ATP Sensing with Anthryl-Functionalized Open-Chain Polyaza-alkanes

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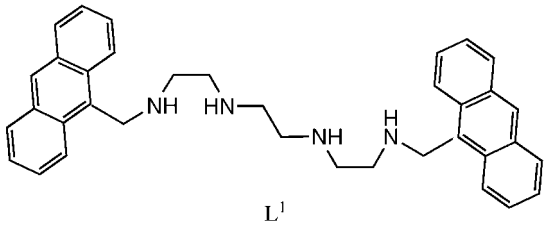
The anthryl-functionalized open-chain polyaza-alkanes **L¹**, **L²**, and **L³** have been synthesized, and their activity as fluorescent chemosensors has been studied in MeCN/H_2O 70:30 (*v*/*v*) and H_2O at 25° against the anions bromide, phosphate, sulfate, ATP, ADP, and GMP. The crystal structure of **L³** has been solved by single-crystal X-ray-diffraction techniques. The emission intensity of **L¹** and **L²** is selectively quenched in the presence of ATP at acidic pH in MeCN/H_2O 70:30 (*v*/*v*). In H_2O, the emission intensity of **L¹** and **L²** is enhanced at neutral pH in the presence of ADP and ATP. The sensing behavior is discussed in terms of H-bonding or electrostatic anion-cation interactions. Receptor **L³** does not show any significant change in fluorescence emission upon addition of anions. Protonation constants of the three ligands and stability constants of **L²** with phosphate and sulfate were determined by potentiometric titration in MeCN/H_2O. The stability constants obtained are compared with those obtained for the interaction of these anions with related open-chain polyamines.

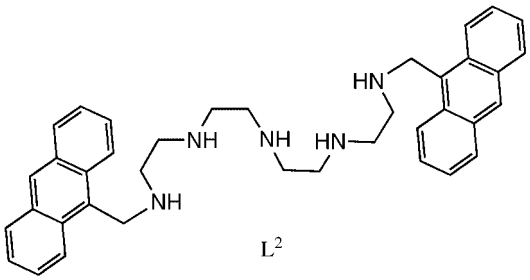
Introduction. – Although a number of molecules for the sensing of metal ions have been widely reported [1–4], less effort has been invested towards the development of sensing receptors for anions [5–7]. Chemical engineering in this field involves the design and synthesis of receptors containing frameworks that are able to coordinate anions and molecular signalling subunits that are able to display selective changes in observable features such as color [8–11], luminescent properties [12–15], electrochemical shifts [16–19], *etc*. upon guest binding. Among different coordination environments for anions, polyamines are especially appealing due to their ability to form highly charged species in solution as a function of pH and H-bonding networks [20–22]. Although there have been a large number of studies dealing with the interaction between polyamines and anions [23–25], there are relatively few references to functionalized polyamines containing suitable signalling subunits for anion sensing [26–28]. Following our interest in the development of potential sensing receptors for anions [29–31], we report here the synthesis of new open-chain polyaza-alkanes functionalized with anthryl groups and their ability as anion-sensing receptors against bromide, phosphate, sulfate, ATP, ADP, and GMP in H_2O and in MeCN/H_2O.

Results and Discussion. – The receptor 1,12-di(anthracen-9-yl)-2,5,8,11-tetraaza-dodecane (**L¹**) has been previously published [32]. Receptor **L²** was synthesized according to a similar reaction procedure. Both **L¹** and **L²** were obtained from condensation between the corresponding free amine and anthracene-9-carbaldehyde in a 1:2 molar ratio, followed by reduction with $LiAlH_4$ in THF. The receptors were isolated as chlorohydrate salts ($(H_4\mathbf{L^1})Cl_4$ and $(H_5\mathbf{L^2})Cl_5$). In contrast, the reaction between triethylenetetramine and anthracene-9-carbaldehyde in a 1:3 molar ratio,

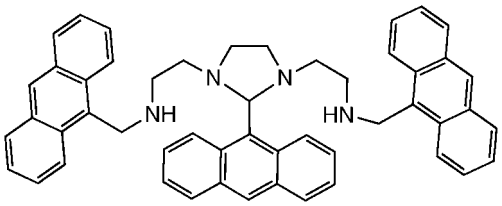
followed by reduction with $LiAlH_4$, gave **L³** as unique product. Both **L¹** and **L²** receptors exhibit the expected ^{1}H-NMR spectra with anrthyl H-atom shifts in the range of 7.45 – 8.30 ppm. The CH_2 groups of the linear polyamine gave overlapped signals between 2.62 and 2.91 ppm, whereas CH_2 groups adjacent to anthryl groups gave resonances at 4.63 ppm. The ^{1}H-NMR spectrum of **L³** is quite complex with well-defined resonances of two *multiplets* at 3.55 and 3.61 ppm of four diastereoisotopic H-atoms of the CH_2 groups of the 1,3-diazolidine ring. The aromatic part also shows the presence of two nonequivalent anthryl groups. The chemical shifts of anthryl H-atoms are in the range of 7.42 – 8.90 ppm. For all three receptors, ^{13}C-NMR and mass spectra, and elemental analysis were also in agreement with the proposed formulation.



