Synthesis, Photophysical Properties, and Complexation Behavior of Three New Luminescent Tetraaza-tetraoxamacrobicyclic Receptors

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Three luminescent receptors **1**–**3** have been synthesized by linking photo-active groups to a tetraaza-tetraoxamacrobicyclic subunit. These multicomponent species constitute a homogeneous series with identical binding subunits, where changes are made to the chromophore and to the spacers. The new compounds exhibit absorption spectra and luminescence properties in acetonitrile dominated by the photo-active components, perturbed by the presence of the nitrogens of the azacrown subunits. Although structurally similar, compounds **1**–**3** exhibit three qualitatively different photophysical properties: **2** emits from a pure π–π^* (^1L_a) level, **3** from both a charge-transfer (CT) level and from an excimeric species, and **1** exhibits emission from CT and ^1L_a levels. The luminescent quantum yields of **1**–**3** are significantly enhanced (up to two orders of magnitude) upon protonation, mainly as a consequence of the removal of the CT excited states from the compounds. Whereas Na^+ and K^+ are not complexed by the luminescent receptors, Ca^{2+} and Mg^{2+} are strongly complexed in a 1:1 fashion and significantly affect the luminescence properties. In particular, selectivity for Ca^{2+} is found. The results suggest that adduct formation is dominated by electrostatic interactions and that the spacers connecting the photo-active and the receptor subunits also play active roles in the stabilization of the adducts.

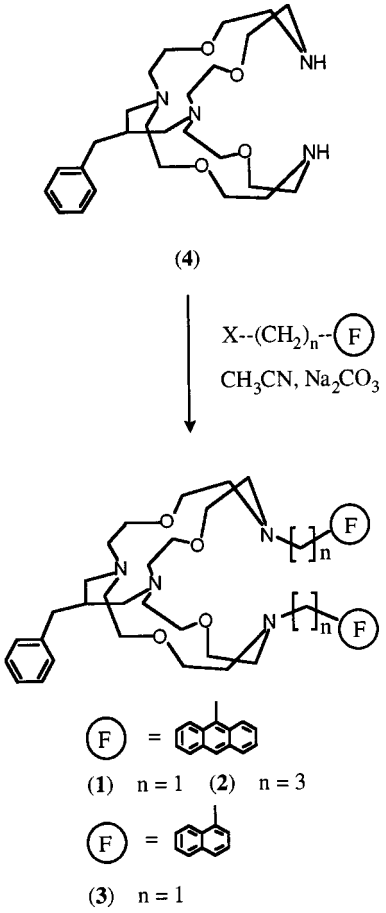
Introduction

Multicomponent species with luminescent and receptor subunits are currently at the center of extensive investigation owing to their possible applications as luminescent sensors for ions and/or small molecules[1] and as constituents of molecular machines and logic devices operating at the molecular level.[2]

These systems are supramolecular species in that they contain photo-active subunit(s), that is, the fluorophore(s), whose output is modified by the presence of suitable substrates complexed to the receptor subunit(s). The sensor function is guaranteed by the coupling of two integrated actions, the luminescence output change and the coordination of the substrate(s), each action is performed by the individual subunits.

We report here the synthesis of three new multicomponent receptors **1**−**3** (Scheme 1), with the same tetraaza-tetraoxamacrobicyclic subunit as a recognition site. A preliminary study carried out on compound **2** showed interesting multistability properties at the molecular level, triggered by a reversible modification of the receptor upon protonation and evidenced by luminescence.[3]

The photophysical properties of compounds **1**−**3** in acetonitrile, as well as their complexation with protons, and alkali and alkaline earth metal cations, have been now thoroughly investigated. Receptors **1**−**3** constitute a homogeneous series in which only the nature of the photo-active and spacer subunits varies. Their considerably different be-



