# Selective Lithium Complexation by Photoactive Aza-Cages Bearing the Anthracene Function

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Three aza-cages with the anthracene-containing photoactive groups **L1**, **L2**, and **L3** have been synthesized. All compounds are able to selectively encapsulate a lithium ion and solid complexes have been isolated. The formation equilibria have been investigated by UV/Vis and $^{1}H$, $^{13}C$ and $^{7}Li$ NMR spectroscopic techniques. The fluorescence emission of both free ligands and lithium complexes have been investigated. Results indicate that the CHEF (chelation enhancement of the fluorescence) effect obtained by lithium coordination exits although lower than that occurring upon full protonation.

## Introduction

The design of new ligands with the ability to bind metal ions, and capable of recognizing the presence of these ions in solution, is of great interest in a wide variety of chemical fields ranging from the study of transport processes in biological systems to industrial and technological applications.[1−6] Macrocyclic compounds are a particularly attractive class of ligands and have thus received much attention in the last few years.[7−10] The development of new synthetic strategies has led to the real possibility of merging theory and experimentation in the design of chemical compounds with specific properties. Lithium is one target of this research and much effort has been dedicated to the synthesis of ligands able to bind it.[11−12] The interest in this ion is due to its significant role not only in industrial applications, but also in medical and biological chemistry.[13][14] Lithium salts have, in fact, been extensively and successfully used in the treatment of manic depression and other neurological and psychiatric disorders.[15][16] Lithium also exhibits antiviral activity against DNA-type viruses.[17] However, the use of lithium salts as drugs is limited by their side effects and toxicity. The mechanisms by which $Li^{+}$ is involved in biological systems are unknown. No natural molecules are known, nor have any synthetic receptors been prepared, that would be selective enough to preferentially bind lithium ions at physiological concentration. Furthermore, easy determination of the lithium level in patients, using selective reactants would be very important. The elucidation of synthetic strategies and coordination properties of $Li^{+}$ should lead to an improved understanding of its biological activity and to the design of better ligands as ionophores for it.

So far, fluorescence methods have proved to be useful in assaying metal ions. The design of molecular systems which combine binding ability and photochemical properties, displaying photoactive features, therefore have a great attraction.[18−20] One of the most used sensors is the anthracene moiety, which presents high fluorescence that could be affected by the molecular surroundings. In this context, three new aza-criptands bearing the anthracene function and characterized by different macrocyclic molecular topologies were synthesized (Chart I). All the ligands present a small three-dimensional cavity able to selectively encapsulate the lithium ion; the aromatic sensor is situated in an external position outside the macrocyclic cavity but in such a way that its optical properties could be perturbed by metal complexation.

The main aim of the present work was to investigate the possibility of employing these anthracene-functionalized aza-cages as selective lithium receptors and chromoionophores. The acid-base behavior of such ligands and their lithium complexation, performed by potentiometric titration, are reported, along with $^{13}C$, $^{1}H$ and $^{7}Li$ NMR spectroscopic analysis.

## Results and Discussion

### Synthesis

All three of the new ligands contain the macrocycle 1,7-dimethyl-1,4,7,10-tetraazacyclododecane; nevertheless, the synthesis was carried out with two different methods, one to obtain **L1** and **L2**, and the other for **L3**. Scheme 1 shows the synthetic pathways for **L1** and **L2**, which were obtained starting from the previously synthesized aza-cage **1** as already reported.[21] To obtain **L1**, compound **1** was functionalized in acetonitrile with the chloroanthracene derivative **2** in an equimolar ratio in the presence of sodium car-

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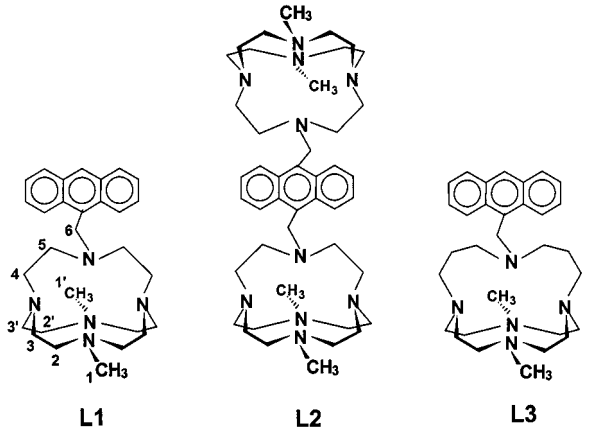
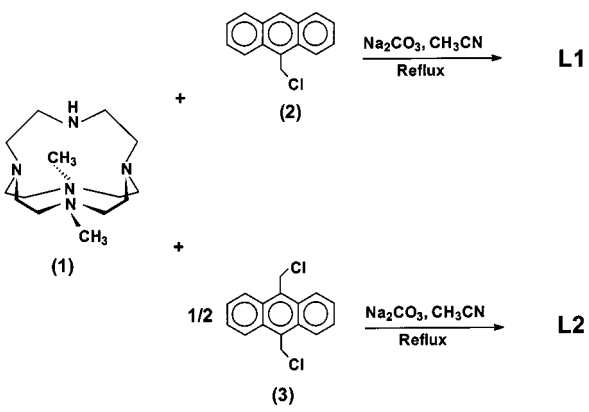
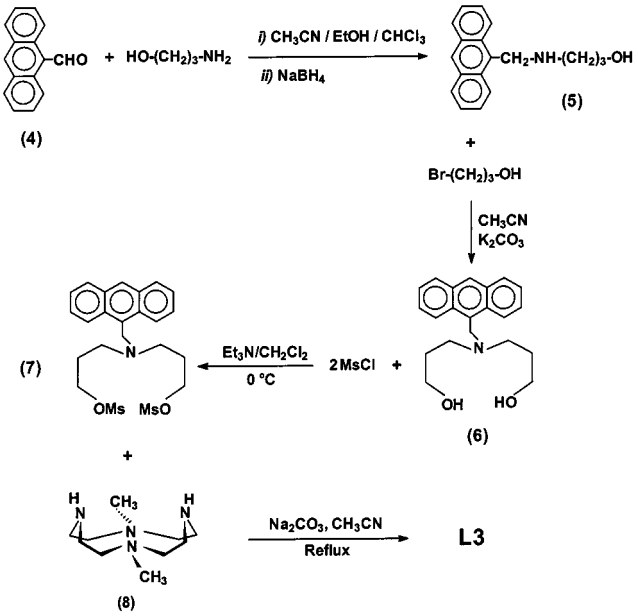