L^1



L^2



L^3

Crystal Structure of **L³**. Suitable crystals for single-crystal X-ray diffraction were obtained by diffusion of hexane into CH_2Cl_2 solutions of **L³**. The molecular structure can be considered as derived from receptor **L¹**, where two H-atoms from two central amino groups have been substituted by one anthrylmethyl group to give a 1,3-diazolidine ring. Selected bond distances are shown in *Table 1*, whereas a view of the molecule is shown in *Fig. 1*. The crystal structure shows the presence of two nonequivalent anthryl moieties, the peripheral ones attached to N(1) and N(4) of the tetramine and the central one attached to N(2) and N(3) N-atoms through a methine

Table 1. *Selected Bond Lengths* [Å] *and Angles* [°] *for* **L**[3]

Distances [Å]			
C(19)–C(18)	1.506(7)	C(2)–C(7)	1.464(8)
C(18)–N(2)	1.450(6)	C(51)–C(46)	1.434(6)
N(2)–C(17)	1.442(6)	C(46)–C(47)	1.412(7)
C(17)–C(16)	1.506(7)	C(41)–C(42)	1.403(8)
C(15)–N(1)	1.137(6)	C(29)–C(34)	1.448(7)
C(20)–C(21)	1.529(6)	C(49)–C(50)	1.359(7)
C(21)–C(34)	1.392(6)	C(37)–C(38)	1.483(6)
C(33)–C(34)	1.447(8)	C(37)–N(4)	1.203(6)
Angles [°]			
C(34)–C(21)–C(20)	120.3(4)	N(1)–C(16)–C(17)	112.2(5)
C(18)–N(2)–C(20)	103.0(3)	C(15)–N(1)–C(16)	123.0(6)
N(4)–C(37)–C(36)	122.4(5)	C(23)–C(22)–C(27)	116.1(5)
N(3)–C(20)–N(2)	103.2(3)	C(8)–C(9)–C(14)	118.3(7)

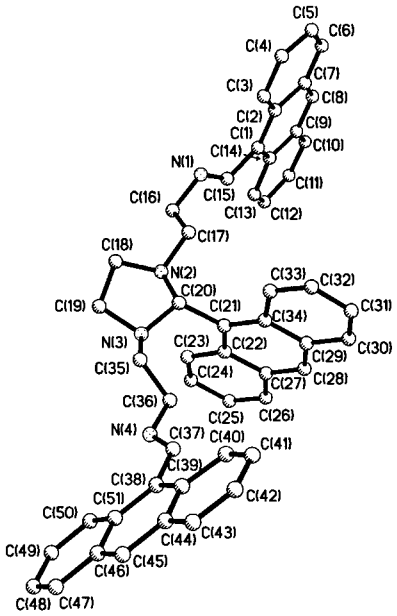


Fig. 1. *Crystal structure of* **L**[3]

spacer. The existence of two nonequivalent anthryl groups is also reflected in ^{1}H- and ^{13}C-NMR spectra and in the emission properties of **L**[3]. Anthryl groups are planar within the experimental error. The dihedral angle between anthryl groups attached to N(1) and N(4) are 37.2°, whereas the central anthryl group gives angles of 65.8° and 74.2° with the peripheral anthryl rings. Aromatic C–C distances range from 1.322(8) Å to 1.464(8) Å, averaging 1.393(8) Å. N–C Bond distances average 1.396(6) Å. Maximum deviation from ideal geometry is found in the diazolidine ring with bond angles of 106.2(4), 103.2(3), 103.0(3), 103.9(4), and 105.1(4)° for C(19)–N(3)–C(20), N(3)–

C(20)–N(2), C(20)–N(2)–C(18), N(2)–C(18)–C(19), and C(18)–C(19)–N(3), respectively.

Protonation Behavior and Anion Coordination. Protonation behavior for **L¹**, **L²**, and **L³** has been studied in MeCN/H_2O (70:30 *v*/*v*) because of their insolubility in other solvents such as H_2O, dioxane/H_2O, or DMSO/H_2O over a wide pH range at working concentrations. Compounds **L¹** and **L³** contain four and **L²** five protonation sites due to the presence of amino groups, and they behave as tetra- (**L¹**, **L³**) and pentaprotic (**L²**) bases (*Table 2*). The protonation behavior is as expected and can be rationalized, bearing in mind electrostatic concepts. The first protonation constants of **L¹**, **L²**, and **L³** are similar due to the structural similarity. The basicity behavior is only slightly reduced in the second protonation step. The third protonation of **L¹** and **L³** has a lower log *K* value than that of **L²**, as expected bearing in mind that the third protonation in **L¹** or **L³** takes place near one already protonated N-atom, whereas the third protonation in **L²** can take place between unprotonated amino groups. A similar effect is observed for the forth protonation process of **L¹** and **L³** ($\log K_4 - \log K_3 = 4.96$ and 2.57 for **L¹** and **L³**, resp.) for which the protons have to be placed between two adjacent ammonium groups. In contrast, for **L²** the forth protonation should take place next to only one ammonium group ($\log K_4 - \log K_3 = 6.89$). Additionally, the last protonation of **L³** has a lower log *K* value than that of **L¹** due to the geometrical structure of the diazolidine ring that imposes the two central N-atoms to be closer than in the more flexible of molecule **L¹**.

