Open-Chain Polyamine Ligands Bearing an Anthracene Unit − Chemosensors for Logic Operations at the Molecular Level

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In this work the absorption and the fluorescence emission properties as well as the protonation sequence of three open chain polyamine ligands of different dimensions bearing an anthracene unit were studied. The protonation and stability constants with Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} have been determined in 0.15 mol·dm^{-3} NaCl at 298.1 ± 0.1 K. The values of both protonation and stability constants follow the expected trends according to the number of nitrogen donors, sequence of chelate rings and hydrophilic–hydrophobic balance. Chelation enhancement of the fluorescence emission (CHEF) was observed for some complexes of these ligands with Zn^{2+} and Cd^{2+}. In contrast the analog complexes containing $Cu^{2+}$and Ni^{2+} exhibit a chelation enhancement of the quenching (CHEQ) except for the complexes with the largest chain where some protonated metal complexes are emissive. These systems are explored from the point of view of chemosensors for logic operations at the molecular level.

Introduction

The tendency towards miniaturization has been a constant objective in many scientific applications, in particular those related to the construction of electronic components. The smaller size is associated with better performance and greater speed.[1,2] However, miniaturization based on top-down approaches, like lithographic techniques, seems to have reached its lower limits.[3,4] One possible alternative to overcome this drawback is the use of the bottom up approach. In this strategy molecules are viewed as elementary components performing a single act, and an assembly of molecular components as a device capable of executing a given function.[4,5]

Molecular analogs of electronic devices are important research tools. There is also a possibility of their future application in a chemical computer.[4−8] In order to mimic semiconductor logic gates, switches based on systems operating in liquid solutions (liquid logic) have been described.[8−13] De Silva and co-workers reported several examples of these systems constituted by a receptor and a fluorophore separated by a spacer.[8,10−13] The input signal (1,0) is obtained through the binding of metal ions or protons to the receptor, while the output signal (0,1) is generally detected by the presence of light emission. In a different approach, based on a pseudo rotaxane, the groups of Balzani and Stoddart were able to describe a conceptual XOR logic gate.[14]

In recent years our groups have been involved in the synthesis and photochemical characterization of chemosensors containing an aromatic hydrocarbon unit and bearing a polyamine receptor unit.[15−19] These molecules are capable of sensing not only cations,[15−18] but also anions.[19] In the case of H^+, Zn^{2+}, and Cd^{2+} we observed an enhancement of the fluorescence emission upon chelation (CHEF), while a quenching effect (CHEQ) can be detected for chelation of ATP, Cu^{2+}, and Ni^{2+}.[8,18,19]

In this work we explore the potential of a series of compounds containing one anthracene moiety, linked to a polyamine chain by an anthrylic carbon atom and their metal complexes. The purpose of this is for mimicking the electronic logic gates.

The systems reported here show a high versatility, because depending on pH, different logic gates, based on metal ion coordination (exhibiting CHEQ and CHEF effects), can be designed.

Results and Discussion

Protonation and Stability Constants

The protonation constants of **L3** and **L4** (Scheme 1) and the stability constants for their interaction with the metal ions Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} are shown in Tables 1, 2,

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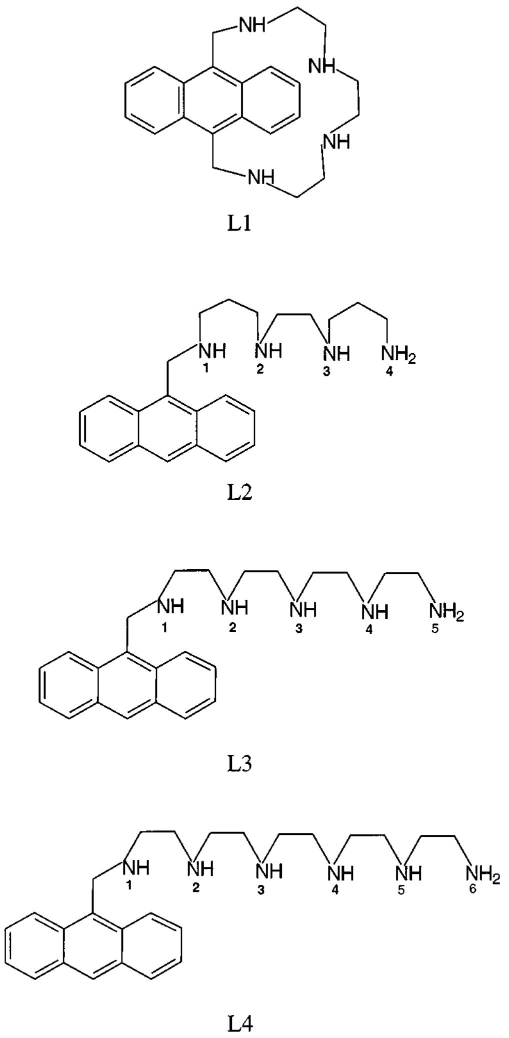