bonate as a base. The reaction gave **L1** in almost quantitative yield and the ligand was transformed into its diperchlorate salt by adding $HClO_4$ during the purification step. The same procedure was adopted to achieve **L2** but, in this case, the dichloroanthracene derivative **3**[22] was added to functionalize cryptand **1** in acetonitrile and employing a molar ratio of 1:2; again, cryptand **L2** was obtained as its perchlorate salt in good yield.




Scheme 1. Synthetic pathway for **L1** and **L2**

Ligand **L3**, however, was synthesized from the tetraaza monocyclic base **8**[23] (see Scheme 2) by reaction with the synthesized dimesyl-*N*-(9-methylanthracene)dipropanolamine (**7**); the complete synthetic pathway is depicted in Scheme 2. Aldehyde **4** was reacted with 3-aminopropanol in a solvent mixture of acetonitrile/ethanol/chloroform in the classic formation of a Schiff base. This compound was not isolated, but the crude solid obtained after evaporating the solvent was reduced in absolute ethanol with sodium borohydride to give compound **5**. This compound was transformed into the dialcohol **6** by *N*-alkylation with 3-bromo-propanol in acetonitrile in the presence of $K_2CO_3$ as base. Attempts to perform direct dialkylation of 9-aminomethylanthracene with two equivalents of 3-bromopropanol to give the dialcohol **6** failed. The methylsulfonyl derivative **7** was obtained using standard methods. Reaction of **7** with the base **8** in the presence of $Na_2CO_3$, a modification of Richman and Atkins′ method gave, after purification, the cryptand **L3**, in quite good yield. The need to use different synthetic pathways to obtain the three ligands is due to the different properties of the precursor cryptand. In fact, while **1** is present as a free amine in alkaline solution, the analogous cryptand with two propylenic (instead of all ethylenic) chains behaves as a proton-sponge and is present as a mono-protonated species in solution; its *N*-alkylation with the compound **2** is thus impeded.




Scheme 2. Synthetic pathway for **L3**

It was possible to isolate the monoprotonated species of the ligand **L1** as its perchlorate salt by extraction of an alkaline suspension of the ligand in chloroform and subsequent precipitation with hexane. The same treatment for **L3** afforded the free amine. The synthesis of the lithium complexes was carried out by reaction of an excess of LiOH with the ligands in methanol at room temperature. The complexes can be easily isolated after removal of the methanol by extracting the solid mixture with chloroform. It should be noted that the $Li^+$ complexes of all the ligands under investigation are very soluble in organic solvents (*ca.* 0.1 M).

## Absorption and Emission Spectroscopy

### Absorption Spectra

The absorption spectra in aqueous solution of the compounds **L1**, **L2** and **L3** present an identical pattern, being characterized by a structured absorption band in the near UV/Visible region of the spectrum. This absorption band can be immediately assigned to the anthracene chromophore. The shape of the absorption spectra of these compounds is only slightly affected by the pH of the solution, allowing us to conclude that the absorption of light by the anthracene moiety occurs independently of the protonation state of the cavity.

### Fluorescence Emission

Excitation of acidic aqueous solutions of the compounds **L1**, **L2** and **L3** into the first singlet state gives rise to a fluorescence emission band which can also be attributed to the anthracene fluorophore. In contrast to the absorption, the fluorescence emission spectra are very dependent on the protonation state of the cavity (see Figure 1). Determination of the protonation constants of these compounds is difficult due to their low solubilities which preclude direct potentiometric measurements. Moreover, as the pH-dependent variations in the absorption spectra are very small, the error associated is large.

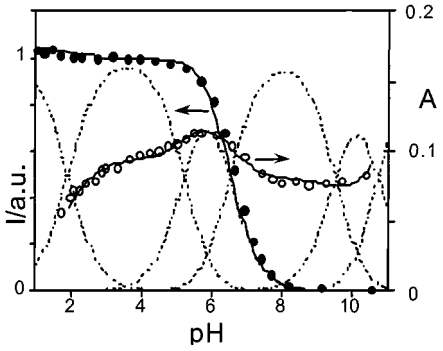



Figure 1. Fluorescence emission (•) and absorption (o) titration, distribution curves of the species (- -), for the compound **L2** in aqueous solution, $5 \times 10^{-5}$ M, $\lambda_{exc} = 398$ nm, $\lambda_{em} = 429$ nm, absorbance at 323 nm

