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 Alarcón, Javier , Aucejo, Ricardo , Albelda, M. Teresa , Alves, Sérgio , Clares, M. Paz , García-España, Enrique , Lodeiro, Carlos , Marchin, Katherine L. , Parola, A. Jorge , Pina, Fernando , De Melo, J. Seixas and Soriano, Conxa(2004) 'Fluorescent Type II Materials from Naphthylmethyl Polyamine Precursors', Supramolecular Chemistry, 16: 8, 573 — 580

To link to this Article: DOI: 10.1080/10610270412331317512

URL: http://dx.doi.org/10.1080/10610270412331317512

Supramolecular Chemistry, December 2004 Vol. 16 (8), pp. 573–580

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Fluorescent Type II Materials from Naphthylmethyl Polyamine Precursors

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Received (in Austin, USA) 21 June 2004; Accepted 21 September 2004

Speciation studies in aqueous solution on the interaction of Cu^{2+} and Zn^{2+} with a series of polyaminic ligands *N*-naphthalen-1-ylmethyl-*N′*-{2-[(naphthalen-1-ylmethyl)-amino]-ethyl}-ethane-1,2-diamine (L1), *N*-naphthalen-1-ylmethyl-*N′*-(2-{2-[(naphthalen-1-ylmethyl)-amino]-ethylamino}-ethyl)-ethane-1,2-diamine (L2) and *N*-naphthalen-1-ylmethyl-*N′*-[2-(2-{2-[(naphthalen-1-ylmethyl)-amino]-ethylamino}-ethylamino)-ethyl]-ethane-1,2-diamine (L3) containing two naphthylmethyl groups at their termini and *N*^{1}-(2-{2-[(naphthalen-1-ylmethyl)-amino]-ethylamino}-ethyl)-ethane-1,2-diamine (L4) containing just one naphthylmethyl group have been carried out at 298.1 K in 0.15 mol dm^{-3} NaCl. In the case of the tetraamines L2 and L4, their coordination capabilities towards Cd^{2+}, Ni^{2+}, Co^{2+} and Pb^{2+} have also been considered. The stability constants follow the general Irving–Williams sequence. The steady-state fluorescence emission studies on the interaction with metal ions show that while Cu^{2+} produces a chelation enhancement of the quenching (CHEQ), the interaction with Zn^{2+} leads to a chelation enhancement of the fluorescence (CHEF). Finally, ligands L1, L2 and L3 have been successfully covalently attached to silica surfaces and some preliminary results of their emissive properties are given.

INTRODUCTION

Nowadays, the design and preparation of fluorescent sensors is a research topic of great interest because of the high demand that these devices have in fields such as analytical chemistry, clinical biochemistry and medical research [1]. Many chemical and biochemical analytes such as hydrogen ions (H^+), metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, etc.), anionic species (halides, carboxylates, phosphates, ATP, etc), neutral molecules (carbohydrates, etc.) or gases (O_2, CO_2, NO, etc.) can be detected by fluorimetric techniques. The interest in measuring emission fluorescence for sensing analytes lies on its high sensitivity [2–10], short response time and capacity for local observation (fluorescence image spectroscopy) [11–13].

One type of fluorescent sensor is based on the phenomenon of photoinduced electron transfer (PET) [14]. Such receptors are built up by joining together a recognition unit for the substrate and a fluorescent fragment whose emission is strongly affected by the interaction of the substrate in the binding unit. The introduction of polyamine molecules as coordination units is interesting because they behave as ambivalent units as a function of the pH; they bind metal ions at pH values when the number of deprotonated amino groups is high enough, while they can coordinate anionic species when the pH is low enough to allow for a sufficient number of protonated amino groups [15]. The mechanism that permits the chemosensor performance of these molecules relies on the fact that the deprotonated amino groups can quench the emission through an electron transfer to the excited fluorophore [16].

One of the developments of this kind of device consists of its incorporation into solid supports.

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ISSN 1061-0278 print/ISSN 1029-0478 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/10610270412331317512

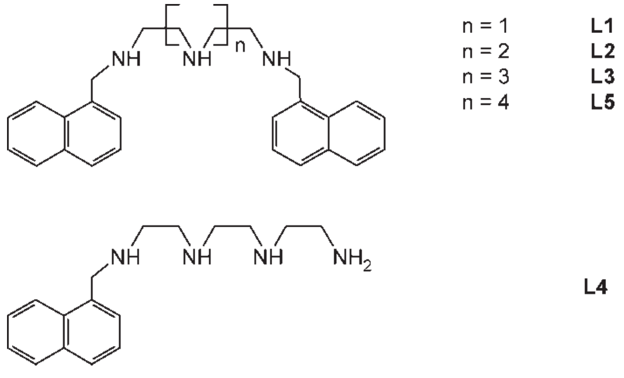
In this way, applications that require a continuous operation can be envisaged [17–28].