Scheme 1

Table 1. Logarithms of the protonation constants for the receptors **L3** and **L4** determined in NaCl 0.15 mol·dm^{-3} at 298.1 ± 0.1 K

Reaction	L3	L4	L2
$H + L \rightleftharpoons HL$[a]	10.27(4)[b]	10.05(1)	10.28
$H + HL \rightleftharpoons H_2L$	9.16(5)	9.18(1)	9.21
$H + H_2L \rightleftharpoons H_3L$	7.83(8)	8.42(1)	7.65
$H + H_3L \rightleftharpoons H_4L$	4.96(1)	6.69(1)	5.59
$H + H_4L \rightleftharpoons H_5L$	2.9(1)	4.22(2)	–
$H + H_5L \rightleftharpoons H_6L$	–	2.33(3)	–
$\log\beta$[c]	35.1	40.9	32.7

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

and 3 respectively. All constants were determined in 0.15 mol·dm^{-3} NaCl at 298.1 ± 0.1 K.

The trend of the protonation constants (Table 1) can be largely interpreted in terms of minimization of coulombic repulsion between same sign charges.[20] **L3** presents three large constants [$\log K_1 - \log K_3 = 2.4$ or $\Delta(\log K_1/K_3) = 2.4$] and two much lower constants for the fourth and fifth protonation steps [$\Delta(\log K_3/K_4) = 2.87$, $\Delta(\log K_4/K_5) = 2.06$]. **L4** displays even higher constants than **L3** in its first three protonation steps [$\Delta(\log K_1/K_3) = 1.63$] an intermediate value for the fourth protonation step [$\Delta(\log K_3/K_4) = 1.75$] and a group of two lower constants for the fifth and sixth protonation steps [$\Delta(\log K_5/K_6) = 1.9$]. The first three protons binding the free polyamine **L3** can bind non-adjacent nitrogen atoms and therefore electrostatic repulsion will not be very large at this stage. The fourth protonation has to occur, however, adjacent to two already protonated nitrogen atoms yielding an important basicity decrease.

For **L4**, the situation is slightly different. The first three protons can bind the receptor through distant enough nitrogen atoms to yield even higher constants than **L3** (see Figure 1). The fourth protonation, however, will have to take place close to only one protonated centre yielding a smaller basicity reduction than that observed for the fourth step of **L3**.

Another point of interest is to compare these protonation constants with those reported in the literature for the polyamines, 1,4,7,10,13-pentaazatridecane (tetren, **L5**) and 1,4,7,10,13,16-hexaazahexadecane (penten, **L6**). The larger hydrophilicity of **L5** and **L6** is denoted in their higher protonation constants. This fact can be ascribed to the greater stabilisation by hydrogen bonding of **L5** and **L6,** containing primary nitrogen atoms at both ends, to the solvent water molecules.

The stability constants of the metal complexes of **L3** and **L4**, presented in Table 2 and Table 3, fulfil some of the general aspects of the coordination chemistry of polyamine ligands. Firstly, the Cu^{2+} complexes of both ligands are the ones displaying the largest stabilities; the stability trend observed $Cu^{2+} > Ni^{2+} > Zn^{2+}$ follows the expected tendency

Table 2. Stability constants for the interaction of **L3** with Cu^{2+}, Zn^{2+}, and Cd^{2+} determined in NaCl 0.15 mol·dm^{-3} at 298.1 ± 0.1 K

Reaction	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
$M + L \rightleftharpoons ML$[a]	13.2(1)	18.15(7)[b]	11.73(1)	8.36(2)
$ML + H \rightleftharpoons MHL$	8.2	7.57	8.28	9.98
$M + LH \rightleftharpoons MHL$	11.1	15.37	9.74	8.07
$MHL + H \rightleftharpoons MH_2L$	5.1	4.61	5.4	5.48
$MH_2L + H \rightleftharpoons MH_3L$	–	3.48	–	–
$ML + OH \rightleftharpoons ML(OH)$	3.3	3.66	5.38	–
$M + L + H_2O \rightleftharpoons ML(OH) + H^+$	2.7(1)	8.1(1)	3.88(8)	–

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

Table 3. Stability constants for the interaction of **L4** with Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} determined in NaCl 0.15 mol·dm^{-3} at 298.1 ± 0.1 K