A fitting to the experimental curves was also performed and the protonation constants thus obtained are reported in Table 1. The best situation was obtained in the case of the compound **L2**. For **L1**, a protonation constant, $pK_a = 6.5$, can only be obtained with sufficient accuracy from fluorescence emission. The most interesting characteristic of the fluorescence emission titration curves of **L1**, **L2** and **L3** is the quenching effect that occurs in the pH 6−9 region. This type of quenching has been described before in chemosensors possessing aromatic units linked to a polyaza chain, and was attributed to an intramolecular electron-transfer process from the deprotonated amine to the excited aromatic moiety.[24] According to the structure of the compounds **L1**, **L2** and **L3** it is likely that quenching occurs upon deprotonation of the apical nitrogen functionalized by the photoactive group, which is the one in the best position to carry out the electron-transfer process. This interpretation is also compatible with the protonation constants obtained by means of the fluorescence data (see Table 1). The log *K* values are very similar for **L1** and **L2** ($pK_a = 6.5$ and 6.8, respectively) and higher for **L3** ($pK_a = 8$). Analyzing these values we propose that the apical nitrogen is involved in the protonation only from the second protonation step of each cage subunit. Furthermore, while **L1** and **L2** have the same cavity, in the case of **L3** it is larger, and the apical nitrogen more basic, because the charge repulsion of the other protonated nitrogen is smaller.

### Potentiometric and NMR Spectroscopic Studies

Due to the presence of the hydrophobic anthracene fragment, the ligands do not show good solubility in aqueous solution. However, in the case of **L2**, and given its topology, it was possible to measure some protonation constants by direct potentiometric methods. The measurements performed in aqueous solution (0.15 M $Me_4NCl$ ionic medium) are summarized in Table 1. The similar log *K* values for the addition of the third and fourth proton, together with the ligand topology, suggest that, in the $[H_4\mathbf{L2}]^{4+}$ species, both amine subunits bind two protons. This hypothesis is also confirmed from a comparison of the log $K_2$ values obtained for **L1** by spectrophotometric methods. Furthermore the basicity constants evaluated with the two different method are in good agreement.

Table 1. Protonation constants of **L1**, **L2** and **L3** (log K) in aqueous solution (298 ± 0.1 K, I = 0.15 M $NMe_4Cl$)

| Reaction | **L1** | **L2** | **L3** |
|---|---|---|---|
| $L + H^+ = HL^+$ | Insoluble | 10.7[a] | Insoluble |
| $HL^+ + H^+ = H_2L^{2+}$ | 6.5[a] | 9.5[a] | 8.0[a] |
| $H_2L^{2+} + H^+ = H_3L^{3+}$ | – | 6.8[a] – 7.0 (1)[b, c] | 6.0[a] |
| $H_3L^{3+} + H^+ = H_4L^{4+}$ | – | 6.2[a] – 6.4 (1)[b] | 1.9[a] |
| $H_4L^{4+} + H^+ = H_5L^{5+}$ | – | 1.9[a] – 1.8(1)[b] | – |

[a] From spectrophotometric measurements. – [b] From potentiometric measurements. – [c] Values in parentheses are standard deviations to the last significant figure.

From a $^1H$ and $^{13}C$ NMR spectroscopic analysis, it was possible to obtain additional information about the chemical properties of **L1** and of the other two ligands. As explained in the "synthesis" section, the free ligand **L1** could not be obtained. The $^1H$ NMR spectrum of the $[H\mathbf{L1}]^+$ species, recorded in $CDCl_3$, is shown in Figure 2a. The spectrum also shows a peak at 10.84 ppm assignable to the deshielded acidic proton. Upon addition of $H_2O$ or $CH_3OH$ to the chloroform solution, the signal at 10.85 ppm did not disappear, indicating a slow exchange on the NMR time scale with the labile protons of the solvent. However, the resonance did disappear when $D_2O$ or $CD_3OD$ were added. The chemical shift, together with the experimental evidence, suggests that the proton is stabilized inside the macrocyclic cavity by a strong hydrogen-bonded network with the amine functions. The other resonance in the $^1H$ NMR spectrum of the $[H\mathbf{L1}]^+$ species in $CD_3OD$ (Figure 2b) is similar to that recorded in $CDCl_3$. It did not change even when a solution of NaOD in methanol was added, thus proving that the acidic proton cannot be removed in alcoholic alkaline solutions. Under the conditions described above, and as reported in the experimental section, **L2** and **L3** are present as free amines. Again, the chemical shift of the $^{13}C$ NMR resonance shows a $C_{2V}$ time-averaged symmetry for **L2** and **L3** in $CDCl_3$ solution. In conclusion, **L2** and **L3** show a lesser basicity in alcoholic solution than **L1** in the first protonation step as evidenced by spectrophoto-