Table 2. *Stepwise Protonation Constants* (log *K*) *of* **L¹**, **L²**, *and* **L³** *Determined in MeCN/H_2O 70:30* v/v *at 298.1 K in 0.1*M *Tetrabutylammonium Perchlorate*

Reaction[a])	log K[b])		
	L¹	**L²**	**L³**
$L + H \rightleftharpoons HL$	9.84(3)	9.88(1)	10.15(1)
$L + 2\,H \rightleftharpoons H_2L$	19.02(2)	19.39(1)	19.24(1)
$L + 3\,H \rightleftharpoons H_3L$	26.38(3)	27.87(1)	25.85(2)
$L + 4\,H \rightleftharpoons H_4L$	31.34(3)	34.76(1)	28.42(4)
$L + 5\,H \rightleftharpoons H_5L$		39.25(2)	
$L + H \rightleftharpoons HL$	9.84	9.88	10.15
$HL + H \rightleftharpoons H_2L$	9.18	9.51	9.09
$H_2L + H \rightleftharpoons H_3L$	7.36	8.48	6.61
$H_3L + H \rightleftharpoons H_4L$	4.96	6.89	2.57
$H_4L + H \rightleftharpoons H_5L$		4.49	

[a]) Charges have been omitted for clarity. [b]) Values in parentheses are standard deviations on the last significant figure.

Anion-coordination investigations were carried out to determine the coordination ability against anions. Unfortunately, stability constants in the presence of ATP could not be determined due to the low solubility in MeCN/H_2O (70:30 *v*/*v*) of the ATP anion. Nevertheless, to determine the magnitude of the anion-cation interaction, potentiometric titrations were carried out in the presence of an equimolar mixture of **L²** and phosphate. The logarithms of the stability constants are shown in *Table 3*. Receptor **L²** forms complexes with phosphate over a wide pH range. The large difference

Table 3. *Logarithms of the Stability Constants of the Interaction of* $\mathbf{L}^2$ *with Sulfate and Phosphate in MeCN/H_2O 70 : 30* v/v (0.1M tetrabutylammonium perchlorate, 25°)

Reaction[a])	Sulfate[b])	Phosphate[b])[c])
$L + H + A \rightleftharpoons HLA$	13.06(2)	
$L + 2\,H + A \rightleftharpoons H_2LA$	22.61(2)	28.23(2)
$L + 3\,H + A \rightleftharpoons H_3LA$	31.61(2)	37.89(2)
$L + 4\,H + A \rightleftharpoons H_4LA$	38.11(2)	46.71(2)
$L + 5\,H + A \rightleftharpoons H_5LA$	44.03(1)	54.77(2)
$L + 6\,H + A \rightleftharpoons H_6LA$	47.29(2)	60.99(1)
$L + 7\,H + A \rightleftharpoons H_7LA$		64.76(3)
$HL + A \rightleftharpoons HLA$	3.18	
$H_2L + A \rightleftharpoons H_2LA$	3.22	8.84
$H_3L + A \rightleftharpoons H_3LA$	3.32	10.02
$H_4L + A \rightleftharpoons H_4LA$	3.33	11.95
$H_5L + A \rightleftharpoons H_5LA$	4.81	15.52
$H_5L + HA \rightleftharpoons H_6LA$	4.19	9.36
$H_5L + H_2A \rightleftharpoons H_7LA$		3.99

[a]) Charges have been omitted for clarity. [b]) Values in parentheses are the standard deviations in the last significant digit. [c]) Basicity constants of phosphate in MeCN/H_2O 70 : 30 *v/v* (0.1M tetrabutylammonium perchlorate, 25°): log $K_1 = 12.38(1)$, log $K_2 = 21.52\ (2)$, and log $K_3 = 25.80(1)$.

