Thermodynamic, NMR and photochemical study on the acid–base behaviour of *N,N'*-dibenzylated polyamines and on their interaction with hexacyanocobaltate(III)

M. Alexandra Bernardo,[a] José A. Guerrero,[b] Enrique García-España,*[,b] Santiago V. Luis,* José M. Llinares,[b] Fernando Pina,*[,a] José A. Ramírez[b] and Conxa Soriano[b]

[a] *Departmento de Química da Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, 2825 Monte de Caparica, Portugal*
[b] *Departamento de Química Inorgànica y Química Orgánica, Facultat de Química, Universitat de València, c/o Dr Moliner 50, 46100 Burjassot (València), Spain*
[c] *Departamento de Ciencias Experimentales, Laboratorio de Química Orgánica, Universitat Jaume I (Castellón), Spain*

The synthesis and protonation behaviour of the dibenzylated open-chain ligands 1,4-dibenzyl-1,4-diazabutane (L^1), 1,7-dibenzyl-1,4,7-triazaheptane (L^2), 1,10-dibenzyl-1,4,7,10-tetraazadecane (L^3), 1,12-dibenzyl-1,5,8,12-tetraazadodecane (L^4) and 1,13-dibenzyl-1,4,7,10,13-pentaazatridecane (L^5) are presented. The protonation behaviour has been studied by means of pH-metric measurements, NMR, absorption UV–VIS and steady-state fluorescence emission spectroscopy. The influence of the aromatic ring on the acid–base behaviour of these ligands is discussed. The association constants of these ligands with $[Co(CN)_6]^{3-}$ have been calculated by steady-state fluorescence emission. The reduction in the quantum yield for the photoaquation reaction of $[Co(CN)_6]^{3-}$ in the presence of L^5 suggests that three out of the six cyanide groups of the anion are involved in the formation of the hydrogen-bond network of the supramolecular adduct.

Recently some of us have reported on the synthesis,[1] protonation,[2–4] metal ion[3,4] and anion coordination chemistry[3,5] of a new family of macrocyclic polyamines characterised by the presence of a *para*-phenylene spacer interrupting polyamine chains with different numbers of nitrogen atoms as well as with different hydrocarbon chains between the nitrogen atoms; L^6–L^9 are representative. The ligand conformations induced by the aromatic spacers resulted in interesting protonation, metal ion and anion coordination behaviour.

On the other hand, these ligands exhibit fluorescence at room temperature. In this respect, we were able to determine their protonation constants by steady-state fluorescence emission or by analysing the variations of the UV–VIS absorption spectra with the pH.[5] Moreover, steady-state fluorescence emission allowed us to obtain the association constants of these macrocycles with the $[Co(CN)_6]^{3-}$ anion.

To better understand the chemistry of macrocycles, comparison with suitable open-chain ligands is often of interest. The open-chain counterparts chosen should match as much as possible the characteristics of the cyclic ligands (number and kind of heteroatoms, hydrophobicity, *etc.*). In this sense, *N,N,'*-dibenzylated open-chain polyamines seemed the most appropriate analogues of these cyclophanes (see L^1–L^5). As most of these ligands were not commercially available and in order to fill this gap we have accomplished the synthesis of this series of compounds.

Aside from these considerations, the chemistry of dibenzylated polyamines has an intrinsic interest due to their use as drugs for a variety of purposes,[6] their activity being very much dependent on the actual charge and charge density they display at physiological pH.

Here, we report on the protonation of polyamines L^1–L^5. Studies have been carried out using potentiometry, NMR, UV–VIS spectroscopy and steady-state fluorescence emission. Additionally, we have determined the association constants of these ligands with hexacyanocobaltate(III) by means of steady-state fluorescence emission. The results are compared both with those of related non-benzylated open-chain polyamines and with those of the cyclophanes series.

Experimental

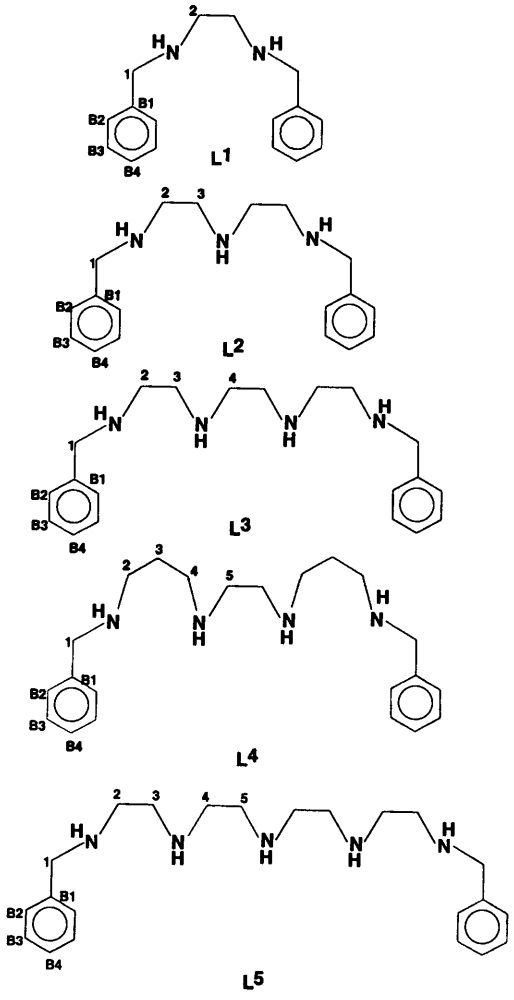
Materials

$NaClO_4$ used as background electrolyte in the potentiometric measurements was purified according to a procedure described in the bibliography.[7] CO_2-free NaOH solutions and HCl, or $HClO_4$ solutions were prepared following the procedure reported in ref. 8. L^1 was purchased from Aldrich and handled as its hydrobromide salt.