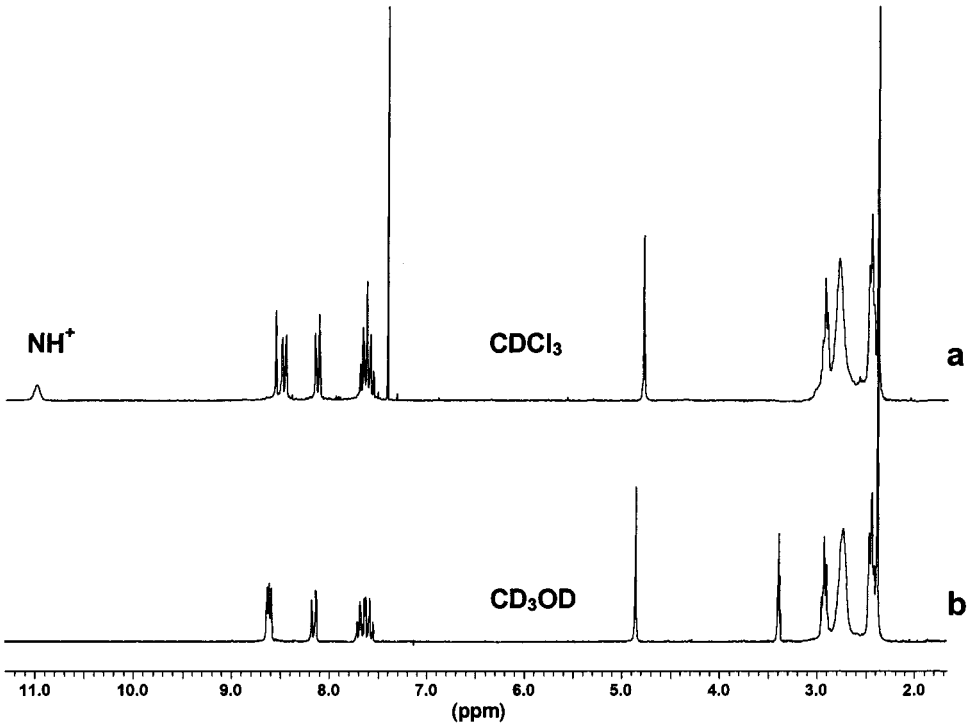



Figure 2. $^{1}H$ NMR spectra of $[HL1]^{+}$ species in $CDCl_3$ (a); in $CD_3OD$ (b)

metric and NMR spectra, this could be ascribed to the larger three-dimensional cavity for **L3**, but other factors like the inductive effect of the methylanthracene group could be important to explain the different behavior of **L1** vs. **L2** and **L3**.

## Lithium Complexation

The coordination of the alkaline metal ions by ligands **L1**, **L2** and **L3** was studied by $^{1}H$, $^{13}C$ and $^{7}Li$ NMR spectroscopic techniques in alcoholic solution. With $^{1}H$ and $^{13}C$

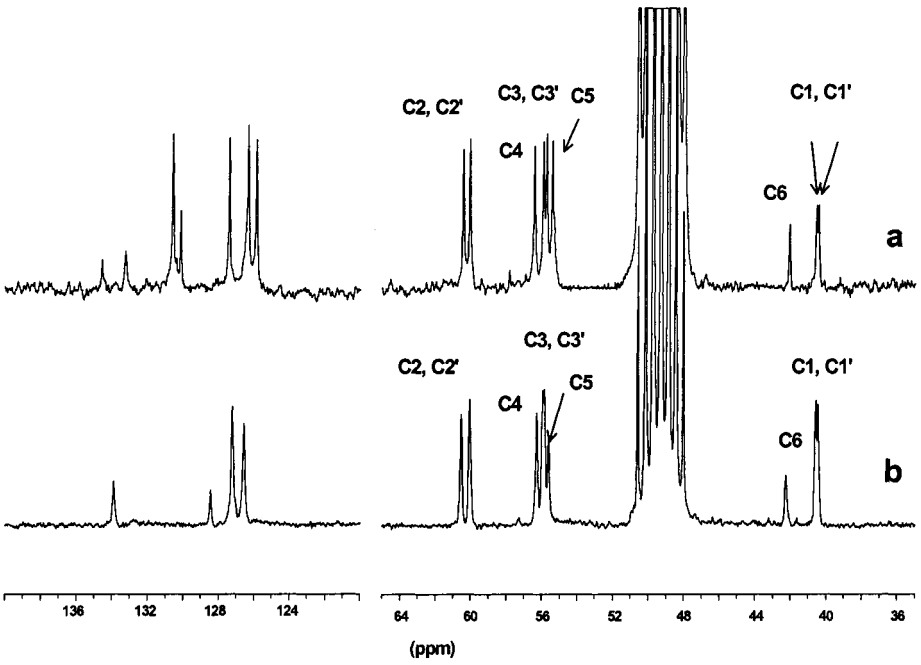



Figure 3. $^{13}C$ NMR spectra in $CD_3OD$ of: $[LiL1]^{+}$ complex (a); $[Li_2L2]^{2+}$ complex (b)

spectroscopy as diagnostic techniques, no evidence was found for complex formation with sodium and potassium ions in alcoholic solution. Instead, all the ligands readily bound the smaller $Li^+$ ion and the solid complexes were isolated as reported in the experimental section. These solid compounds are soluble in organic solvents such as $CDCl_3$ and their $^7Li$ NMR spectra present a sharp peak, shifted downfield with respect to the free ion. $Li^+$ coordination is clearly shown by the $^{13}C$ and $^7Li$ NMR spectra of a methanol solution containing **L1**, **L2** or **L3** and $Li^+$ in the presence of a base. In all three cases, upon the addition of an excess of $Li^+$ to an alkaline solution of the ligands, the $^7Li$ NMR spectrum shows two sharp peaks, one due to the free lithium ion and the other, shifted downfield, due to the complexed lithium ion. The changes in chemical shift of the complexed ion are 3.29, 3.26, and 1.39 ppm with respect to the solvated ion, for **L1**, **L2**, and **L3**, respectively. The simultaneous presence of the two peaks denotes a slow exchange of the complexed lithium ion with the free ion on the NMR time scale. These chemical shifts were conserved when the solvent was changed to $CD_3CN$ or $CDCl_3$, and are the same as observed by solubilizing the solid complexes.

