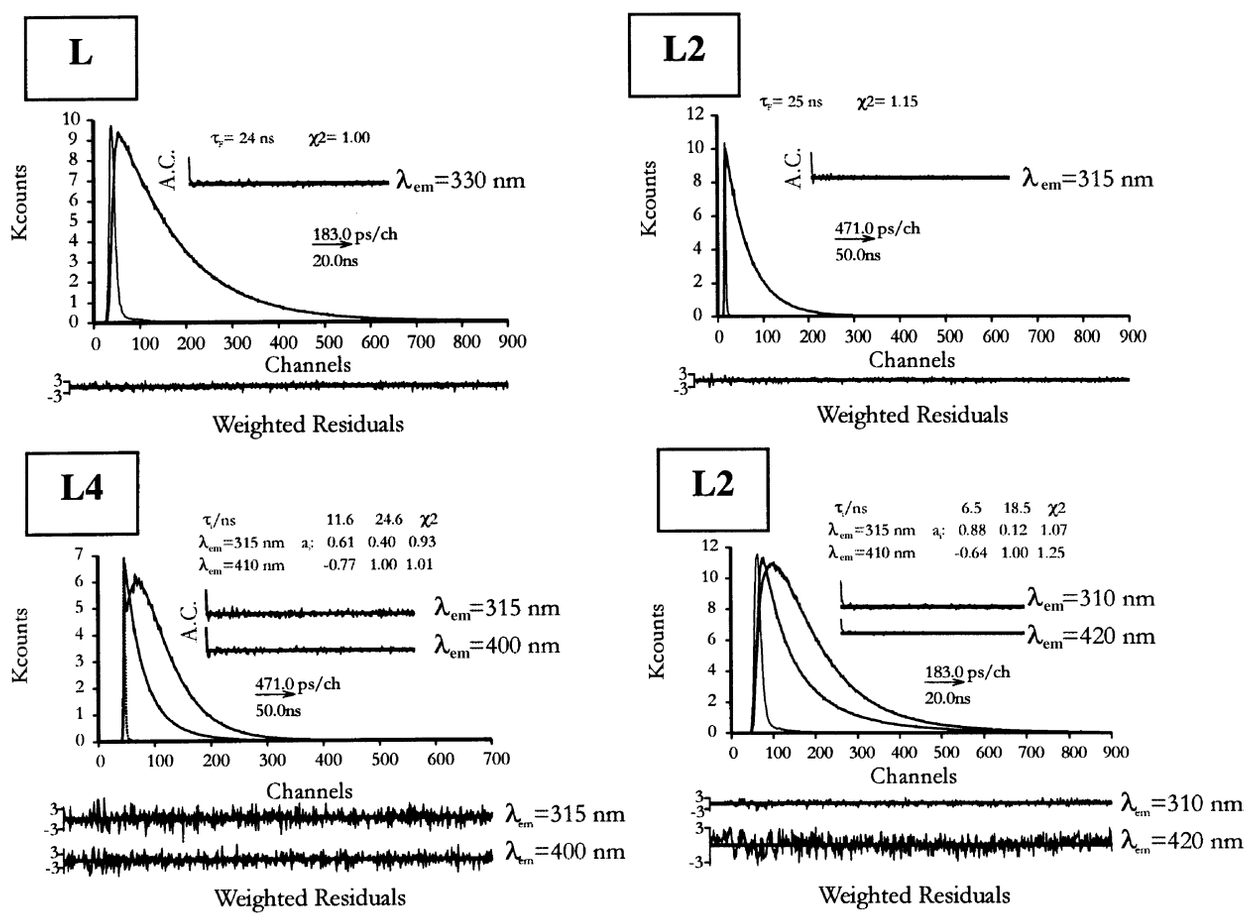


Fig. 3 Fluorescence decays and pulse instrumental response, with λ_{exc} = 281 nm, for **L2** at pH = 0.85 (top panel) and 4.64 (bottom panel). Shown as insert are the decay times (τ/ns) and the normalized pre-exponential factors (a_i). For judging the quality of the fit, chi-squares (χ2), autocorrelation functions (AC) and weighted residuals (WR) are also shown.

decrease is followed by a clear increase in the excimer emission. The lack of excimer emission, for **L5**, was also confirmed at lower temperatures.

The variation of the excimer to monomer intensities ratio (I_E/I_M) in the framework of a Birks kinetic scheme[24] should be described by eqn. (1)

$$\frac{I_E}{I_M} = \frac{k'_f}{k_f} \times \frac{k_1}{k_{-1} + k_E} \quad (1)$$

where k'_f and k_f are the excimer and monomer radiative rate constants respectively and k_1 and k_{-1} are the excimer formation and dissociation rate constants described above (Scheme 2).