1,7-Dibenzyl-*N,N',N''*-tris(*p*-tolylsulfonyl)-1,4,7-triazaheptadecane (1) and 1,10-dibenzyl-*N,N',N'',N'''*-tetrakis(*p*-tolylsulfonyl)-1,4,7,10-tetraazadecane (2). These compounds were prepared by the general procedure described in ref. 1 which consists of reaction in CH_3CN of benzyl chloride with the tosylated polyamine using K_2CO_3 as a base. Melting points, NMR characterisation and elemental analysis of compounds (**1**) and (**2**) were in agreement with those previously published.[7]

1,13-Dibenzyl-*N,N',N'',N''',N''''*-pentakis(*p*-tolylsulfonyl)-1,4,7,10,13-pentaazatridecane (3). This compound was prepared from *N,N',N'',N''',N''''*-penta-*p*-tolysulfonyl-1,4,7,10,13-pentaazatridecane by using the same procedure described above: 80% yield, mp 193–195 °C; *J* in Hz. δ_H 2.31 (s, 9 H), 2.35 (s, 6 H), 2.76 (t, *J* 8, 4 H), 3.07 (s, 8 H), 3.25 (t, *J* 8, 4 H), 4 17 (s, 4 H), 7.66–7.72 (m, 8 H); δ_C 21.5, 48.3, 49.1, 49.4, 49.5, 53.7, 127.3, 127.6, 127.9, 128.7, 128.9, 129.7, 129.9, 134.5, 135.8, 136.1, 143.5.

1,7-Dibenzyl-1,4,7-triazaheptane tris(hydrobromide) $L^2 \cdot 3HBr$. Tritosylated amine **1** (5 g, 6.7 mmol) and phenol (70 g, 268 mmol) were suspended in HBr–AcOH (33%, 26.8 ml). The mixture was stirred at 90 °C for 24 h and then cooled. The precipi-



tate was filtered and washed several times with Cl_2CH_2, EtOH and diethyl ether: 33% yield, mp 254–257 °C; δ_H 3.38 (s, 8 H), 4.19 (s, 4 H), 7.36 (s, 10 H); δ_C 43.4, 44.5, 52.7, 130.4, 130.9, 131.0. Anal. Calc. for $C_{18}Br_3H_{28}N_3$: C, 41.0; H, 5.3; N, 8.0. Found: C, 41.3; H, 5.4; N, 7.6%.

1,10-Dibenzyl-1,4,7,10-tetraazadecane tetrahydrobromide L^1·4HBr. This compound was obtained in 42% yield, mp 205–207 °C; δ_H 3.43–3.46 (m, 12 H), 4.20 (s, 4 H), 7.39 (s, 10 H); ^{13}C NMR 43.5, 44.5, 44.6, 52.8, 130.5, 131.0, 131.1, 134.1. Anal. Calc. for $C_{20}Br_4H_{34}N_4$: C, 36.9; H, 5.3; N, 8.6. Found: C, 36.7; H, 5.3; N, 8.7%.

1,13-Dibenzyl-1,4,7,10,13-pentaazadecane pentahydrobromide L^5·5HBr. This compound was obtained in 53% yield, mp 256–257 °C; δ_H 3.38–3.42 (m, 16 H), 4.19 (s, 4 H), 7.35 (s, 10 H); δ_C 43.4, 44.5, 44.6, 52.8, 130.5, 131.0, 131.1, 149.6. Anal. Calc. for $C_{22}Br_5H_{40}N_5$: C, 34.1; H, 5.2; N, 9.0. Found: C, 33.9; H, 5.2; N, 9.1%.

Ligand L^4. L^4 was synthesised by an alternative procedure consisting of the direct reaction of the free amine with benzaldehyde. 1,12-Bis(benzylidene)-1,5,8,12-tetraazadodecane was prepared by the general method of Coleman and Taylor.[9] To a solution 1,12-bis(benzylidene)-1,5,8,12-tetraazadodecane (1.7 g, 4.9 mmol) in ethanol (50 ml) was added sodium borohydride (0.38 g, 10 mmol). The mixture was stirred at room temp. for 2 h. The ethanol was removed under vacuum and the residue treated with water and the amine taken up with dichloromethane. The solution was dried over anhydrous sodium sulfate and the solvent evaporated to yield the free amine which was dissolved in methanol and precipitated as its hydrobromide salt (yield 53%), mp 284–286 °C; δ_H 1.98–2.21 (m, 4 H), 3.10–3.20 (m, 8 H), 3.37 (s, 4 H), 4.17 (s, 4 H), 7.39 (s, 4 H); δ_C 22.6, 44.1, 44.7, 46.1, 52.2, 130.3, 130.7, 130.8, 131.3. Anal. Calc. for $C_{22}Br_4H_{38}N_4$: C, 39.0; H, 5.7; N, 8.8. Found: C, 39.1; H, 5.9; N. 8.6%.

EMF measurements

The potentiometric titrations were carried out in 0.15 mol dm^{-3} $NaClO_4$ or 0.15 mol dm^{-3} NaCl at 298.1 ± 0.1 K, by using the experimental procedure (burette, potentiometer, cell, stirrer, microcomputer, *etc.*) that has been described fully elsewhere.[10] The acquisition of the EMF data was performed with the computer program PASAT.[11] 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 precise amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by the Gran's method,[12] which gives the standard potential, E^{OI}, 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.

The computer program SUPERQUAD[13] was used to calculate the protonation and stability constants. The DISPO[14] program was used to obtain the distribution diagrams. The titration curves for each system (*ca.* 200 experimental points corresponding to at least three measurements, pH range investigated 2–10.5, concentration of ligands ranging from 1×10^{-3} to 5×10^{-4} mol dm^{-3}) were treated either as a single set or as separated curves without significant variations in the values of the stability constants. Finally, the sets of data were merged and treated simultaneously to give the final stability constants.