Scheme 1. Synthesis of receptors **1**−**3**

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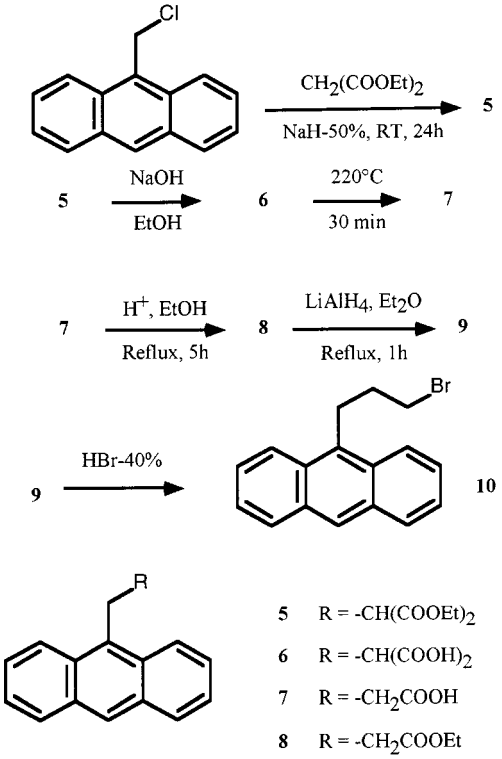
havior, discussed in this paper, illustrates the versatility of the multicomponent approach in selective luminescent sensor design.

Results and Discussion

Synthesis

Receptors **1**−**3** were synthesized by alkylation of the tetraaza-tetraoxamacrobicyclic bis-amine **4**[4] with commercially available 9-chloromethylanthracene and 1-chloromethylnaphthalene for **1** and **3**, respectively, while **2** required 9-(3-bromopropyl)anthracene **(10)** prepared by modification of known procedures.[5] All reactions were carried out in acetonitrile at reflux and in the presence of solid Na_2CO_3 as base, and all products were purified by column chromatography (Schemes 1 and 2). Details are given in the Experimental Section.



Scheme 2. Synthesis of 9-(3-bromopropyl)anthracene

Absorption Spectra and Luminescence Properties of the Multicomponent Species 1−3

Absorption Spectra

The absorption spectra of the anthracene-containing species **1** and **2** in acetonitrile (Figure 1, Table 1) are similar and are dominated by the anthracene subunits. At relatively low energies, the typical structured anthracene band is present as are peaks for both the compounds around 360 nm, with moderate intensity ($\varepsilon \approx 10000$ м$^{-1}$ cm^{-1}). This peak is assigned to the $\pi \rightarrow \pi^*$ electronic transition, which populates the ^1L_a excited state.[6]

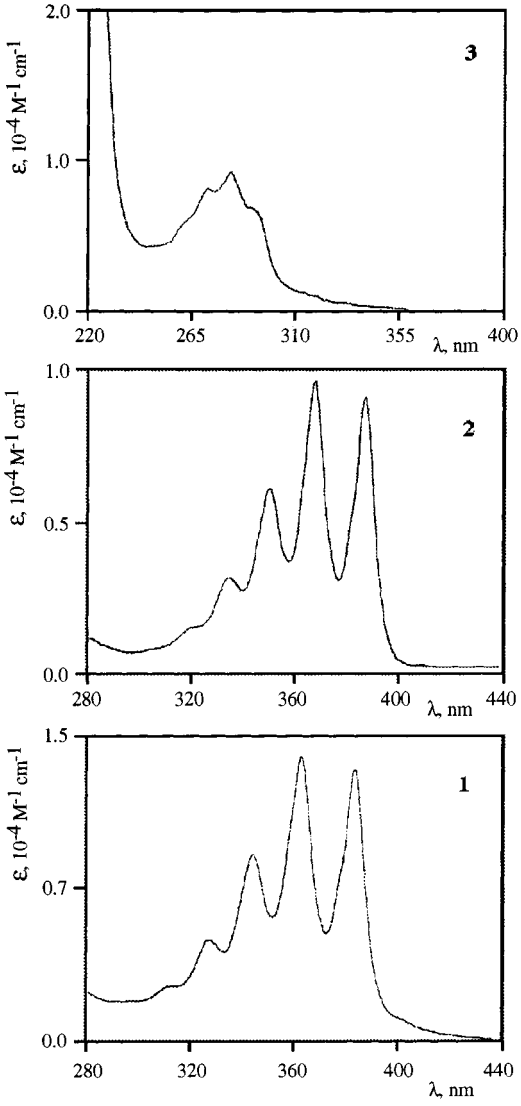


Figure 1. Absorption spectra in acetonitrile solution of **1**, **2**, and **3**

Table 1. Spectroscopic and photophysical data of the new compounds in acetonitrile

Compounds	Absorption λ_{max}, nm (ε, м$^{-1}$ cm^{-1})		Luminescence λ_{max}, nm	τ, ns	Φ
1	365	(13500)	419[a]	3.7	3.6×10^{-3}
1·(H$^+$)	371	(8500)	428	5.4	0.70
2	366	(9900)	414	4.7	0.03
2·(H$^+$)	366	(9900)	414	5.2	0.11
3	280	(8350)	358[a]	3.0	0.01
3·(H$^+$)	280	(8200)	330	9.5	0.26
Anthracene	375	(7200)	398	5.8	0.18
	338	(5100)			
Naphthalene	275	(4300)	327	9.3	0.17

[a] A weak emission band at lower energy is also present (see text). **n•(H$^+$)** represents the species totally protonated, without reference to the adduct stoichiometry.