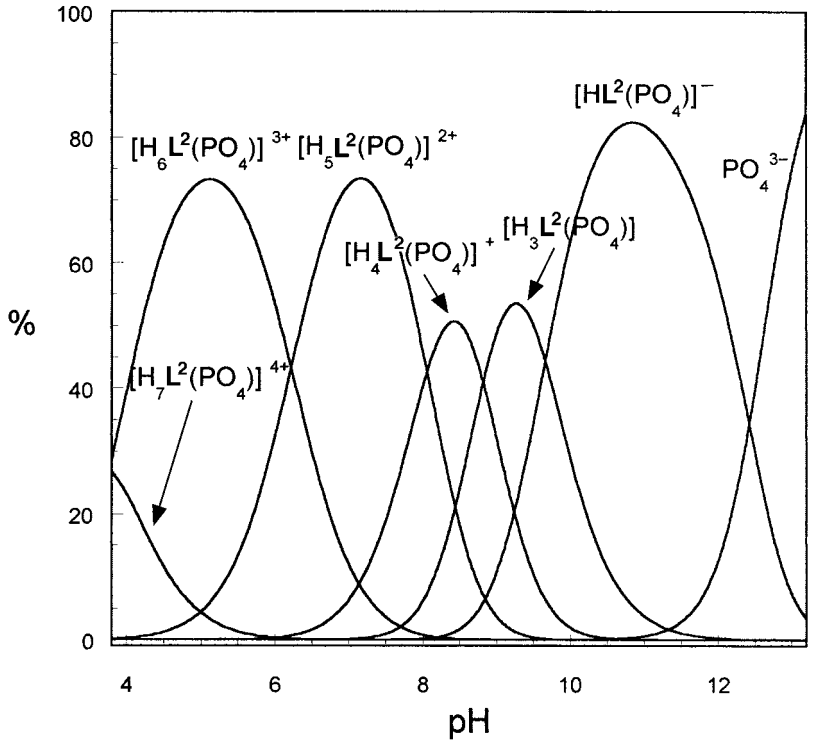


Fig. 2. *Distribution diagram of the* $\mathbf{L}^2$*-H^+-phosphate system in MeCN/H_2O 70 : 30* v/v

between the first protonation of the phosphate ($H^+ + PO_4^{3-} \rightleftharpoons HPO_4^{2-}$, $\log K_1 = 12.38$) and the last protonation of the free ligand ($H^+ + (H_4\mathbf{L^2})^{4+} \rightleftharpoons (H_5\mathbf{L^2})^{5+}$, $\log K = 4.49$) makes it difficult to assign which are the species involved in the formation of the $[\mathbf{L^2}H_jPO_4]^{j-3}$ complexes. At least two complexes must deal with the interaction with HPO_4^{2-} and $H_2PO_4^-$ species, taking into account that the complexes $[\mathbf{L^2}H_6PO_4]^{3+}$ and $[\mathbf{L^2}H_7PO_4]^{4+}$ exist. The distribution diagram of the species for the system L–H^+-phosphate is shown in *Fig. 2*.

Sulfate also forms $[\mathbf{L^2}H_jSO_4]^{j-2}$ complexes with receptor $\mathbf{L^2}$. The last protonation constant for $\mathbf{L^2}$ and the first protonation constant of the sulfate anion have a similar value, and, therefore, it can be argued that the species in the L–H^+-sulfate systems are related to the interaction of the dianion SO_4^{2-} with the $H_j(\mathbf{L^2})^{j+}$ cations. At least one complex, $[\mathbf{L^2}H_6SO_4]^{4+}$, involves the interaction of HSO_4^- with $(H_5\mathbf{L^2})^{5+}$.

The results obtained are in line with those obtained for the interaction of 1,15-diferrocenyl-2,5,8,11,14-pentaazapentadecane ($\mathbf{L^4}$; receptor similar to $\mathbf{L^2}$ but replacing anthryl by ferrocenyl groups) with phosphate [33]. $\mathbf{L^4}$ forms $[\mathbf{L^4}H_3PO_4]$, $[\mathbf{L^4}H_4PO_4]^+$, $[\mathbf{L^4}H_5PO_4]^{+2}$, and $[\mathbf{L^4}H_6PO_4]^{+3}$ complexes with slightly higher stability-constant values than those obtained for $\mathbf{L^2}$ and phosphate. For instance, logarithms of the stability constants for the processes $(H_3L)^{3+} + PO_4^{3-} \rightleftharpoons [LH_3PO_4]$, $(H_4L)^{4+} + PO_4^{3-} \rightleftharpoons [LH_4PO_4]^+$, and $(H_5L)^{5+} + PO_4^{3-} \rightleftharpoons [LH_5PO_4]^{2+}$ are 9.99, 14.7, and 18.28, respectively, for $L = \mathbf{L^4}$ and 10.02, 11.95, and 15.52 for $L = \mathbf{L^2}$. A similar trend was found for sulfate. This difference might be attributed to the use of a different medium; MeCN/H_2O (70:30 *v*/*v*) for $\mathbf{L^2}$ and THF/H_2O 70:30 (*v*/*v*) for $\mathbf{L^4}$. Bearing in mind the similarity between $\mathbf{L^2}$ and $\mathbf{L^4}$, both containing peripheral bulky groups, the larger permittivity in MeCN/H_2O than in THF/H_2O could account for this difference.