Spectroscopy

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 DMSO solutions. For the ^{13}C NMR spectra dioxane was used as a reference standard (δ 67.4) and for the ^1H spectra the solvent signal. The pH was calculated from the measured pD values using the correlation, pH = pD − 0.4.[15]

Spectrophotometric and spectrofluorimetric titrations

Absorption spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer and fluorescence emission on a SPEX F111 Fluorolog spectroflouorimeter. $HClO_4$ and NaOH were used to adjust the pH values that were measured on a Metrohm 713 pH meter. Errors in quantum yields are estimated to be *ca.* 10%.

Irradiation experiments

Irradiation at 313 nm (Oriel filters) was carried out using a xenon-mercury medium pressure lamp (PTI model A1010). The intensity of incident light was 1.43×10^{-6} einstein min^{-1} as measured by iron(III) oxalate actinometry.[16] Concentrations of $K_3[Co(CN)_6]$ were *ca.* 10^{-3} mol dm^{-3}; an excess of L^5 was used in order to obtain at least 90% association. The pH value was selected such that only the fully protonated form of L^5 exists in solution.

Results and discussion

Protonation

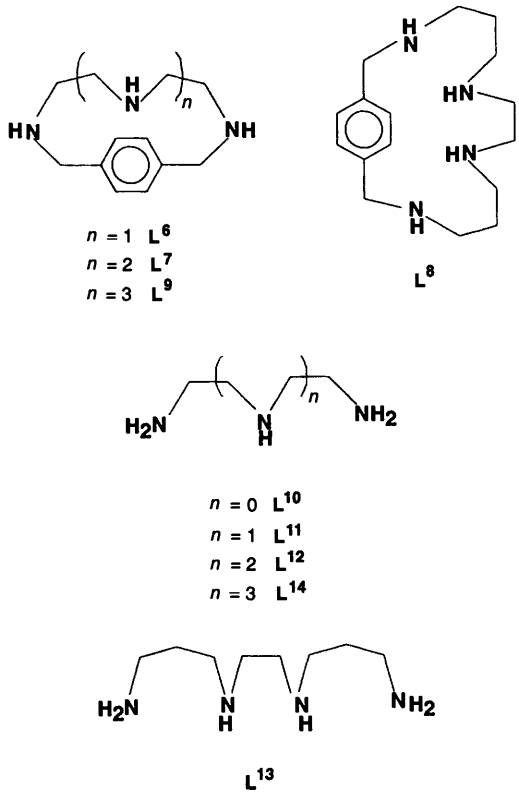
In Table 1 are presented the stepwise basicity constants of the ligands L^1–L^5 determined in 0.15 mol dm^{-3} $NaClO_4$ or NaCl at 298.1 ± 0.1 K together with those we have previously determined[2–4] for the azaparacyclophanes L^6–L^9 and those of the related non-benzylated open-chain polyamines ethylenediamine (L^{10}), 3-azapentane-1,5-diamine (L^{11}), 3,6-diazaoctane-1,8-diamine (L^{12}), 4,7-diazadecane-1,11-diamine (L^{13}) 3,6,9-triazaundecane-1,11-diamine (L^{14}) taken from the bibliography.[17] The overall basicities of these polyamines are also included in Table 1.

It is well known that protons bind polyamine molecules in such a way that minimum electrostatic repulsions between protonated sites are achieved in each protonation stage. This is

Table 1 Logarithms of the stepwise basicity constants for L^1, L^2, L^3, L^4,. L^5, L^6, L^7, L^8, L^9, L^{10}, L^{11}, L^{12}, L^{13} and L^{14} determined at 298.1 K in 0.15 mol dm^{-3} $NaClO_4$

Reaction	L^1	L^{1c}	L^2	L^3	L^{4c}	L^5	L^{6d}	L^{7e}	L^{8f}	L^{9e}	L^{10g}	L^{11}	L^{12}	L^{13}	L^{14}
$L + H \rightleftharpoons HL$	9.11(2)	9.18(1)	9.382(4)	9.30(2)	9.68(2)	9.85(2)	9.42	9.39	9.93	10.68	10.56	9.84	9.74	10.53	9.70
$HL + H \rightleftharpoons H_2L$	6.23(3)	6.25(2)	8.290(5)	8.62(2)	8.87(4)	8.89(3)	7.31	8.45	9.09	9.29	8.76	9.02	9.07	9.77	9.14
$H_2L + H \rightleftharpoons H_3L$	—	—	3.992(8)	6.41(3)	7.37(6)	7.99(3)	3.26	5.38	7.44	8.66	—	4.23	6.59	8.30	8.05
$H_3L + H \rightleftharpoons H_4L$	—	—	—	3.77(6)	4.90(8)	4.93(5)	—	2.51	3.61	7.23	—	—	3.27	5.59	4.70
$H_4L + H \rightleftharpoons H_5L$	—	—	—	—	—	2.75(8)	—	—	—	3.93	—	—	—	—	2.97
$L + nH \rightleftharpoons H_nL$[h]	15.34	15.43	21.66	28.10	30.82	34.41	19.99	25.73	30.07	39.79	19.32	23.09	28.67	34.19	34.56

[a] Charges have been omitted for clarity. [b] Numbers in parentheses are standard deviations in the last significant figure. [c] Constants determined in 0.15 mol dm^{-3} NaCl at 298.1 K. [d] Taken from ref. 2, 0.15 mol dm^{-3} $NaClO_4$, 298.1 K. [e] Taken from ref. 4, 0.15 mol dm^{-3} $NaClO_4$, 298.1 K. [f] Taken from ref. 3, 0.15 ml dm^{-3} $NaClO_4$, 298.1 K. [g] Basicity constants of polyamines L^{10}–L^{14} have been taken from ref. 17. [h] Overall cumulative basicities.