The vibrational progression is due to the C=C stretching modes (about 1600 cm^{-1}) coupled with the electronic transitions. At higher energies a much more intense band (data

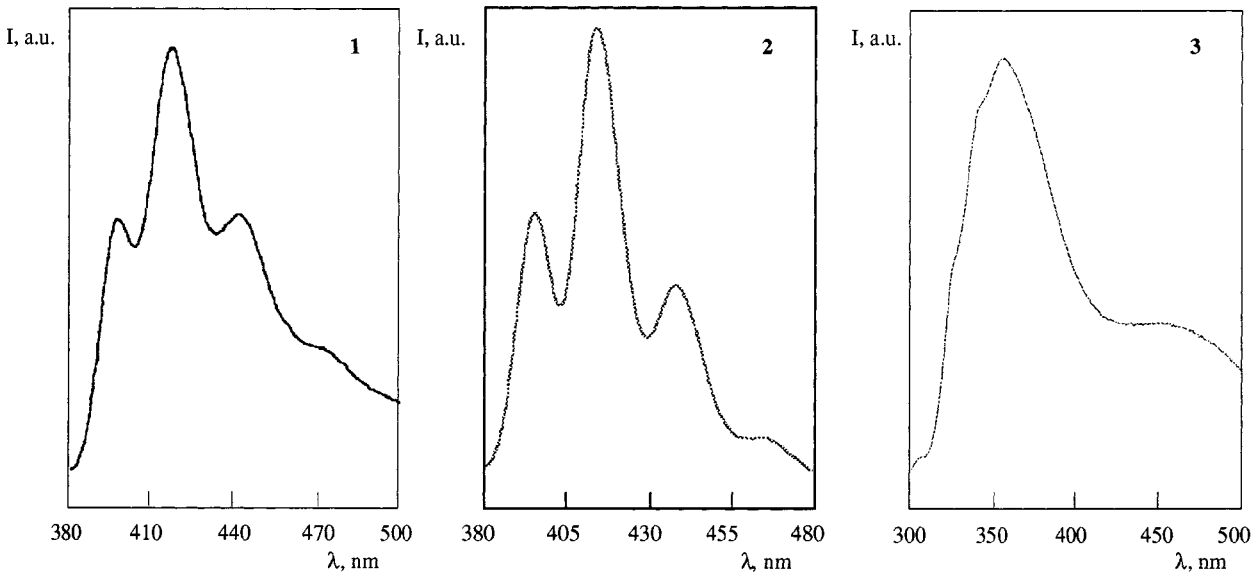


Figure 2. Emission spectra in acetonitrile solution of **1** (left), **2** (middle), and **3** (right); excitation wavelength is 260 nm in all the cases

not shown) is present in both the compounds ($\varepsilon \approx 10^5$ M^{-1} cm^{-1}), which peaks at about 250 nm. This band also arises from the anthracene moieties, and is attributed to the transition which populates the ^1B_b excited state.[6] The main difference between the absorption spectra of **1** and **2** is the presence for **1** of a weak absorption around 400 nm. This absorption is tentatively assigned to a charge-transfer (CT) transition from the azacrown nitrogens to the anthryl groups, in agreement with the expected electron-donor ability of the nitrogens of the polyazamacrocycle; similar CT bands have been reported in the literature for analogous compounds.[7] Such a band is absent in **2**, probably because the longer alkyl chains reduce the electronic interaction between donor and acceptor orbitals, so making the oscillator strength of the corresponding transition negligible.

The absorption spectrum of **3** (Figure 1, Table 1) exhibits the characteristic features of naphthalene derivatives. The structured band centered at 280 nm is assigned to the transition which populates the ^1L_a excited state, while the tail at lower energies arises from the transition populating the ^1L_b level.[6] A CT band analogous to that in the absorption spectrum of **1** is expected but is not clearly observed, probably because it is obscured by the ^1L_b band.