These materials can exist within two very different classes. In the first, type I materials, the organic and inorganic constituents interact through weak forces such as hydrogen bonding, van der Waals forces, etc. In the second, type II hybrids, the organic and inorganic components are connected through covalent or ionic–covalent bonds [29].

Over the past few years we have been interested in the analysis of the coordination and emissive capabilities of different families of polyamines containing anthracene and/or naphthalene moieties as sensing units in solution [30].

In the present work we analyse the coordination chemistry of Cu^{2+} and Zn^{2+} with polyaminic ligands *N*′-naphthalen-1-ylmethyl-*N*-{2-[(naphthalen-1-ylmethyl)-amino]-ethyl}-ethane-1,2-diamine (**L1**), *N*-naphthalen-1-ylmethyl-*N*′-(2-{2-[(naphthalen-1-ylmethyl)-amino]-ethylamino}-ethyl)-ethane-1,2-diamine (**L2**) and *N*-naphthalen-1-ylmethyl-*N*′-[2-(2-{2-[(naphthalen-1-ylmethyl)-amino]-ethylamino}-ethylamino)-ethyl]-ethane-1,2-diamine (**L3**), which contain napthylmethyl groups at their two termini. The fluorescence behaviour in solution is also considered. In addition, we also report on the coordination chemistry and fluorescent behaviour of the monochromophoric ligand N^1-(2-{2-[(naphthalen-1-ylmethyl)-amino]-ethylamino}-ethyl)-ethane-1,2-diamine (**L4**) with only one naphthylmethyl group (Scheme 1) in solution. In the case of the bisfluorophoric and monofluorophoric tetraamines **L2** and **L4**, we have also extended our solution studies to the divalent metal ions Co^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+} in order to examine the behaviour of other bivalent transition and post-transition metal ions.

Finally, we report on the covalent binding of the polyamines **L1–L3** to functionalized silica surfaces to give type II materials and we present several general features of their emissive behaviour.



SCHEME 1

EXPERIMENTAL

Materials

Receptors **L1–L3** and **L4** were prepared as described previously [30] and gave satisfactory elemental analysis and spectroscopic characterization. The 4-bromopropyl-functionalized silica gel was purchased from Aldrich and used without further purification.

Synthesis of the Grafted Materials

To prepare the grafted materials the free amines **L1–L3** were reacted in CH_3CN under reflux with stoichiometric amounts of 4-bromopropyl-functionalized silica gel using K_2CO_3 as a base (Scheme 2).

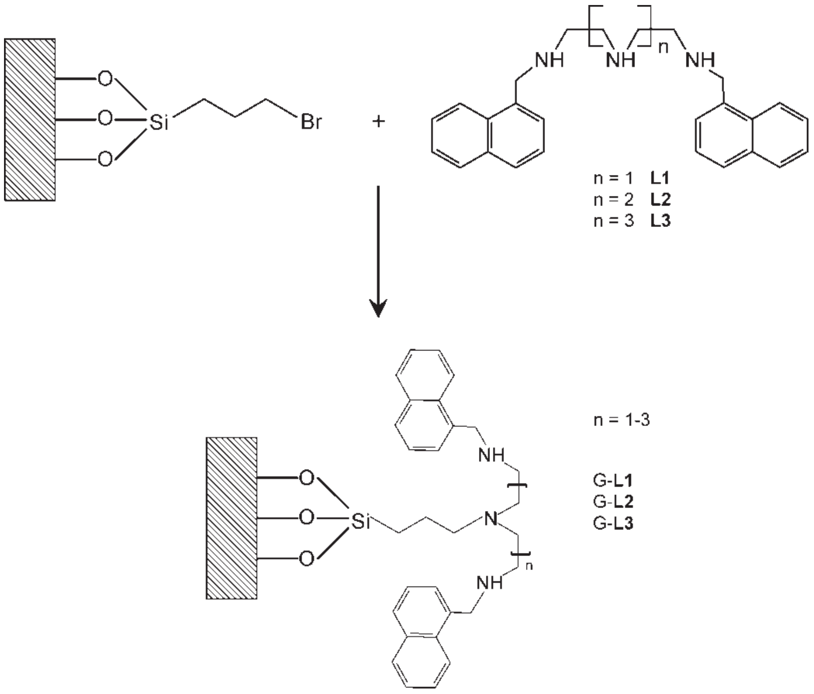
Grafted L1 (G-**L1**). In a round-bottom flask 0.50 g (1.30 mmol) of **L1**, 2.72 g of 4-bromopropyl-functionalized silica gel and 1.06 g (7.67 mmol) of anhydrous K_2CO_3 were mixed with 200 cm^3 of dry CH_3CN and the mixture refluxed for 24 h in an Ar atmosphere. The excess of K_2CO_3 was neutralized with HCl. The product was washed repeatedly with ethanol/water, and then washed with refluxing ethanol in a Soxhlet apparatus. Finally, it was dried under vacuum at 60°C for 24 h. Anal. (%): N, 0.82; C, 10.94; H, 1.66. Yield of functionalization with respect to the estimated number of bromopropyl substituents: 40.88%.