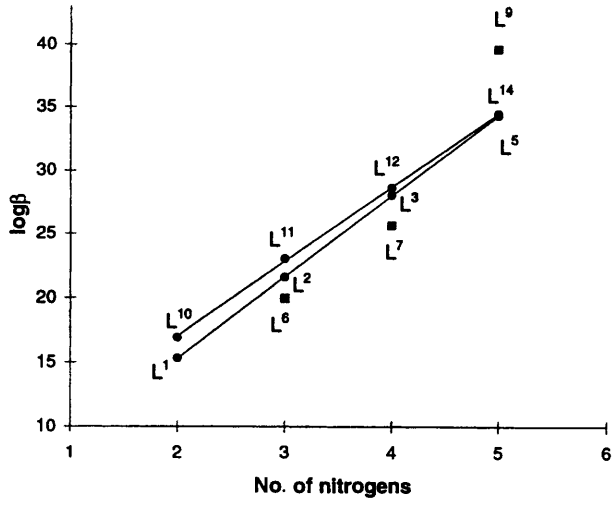


Fig. 1 Plot of the cumulative basicity (log β; $L + pH \rightleftarrows H_pL$) *vs.* the number of nitrogens in the chain for dibenzylated polyamines (L^1–L^3, L^5), cyclophanes (L^6, L^7, L^9) and open-chain polyamines (L^{10}–L^{12}, L^{14})

clearly reflected in the stepwise protonation constants of the ligands L^1–L^5. L^1 presents a relatively high first basicity constant [$\log K_{HL} = 9.11(2)$] and an intermediate one [$\log K_{H_2L} = 6.23(3)$]; L^2 displays two relatively large constants [$\log K_{HL} = 9.382(4)$, $\log K_{H_2L} = 8.290(5)$] and a much lower third one; L^3 presents two relatively large constants [$\log K_{HL} = 9.30(2)$, $\log K_{H_2L} = 8.62(2)$] an intermediate one [$\log K_{H_3L} = 6.41(3)$] and a much reduced one for the last protonation step [$\log K_{H_4L} = 3.77(6)$]; L^4 has relatively high basicities in its three first protonation steps and much reduced basicity in the fourth one [$\log K_{H_4L} = 4.90(8)$]; finally, L^5 presents three relatively large constants and much lower constants for its last two protonation steps. All these groupings of constants may be explained just taking into account electrostatic considerations. For instance, the second protonation of L^2 may occur on a nitrogen atom separated from the protonated site by a non-protonated nitrogen and, therefore, the basicity constant associated with this step is still high. The third protonation, however, will occur on a nitrogen, next to two protonated nitrogens yielding a considerable reduction in basicity. In L^3, while both first protonations take place at nitrogen atoms far enough apart not to be significantly affected by unfavourable electrostatic contributions, the third one should occur next to one protonated site yielding an intermediate constant and the fourth one necessarily occurs between already protonated sites yielding a further drop in basicity. Similar considerations may explain the trend in the constants for L^5 for which the three first protonations may occur in alternate nitrogens of the molecule while the fourth and fifth ones have to take place between already protonated polyammonium sites giving the pattern of three high and two much lower basicity constants. In L^4 the presence of the propylenic chains is reflected in its basicity trends; namely, the higher values of its first protonation constants in comparison with those of L^3 denote the lower repulsions between protonated sites when propylenic chains are included in the polyamine framework.

Perhaps of more novelty is to analyse how other factors like hydrophobic effects and hydrogen bonding modulate the overall and stepwise basicity of the ligands. A plot of the overall basicities of the ligands containing only ethylenic chains between the nitrogen atoms as a function of the number of nitrogen atoms in the molecule allows several general trends to be derived. First, both the benzylated ligands, L^1–L^3, L^5, and the non-benzlated ones, L^{10}–L^{12}, L^{14}, fit very well straight lines of slopes 6.2 and 5.7, respectively (see Fig. 1). The overall basicities of the non-benzylated tri- and tetra-amines are higher than those of the respective benzylated ones while the benzylated and non-benzylated pentaamines display the same overall basicity. On the other hand, the cyclic tri- and tetra-aza paracyclophanes L^6 and L^7 display lower overall basicity than any one of the open-chain polyamines while, contrarily, the basicity of L^9 is higher than that of the corresponding open-chain pentaamines. This reduced basicity of the azaparacyclophanes L^6 and L^7 with respect to analogous saturated polyamines was ascribed to an entropy driven stabilisation of the protons in the benzylic sites.[4] For the pentaamine L^9 such an effect was no longer observed.

In order to decide if the reduced basicity of L^1, L^2 and L^3 and the identical basicity of L^5 with respect to the non-benzylated open-chain polyamines L^{10}–L^{12}, L^{14} could have a similar origin we have performed an NMR study on their protonation. The ^1H NMR spectrum in D_2O of L^2 at pH 10.5 where the non-protonated free amine predominates consists for the aliphatic protons of two signals at 2.65 and 3.69 ppm integrating in the ratio 2:1 which can be assigned to protons H-2, H-3 and to the benzylic protons H-1, respectively. The aromatic protons HB-2, HB-3 and HB-4 appear at this pH as a broad multiplet centred at 7.23 ppm. The ^{13}C NMR spectrum at the same pH consists of signals at 47.2, 47.6, 53.1, 129.0, 129.9 (two signals), 130.99, 131.05 and 138.1 ppm that can be assigned to carbon atoms C-2, C-3, C-1, CB-4, CB-3, CB-2 and CB-1 respectively (numbering as on structural diagram). All the assignments have been performed on the basis of two-dimensional ^1H–^1H correlations as well as taking into account the data in the bibliography for similar systems. It is well known that upon protonation the carbon signals placed β to protonated nitrogen atoms are the ones shifting most.[18] Particularly, to establish the protonation pattern of these ligands, it is very helpful to follow the variations in the chemical shift of CB-1 since it is placed in the β-position to the benzylic nitrogens N-1.[4] In Fig. 2(*a*) it can be seen that this signal experiences a remarkable upfield shift in the pH range 11–8 where L^2 bears its two first protonations and remains practically unchanged below pH 6 where L^2 takes up the last proton. Additionally the signal of C-2 placed β to the central nitrogen atom shifts upfield below pH 6 in correspondence with the last protonation. All these data strongly suggest that the first two protonations occur on the benzylic nitrogens of L^2.