ATP Sensing. In a first step, anion-sensing investigations on receptors $\mathbf{L^1}$, $\mathbf{L^2}$, and $\mathbf{L^3}$ against bromide, phosphate, sulfate, ATP, ADP, and GMP have been performed as a function of pH in the same medium in which the potentiometric data were taken (MeCN/H_2O 70:30 *v*/*v*). Receptors $\mathbf{L^1}$ and $\mathbf{L^2}$ show typical absorption and emission bands due to the presence of two equivalent anthryl groups. In contrast, $\mathbf{L^3}$ displays more complex behavior attributed to the superposition of the spectra of two nonequivalent anthracene moieties. Emission intensities of both $\mathbf{L^1}$ and $\mathbf{L^2}$ show a large dependence on pH. There is a quenching of the emission intensity at basic pH whereas the emission intensity is higher at acidic pH. This behavior has already been reported for other anthryl-functionalized amines and attributed to the partial inhibition of the photoelectron-transfer process (from the lone pair of the amine to the photo-excited anthryl group) at acidic pH where protonation of the amino groups occurs [34]. The difference in emission behavior at acidic and basic pH is larger for $\mathbf{L^2}$ than for $\mathbf{L^1}$ (I(pH 3)/I(pH 10) = 12 for $\mathbf{L^1}$ and 30 for $\mathbf{L^2}$).

Fig. 3 shows the relative fluorescence intensity *vs.* pH for the $\mathbf{L^1}$–H^+–A and $\mathbf{L^2}$–H^+–A (A = bromide, phosphate, sulfate, ATP, ADP, or GMP) systems. At basic pH, there is no change in the emission properties of $\mathbf{L^2}$ upon addition of anions. At acidic pH, neither bromide, phosphate, sulfate, ADP, nor GMP modify significantly the emission behavior of $\mathbf{L^2}$. In contrast, in the presence of ATP, there is substantial quenching of the emission intensity in a wide pH range with a maximum difference between $\mathbf{L^2}$ and the $\mathbf{L^2}$-ATP system at acidic pH. Similar behavior was found for the $\mathbf{L^1}$–H^+–ATP system (see *Fig. 3*,*a*). Although, unfortunately, we have been unable to

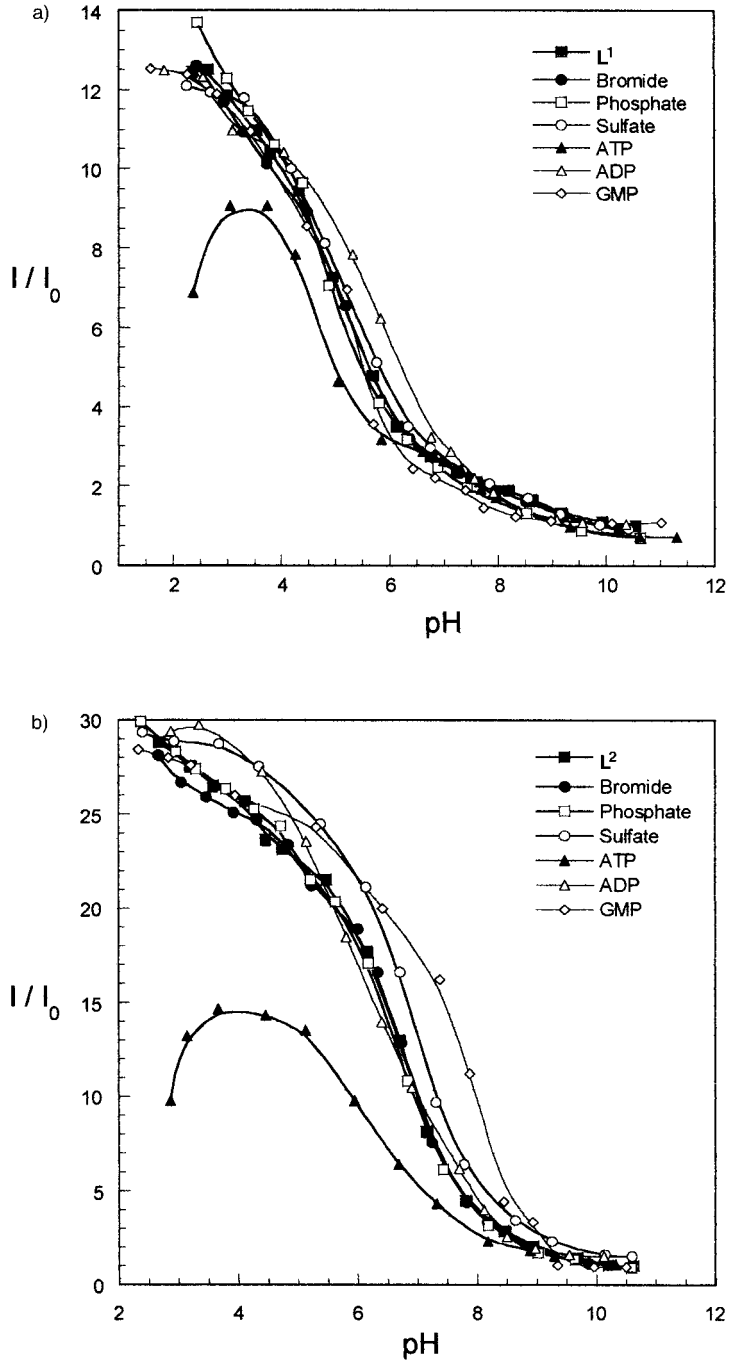


Fig. 3. *Fluorescence intensity* vs. *pH in MeCN/H_2O 70:30* v/v *for the* a) **L^1**-H^+-*A and* b) **L^2**-H^+-*A systems* (A = bromide, phosphate, sulfate, ATP, ADP, and GMP; $\lambda_{exc} = 368$ nm, $\lambda_{em} = 420$ nm)

determine stability constants for the interaction between the receptors and ATP, the larger fluorescence-emission difference found in the interaction of ATP with **L²** than with **L¹** may be attributed to a larger interaction between the pentamine **L²** and ATP than between the tetramine **L¹** and ATP [35].