Grafted L2 (G-**L2**). The above method was repeated using 0.34 g (0.39 mmol) of **L2**, 3.09 g of 4-bromopropyl functionalized silica gel and 1.23 g (8.83 mmol) of K_2CO_3. Anal. (%): N, 1.94; C, 13.30; H, 2.02. Yield of functionalization: 50.83%.

Grafted L3 (G-**L3**). The above method was repeated using 0.96 g (1.48 mmol) of **L3**, 1.25 g of 4-bromopropyl functionalized silica gel and 0.49 g (3.55 mmol) of K_2CO_3. Anal. (%): N, 1.37; C, 12.44; H, 2.02. Yield of functionalization: 58.28%.

Emf Measurements

Potentiometric titrations were carried out at 298.1 ± 0.1 K using NaCl 0.15 mol dm^{-3} as the supporting electrolyte. The experimental procedure (burette, potentiometer, cell, stirrer, microcomputer, etc.) has been described fully elsewhere [31]. Acquisition of the emf data was performed with the computer program PASAT [32]. The reference electrode was an Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen-ion concentration probe by titration of previously standardized amounts of HCl with CO_2-free NaOH solutions and determination of the equivalent point by the Gran method [33,34], 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 used were determined



SCHEME 2

gravimetrically by standard methods. NaCl was used as the supporting electrolyte instead of the usual $NaClO_4$ because of the slightly higher solubility of the receptors in this medium.

The computer program HYPERQUAD was used to calculate the protonation and stability constants [35,36]. The pH range investigated was 2.5–11.0. The different titration curves for each ligand 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. Values for the protonation constants of ligands **L1**–**L4** were taken from the literature [30].

Spectrofluorimetric Measurements

The solvents used were of spectroscopic or equivalent grade. Water was twice distilled and passed through a Millipore apparatus. All aqueous solutions were prepared in $0.15\,\text{mol}\,\text{dm}^{-3}$ NaCl. pH values were measured with a Crison micropH 2000 and adjustments of the hydrogen-ion concentration of the solutions were made with diluted HCl and NaOH solutions.

Absorption and fluorescence spectra were recorded on a Shimadzu UV-2100 and a Horiba–Jobin–Yvon–Spex Fluorolog 3.22 spectrophotometer, respectively.

Fluorescence spectra of the grafted molecules were recorded on the spectrofluorimeter using $\lambda_{exc} = 280\,\text{nm}$ for the solid compounds. Emission spectra were recorded in the range 300–500 nm, using a fibre optic system connected to the spectrofluorometer.

Fluorescence decays were measured using a home-built time-correlated single-photon timing apparatus described previously [37]. In brief, it consists of a D_2 or N_2 gas-filled IBH 5000 coaxial flashlamp as excitation source, Jobin–Yvon monochromators, a Philips XP2020Q photomultiplier, and a Canberra instruments time-to-amplitude converter and multichannel analyser. Alternate measurements (1000 counts per cycle at the maximum) of the pulse profile at 285 nm (or 295 nm) and the sample emission were performed until $(4–10) \times 10^3$ counts at the maximum were reached. Fluorescence decays were analysed on a Pentium 500 PC, running LINUX Red Hat as the operating system, using the method of modulating functions of Striker with automatic correction for the photomultiplier 'wavelength shift' [38].