When the temperature is increased k_{-1} grows faster than k_E and ultimately, above some temperature, the limit where $k_{-1} \gg k_E$ (high temperature limit) is reached and eqn. (1) simplifies to eqn. (2).

$$\frac{I_E}{I_M} = \frac{k'_f}{k_f} \times \frac{k_1}{k_{-1}} \quad (2)$$

In this limit the ratio of I_E/I_M is a simple function of the equilibrium constant for excimer formation. The ratio k'_f/k_f is temperature independent, and a plot of ln (I_E/I_M) *vs.* $1/T$ (Stevens–Ban plot[25]) yields a straight line whose slope leads to the value of the enthalpy for excimer formation (excimer binding energy), ΔH^* (see inset in Fig. 4). The value of ΔH^* obtained for compounds **L** to **L4**, at several pH values, is also presented in Table 2.

As expected, the binding energy for the excimer formation is negative in all cases, showing that the process possesses a favourable enthalpic factor. Through this work we have verified that **L** gives rise to an atypical excimer and this was confirmed by the fact that it does not follow the trend of properties observed for the series **L1** to **L4**, see below.

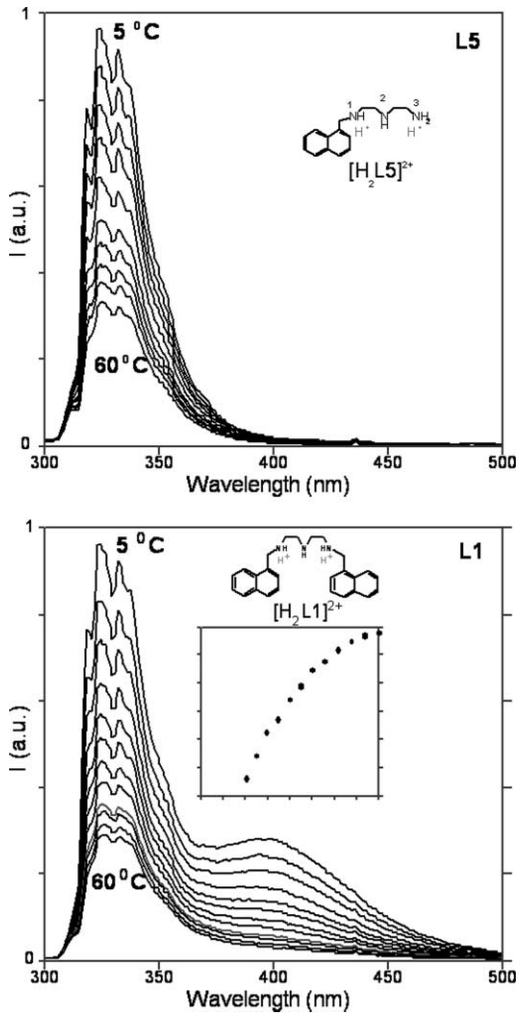


Fig. 4 Temperature dependence of the fluorescence emission at λ_{exc} = 280 nm, pH = 5.9 and 6.3 respectively for **L5** and **L1** . Inset: plot of ln (I_E/I_M) *vs.* $1/T$ for **L1** at pH = 6.0.

Inspection of Table 2 clearly shows that for the same charge of the chain, the binding energy for the excimer formation, ΔH^* (entries 3 and 6, 5 and 9, 4 and 8 respectively for the charges 3+, 4+ and 5+), becomes more negative with increasing chain length. This behaviour is probably associated with an increase in the flexibility that allows the formation of more stable excimers. In other words, the flexibility of the chain increases with the increasing of its length. On the other hand maintaining constant the length of the chain, the binding energy becomes more negative on decreasing the charge, (entries 4, 5, 6 for **L3**, and 7, 8, 9 for **L4**). These results can be explained by the lower electrostatic repulsion of the less protonated species.

The influence of the chain length and its protonation stage on the rate constant of the excimer formation and dissociation, k_1 and k_{-1}, is shown in Table 2 and plotted in Fig. 5, for **L3** and **L4**. Once more, except in the case of **L**, for the same charge k_1 increases with increasing length and for the same length decreases by increasing the charge of the chain. The same type of arguments used to explain the excimer binding energy variation can be employed in this case. On the other hand, k_{-1} only presents a modest increase. In other words the disruption of the excimer is more or less independent of the chain length and charge, at least in the case of **L3** and **L4**. In effect only a small separation of the two naphthalene units is needed to allow the collapse of the excimer.