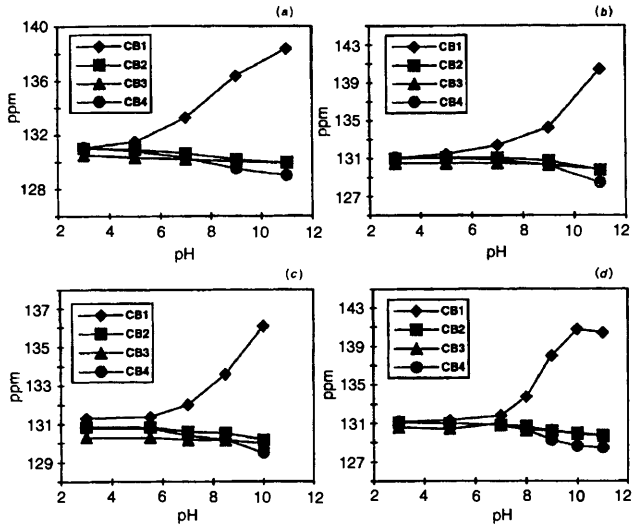


Fig. 2 Representation of the variation of the chemical shifts with pH of the aromatic carbon atoms for the ligands L^2–L^5

For L^3, again the variation in the chemical shift of the signal of the aromatic carbon (CB-1) very clearly implies the protonation pattern of the ligand. The chemical shift of CB-1 strongly varies in the 11–6 pH range where L^3 binds the first three protons [see Fig. 2(*b*)]. These data imply that the first protonation of L^3 occurs again on the benzylic nitrogens and that these nitrogens are involved in two out of the three first protonations. The last protonation will occur on the central nitrogens as shown by the fact that below pH 6 the largest upfield variations in the ^{13}C chemical shifts are observed for C-3 and C-4.

The chemical shift of the CB-1 signal in the ^{13}C NMR spectrum of L^4 strongly varies in the pH range 10–6 sharing a similar behaviour to that presented by L^3 [Fig. 2(*c*)]. Again in this ligand the spectral changes suggest that first protonation occurs on the benzylic nitrogens. Additionally, the shifts in the ^1H and ^{13}C NMR signals would indicate that the two benzylic nitrogens would be involved in two out of the three first protonations.

Finally, for L^5 the variations with the pH of the chemical shift of CB-1 are somewhat different from those of L^2 and L^3, since in this case no significant upfield shift of the signal is observed until pH 9.5 where L^5 starts to incorporate the second proton [Fig. 2(*d*)]. However above pH 9.5, variations in the chemical shift of the central signals of the ethylenic chains occur suggesting therefore that the first protonation most likely implies the central nitrogen instead of the benzylic ones. Second and third protonations would involve the benzylic nitrogen atoms.

Summarising all these results one can conclude that obviously in L^1, but also in L^2 and L^3, the first protonation affects the benzylic nitrogen while in L^5 such protonation occurs on the middle nitrogens of the polyamine. Protonation on the benzylic nitrogens results in lower overall and stepwise basicities of the ligands as shown in Table 1 and Fig. 1 in comparison with related polyamines. In fact L^5, in which such behaviour is not observed, displays the same basicity as the related non-benzylated polyamine L^{14}. Protonation studies previously performed on the azaparacyclophanes L^6–L^8 also provided evidence for similar behaviour. Macrocycles L^6 and L^7 which bind their first proton on the benzylic nitrogens display low first protonation constants which are comparable to the first protonation constants of the benzylated ligands L^2 and L^3. The lower overall basicity of L^6 and L^7 could probably be attributed to stronger repulsions promoted by the cyclic topology. L^9 which protonates first on the nitrogens in the middle of the polyamine bridge, analogously to L^5, presents a much higher basicity. In the latter ligands the possibility of the proton sharing several equivalent sites and the probable formation of hydrogen bonds would compensate the entropic stabilisation yielded by a protonation occurring on the benzylic nitrogens.

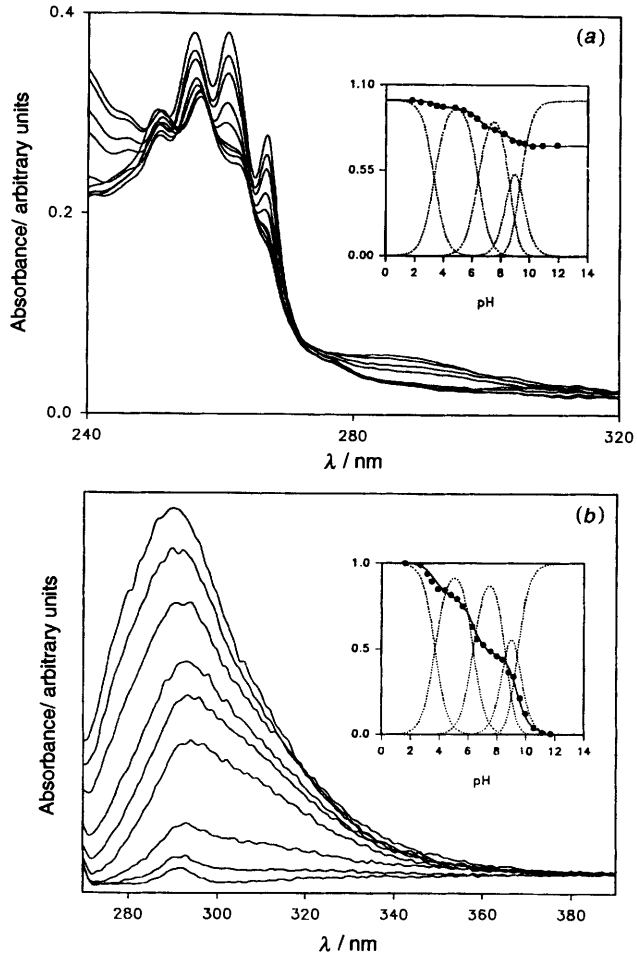


Fig. 3 (*a*) pH dependence of the absorption spectra of L^3; *inset* full line titration curve at 261 nm; dotted lines molar fractions distributions. (*b*) pH dependence of the fluorescence emission spectra of L^3; *inset* full line titration curve at the excitation and emission wavelengths respectively 264 nm and 290 nm; dotted lines molar fractions distributions.