RESULTS AND DISCUSSION

Synthesis of the Grafted Materials

The covalent attachment of polyamines **L1**–**L3** was accomplished by means of nucleophilic attack of the bromopropyl functionalized silica to the secondary nitrogens of the fluorophoric amine (Scheme 2). Functionalization can occur on any one of the nitrogens of the polyamine. However, a double functionalization of a single molecule is very unlikely because of the distribution of the bromopropyl groups attached to the silica, which lie very far apart. The nitrogen percentages in the elemental analysis can be used to

TABLE I Stability constants for the interaction of **L1**, **L2** and **L3** with the metal ions Cu^{2+} and Zn^{2+} determined in NaCl 0.15 mol dm^{-3} at 298.0 ± 0.1 K

	L1		**L2**		**L3**		**L4**	
Reaction	Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}	Cu^{2+}	Zn^{2+}
$\mathrm{M + L \rightleftarrows ML}$*	14.92(2)†	8.25(4)	16.43(6)	9.05(4)	18.81(9)	9.62(6)	20.29(8)	13.19(4)
$\mathrm{M + L + H \rightleftarrows MHL}$	–	–	21.35(3)	14.77(9)	23.26(9)	17.66(2)	25.73(3)	19.81(1)
$\mathrm{M + L + 2H \rightleftarrows MH_2L}$	–	–	–	5.72	27.90(3)	–	30.04(3)	–
$\mathrm{ML + H \rightleftarrows MHL}$	–	–	4.92	–	4.45	8.04	5.44	6.62
$\mathrm{MHL + H \rightleftarrows MH_2L}$	–	–	–	–	4.64	–	4.31	–
$\mathrm{M + L + OH \rightleftarrows ML(OH)}$	–	− 1.04(1)	7.03(5)	–	–	–	–	3.25(6)

*Charges omitted by clarity. †Values in parentheses are standard deviations of the last significant figure.

derive the amount of polyamine incorporated in the silica. In the case G-**L1**, 0.743 g of **L1** was attached per gram of material; for **L2** 0.1043 g was attached, and for **L3** 0.1332 g was incorporated per gram of material.

Stability Constants of Metal Complexes

To determine the behaviour of the silica-supported materials, the coordination behaviour of the free polyamines in aqueous solution must first be known. The nitrogen protonation constants of **L1**–**L4** taken from the literature [30] show the typical sequence for these open-chain polyamines in which electrostatic forces and the presence of aromatic substituents control the values of the protonation constants.

Table I contains the values of the stepwise stability constants for the formation of Cu^{2+} and Zn^{2+} complexes of **L1**–**L4** determined by potentiometric methods at 298.1 K in 0.15 mol dm^{-3} NaCl aqueous solutions. Tables II and III present the formation constants of the Co^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+} complexes of the tetraamines **L2** and **L4**, respectively.

Analysis of the stability constants of these systems confirms the general trends observed for these types of polyamines [39,40] and can be summarized in the following.

If we first focus on the $[ML]^{2+}$ complexes ($M = Cu^{2+}$, Zn^{2+}) of the bis(chromophoric) receptors **L1**–**L3**, we observe that, as expected, the Cu^{2+} complexes exhibit higher stability constants than those of Zn^{2+} for all the ligands studied. On the other hand, as the number of nitrogen donors and the length of the chain increase, the stability of both the Zn^{2+} and Cu^{2+} complexes also increases. The maximum is reached for **L3** with five nitrogen donors. However, the analogous bis(chromophoric) receptor (**L5**) with six nitrogen atoms does not exhibit a further increase in the stability constant [$\log K(\mathrm{Cu}\mathbf{L5}/\mathrm{Cu}\cdot\mathbf{L5}) = 17.13(6)$, $\log K(\mathrm{Zn}\mathbf{L5}/\mathrm{Zn}\cdot\mathbf{L5}) = 9.48(6)$] [41]. These data suggest that five is, in this series of ligands, the maximum number of nitrogen atoms that can be involved in the first coordination sphere of the metal.

If the stability constants of the mono-(chromophoric) and bis(chromophoric) tetraamines **L2** and **L4** with the different metal ions are analysed, we observe that in both cases the general Irving–Williams order of stability is followed. Also within each series the stability constants of the $[ML]^{2+}$ complexes of Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} are fairly similar. Comparison between the stability constants of the complexes of **L2** and **L4** always shows higher values for the complexes of the mono(methylnaphthyl) compound **L4**, which is in agreement with its higher affinity for hydrogen ions [30].

Absorption and Fluorescence Emission Spectroscopy

For all the systems studied, the mole fraction distribution of the different species in solution was calculated with the constants determined by potentiometry, and used to fit the absorption and the fluorescence emission titration curves.

Zn^{2+} Complexes

It has been well established that when amines are coordinated to Zn^{2+}, the quenching effect by electron

TABLE II Stability constants for the formation of Co^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+} complexes of polyamine **L2** determined in 0.15 M NaCl at 298.1 K

Reaction	Co^{2+}	Ni^{2+}	Cd^{2+}	Pb^{2+}
M + L + H Δ MHL*	14.53(4)†	16.51(3)	14.97(2)	15.01(4)
$\mathrm{M + L \rightleftarrows ML}$	7.88(3)	10.61(4)	‡	9.15(1)
$\mathrm{ML + H \rightleftarrows MHL}$	6.7	5.9		5.9

*Charges omitted by clarity. †Values in parentheses are standard deviations of the last significant figure. ‡Precipitation prevented to obtain this stability constant.