From the data reported in Table 2, the Gibbs energy, $\Delta G°^*$, of the equilibrium between the excited monomer and the excimer, can be calculated ($\Delta G°^* = -RT\ln(k_1/k_{-1})$), and by consequence the respective entropy variations, $\Delta S°^*$. In all cases

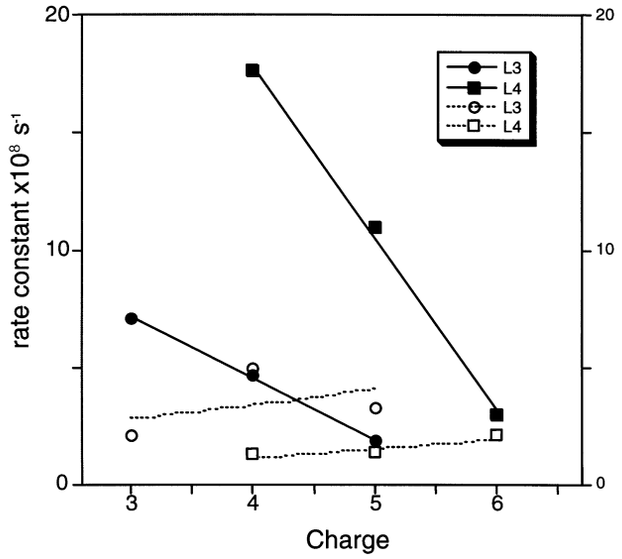


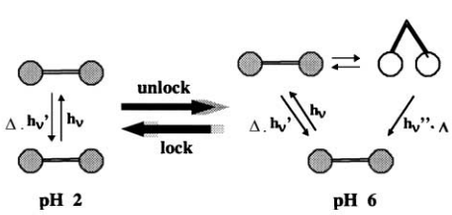
Fig. 5 Variation of the rate constants for excimer formation (k_1, closed symbols) and dissociation (k_{-1}, open symbols) for compounds **L3** and **L4** at T = 20 °C as a function of the charge (degree of protonation) of the ligand (see also Table 2).

the entropy of the excimer formation is negative because the excimer is more ordered than the initially separated monomers. Maintaining the charge, a decrease of the entropy by increasing the length of the chain is observed. Larger chain length leads to more flexible species. A decrease of entropy is also observed by decreasing the charge in the same compound. Less protonated chains are more flexible.

Conclusions

In previous work it was established that temperature, viscosity of the solvent and chain dimension are important factors contributing to intramolecular excimer formation, which are now well-discussed issues in the literature, see for instance ref. 26. In the present case we have added a completely different, and new, external factor contributing to excimer formation: the hydrogen-ion concentration of the medium.

The compounds here described present pH dependent conformational changes easily proved through excimer formation. The on–off switch action of pH leads to the elementary molecular movements that are illustrated in Scheme 3. At pH values



Scheme 3

below 2, for the case of compound **L1**, electrostatic repulsion avoids folded conformations, as proved by the absence of excimer emission; at this state the system is locked. The unlock step takes place following a pH jump to 6. For this pH value, light absorption by the monomer leads to excimer formation, signalling the presence of folded conformations.

References

1 (*a*) *Supramolecular Chemistry of anions*, A. Bianchi, K. Bowman-James and E. Garcia-España ed., Wiley-VCH, New York, 1996; (*b*) *Transition Metals in Supramolecular Chemistry*, J.-P. Sauvage ed., John Wiley & Sons, Chichester, 1999; (*c*) F. Pina, M. A. Bernardo and E. García-España, *Eur. J. Inorg. Chem.*, 2000, 2143–2157.