Absorption and emission measurements

In Fig. 3 are shown the spectral variations of both absorption and fluorescence emission as a function of pH, for a representative member of the series of benzylated ligands. Similarly to what has been previously observed with the parent compounds of the polyazacyclophane family,[5] in the present series, both chromophores and fluorophores can be mainly assigned to the aromatic component.

The compounds of the present series are involved in n multiple acid–base equilibria according to the general equilibrium, eqn. (1), n being the total number of the nitrogens in the chain,

$$AH_{n-q}^{(n-q)+} + H_2O \underset{}{\overset{K_{n,q}}{\rightleftharpoons}} AH_{n-q-1}^{(n-q-1)+} + H_3O^+ \qquad (1)$$

and q the number of the non-protonated nitrogens in a given species.

The absorbance at a given wavelength, divided by the absorption from the totally protonated form A_0 (obtained at sufficiently acidic pH), may be described by the general eqn. (2),

$$\frac{A}{A_0} = \sum_{i=0}^{n} C_i \chi AH_{(n-i)}^{(n-i)+} \qquad (2)$$

in which $\chi AH_{(n-i)}^{(n-i)+}$ is the molar fraction of the species containing $(n - i)$ protons and of positive charge $(n - i)$, C_i the ratio between the molar absorption coefficients of the species with $(n - i)$ protons and the totally protonated form ($C_0 = 1$).

In the absence of the excited-state proton transfer,[19] eqn. (2) can also be applied to the fluorescence emission titration curves, in this case A/A_0 being substituted by I/I_0 (if necessary, after

Table 2 Logarithms of the stepwise basicity constants for L^1, L^2, L^3, L^4 and L^5[a]

	L^1[b]	L^2	L^3	L^4[b]	L^5
$H + L \rightleftharpoons HL$[b]	9.6(1), 9.2(1)	9.4(1),[c,d]	9.3(1), 9.4(1)	9.7(1), 9.7(1)	9.9(1),[c] 9.9(1)
$HL + H \rightleftharpoons H_2L$	6.2(1), 6.2(1)	8.4(1),[c] 8.2(1)	8.6(1), 8.6(1)	8.7(1), 8.7(1)	7.7(1),[c] 8.9(1)
$H_2L + H \rightleftharpoons H_3L$	—	3.6(1),[c] 3.9(1)	6.4(1), 6.4(1)	7.4(1), 7.3(1)	7.5(1),[c] 7.9(1)
$H_3L + H \rightleftharpoons H_4L$	—	—	3.4(1),[c] 3.7(1)	5.1(1),[c] 5.1(1)	4.4(1),[c] 4.4(1)
$H_4L + H \rightleftharpoons H_5L$	—	—	—	—	2.8(1),[c] 2.8(1)
$\varepsilon_{H_{n-1}L^{(n-1)+}}/\varepsilon_{H_nL^{n+}}$	0.79	0.93	0.95	0.86	0.98
$\varepsilon_{H_{n-2}L^{(n-2)+}}/\varepsilon_{H_nL^{n+}}$	0.69	0.67	0.81	0.75	0.93
$\varepsilon_{H_{n-3}L^{(n-3)+}}/\varepsilon_{H_nL^{n+}}$	—	0.67	0.73	0.63	0.90
$\varepsilon_{H_{n-4}L^{(n-4)+}}/\varepsilon_{H_nL^{n+}}$	—	—	0.71	0.55	0.82
$\varepsilon_{H_{n-5}L^{(n-5)+}}/\varepsilon_{H_nL^{n+}}$	—	—	—	—	0.85
$\varphi_{H_{n-1}L^{(n-1)+}}/\varphi_{H_nL^{n+}}$	0.85	0.38	0.75	0.93	0.85
$\varphi_{H_{n-2}L^{(n-2)+}}/\varphi_{H_nL^{n+}}$	0.00	0.02	0.45	0.60	0.55
$\varphi_{H_{n-3}L^{(n-3)+}}/\varphi_{H_nL^{n+}}$	—	0.00	0.43	0.15	0.25
$\varphi_{H_{n-4}L^{(n-4)+}}/\varphi_{H_nL^{n+}}$	—	—	0.00	0.00	0.15
$\varphi_{H_{n-5}L^{(n-5)+}}/\varphi_{H_nL^{n+}}$	—	—	—	—	0.00

[a] Constants determined in 0.15 mol dm^{-3} $NaClO_4$. Charges have been omitted for clarity. For each compound values obtained from UV–VIS spectroscopy [eqn. (2)] and fluorescence emission [eqn. (11)] are respectively first and second. Numbers in parentheses are standard deviations in the last significant figure. [b] Constants determined in 0.15 mol dm^{-3} NaCl at 298.1 K. [c] Values for which accuracy is not high, due to the small differences between the respective molar absorption coefficients. [d] Quantum yield for fluorescence too low for quantitative measurements.