Reaction	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
$M + L \rightleftharpoons ML$[a]	15.2(1)[b]	18.45(5)	12.84(5)	10.07(5)
$ML + H \rightleftharpoons MHL$	7.31	9.31	8.21	9.82
$M + LH \rightleftharpoons MHL$	12.5	17.71	11.0	9.85
$MHL + H \rightleftharpoons MH_2L$	6.12	5.03	6.22	6.62
$MH_2L + H \rightleftharpoons MH_3L$	–	3.58	–	–
$ML + OH \rightleftharpoons ML(OH)$	–	–	4.9	–
$M + L + H_2O \rightleftharpoons ML(OH) + H^+$	–	–	4.01(4)	–

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

according to the general Irving−Williams order of stability for octahedral complexes. The stability of the Cd^{2+} complexes is, for the two ligands, slightly lower than that found for the Zn^{2+} complexes. It is interesting to note that, particularly for Cu^{2+}, the stability constants of the different complexes do not increase much from **L3** to **L4**. Although deriving coordination numbers from values of the free energy terms alone can often be misleading, comparison of the values of the stability constants with those presented by analogous complexes can provide useful information with respect to this. The stability of the $[CuL]^{2+}$ complexes of **L3** and **L4** (see Table 2 and Table 3) is clearly lower than those presented by the $[CuL]^{2+}$ complexes of **L5**, log K_{CuL} = 22.8, and **L6**, log K_{CuL} = 22.40(5),[21] and even slightly lower than that presented by the open-chain tetraamine 1,4,7,10-tetraazadecane, log K_{CuL} = 20.05. Therefore, all of this data, together with the presence of different protonated complex species seem to suggest that four nitrogen atoms are involved in the coordination sphere of the Cu^{2+} complexes of both polyamines. This point is further supported by comparison with the tetraamine **L2**, that also contains an anthracene fragment. The complex $[Cu\mathbf{L2}]^{2+}$ whose crystal structure denoted a 4-coordination of the Cu^{2+} by the nitrogen donors of the ligand,[18] presents a slightly higher stability than $[Cu\mathbf{L3}]^{2+}$ and $[Cu\mathbf{L4}]^{2+}$, again suggesting the same number of co-ordinated nitrogens. The higher stability of $[Cu\mathbf{L2}]^{2+}$ (log K_{CuL2} = 19.45) with respect to $[Cu\mathbf{L3}]^{2+}$ and $[Cu\mathbf{L4}]^{2+}$ can be ascribed to the better bite produced by an alternated sequence of five and six-membered chelate rings. For the other metal ions studied, Ni^{2+}, Zn^{2+}, and Cd^{2+}, similar comparisons with related polyamines also suggest four as the most likely number of nitrogen donors involved in the first co-ordination sphere of the metals (log K_{NiL2} = 11.61, log K_{ZnL2} = 8.62, log K_{CdL2} = 8.20, ref.[18]).

Electronic Absorption and Fluorescence Emission Studies

For all systems the molar 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.

Protonation Effects

The electronic absorption spectra of the free ligands reported in Scheme 1 do not change significantly with pH, in contrast with the fluorescence emission intensities which are dramatically dependent on the protonation state of the compounds (see Figure 1). In previous work carried out with the smaller ligands **L1** and **L2**, we reported that their fully protonated forms exhibit the highest emission intensity.[18] According to the NMR spectroscopic data, the first and second deprotonation steps occur on the two central