TABLE III Stability constants for the formation of Co^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+} complexes of polyamine **L4** determined in 0.15 M NaCl at 298.1 K

Reaction	Co^{2+}	Ni^{2+}	Cd^{2+}	Pb^{2+}
M + L + H Δ MHL*	15.65(6)†	17.63(6)	15.62(3)	15.74(2)
$\mathrm{M + L \rightleftarrows ML}$	9.56(2)	12.73(2)	9.40(1)	9.11(2)
$\mathrm{ML + H \rightleftarrows MHL}$	6.1	4.9	6.2	5.6

*Charges omitted by clarity. †Values in parentheses are standard deviations of the last significant figure.

transfer is not efficient [42–44]. In that situation, the positive charge of the metal, like protons, is expected to increase the oxidation potential of the amines. On the other hand, Zn^{2+} possesses a d^{10} electronic configuration, and no quenching by energy transfer is predicted to occur. In Fig. 1 the titration curves for the Zn^{2+} complexes with **L1**-**L4** are presented.

The ZnL^{2+} form is the dominant species in the case of the complexes involving **L1** and **L2**. In both compounds all of the nitrogens are expected to be involved in the coordination, and in some way protected from the electron transfer process.

In contrast, the hydroxylated complexes are not emissive. Two reasons may explain the lack of emission in the case of the hydroxylated species: (i) the hydroxyl group takes one coordination position of the metal, forcing one of the amines to detach, which then becomes free to quench, and (ii) the hydroxyl moiety introduces new deactivation channels.

All the compounds reported in Fig. 1 give rise to an enhancement of the emission upon chelation (CHEF) [42–44]. The performance of the chemosensor can be checked by the increase in the emission from the free ligand to the complex. **L1** is very efficient in the pH range 8–11, **L2** in the pH range 7–11 and **L3** in the pH range 6–11, while the mono(chromophoric) **L4** has this effect in the pH range 6–12. At this point **L3** and **L4** are the best candidates to be used as chemosensors at the biological pH value of 7.4.

In contrast to the behaviour of Zn(II) complexes with ligands **L1**–**L3**, the hydroxylated Zn(II) complex of **L4** is emissive. While the former contain two fluorophoric units that confer strong stereochemical