The behavior of receptor **L³** is in contrast to that observed for **L¹** and **L²**. First, the difference in emission intensity at acidic and basic pH is very small ($I(\mathrm{pH}=10)/I(\mathrm{pH}=3)=1.6$), and, additionally, there is no fluorescence-emission change upon addition of anions. The existence of a diazolidine cycle that could impose some constraints on the polyammonium-anion interaction may account for this low fluorescent response upon guest binding.

The influence of different solvents or solvent mixtures on the emission properties of fluorescent receptors upon addition of target guests is not usually studied. It is known that the origin of the quenching or enhancement effects is very subtle and, in some cases, unpredictable due to the competition of several processes, namely changes in photoelectron-transfer or energy-transfer paths, changes in redox properties of the receptor, *etc*. In a similar manner, the solvent could modulate the type and strength of the anion-cation interaction and, therefore, have a direct effect on the fluorescence behavior of the anion-cation supermolecule.

Towards the analysis of this effect, we have carried out studies on the variation of the pH-fluorescence profiles of receptors **L¹** and **L²** upon addition of anions in H_2O. **L¹** and **L²** are not water-soluble at the concentration necessary to carry out potentiometric experiments but are soluble enough to carry out photochemical studies (ligand conc. $1.5\cdot10^{-4}$ M). In H_2O, the fluorescence intensity ($\lambda_{exc}=368$ nm, $\lambda_{em}=420$ nm) of **L¹** and **L²** is also pH-dependent. Again, the difference in emission at acidic and basic pH is larger for **L²** than for **L¹** ($I(\mathrm{pH}=3)/I(\mathrm{pH}=10)=5$ for **L¹** and 17 for **L²**). The emission behavior of **L¹** and **L²** in H_2O is quite similar with an increase from basic to acidic pH until *ca*. 3 and a further decrease from pH 3 to 1.5. Such a decrease has been observed in related chemosensors and has been attributed to an acid-catalyzed photochemically-induced decomposition [36].

The fluorescence behavior of **L¹** and **L²** does not change in the presence of bromide, phosphate, sulfate, and GMP. In contrast, ATP and ADP gave a significant response over a wide pH range [37][38]. There is a maximum enhancement of the emission intensity at pH of *ca*. 6 in the presence of ATP for both **L¹** and **L²**, and at pH of *ca*. 5.5 for **L¹** and at pH of *ca*. 7 for **L²** in the presence of ADP. This intensity enhancement is more remarkable for ATP than for ADP. *Fig. 4* shows the relative fluorescence intensity *vs*. pH for the $\mathbf{L^1}-H^+-A$ and $\mathbf{L^2}-H^+-A$ systems (A = bromide, phosphate, sulfate, ATP, ADP, or GMP).

A quite different response to ATP and ADP was found in H_2O or $MeCN/H_2O$ (compare *Figs. 3* and *4*). Polyamines are well-known to bind anions *via* favorable ammonium-anion electrostatic or H-bonding interactions. H-Bonding between the ATP or ADP and the N-atoms attached to the anthrylmethyl groups is expected to result in a reduction of the PET quenching mechanism and, therefore, an enhancement of the emission intensity would be expected. This H-bonding interaction is most likely responsible for the enhancement in H_2O at neutral pH (see *Fig. 4*) in the presence of those anions. In contrast, anion-cation electrostatic interactions are presumably the type of interaction responsible for the quenching observed for ATP at acidic pH in