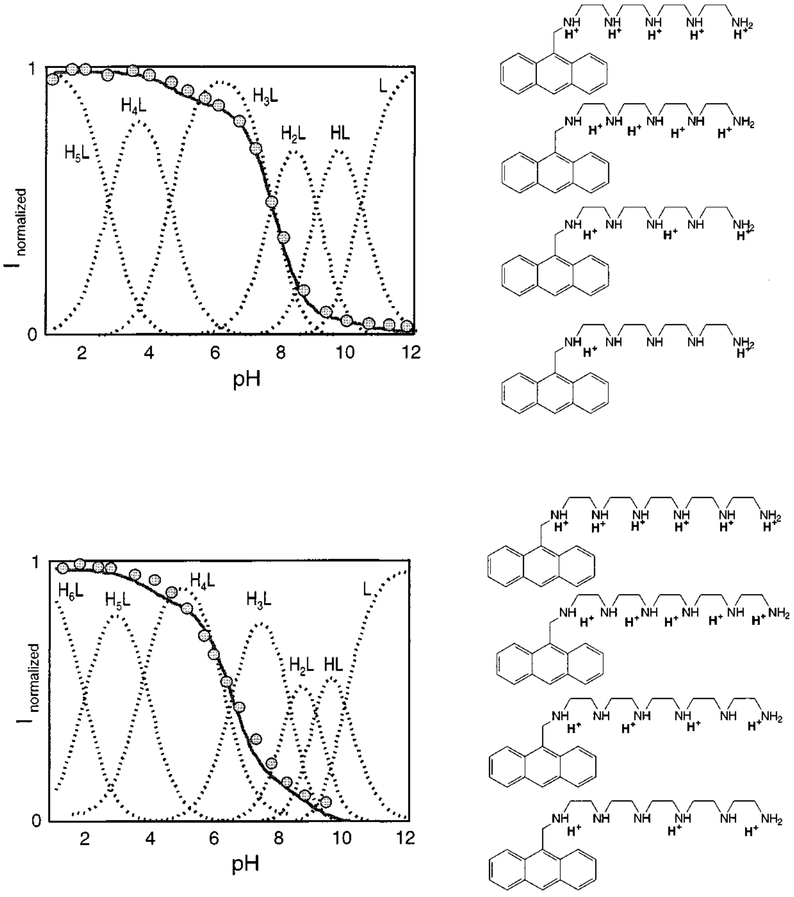


Figure 1. Fluorescence emission titration curves and molar fraction distributions of the ligands in the absence of metal ions; **L3**: λ_{exc} = 387 nm, λ_{em} = 420 nm; **L4**: λ_{exc} = 378 nm, λ_{em} = 418 nm

nitrogens of the chain. However, while the first deprotonation has only a small effect in the intensity of the fluorescence emission, the second one gives rise to its complete disappearance. The quenching effect can be accounted for by the thermodynamically favourable intramolecular photo-induced electron transfer from the lone pairs of the amine to the excited anthracene unit. This process is prevented by the protonation of the nitrogens, because protonation increases the oxidation potential by amounts of the order of 2 eV, changing the process from exergonic to endergonic. In the case of the macrocycle **L1** and its open-chain analog compound **L2**, the existence of one proton shared by the two central nitrogen atoms seems to be sufficient to prevent the quenching process. For this reason the complete quenching effect is only observed when both central nitrogens 2 and 3 are not protonated.

This pattern is repeated in the case of the compounds **L3** and **L4**.

A large quenching effect is observed only for the forms in which nitrogens 2 and 3 are completely deprotonated. It is worthwhile noting that deprotonations occurring on nitrogen atoms located at large distances from the anthracene ($n \geq 4$) do not produce significant quenching effects. This result can be explained by the well-known decrease of the electron transfer efficiency with the distance. According to CPK models the most suited nitrogen atoms for such a transfer seem to be those located at positions 2 and 3.

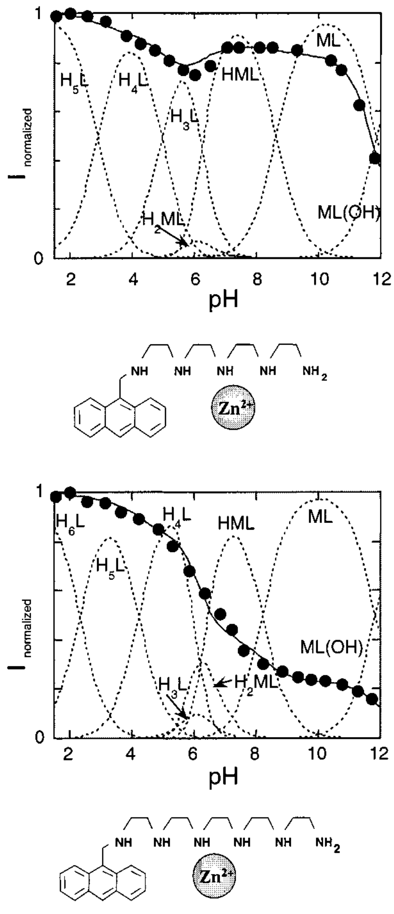


Figure 2. Fluorescence emission titration curves and molar fraction distributions of the ligands in the presence of Zn^{2+}; **L3**: λ_{exc} = 388 nm, λ_{em} = 420 nm; **L4**: λ_{exc} = 379 nm, λ_{em} = 418 nm

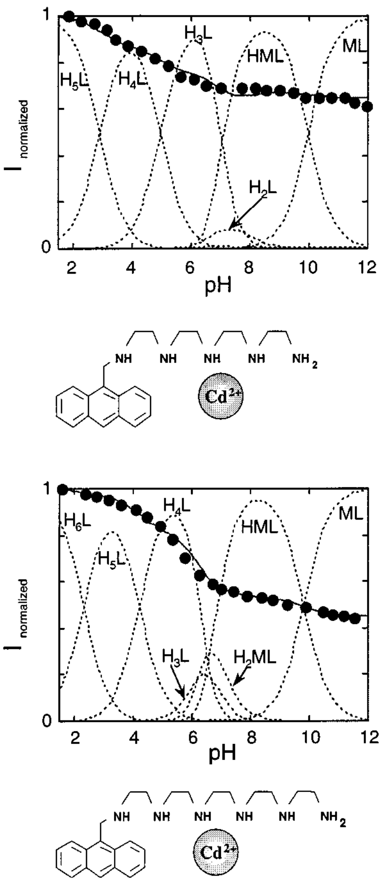


Figure 3. Fluorescence emission titration curves and molar fraction distributions of the ligands in the presence of Cd^{2+}; **L3**: λ_{exc} = 380 nm, λ_{em} = 419 nm; **L4**: λ_{exc} = 382 nm, λ_{em} = 418 nm