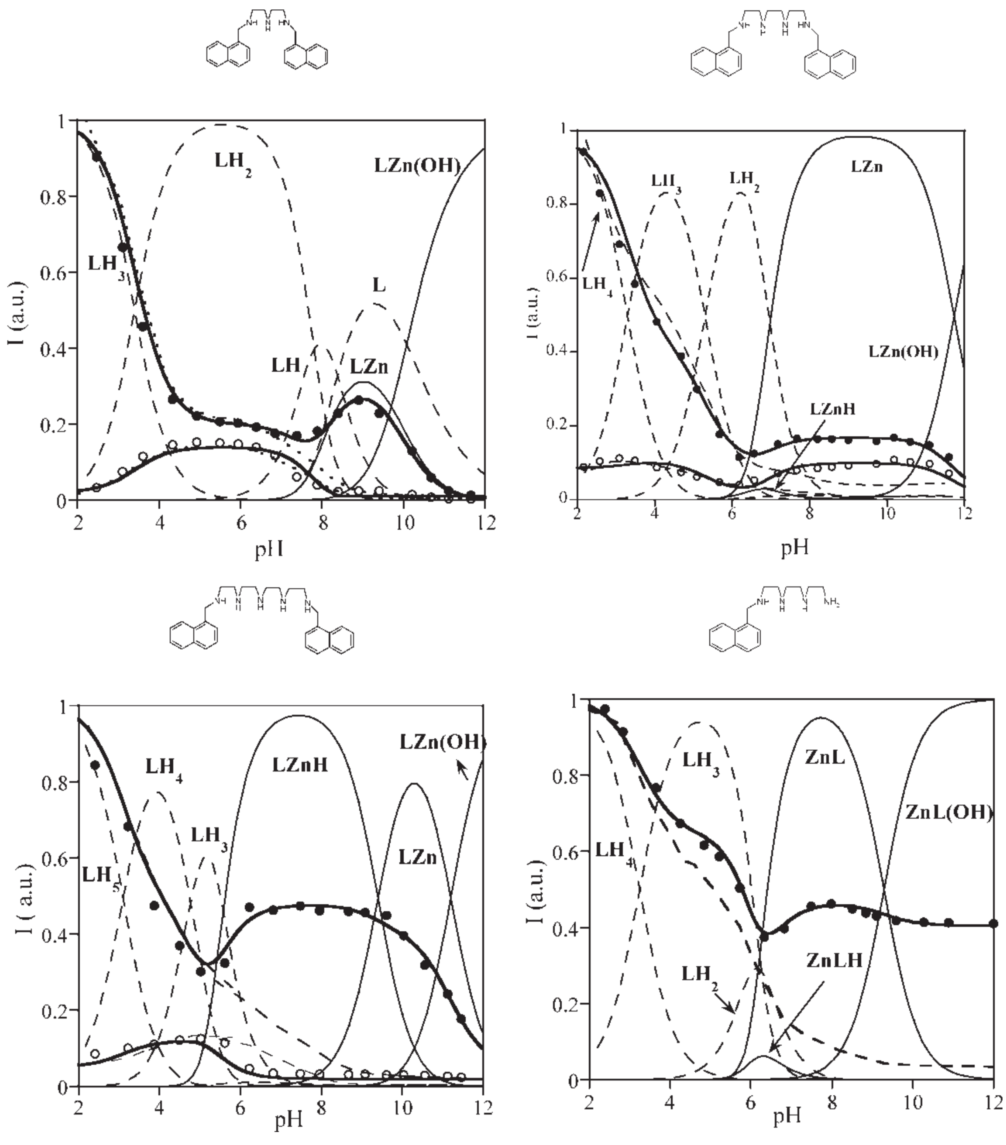


FIGURE 1 Steady-state fluorescence emission titrations curves (● monomer and ○ excimer) of **L1**, **L2**, **L3** and **L4** and molar fractions of the protonated (dashed lines) and complexed species (full lines) in the presence of Zn(II) (1:1 molar ratio) as a function of pH ([**L**] = 1.5×10^{-5} M; I = 0.1 M). Charges of the complexes are omitted for clarity. (λ_{exc} = 280 nm, λ_{em} = 334 nm; temperature = 298 K). The dashed line is relative to the fluorescence emission of the free ligands.

TABLE IV Fluorescence decay times (τ_i) and normalized pre-exponential factors (A_i) at different pH values, for the Zn^{2+} complexes of **L1**, **L2** and **L3**

Compound	pH	λ_{em}	τ_2/ns	τ_1/ns	τ_3/ns	A_1	A_2	A_3	χ^2
ZnL1	9.11	315	8.6		27	0.28		0.72	0.97
ZnL2	9.15	330	9		23	0.36		0.64	0.94
ZnL2	9.15	315	6.4	19.4	32	0.263	0.654	0.084	0.98
		410				− 0.148	0.734	0.266	1.05
ZnL3	8.99	330	5.32		27.5	0.112		0.888	1.18
ZnL5	6.5	330	4.6		21.5	0.7		0.3	1.02

requirements on the formation of the complexes, the latter is monofluorophoric. Coordination of a hydroxyl anion to any of the complexes should involve detachment of a nitrogen, with a consequent decrease in emission, if the nitrogen is near the fluorophore. In the case of the monofluorophoric **L4** ligand, there is a larger probability of this nitrogen being far from the emissive unit.

A final remark concerns the excimer emission. Only in the case of **L2** was the formation of the excimer for the species ZnL^{2+} observed. In this compound the four nitrogens should be involved in