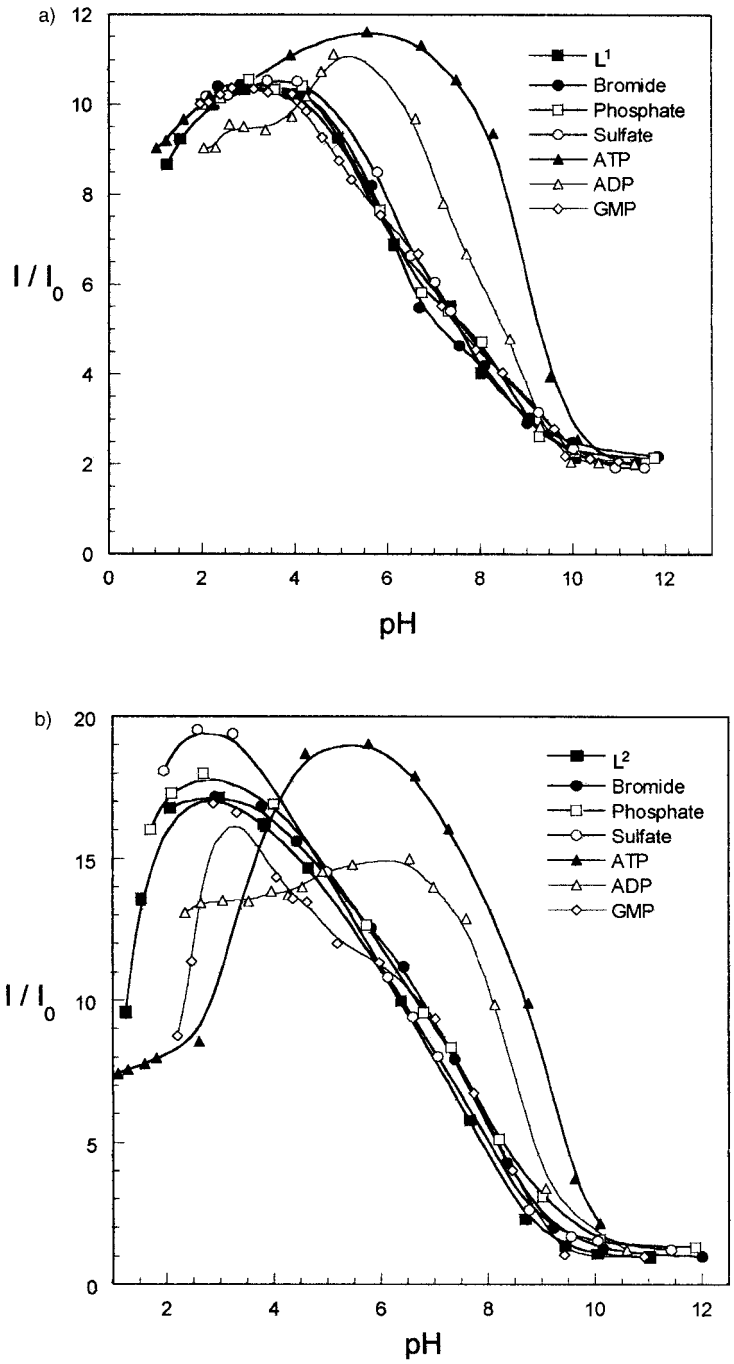


Fig. 4. *Fluorescence intensity* vs. *pH in* H_2O *for the* a) $\mathbf{L^1}$-H^+-*A and* b) $\mathbf{L^2}$-H^+-*A systems* (A = bromide, phosphate, sulfate, ATP, ADP, and GMP; $\lambda_{exc} = 368$ nm, $\lambda_{em} = 420$ nm)

$MeCN/H_2O$. Additionally, the reduction of the dielectric constant in $MeCN/H_2O$ when compared with H_2O would lead to larger electrostatic anion-cation interactions favoring energy-transfer paths or π-staking binding modes that would also lead to quenching of the fluorescence.

Conclusions. – It could be concluded that polyamines functionalized with fluorescent anthryl groups **L¹** and **L²** are good candidates for the sensing of ATP in $MeCN/H_2O$ based on fluorescence measurements. Additionally, the use of H_2O leads to an enhancement in the fluorescence intensity at neutral pH in the presence of both ATP and ADP.

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Experimental Part

Physical Measurements. Potentiometric titrations were carried out in $MeCN/H_2O$ (70:30 *v/v*, 0.1M tetrabutylammonium perchlorate, 25°) for **L¹** and **L²**, in a reaction vessel water-thermostatted at $25.0° \pm 0.1°$ under N_2. The titrant was added by a *Crison Microburette 2031*. The potentiometric measurements were made with a *Crison 2002* pH-meter and a combined glass electrode. A PC automatically controlled the titration system. The electrode was calibrated as a H^+ conc. prove by titration of well-known amounts of HCl with CO_2-free KOH soln. and by determining the equiv. point by *Gran*'s method [39], which gives the standard potential E'^0 and the ionic product of H_2O ($K'_w = [H^+][OH^-]$). The computer program SUPERQUAD [40] was used to calculate the protonation and stability constants. The titration curves for each system (*ca.* 250 experimental points corresponding to at least three titration curves, $pH = -\log[H^+]$ range investigated 2.5–10, conc. of the ligand and anions was *ca.* $1.2 \cdot 10^{-3}$ M) were treated either as a single set or as separated entities without significant variations in the values of the stability constants.

Fluorescence measurements were made on a *Edinburgh Analytical Instrument* with **L¹**, **L²**, and **L³** at a conc. of $1.5 \cdot 10^{-4}$ M in $MeCN/H_2O$ 70:30 *v/v* ($\lambda_{exc} = 368$ nm, $\lambda_{em} = 420$ nm for **L¹** and **L²**, and $\lambda_{exc} = 371$ nm, $\lambda_{em} = 448$ nm for **L³**) and H_2O ($\lambda_{exc} = 368$ nm, $\lambda_{em} = 420$ for **L¹** and **L²**, and $\lambda_{exc} = 371$ nm, $\lambda_{em} = 448$ for **L³**) in the presence of different anions (anion-to-ligand ratio 1:1) as a function of pH.