Chelation Enhancement of the Fluorescence Emission (CHEF)

It is well documented that metal cations like Zn^{2+} and Cd^{2+}, can give rise to complexes exhibiting fluorescence emission.[18,22,23] Figure 2 and Figure 3 show the fluorescence emission titration curves of the compounds **L3** and **L4**, in the presence of equimolar quantities of Zn^{2+} and Cd^{2+}, respectively. As reported in previous work, the zinc complexes of ligands containing a polyamine chain linked to an aromatic hydrocarbon unit are generally emissive except for the hydroxo species.[17,18] In principle, any positively charged substrate capable of binding to the nitrogen lone pairs could prevent the electron transfer. However, the interaction with metal cations can also give rise to other non-emissive excited states (charge transfer) or promote the quenching by energy transfer involving the metal. This is not the case for Zn^{2+} and Cd^{2+}, because these metal cations posses a d^{10} electronic configuration and, thus no charge transfer process (except metal-ligand CT when low energy empty ligand orbitals are available) or energy transfer is expected to occur. Therefore, for ligands **L2**−**L4** coordination of Zn^{2+} and Cd^{2+} produce a chelation enhancement of the fluorescence emission (CHEF effect).

On this basis, the species $[ZnL4]^{2+}$ showing a lower emission intensity than its analogous $[ZnL2]^{2+}$ [18] and $[ZnL3]^{2+}$ is an exception. This behaviour can be explained by the fact that Zn^{2+} is coordinated by only four nitrogen atoms. In the case of the species $[ZnL4]^{2+}$ there would be two non-coordinated deprotonated nitrogens (one more than in **L3**), and probably one of these nitrogens can get closer to the anthracene. Attempts to obtain suitable crystals of these complexes for X-ray diffraction in order to support our interpretation have unfortunately been unsuccessful.

In general, there is an important difference between Zn^{2+} and Cd^{2+} complexes in the basic pH region, because Cd^{2+}, differently from Zn^{2+}, does not easily form the non-emissive hydroxo complexes. This fact permits the existence of strong emissions, for example at pH = 12, which can be explored for practical purposes, vide infra. Finally, the species $[CdL4]^{2+}$ is also less emissive than its analogs $[CdL3]^{2+}$ and $[CdL2]^{2+}$, probably by the same reason pointed out for the Zn^{2+} complexes.

Chelation Enhancement of the Quenching (CHEQ)

Contrarily to Zn^{2+} and Cd^{2+}, many other metal cations are able to quench the emission when forming the corresponding complexes giving rise to the appearance of CHEQ effects. Cu^{2+} and Ni^{2+} are representative examples (see Figure 4 and Figure 5, respectively). This quenching effect can be explained by the existence of deactivation channels involving the metal orbitals. Energy transfer for both metal ions as well as electron transfer in the case of Cu^{2+}, have been claimed as possible mechanisms of deactivation.

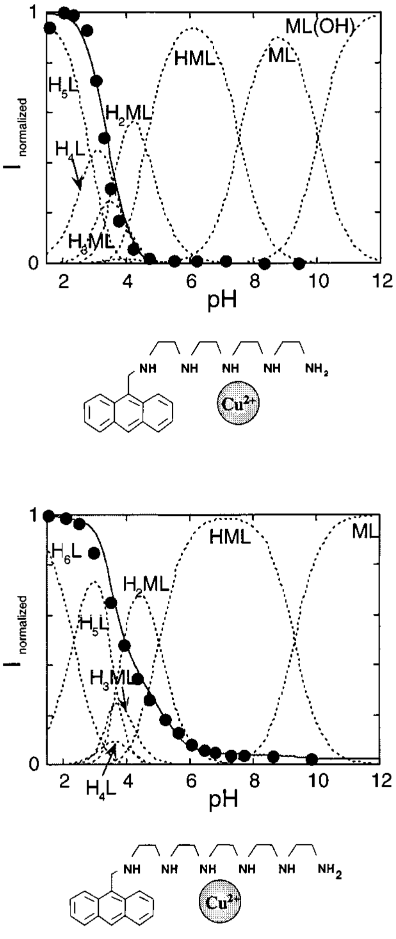


Figure 4. Fluorescence emission titration curves and molar fraction distributions of the ligands in the presence of Cu^{2+}; **L3**: λ_{exc} = 391 nm, λ_{em} = 418 nm; **L4**: λ_{exc} = 379 nm, λ_{em} = 418 nm