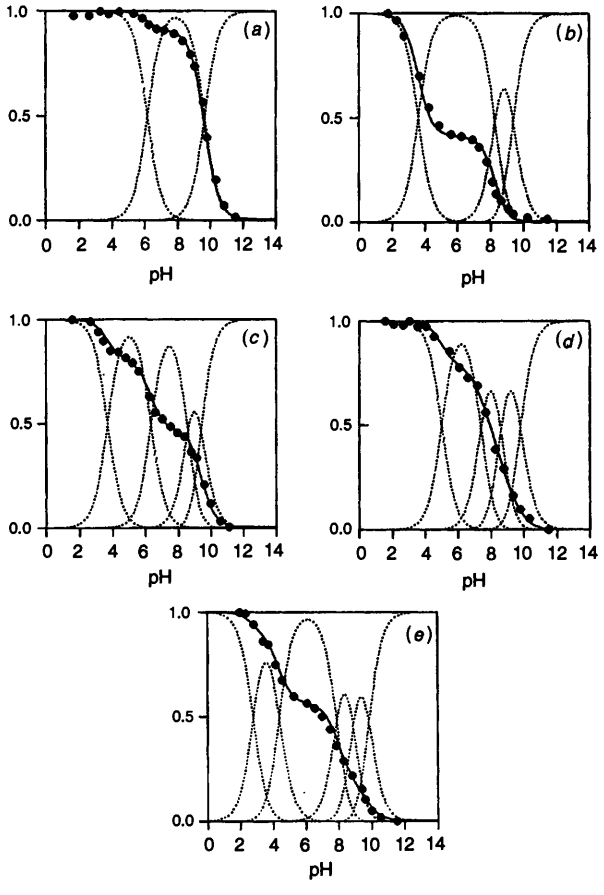


Fig. 4 Steady-state fluorescence emission titration curves of: (*a*) L^1; (*b*) L^2; (*c*) L^3; (*d*) L^4 and (*e*) L^5 (full line). Molar fractions distribution (dotted line).

correction for the fraction of the absorbed light; see Appendix 1), the emission at any pH value and the emission from the totally protonated form. The constant C_i, in this case, depends on the emission quantum yields and on the molar absorption coefficients according to eqn. (11*a*) (Appendix 1).

The molar fractions appearing in eqn. (2) can easily be expressed in terms of the *n* equilibrium constants, and fitting of the titration curves can thus be achieved by adjusting these constants, and the parameters C_j.

In Fig. 4 are represented the titration curves obtained by steady-state fluorescence emission spectroscopy, as well as the respective fitting. The experimental results obtained for several pK_a values are in good agreement with those calculated by means of the potentiometric method; see Table 2.

The decrease observed in the fluorescence emission as nitrogens are deprotonated is identical to what has been detected for the polyazacyclophane analogues,[5] and can be attributed to the same reasons, *i.e.* to an intramolecular quenching effect by electron transfer involving deprotonated amines and benzene rings. Inspection of Fig. 4 shows for all the series a different behaviour on the fluorescence emission curves upon loss of the first proton. For the first member of the series L^1, deprotonation of the first benzylic nitrogen gives rise to a small decrease in the fluorescence emission, probably due to the lack of overlap between n molecular orbitals of the amine donor and π^* orbitals of the benzene ring receptor. For the second member, L^2, a dramatic effect upon first deprotonation can be observed. This seems to be associated with the fact that, as proved by ^1H NMR, the first proton to leave the molecule is that from nitrogen at the middle of the chain (N-2). According to space filling models overlap between n and π^* molecular orbitals is in this case much more efficient, explaining the observed large quenching effect. Moreover, the two benzene rings have the same probability of accepting the electron because of the symmetry of the deprotonated nitrogen. The situation is similar in the case of L^3. As in L^2, the first deprotonated nitrogen is not a benzylic one, but one of the other two middle nitrogens of the chain. However, unlike the last molecule only one benzene ring is well positioned to transfer the electron, because the second benzene becomes more distant, and distance is a critical parameter on electron transfer. In addition, the total positive charge of the first deprotonated species increases from L^2 to L^3 which is another factor hindering electron transfer.

The effect of distance on efficiency of electron transfer can easily be observed when comparing the fluorescence emission titration curves of L^3 and L^4. These compounds have the same number of nitrogens and consequently the same charge. However, the first nitrogen at which deprotonation takes place in L^4 is one methylene group further away from the benzene ring which leads to a less efficient quenching effect.

Finally, in the last member of the series, L^5, the ^1H NMR data have shown that as in the previous cases the deprotonated nitrogen is located in the middle of the chain. The distance and charge used to explain the relative behaviour of L^2, L^3 and L^4 can once more be used to explain why in L^5 the quenching is less efficient.

Comparison between previously published results with polyazacyclophanes can be done between the open chain ligands L^3 and L^4 and the related L^7 and L^8. In both cases it is the central nitrogen that is deprotonated first but the effect is

Table 3 Association constants (in log units) of the adducts formed between hexacyanocobaltate(III) and the full protonated forms of the L^1–L^5 ligands, in 0.15 mol dm^{-3} $NaClO_4$ determined by quenching of the steady-state fluorescence emission[a]

Receptor	
L^{1b}	2.41(1)
L^2	2.45(1)
L^3	2.47(1)
L^{4b}	2.51(1)
L^5	2.60(1)

[a] Numbers in parentheses are standard deviations in the last significant figure. [b] Constants determined in 0.15 mol dm^{-3} NaCl at 298.1 K.

larger in L^7 and L^8 than in L^3 or L^4. This can be explained by the fact that in these cyclic ligands the nitrogens are forced to stay over the benzene. This results in a more effective overlap between n and π^* acceptor molecular orbitals.

Supramolecular adducts with $[Co(CN)6]^{3-}$

The emission of the fully protonated forms of the polyamines L^1–L^5 were followed as a function of the added concentration of hexacyanocobaltate(III) in 0.15 mol dm^{-3} $NaClO_4$ or NaCl. As in the polyazacyclophanes family,[5] addition of the anion gives rise to a quenching effect on the emission of the fully protonated form of the receptor. Similarly to what has been observed for the adducts of this anion with polyazacyclophanes, no dynamic quenching was observed, and only total quenching of the ground state is operative allowing the calculation of the association constant,[5] shown in Table 3.