2 (*a*) M. A. Bernardo, S. Alves, F. Pina, J. Seixas de Melo, J. M. T. Albelda, E. Garcia-España, J. M. Llinares, C. Soriano and S. V. Luis, *Supramol. Chem.*, 2001, **13**, 435; (*b*) M. T. Albelda, M. A. Bernardo, P. Díaz, E. García-España, J. Seixas de Melo, F. Pina, C. Soriano and S. V. Luis, *Chem. Commun.*, 2001, 1520.
3 (*a*) P. D. Boyer, *Angew. Chem., Int. Ed.*, 1998, **37**, 2296; (*b*) J. E. Walker, *Angew. Chem., Int. Ed.*, 1998, **37**, 2308; W. Junge, *Proc. Natl. Acad. Sci. USA*, 1999, **96**, 4735.
4 (*a*) V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2000, **39**, 3348; (*b*) V. Balzani, A. Credi and M. Venturi, *Supramolecular Science: Where it is and where it is going*, R. Ungaro and E. Dalcanale ed., NATO ASI series, Kluwer, Dordrecht, 1999; (*c*) V. Balzani, M. G-López and J. F. Stoddart, *Acc. Chem. Res.*, 1998, **31**, 405.
5 A. P. Davies, *Angew. Chem., Int. Ed.*, 1998, **37**, 909; M. Consuelo Jiménez, C. Dietrich-Buchecker and J.-P. Sauvage, *Angew. Chem., Int. Ed.*, 2000, **39**, 3284.
6 (*a*) T. R. Kelly, H. Silva and R. A. Silva, *Nature*, 1999, **401**, 150; (*b*) T. R. Kelly, M. C. Bowyer, K. V. Bhaskar, D. Bebbington, A. Garcia, F. Lang, M. H. Kim and M. P. Jette, *Angew. Chem., Int. Ed.*, 1997, **36**, 1866; (*c*) T. R. Kelly, R. A. Silva and G. Finkenbeiner, *Tetrahedron Lett.*, 2000, **41**, 9651.
7 (*a*) R. A. Bissel, A. P. de Silva, H. Q. N. Gunaratne, P. L. M. Lynch, G. E. M. Maguire and K. R. A. S. Sandanayake, *Chem. Soc. Rev.*, 1992, 187; (*b*) A. P. de Silva, H. Q. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515.
8 (*a*) E. Kimura and T. Koike, *Chem. Commun.*, 1998, 1495; (*b*) M. Shionoya, E. Kimura and M. Shiro, *J. Am. Chem. Soc.*, 1993, **115**, 6730.
9 B. König, M. Pelka, H. Zieg, T. Ritter, H. Bouas-Laurent, R. Bonneau and J. P. Desvergne, *J. Am. Chem. Soc.*, 1999, **121**, 1681.
10 F. McLaren, P. Moore and A. M. Wynn, *J. Chem. Soc., Chem. Commun.*, 1989, 798.
11 L. Fabbrizzi (ed.), *Coord. Chem. Rev.*, 2000, **205**, 3.
12 C. Lodeiro, A. J. Parola, J. Seixas de Melo, F. Pina, A. Bencini, A. Bianchi, A. Masotti and B. Valtancoli, *Chem. Commum.*, 2000, 1639.
13 E. García-España, M. J. Ballester, F. Lloret, J. M. Moratal, J. Faus and A. Bianchi, *J. Chem. Soc., Dalton Trans.*, 1998, 101.
14 M. Fontanelli and M. Micheloni, *Proceedings of the I Spanish–Italian Congress on Thermodynamics of Metal Complexes*, Diputación de Castellón, Spain, 1990.
15 G. Gran, *Analyst (London)*, 1952, **77**, 881; F. J. Rossotti and H. J. Rossotti, *J. Chem. Educ.*, 1965, **42**, 375.
16 A. Sabatini, A. Vaca and A. Gans, *Coord. Chem. Rev.*, 1992, **120**, 389.
17 A. K. Convington, M. Paabo, R. A. Robinson and R. G. Bates, *Anal. Chem.*, 1968, **40**, 700.
18 (*a*) G. Striker, V. Subramaniam, C. A. M. Seidel and A. Volkmer, *J. Phys. Chem. B*, 1999, **103**, 8612; (*b*) M. Goldenberg, J. Emert and H. Morawez, *J. Am. Chem. Soc.*, 1978, **100**, 7171.
19 M. A. Bernardo, J.-A. Guerrero, E. García-España, S. V. Luis, J. M. Llinares, F. Pina, J. A. Ramírez and C. Soriano, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2335.
20 A. Bencini, A. Bianchi, E. García-España, M. Micheloni and J. A. Ramírez, *Coord. Chem. Rev.*, 1999, **188**, 97.
21 M.-A. Bernardo, F. Pina, E. García-España, J. Latorre, S.-V. Luis, J.-M. Llinares, J. A. Ramírez and C. Soriano, *Inorg. Chem.*, 1998, **37**, 3935.
22 S. Alves, F. Pina, M.-T. Albelda, E. García-España, C. Soriano and S. Luis, *Eur. J. Inorg. Chem.*, 2001, 405.
23 E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, 1971, **9**, 393.
24 J. B. Birks, *Prog. React. Kinet.*, 1970, **5**, 181.
25 B. Stevens and M. I. Ban, *Trans. Faraday Soc.*, 1964, **60**, 1515.
26 (*a*) K. A. Zachariasse, G. Duveneck and R. Busse, *J. Am. Chem. Soc.*, 1984, **106**, 1045; (*b*) K. A. Zachariasse, W. Kühnle, U. Leinhos, P. Reynders and G. Striker, *J. Phys. Chem.*, 1991, **95**, 5476.