Synthesis of **L²**. Anthracene-9-carbaldehyde (1000 mg, 4.85 mmol) and tetraethylenpentamine (460 mg, 2.43 mmol) were heated to reflux in CH_2Cl_2 (20 ml) and over 4-Å molecular sieve for 4 h. The soln. was evaporated to dryness, dissolved in THF (30 ml) and the compound reduced with $LiAlH_4$ under reflux and Ar for 4 h. After careful addition of H_2O, the mixture was filtered, and the resulting soln. evaporated to dryness. The residue was dissolved in acetone, and 35% HCl was added dropwise until total precipitation of the polyamine in its chlorohydrate form. The solid was filtered off and dried. *1,15-Di(anthracen-9-yl)-2,5,8,11,14-pentaazapentadecane* (**L²**; 1000 mg, 60.3%). ^{1}H-NMR ($CDCl_3$): 2.63 (*m*, 12 H); 2.90 (*t*, 4 H); 4.63 (*s*, 4 H); 7.45 (*m*, 8 H); 7.92 (*d*, 4 H); 8.30 (*t*, 6 H). ^{13}C-NMR ($CDCl_3$): 46.12, 49.76, 49.79, 50.17 (CH_2); 124.76, 125.48, 126.60, 127.71, 129.71, 130.83, 132.09, 132.33 ($C_{14}H_9$). MS: 642 ($[M + H + 2\,HCl]^+$), 570 ($[M + H]^+$), 380, 337, 294, 251, 207, 191. Anal. calc.: C 51.84, H 6.50, N 8.47; found: C 51.88, H 6.79, N 8.12.

Synthesis of 2-(Anthracen-9-yl)-1,3-bis(2-{[(anthracen-9-yl)methyl]amino}ethyl)-1,3-diazolidine (**L³**). Anthracene-9-carbaldehyde (1000 mg, 4.85 mmol) and triethylenetetramine hydrate (350 mg, 1.62 mmol) were heated under reflux in benzene (20 ml) with a *Dean-Stark* destillator for 2 h. The soln. was evaporated to dryness, and the residue dissolved in THF (25 ml) and reduced with an excess of $LiAlH_4$ under reflux for 2 h. After careful addition of small amounts of H_2O, the mixture was filtered, and the resulting soln. evaporated to dryness. Basic aq. soln. and CH_2Cl_2 were added, and the org. phase was dried ($MgSO_4$), filtered, and evaporated to dryness. The orange oil was recrystallized (CH_2Cl_2/hexane) to give an orange crystalline solid (2000 mg, 58%). ^{1}H-NMR ($CDCl_3$): 3.00 (*m*, 8 H); 3.55 (*m*, 2 H); 3.61 (*m*, 2 H); 3.85 (*m*, 4 H); 5.61 (*s*, 1 H); 7.40 (*m*, 12 H); 7.95 (*d*, 6 H); 8.28 (*d*, 4 H); 8.42 (*t*, 3 H); 8.90 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 52.87. 54.25, 61.91, 84.49 (CH); 123.52, 124.83, 125.06, 125.18, 125.30, 125.67, 126.38, 126.87, 128.18, 128.63, 128.80, 129.02, 129.11, 129.28, 129.80, 131.15, 134.13, 135.22 ($C_{14}H_9$). MS: 711, 549, 533, 492, 437, 391, 307, 281, 231, 218, 191, 154, 136. Anal. calc.: for C 79.49, H 5.98, N 7.11; found: C 79.79, H 6.13, N 7.16.

Structure Determination of $\mathbf{L^3}$. $C_{51}H_{46}N_4$, $M = 714.91$, monoclinic, space group $P2_1/c$, $a = 20.261(5)$, $b = 9.935(4)$, $c = 19.360(7)$ Å, $\beta = 103.05(2)^\circ$, $Z = 4$, $V = 3797(2)$ Å^3, $D_c = 1.25$ g cm^{-3}, λ(Mo-K$_\alpha$) = 0.71069 Å, $T = 296(2)$ K, μ(MoK$_\alpha$) = 0.073 mm^{-1}. Measurements were made with a *Siemens P4* diffractometer with graphite monochromated Mo-K$_\alpha$ radiation on a yellow crystal of $\mathbf{L^3}$, of dimensions $0.10 \cdot 0.35 \cdot 0.40$ mm. A total of 5131 reflections were collected of which 4948 were unique ($R_{int} = 0.0238$). *Lorentz* and polarization corrections were applied. The structure was solved by direct methods (SHELXTL) [41] and refined by full-matrix least-squares analysis on F^2 (SHELXTL). The refinement converged at $R1$ 0.082 ($F > 4\sigma(F)$) and $wR2$ 0.383 (all data). Largest peak and hole in the final difference map $+0.34$, -0.34 e Å^{-3}.

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