The solvent-independence of the $^7Li$ chemical shift and the slow exchange on the NMR time scale between free and bound lithium indicate that the ion is encapsulated inside the macrocyclic cavity and thus quite isolated from the medium. Comparison of the $^{13}C$ NMR spectra of the free amines with those of the lithium complexes, as shown for example in the case of **L1** (Figure 3a), revealed that the complexation of the $Li^+$ ion produces a decrease in molecular symmetry, on the NMR time scale, for all three ligands. In fact while the free ligand **L1** presents fourteen peaks for a $C_{2v}$ time-averaged symmetry, the spectrum of the complex presents seventeen peaks indicating a $C_s$ symmetry. Analyzing the spectrum of the complex, the element of symmetry lost is the plane passing through the bridgehead nitrogen and the nitrogen atom having the anthracene group, while the other plane, which contains the methylated nitrogen atoms, is preserved.

For ligand **L1** the coordination of the lithium ion leads to removal of the acidic proton resonance at 10.85 ppm which is not present in the $^1H$ NMR spectrum of the complex. Ligand **L2** is able to bind two lithium ions but only one resonance was obtained in the $^7Li$ spectra, with the same value as for the **L1** complex. The aliphatic resonances for the $[Li_2\mathbf{L2}]^{2+}$ complex (Figure 3b), show the same environment around the lithium ions from the two subunits, and are similar to those found for the $Li\mathbf{L1}^+$ species (Figure 3a). These experimental data provide evidence that, for **L2**, only one ion is lodged in the subunit and the coordination around the ion is equal in the two subunits on the NMR time scale and similar to that of the **L1** complex. It is noteworthy that these spectral features do not change even in the presence of a large excess of $Na^+$. In other words, lithium complexation is not influenced by the presence of the $Na^+$ ion, even at high concentrations, indicating that ligands **L1**–**L3** are able to discriminate completely between $Li^+$ and $Na^+$. Such selectivity is related to the small dimensions of the macrobicyclic cavity, in which the larger $Na^+$ cannot be encapsulated.

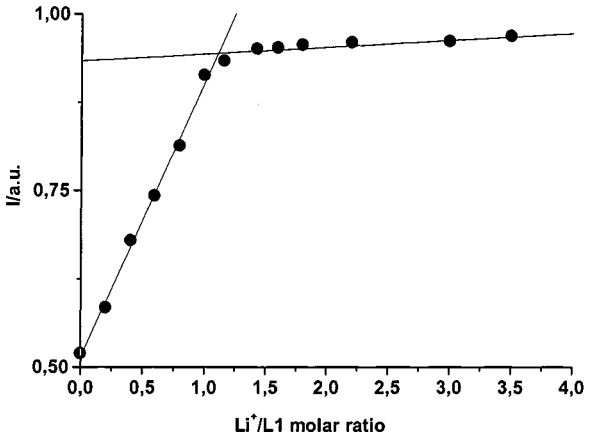



Figure 4. Variation of the fluorescence emission intensity of **L1** ($1 \times 10^{-5}$ M) in methanol with tetrabutylammonium hydroxide, at $\lambda_{em}$ = 412 nm, as a function of $Li^+$/**L1** molar ratio

## Sensing Lithium

A plot of the fluorescence emission variations that occur upon addition of different concentrations of lithium to an alkaline methanol solution of compound **L1**, at 25°C is shown in Figure 4. A similar behavior was also observed for **L2**. The fit of the experimental data points is in good agreement with a $Li^+$:L ratio of 1:1 for the lithium complex of **L1** and a 2:1 ratio for **L2**. The trend of chelation enhancement of the fluorescence (CHEF) effect, obtained by coordination of $Li^+$ into the cavity by increasing the lithium equivalents, shows that the complexes are completely formed by the addition of one or two equivalents of ion for **L1** and **L2,** respectively. The spectrum of the lithium complexes is quite similar to the sensor in the absence of lithium, but is approximately twice as intense and slightly shifted to the red, as shown in Figure 5 for the $[Li\mathbf{L3}]^+$ species.

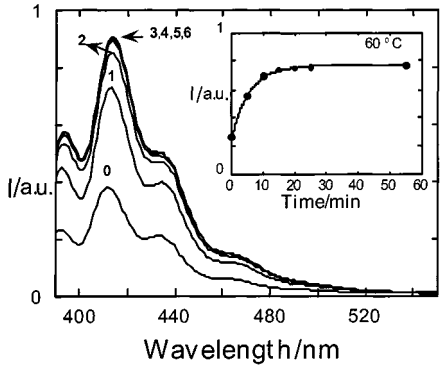



Figure 5. Spectral variations of the fluorescence emission of **L3** in methanol with addition of tetrabutylammonium hydroxide (0); immediately after addition of lithium excess(1); after 5 min (2); 10 min (3); 15 mim (4); 20 min (5); 55 min (6). $\lambda_{exc}$ = 380 nm. Inset variation of the fluorescence emission intensity at $\lambda_{em}$ = 420 nm as a function of time

In this case the coordination of the lithium is time-dependent but the equilibrium state is reached in less than twenty minutes at 60°C. In the equilibrium state, a behavior similar to that of the previous two ligands was also observed for **L3**. The CHEF effect obtained by coordination of lithium into the cavity is, however, much lower than that occurring upon full protonation. A possible explanation for this behavior is the fact that coordination of the metal has only a small influence on the quenching mechanism.