Irradiation experiments

Irradiation of hexacyanocobaltate(III) at 313 nm was only performed in the presence of L^5 due to solubility problems of the other compounds when irradiated. Corrections were made for the amount of adduct associated. The photoaquation quantum yields obtained were 0.31 for $K_3[Co(CN)_6]$ with no receptor present and 0.15 for the complex (errors in these values are *ca.* 10%). This reduction by a factor of two agrees with the ones found for the polyazacyclophane family,[5] and can be interpreted by assuming that three out of the six cyanides of hexacyanocobaltate(III) are involved in hydrogen bonding with the protonated polyamine.

Appendix

Let us consider consecutive acid base equilibria as in eqns. (1*a*)–(3*a*), in which charges are omitted.

$$LH_n \rightleftarrows LH_{n-1} + H^+ \qquad (1a)$$

$$LH_{n-1} \rightleftarrows LH_{n-2} + H^+ \qquad (2a)$$

$$\cdots$$

$$LH \rightleftarrows L + H^+ \qquad (3a)$$

The total emission at any wavelength and pH value is the sum of the emission from each species present in solution:

$$I = I_{LH_n} + I_{LH_{n-1}} + I_{LH_{n-2}} + \cdots + I_L \qquad (4a)$$

According to the definition of fluorescence emission quantum yield, for each species:

$$\varphi_{RHi} = \frac{I_{RHi}}{I_{abs(RH_i)}} \qquad (5a)$$

In eqn. (5*a*) φ is the fluorescence emission quantum yield, I the fluorescence emission intensity and $I_{abs(RH_i)}$ the intensity of the absorbed light by the species RH_i. Experimentally, it is not possible to collect all the emissive light and eqn. (6*a*) must be used, in which G is a constant geometrical factor depending on the spectrofluorimeter characteristics.

$$I_{RHi} = G\varphi_{RHi}I_{abs(RH_i)} \qquad (6a)$$

In case that several species are competing for the excitation light, eqn. (6) has to be corrected according to eqn. (7*a*):

$$I_{RHi} = G\varphi_{RHi}I_{inc}(1 - 10^{-A})\frac{\varepsilon_{RHi}[RH_i]}{A} \qquad (7a)$$

In eqn. (7*a*) I_{inc} is the incident light, A the total absorbance of the solution, ε_{RH_i} the molar absorption coefficient of the species RH_i and $[RH_i]$ its concentration.

Considering now I/I_0 the total emission at any wavelength and pH value, divided by the emission of the totally protonated form, obtained at a pH value sufficiently acidic to consider RH_n as the sole species present in solution.

$$\frac{I}{I_0} = \frac{(1 - 10^{-A})}{(1 - 10^{-A_0})}\frac{A_0}{A}\frac{[RH_n]}{C_0} + \frac{\varepsilon_{RH_{n-1}}}{\varepsilon_{RH_n}}\frac{\varphi_{RH_{n-1}}}{\varphi_{RH_n}}\frac{(1 - 10^{-A})}{(1 - 10^{-A_0})}\frac{A_0}{A}\frac{[RH_{n-1}]}{C_0} + \cdots + \frac{\varepsilon_R}{\varepsilon_{RH_n}}\frac{\varphi_R}{\varphi_{RH_n}}\frac{(1 - 10^{-A})}{(1 - 10^{-A_0})}\frac{A_0}{A}\frac{[R]}{C_0} \qquad (8a)$$

I_0 being defined according to eqn. (9*a*):

$$I_0 = G\,\varphi_{RH_i}\,I_{inc}\,(1 - 10^{-A_0})\frac{\varepsilon_{RH_n}C_0}{A_0} \qquad (9a)$$

Eqn. (8*a*) can be rewritten as in eqn. (10*a*):

$$\frac{I}{I_0}\frac{(1 - 10^{-A_0})}{(1 - 10^{-A})}\frac{A}{A_0} = \frac{[RH_n]}{C_0} + \frac{\varepsilon_{RH_{n-1}}}{\varepsilon_{RH_n}}\frac{\varphi_{RH_{n-1}}}{\varphi_{RH_n}}\frac{[RH_{n-1}]}{C_0} + \cdots + \frac{\varepsilon_R}{\varepsilon_{RH_n}}\frac{\varphi_R}{\varphi_{RH_n}}\frac{[R]}{C_0} =$$

$$\chi_{RH_n} + \frac{\varphi_{RH_{n-1}}}{\varphi_{RH_n}}\frac{\varepsilon_{RH_{n-1}}}{\varepsilon_{RH_n}}\chi_{RH_{n-1}} + \cdots + \frac{\varphi_R}{\varphi_{RH_n}}\frac{\varepsilon_R}{\varepsilon_{RH_n}}\chi_R \qquad (10a)$$

In eqn. (10*a*) χ_{RH_i} is the molar fraction of the species RH_i, the other symbols as stated previously, namely the coefficients C_i as defined in eqn. (2) of the main text.

Inspection of eqn. (10*a*) shows its similarity with eqn. (2), the only difference being the fact that molar fractions are also multiplied by the ratio of the quantum yields $\varphi_{RH_i}/\varphi_{RH_n}$.

Whenever the absolute values of the absorbance are low over all the pH region, as usually used in fluorescence measurements, upon development of the exponential terms in series, a simplification can be obtained as shown in eqn. (11*a*).

$$\frac{I}{I_0} = \chi_{RH_n} + \frac{\varphi_{RH_{n-1}}}{\varphi_{RH_n}}\frac{\varepsilon_{RH_{n-1}}}{\varepsilon_{RH_n}}\chi_{RH_{n-1}} + \cdots + \frac{\varphi_R}{\varphi_{RH_n}}\frac{\varepsilon_R}{\varepsilon_{RH_n}}\chi_R \qquad (11a)$$

In the cases where it is possible to choose a wavelength for which the absorbance can be considered almost constant for all pH values, the right-hand term of eqn. (11*a*) is exactly reduced to the right-hand term of eqn. (2).

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