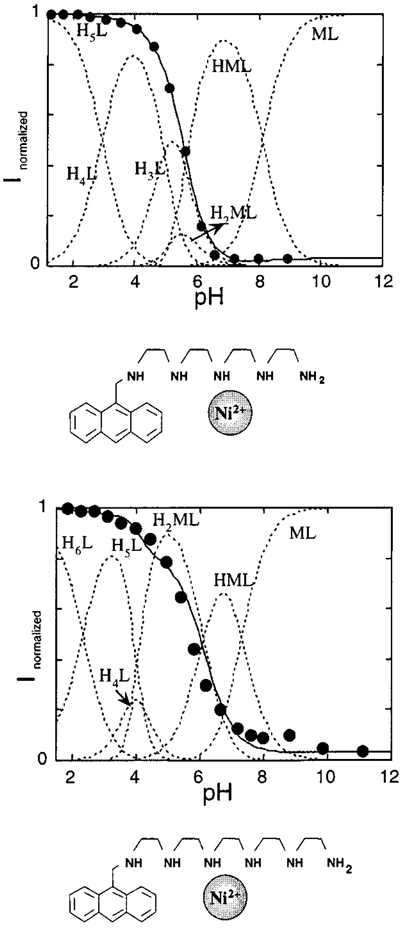


Figure 5. Fluorescence emission titration curves and molar fraction distributions of the ligands in the presence of Ni^{2+}; **L3**: λ_{exc} = 378 nm, λ_{em} = 418 nm; **L4**: λ_{exc} = 379 nm, λ_{em} = 418 nm

In Figure 4, the fluorescence emission titration curves of the ligands in the presence of Cu^{2+} are shown. As in the previous examples the dimension of the chain affects the emissive properties of the complexes. Comparing the Cu^{2+} complexes of these ligands, the most interesting feature is the existence of a slightly emissive $[CuH_2L4]^{4+}$ species, and a relatively strong emissive species, $[CuH_3L4]^{5+}$. In this case, we can expect that the metal ion to be coordinated by nitrogens 4, 5 and 6, is far enough away from the anthracene so as to decrease the metal-chromophore interaction.

Inspection of Figure 5, shows that while the $[NiL]^{2+}$ complexes are not emissive, strong emissions can be detected for some of the protonated complexes. Once more the most intense emission is observed for the ligand possessing the largest chain, $[NiH_2L4]^{4+}$. This behaviour can be explained as follows: i) by increasing the length of the chain, metal adducts containing protonated nitrogens are allowed to be formed ii) in these species the metal is more distant from the fluorophore making their interactions difficult.

Logic Gates

In Figure 6 we represent the fluorescence emission titration curves of the complexes formed between **L3** and equimolar quantities of the metal cations Zn^{2+}, Cd^{2+},Cu^{2+}, and Ni^{2+}. This figure constitutes the basis for the following discussion.

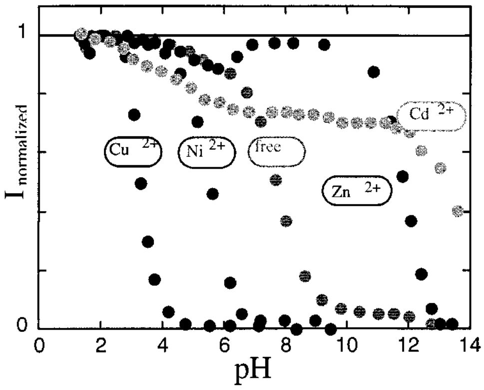
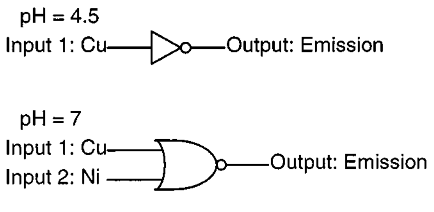


Figure 6. Comparison of the fluorescence emission of **L3** at 420 nm for the various metal ions; excitation wavelengths: Free − 387 nm; Zn^{2+} − 388 nm; Cd^{2+} − 380 nm; Cu^{2+} − 391 nm; Ni^{2+} − 378 nm

As reported previously by other authors[8,14] switching systems based on external impulses can be designed. In the present system we consider the impulses as the addition of a metal (symbol 1), or non addition, (symbol 0). Fluorescence emission intensity was used as an output signal as follows: i) if the emission reaches more than 60% of the maximum emission intensity of the free ligand at the considered wavelength the output is considered (1); ii) if the emission lies below 10% of the maximum emission intensity, the output is considered (0). It should be noted that this treatment is similar to the one used in electronics: for example in the case of the TTL family of logic gates the 1 level is considered approximately between 2 and 5 V, and the 0 level is between 0 and 0.8 V.[24]

Logic Gates Based on a CHEQ-CHEQ Pair

The first example concerns the use of a pair of metal ions both giving rise to CHEQ effects (Scheme 2).