## Conclusions

The molecular topology of the polyamines **L1**-**L3** is characterized by the presence of both a three-dimensional cavity and an anthracene moiety. It has been shown that **L1** behaves as a "proton sponge" in alcoholic solution. All three ligands are able to selectively bind the lithium ion in alcoholic solution while the other alkali metal ions are not complexed. Such remarkable selectivity is due to the small dimensions of the macrocyclic cavity, in which alkali metals larger than lithium cannot be encapsulated. The solid lithium complexes, which were isolated and fully characterized, are soluble in organic solvents such as $CDCl_3$. **L2** forms a binuclear lithium complex with each ion lodged in a single cage subunit. The photochemical properties of the ligands are strongly influenced by protonation; moreover, on lithium complexation an increase in the fluorescence emission of the sensor, relative to that of the free ligand, is observed in methanol. Unfortunately, the presence of the anthracene moiety renders the ligands insoluble in aqueous solutions preventing the complexation of the lithium in this medium.

## Experimental Section

**General:** $^1H$, $^{13}C$ and $^7Li$ NMR spectra were recorded on a Bruker AC-200 instrument, operating at 200.13, 50.33 or 77.78 MHz, respectively. $^1H$ NMR peak positions are reported relative to HOD (4.75 ppm), dioxane was used as reference standard in $^{13}C$ NMR spectra ($\delta$ = 67.4 ppm). For the spectra recorded in $CDCl_3$, the peak positions are reported relative to TMS. $^7Li$ NMR peaks are reported relative to free $LiClO_4$. $^1H$-$^1H$ and $^1H$-$^{13}C$ correlation experiments were performed to assign the signals. Solvents and starting material were used as purchased.

**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 tetrabutylammonium hydroxide were used to adjust the pH values, which were measured on a Metrohm 713 pH meter. The acidification constants were obtained from a fit of the theoretical equations to the experimental titration data by least-squares analysis using the bracketing technique.

**Potentiometric Measurements:** All potentiometric measurements were carried out in 0.15 M $Me_4NCl$ at 298.1 ± 0.1 K, in the pH range 2.5–10, using the fully automatic equipment that has been already described.[25] The acquisition of the emf data was performed with the PASAT computer program. The electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with $CO_2$-free $Me_4NOH$ solutions and determining the equivalent point by Gran's method,[26] which gives the standard potential E° and the ionic product of water $K_w$. At least three measurements were performed. The HYPERQUAD computer programs were used to process the potentiometric data and calculate the protonation constants.[27]

Compounds **1**, **3**, **8** were synthesized as reported in the literature.[21–23] Compounds **2** and **4** were purchased from Aldrich Chemical Co. All reactions were carried out under an inert atmosphere.

**Caution:** Perchlorate salts of organic compounds are potentially explosive; these compounds must be handled with great caution!

**(1,7,-Dimethyl-1,4,7,10,15-pentaazabicyclo-[5.5.5]-heptadecan-15-yl)-9-methylanthracene Diperchlorate (L1·2HClO$_4$)**: Cryptand **1** (0.54 g, 2 mmol) and $Na_2CO_3$ (0.64 g, 6 mmol) were suspended in refluxing $CH_3CN$ (100 mL). To this mixture, a solution of **2** (0.68 g, 3 mmol) in 50 mL of acetonitrile was added dropwise in 2 h. After the addition was completed, the suspension was refluxed for 2 h. The mixture was evaporated to dryness under vacuum, and the solid obtained was suspended in chloroform. The organic layer was filtered and solvents removed under vacuum to give a yellow solid, which was dissolved in ethanol. The suspension was filtered to eliminate the excess of **2,** and then treated with 65% perchloric acid to give the diperchlorate salt as a yellowish solid. Yield: 0.85 g (90%). – $C_{29}H_{43}Cl_2N_5O_8$: calcd. C 52.73, H 6.56, N 10.60; found C 52.6, H 6.6, N 10.5.

**L1·HClO$_4$:** The monoprotonated species was obtained by suspending the diperchlorate salt in 1 M NaOH aqueous solution and extraction of the resulting suspension with chloroform. The volume of the organic phase was reduced and the H**L1**$^+$ was precipitated with hexane in almost quantitative yield. – $C_{29}H_{42}ClN_5O_4$: calcd. C 62.18, H 7.56, N 12.50; found C 62.0, H 7.5, N 12.3. – MS (ESI) $m/z$ = 461 $[M + H]^+$. – $^1H$ NMR ($CDCl_3$): $\delta$ = 2.24 (s, 6 H) 2.30 (t, 4 H), 2.64 (bb, 16 H), 2.78 (t, 4 H), 4.65 (s, 2 H), 7.46 (m, 4 H), 7.97 (d, 2 H), 8.32 (d, 2 H), 8.41 (s, 1 H), 10.84 (bb, 1 H). – $^{13}C$ NMR ($CDCl_3$): $\delta$ = 43.5, 49.4, 50.2, 52.9, 53.0, 53.5, 124.2, 125.1, 126.5, 128.3, 128.4, 129.5, 130.9, 131.3.