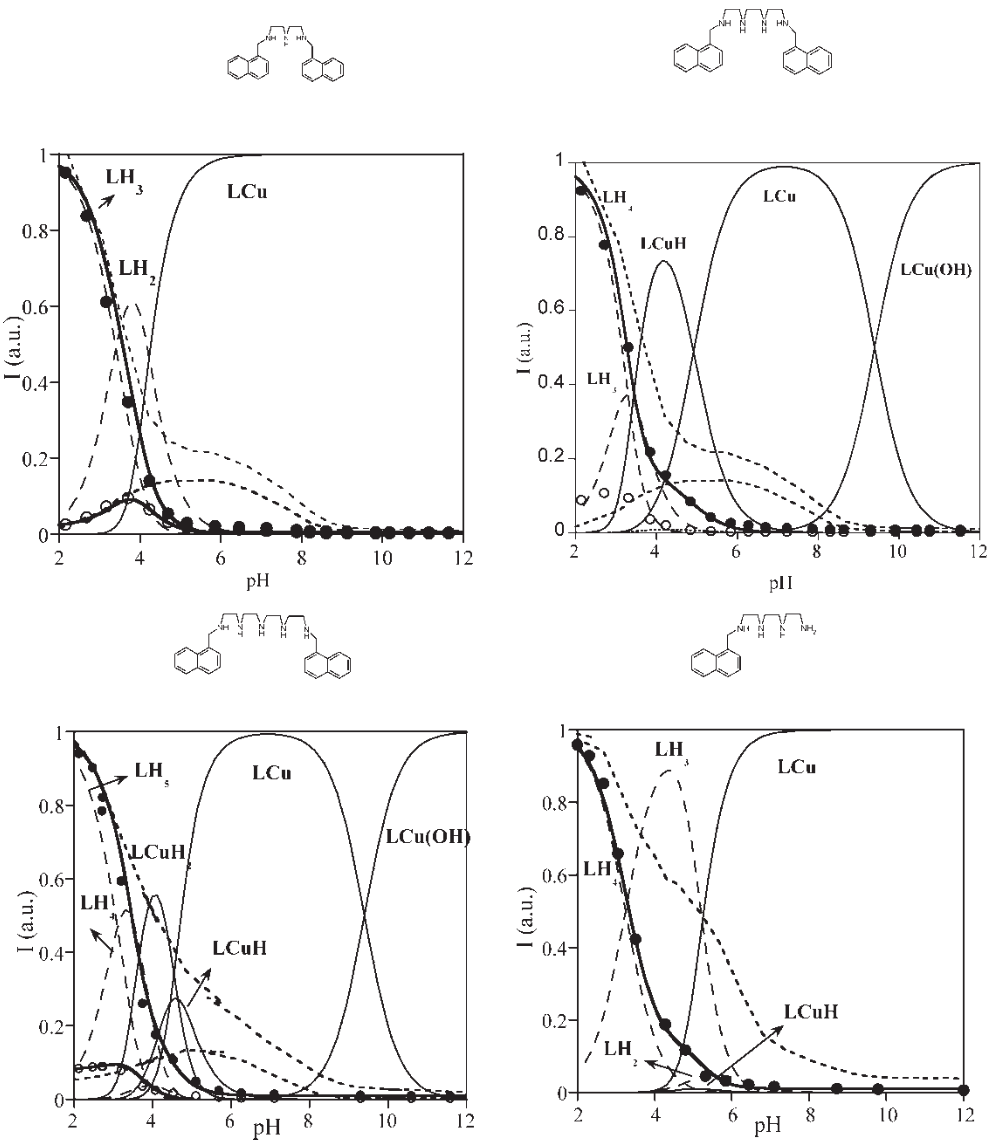


FIGURE 2 Steady-state fluorescence emission titrations curves (● monomer and ○ excimer) of **L1**, **L2**, **L3** and **L4** and molar fractions of the protonated (dashed lines) and complexed species (full lines) in the presence of Cu(II) (1:1 molar ratio) as a function of pH ([*L*] = 1.5×10^{-5}M; I = 0.1 M). Charges of the complexes are omitted for clarity. (λ_{exc} = 280 nm, λ_{em} = 334 nm; temperature = 298 K.) The dashed line is relative to the fluorescence emission of the free ligands.

the binding and the two naphthalene units should be close enough to allow interaction in the excited state. This seems to represent another example of a chain dimension effect in the excimer formation. In **L1** the chain is too short, and in **L3** and **L4** it is too large. However, no movement is expected to occur, because in the ground state the two fluorophores are still nearby.

With respect to the photophysics, the excited-state behaviour observed when zinc is added to a solution of the ligand **L** is a result of the coexistence of free ligand and complexed species. Double exponential fits were obtained for the compounds when zinc was bound to the ligand, usually at high pH values (see Table IV). The τ_2 lifetime is clearly identified as that of the ZnL^{2+} species and the longer one (τ_3) as that of the free species. The sole exception occurs with **L2** at pH $\sim$ 9. In this case excimer formation occurs leading to the appearance of a third lifetime (τ_1) and a negative pre-exponential factor (rise-time) at longer wavelengths, indicating that the excimer is being formed in the excited state at the expense of the ZnL^{2+} species. This is most probably because the Zn^{2+} complex in this case leads to a favourable sandwich-type conformation in the excited state allowing the overlap between the naphthalene chromophores.