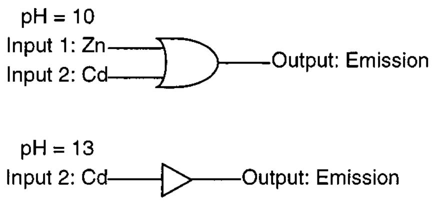
Cu^{2+}	Ni^{2+}	pH = 4.5	pH = 7
0	0	1	1
0	1	1	0
1	0	0	0
1	1	0	0
		NOT Cu^{2+}	NOR

Scheme 2

At pH = 1 the ligand is completely protonated and thus the system behaves independently of the metals giving in all case an output of 1. In terms of the electrical circuit analogy it means that the current flows in all circumstances and the output is 1 (third column in the table of Scheme 2). At pH = 4.5 (fourth column in the table), the situation is different. When neither Cu^{2+} nor Ni^{2+} are added to the solution of **L3** (inputs 0 in first and second column), the emission from the free ligand is observed, and the output is 1 (see Figure 6). Exclusive addition of Ni^{2+} at this pH value (input 0 for Cu^{2+}, input 1 for Ni^{2+}) gives rise to an emissive situation (output 1), while exclusive addition of Cu^{2+} leads to a quenching effect (output 0). When both metals are added (inputs 1 for Cu^{2+} and Ni^{2+}) it can be noted that the binding constant of Cu^{2+} is much higher than that of Ni^{2+}, resulting in a quenching effect (output 0). In terms of the logic table it can be considered as **NOT Cu^{2+}** since this column shows a positive answer (output 1) only when Cu^{2+} is absent. At pH = 7.0, both metal ions give rise to a quenching effect and the result is a **NOR** logic gate. The addition of any metal ion separately or both simultaneously gives an output of 0. Finally at pH = 10.0 the emission is quenched by electron transfer even in the absence of metal ions (output 0 in all cases). This means that no current can flow through the electrical circuit.

Logic Gates Based on a CHEF-CHEF Pair

When Zn^{2+} and Cd^{2+}, both exhibiting CHEF effects are used, a different set of logical gates is obtained, Scheme 3. At pH < 7 the situation is similar to that observed for $Ni^{2+}$and Cu^{2+} at pH = 1 and the output is always 1. At pH = 10.0, however, both metals compete for binding to the chemosensor and the two adducts show fluorescence emission, a situation that leads to an **OR** logic gate. At pH = 12.7 the response of the system is equal to the input of Cd^{2+}, because the association constant of $[CdL]^{2+}$ is much higher than the non emissive $[ZnL(OH)]^{+}$.

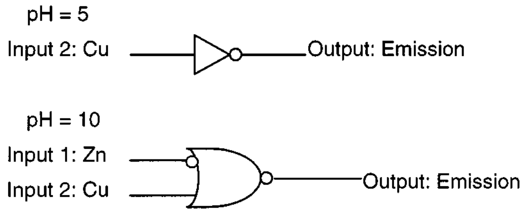


Zn^{2+}	Cd^{2+}	pH = 10	pH = 13
0	0	0	0
0	1	1	1
1	0	1	0
1	1	1	1
		OR	Cd^{2+}

Scheme 3

Logic Gates Based on a CHEF-CHEQ Pair

Another possibility is to combine metal ions that show CHEF and CHEQ effects (Scheme 4). In the case of Zn^{2+} and Cu^{2+}, the logic gates at pH = 1.0 (output 1 in all cases) and 5.0 (**NOT Cu^{2+}**) are similar to those described for Cu^{2+} and Ni^{2+} at pH = 1.0 and 4.5, respectively. However, in the



Zn^{2+}	Cu^{2+}	pH = 5	pH = 10
0	0	1	0
0	1	0	0
1	0	1	1
1	1	0	0
		NOT Cu^{2+}	NOT(Zn^{2+} ⇒ Cu^{2+})

Scheme 4

case of the logic gate at pH = 10, the complexes with Cu^{2+} are stronger than those of Zn^{2+} leading to a set of outputs which are equivalent to a negation of the implication **Zn^{2+} ⇒ Cu^{2+}** . In this case an output 1 is obtained only when Zn^{2+} is present but Cu^{2+} is absent.