**(1,7,-Dimethyl-1,4,7,10,15-pentaazabicyclo-[5.5.5]-heptadecan-15-yl)-9,10-dimethylanthracene Tetraperchlorate (L2·4HClO$_4$)**: Cryptand **1** (1.1 g, 4 mmol) and $Na_2CO_3$ (1.3 g, 12 mmol) were suspended in refluxing $CH_3CN$ (100 mL). To this mixture, was added a solution of **3** (0.55 g, 2 mmol) in $CH_3CN$ (100 mL) dropwise in 2 h. After the addition was completed, the suspension was refluxed for 3 h. The mixture was vacuum evaporated, and the solid obtained was suspended in chloroform. The organic layer was filtered and vacuum evaporated to give a yellow solid. The solid was dissolved in a minimum amount of chloroform and chromatographated on neutral alumina with $CH_2Cl_2$/MeOH mixture (10:1) as eluent. The eluted fractions were collected and evaporated to dryness to obtain a yellow solid. The solid was further purified by dissolving it in ethanol and the solution treated with 65% perchloric acid to give the tetraperchlorate salt in almost quantitative yield. Yield: 1.65 g (72%). – $C_{44}H_{76}Cl_4N_{10}O_{16}$: calcd. C 46.24, H 6.70, N 12.26; found C 46.0, H 6.6, N 12.1. – MS (ESI) $m/z$ = 742 $[M + H]^+$. – $^1H$ NMR ($D_2O$, pD = 3):$\delta$ = 2.56 (s, 12 H) 2.69 (t, 8 H), 2.87 (bb, 32 H), 2.95 (t, 8 H), 4.70 (s, 4 H), 7.39 (d, 4 H), 8.26 (d, 4 H), 10.68 (bb, 2 H). – $^{13}C$ NMR ($D_2O$, pD = 3):$\delta$ = 42.2, 49.1, 50.6, 53.0, 53.2, 53.7, 127.1, 128.9, 129.4, 136.2.

***N*-(Anthracene-9-methyl)-aminepropanol (5):** Reagent **4** (20.6 g, 0.10 mol) was added together with 3-amino-propanol to 150 mL of $CH_3CN/CH_3CH_2OH/CHCl_3$ mixture (5:15:70). This solution was kept stirred at room temperature for 24 h and then vacuum evapo-

rated to give a yellow solid, which was dissolved in hot absolute ethanol (500 mL). The solution was cooled at room temperature and then added of $NaBH_4$ (8 g, 0.2 mol). The suspension obtained was refluxed for 4 h and then vacuum evaporated. The solid was suspended in water (120 mL) and extracted with chloroform ($3 \times 100$ mL). The organic phase was dried over anhydrous $Na_2SO_4$, and its volume vacuum reduced. Ethyl ether was added to this solution to complete precipitation of a yellow solid, which was recrystallized from hot $CH_3CN$. Yield: 20.5 g (77%). − $C_{18}H_{19}NO$: calcd. C 81.48, H 7.22, N 5.28; found C 81.6, H 7.3, N 5.2. − M.p., 79−81°C. − $^1$H NMR ($CDCl_3$): δ = 1.82 (m, 2 H), 2.41 (t, 2 H), 3.38 (t, 2 H), 3.51 (b, 1 H), 4.26 ( s, 2 H), 4.76 (b, 1 H) 7.47 (m, 4 H), 8.04 (d, 2 H), 8.29 (d, 2 H), 8.44 (s, 1 H). − $^{13}$C NMR ($CDCl_3$): δ = 28.5, 48.5, 53.6, 62.4, 124.0, 124.8, 126.0, 128.6, 129.7, 131.1, 131.3.

***N*-(Anthracene-9-methyl)-dipropanolamine (6):** A sample of **5** (5.3 g, 0.02 mol) was added with 3-bromine-propanol (2.8 g, 0.02 mol) and $K_2CO_3$ (3.0 g, 0.022 mol) to 80 mL of $CH_3CN$. This mixture was slowly warmed to 50°C and kept with stirring over a period of 5 h. After this period the suspension was refluxed for 2 h. The reaction mixture was allowed to cool to room temperature and then 100 mL of 0.1 mol $dm^{-3}$ NaOH aqueous solution added. The extracted organic phase, was dried over sodium sulfate. The solvent was removed under reduced pressure to obtain a solid which was recrystallized from $CH_3CN$. Yield 3.6 g (56%). − $C_{21}H_{25}NO_2$: calcd. C 77.98, H 7.79, N 4.33; found C 78.2, H 7.9, N 4.3. − $^1$H NMR ($CDCl_3$): δ = 1.79 (p, 4 H), 2.76 (t, 4 H), 3.48 (t, 4 H), 3.62 (b, 2 H), 4.53 ( s, 2 H), 7.51 (m, 4 H), 8.01 (d, 2 H), 8.37 (d, 2 H), 8.45 (s, 1 H). − $^{13}$C NMR ($CDCl_3$): δ = 28.7, 51.4, 52.5, 62.2, 124.3, 125.0, 126.2, 128.9, 129.3, 131.3, 131.4.