Cu^{2+} Complexes

As reported elsewhere for ligands bearing an anthracene attached to a polyamine chain [45], the Cu^{2+} complexes with **L1**–**L4** show a chelation enhancement of the quenching (CHEQ) [42–45]. Nevertheless, some residual emission can be observed for the species also containing some nitrogens involved in the binding and some others protonated. This is particularly true for the species CuH$_3$L^{5+} of the compound possessing the largest chain, **L5** [42]. In this compound it is reasonable to suppose that the structure adopts a symmetric configuration, in which the Cu^{2+} is bound to the central nitrogen atoms while the naphthylic nitrogens remain protonated. This leads to a situation where the metal is not very close to the fluorophore and thus the quenching effect may be reduced (Fig. 2).

Steady-state Fluorescence Emission Studies of the Grafted Materials

We also carried out steady-state fluorescence emission studies of the grafted materials G-**L1**, G-**L2** and G-**L3**. The studies were performed by using an optical fibre device connected to a Horiba–Jobin–Yvon–Spex Fluorolog 3.22 spectrofluorometer.

Figure 3 shows the excitation and emission spectra of the three grafted materials. In general, the spectra of the grafted materials were less resolved than those recorded in solution, possibly due to a light-scattering phenomenon. As can be seen in the figure, in all cases the characteristic fluorescence emission of the naphthalene moiety is accompanied by a red-shifted emission whose shape and energy suggest the presence of an excimer. This emission pattern is similar to that displayed by the polyamine sensors dissolved in water [30]. Unfortunately, in the case of the grafted materials it is difficult to know which is the mean protonation state of the polyamine chain,

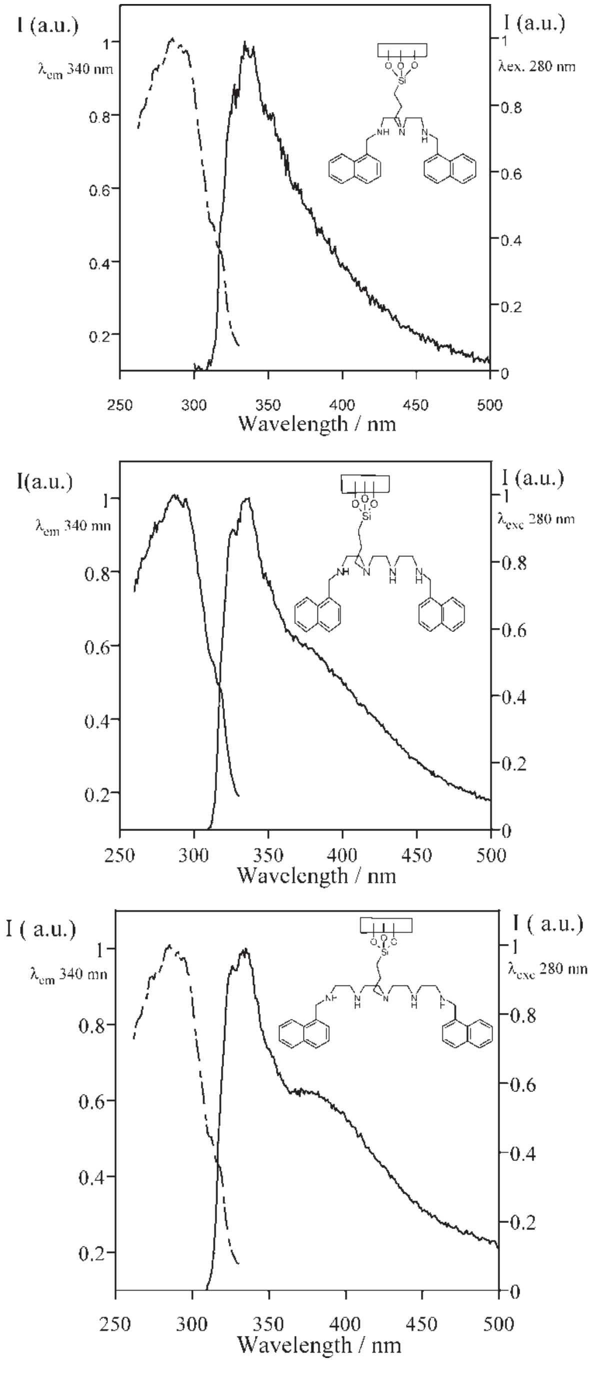


FIGURE 3 Fluorescence emission (right) and excitation spectra (left) of solids G-**L1**, G-**L2** and G-**L3**. (λ_{exc} = 280 nm, λ_{em} = 334 nm and temperature of 298 K.)

and thus quantitative comparisons are hampered. It is noticeable that for the solid compounds, the excimer emission increases with the chain dimension (see Fig. 3). This is probably because the binding of the chain to the silica support allows for a more efficient approach of the two fluorophores at the chain termini. Further studies on the coordination behaviour of the grafted material are under way.

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