Experimental Section

Materials: Synthesis of receptors **L1−L2** has been accomplished as described in ref.[18]

N^1-(2-Aminoethyl)-N^2[2-{[2-(anthrylmethyl)aminoethyl]amino}-ethyl]ethane-1,2-diamine: Compound L3 was synthesised by an alternative procedure consisting of the reaction of a five-fold excess of the free amine tetraethylenepentaamine (3.76 g 20 mmol) with anthracene-9-carbaldehyde (0.82 g 4 mmol) to give the imine. To the solution in ethanol (75 mL) sodium borohydride (0.33 g 8.6 mmol) was added and the mixture was stirred at room temperature for 24 hours. The ethanol was removed at reduced pressure. The resulting residue was treated with water and the functionalised amine was extracted with dichloromethane (3 × 30 mL). The organic phase was washed with water and dried with anhydrous sodium sulfate and the solvent evaporated to yield the free amine, which was dissolved in ethanol and precipitated as a hydrochloride salt. (Yield 62%; 1.4 g). mp: 219−222 °C. − ^{1}H NMR (D_2O): δ_H = 3.15−3.32 (m, 14 H); 3.51 (t, 2 H), 5.19 (s, 2 H); 7.45 (t, 2 H); 7.56 (t, 2 H); 8.00 (d, 2 H); 8.12 (d, 2 H); 8.55 (s, 1 H). − ^{13}C NMR (D_2O): δ_C = 35.6, 43.7, 44.0, 44.7, 122.8, 125.9, 128.2, 129.8, 130.7, 131.2. − $C_{23}N_5H_{38}Cl_5$ (561.85): calcd. C 49.17, N 12.47, H 6.82; found C, 49.3, N, 12.6, H, 7.0.

N^1-[2-{(2-Aminoethyl)amino}ethyl]-N^2-[{2-[{2-(anthrylmethyl)-amino}ethyl]amino}ethyl]ethane-1,2-diamine: Compound **L4** was prepared as **L3**, by reaction of penthaethylenehexaamine and anthracene-9-carbaldehyde. (Yield 63%; 1.61 g) m.p. 189−192 °C. − ^{1}H NMR (D_2O) δ_H = 3.34−3.44 (m, 20 H); 4.94 (s, 2 H); 7.42 (t, 2 H); 7.53 (t, 2 H); 7.86 (d, 2 H); 7.97 (d, 2 H); 8.29 (s, 1 H). − ^{13}C NMR (D_2O): δ_C = 35.5, 43.5, 43.6, 44.8, 119.7, 122.5, 125.6, 127.9, 129.5, 130.2, 130.7. − $C_{25}N_6H_{44}Cl_6$ (641.38): calcd. C 46.7, N 13.09, H 6.9; found C, 47.1, N, 13.3, H, 7.2.

NaCl used as a background electrolyte, was a Merck suprapur product. CO_2-free NaOH and HCl solutions were prepared following the procedure reported in ref.[20]

Spectrophotometric and Spectrofluorimetric Titrations: Absorption spectra were recorded on a Perkin−Elmer Lambda 6 spectrophotometer and fluorescence emission on a SPEX F111 Fluorolog spectrofluorimeter. HCl and NaOH were used to adjust the pH values that were measured on a Metrohm 713 pH meter. Linearity of the fluorescence emission was checked in the concentration range 10^{-5} mol·dm^{-3} to 10^{-6} mol·dm^{-3}. The absorbance of the excitation wavelength was maintained lower than ca. 0.15. When excitation was carried out at wavelengths different from the isosbestic points, a correction for the absorbed light was performed.

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.) have been fully described elsewhere.[25] The acquisition of the emf data was performed with the computer program PASAT.[26] 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 the equivalent point was determined by the Gran's method,[27] which gives the standard potential, $E°'$, 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 more usual $NaClO_4$, due to the slightly higher solubility of the receptors in this medium.

The computer program HYPERQUAD,[28] 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 $1 \cdot 10^{-3}$ to $5 \cdot 10^{-3}$ mol·dm^{-3}) were treated either as a single set or as separate curves without significant variations in the values of the stability constants. Finally, the data sets were merged together to give the final stability constants. Moreover, in the case of Ni^{2+}, measurements were made both in formation and in dissociation (from acid to alkaline pH and vice versa) to check the reversibility of the reactions.

NMR Measurements: The ^{1}H and ^{13}C NMR spectra were recorded on Varian UNITY 300 and UNITY 400 spectrometers, operating at 299.95 and 399.95 MHz for ^{1}H 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) and the solvent signal for the ^{1}H spectra. The probe temperature was regulated with 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.[29]

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