***N*-(Anthracene-9-methyl)-*O*-dimesyl-dipropanolamine (7):** A sample of **6** (3.2 g, 0.01 mol) and triethylamine (5.1 g, 0.05mol) in 60 mL of anhydrous dichloromethane was cooled at −5°C. To this solution was added dropwise over a period 3 h, with stirring, a solution of methanesulfonil chloride (2.9 g, 0.025 mol). The reaction mixture was kept to −5°C for further 30 min and then was allowed to warm up to room temperature. The resulting suspension was washed twice with a 0.1 M NaOH aqueous solution and then with water. The organic phase was dried over anhydrous $Na_2SO_4$ and evaporated to dryness to obtain **7** as a yellowish solid. Yield: 4.4 g (91%). − $C_{23}H_{29}NO_6S_2$: calcd. C 57.60, H 6.09, N 2.92; found C 57.7, H 6.1, N 3.0. − $^1$H NMR ($CDCl_3$): δ = 1.52 (m, 4 H), 2.71 (t, 4 H), 2.83 (s, 6 H), 3.38 (s, 2 H), 4.25 (t, 4 H), 7.53 (dd, 2 H), 7.72 (dd, 2 H), 8.07 (d, 2 H), 8.33 (dd, 2 H), 8.59 (s, 1 H). − $^{13}$C NMR ($CDCl_3$): δ = 24.3, 37.5, 39.7, 54.1, 59.7 123.1, 125.7, 127.2, 129.0, 129.5, 129.9, 132.2, 132.8.

**1,7,-Dimethyl-1,4,7,10,16-pentaazabicyclo-[5.5.7]-nonadecan-16-yl-9-methylanthracene (L3):** To a refluxing suspension of **8** (1.8 g, 0.009 mol) and $Na_2CO_3$ (5.3 g, 0.05 mol) in 150 mL of acetonitrile was added, over a period of 6 h, a solution of **7** (4.3 g, 0.009 mol) in 100 mL of acetonitrile. The reaction mixture was maintained at reflux for a further 2 h. After the mixture was cooled to room temperature, the resulting suspension was filtered and evaporated under reduced pressure to give a yellowish solid, which was dissolved in a minimum amount of $CHCl_3$ and chromatographed on neutral alumina with an eluent mixture of $CHCl_3/CH_3OH$ (100:5). The eluted fractions were collected and evaporated to dryness to obtain a yellow solid. The solid was further purified by dissolving it in ethanol and the solution treated with 65% perchloric acid to give the diperchlorate salt in almost quantitative yield. Yield: 3.6 g (58%). − $C_{31}H_{45}N_5$: calcd. C 76.34, H 9.30, N 14.36; found C 76.2, H 9.3, N 14.3. − MS FAB *m/z* = 489 $[M + H]^+$. − $^1$H NMR ($CDCl_3$): δ = 1.56 (m, 4 H) 2.52 (s, 6 H), 2.58 (t, 4 H), 2.66 (t, 4 H), 2.92 (m, 16 H), 4.48 (s, 2 H) 7.43 (m, 4 H), 7.95 (d, 2 H), 8.36 (s, 1 H), 8.40 (d, 2 H). − $^{13}$C NMR ($CDCl_3$): δ = 25.2, 41.5, 50.6, 51.4, 53.2, 54.8, 55.5, 124.7, 124.8, 125.6, 127.5, 129.1, 130.0, 131.1, 131.3.

**Preparation of the Complexes. [LiL1]$ClO_4$ (9):** A solution of LiOH (10 mg, 0.44 mmol) and $NaClO_4 \cdot H_2O$ (100 mg, 0.7 mmol) in 15 mL of methanol was added to a solution of **L1**· $HClO_4$ (56 mg, 0.1 mmol) in methanol (15 mL). The reaction mixture was stirred for 15 min and then evaporated to dryness. The yellow solid was suspended in 20 mL of $CHCl_3$, and the mixture filtered to separate the inorganic excess and the organic solution dried over $Na_2SO_4$. On addition of cyclohexane (25 mL) a yellow precipitated formed, yield 41 mg (73%). − $C_{29}H_{41}ClLiN_5O_4$: calcd. C 61.53, H 7.30, N 12.37; found C 61.4, H 7.4, N 12.3. − MS (ESI) *m/z* = 467 $[Li\mathbf{L1}]^+$. − $^{13}$C NMR ($CDCl_3$):δ = 39.8, 39.9, 41.0, 54.3, 54.4, 54.5, 55.1, 58.6, 58.9, 124.0, 124.7, 125.1, 126.5, 129.0, 129.2, 131.3, 132.8.

**[$Li_2$L2]($ClO_4$)$_2$ (10):** This compound was synthesized from **L2**·2$HClO_4$ (47 mg, 0.05 mmol) following the same procedure reported for **9** giving **10** as a yellowish solid, yield 36 mg (76%). − $C_{44}H_{72}Li_2Cl_2N_{10}O_8$: calcd. C 55.40, H 7.61, N 14.68; found C 55.5, H 7.6, N 14.8. − MS (ESI) *m/z* = 854 ($Li_2\mathbf{L2}ClO_4^+$). − $^{13}$C NMR ($CDCl_3$):δ = 40.1, 40.3, 42.2, 55.4, 55.6, 55.8, 55.1, 60.2, 60.8, 126.3, 127.1, 128.4, 134.0.

**[LiL3]$ClO_4$ (11):** This compound was synthesized from **L3**·2$HClO_4$ (34 mg, 0.05 mmol) following the same procedure reported for **9** giving **11** as a yellowish solid, yield 36 mg (76%). − $C_{31}H_{45}ClLiN_5O_4$: calcd. C 62.67, H 7.63, N 11.79; found C 62.5, H 7.6, N 11.7. MS (ESI) *m/z* = 495 $[Li\mathbf{L3}]^+$. − $^{13}$C NMR ($CDCl_3$):δ = 26.4, 44.4, 52.2, 53.0, 53.5, 54.4, 54.9, 126.1, 126.2, 126.6, 129.7, 130.1, 130.3, 132.8, 134.2.

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