Luminescence Properties

The emission spectra of **1** and **2** in acetonitrile (Figure 2, Table 1) are dominated by the typical structured fluorescence of the ^1L_a excited state of anthracene derivatives.[6] However, interesting differences between the emission properties of **1** and **2** appear.

First of all, the luminescence quantum yields of the two compounds are significantly reduced with respect to the free anthracene ($\varphi = 0.18$ under the same experimental conditions) and are also quite different from one another — the quantum yield of **1** is one order of magnitude lower than the quantum yield of **2**. Moreover, the emission spectrum of **1** exhibits a tail towards the red, which is absent in **2**; this suggests the presence of a composite emission feature.

On the basis of literature data,[6] and on the structured shape of the emission spectrum, we assign the emission of **2** to a pure anthracene $\pi\rightarrow\pi^*$ (^1L_a) excited state, partially quenched with respect to the free anthracene by reductive electron transfer from the azacrown nitrogens to the excited chromophore. In the luminescence of **1**, the electron-transfer quenching (which leads to reduction of the $\pi\rightarrow\pi^*$ emission) is expected to be more effective because of the close proximity of the nitrogen quenchers. However, with **1** the CT state formed upon electron transfer is also significantly deactivated by a radiative process, and gives a CT contribution which dominates the low-energy tail of the emission spectrum. The two emissions give rise to a monoexponential luminescence lifetime. Moreover, the luminescence spectrum and lifetime are constant on changing excitation or emission wavelengths. These latter experimental results suggest that the CT and $\pi\rightarrow\pi^*$ states could be thermally equilibrated.[8]

The luminescence properties of **3** are significantly different from those of free naphthalene (Figure 2, Table 1); the emission spectrum is displaced to lower energies and is unstructured. Furthermore, a broad emission band which peaks at about 450 nm is also present. The emission of **3** at higher energy is assigned to a CT state between the proximate azacrown nitrogens and the naphthalene subunits. In contrast to **1**, the contribution of the $\pi\rightarrow\pi^*$ levels to the emission of **3** is negligible. The emission at about 450 nm is assigned to an excimer-type species, commonly observed in compounds with two aromatic hydrocarbon subunits which can move close to each other.[7b,9]

The energy level schemes for **1**, **2** and **3** are shown in Figure 3. It is interesting to note that, although structurally similar to one another, compounds **1**−**3** exhibit three qual-

itatively different photophysical properties: **2** emits from a pure $\pi\rightarrow\pi^*$ (^1L_a) level, **3** from both a CT level and from an excimeric species, and **1** exhibits emission from both CT and $\pi\rightarrow\pi^*$ (^1L_a) levels. However, the presence of an additional excimer-type emission cannot be totally excluded in the case of **1** and **2** because the larger quantum yields of the $\pi\rightarrow\pi^*$ emission in these compounds could make the detection of the excimeric emission difficult.

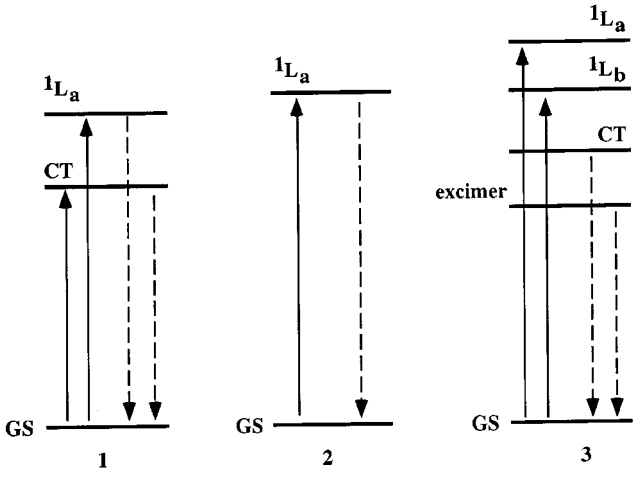


Figure 3. Energy level diagrams of the three complexes; GS is the ground state level; absorption (full lines) and radiative deactivation transitions (dashed lines) are also evidenced

Receptors 1−3 as Luminescent Sensors

Behavior in the Presence of Protons

As demonstrated above, CT excited states which involve basic sites affect the luminescence properties of **1**−**3** in acetonitrile solution. It was therefore expected that the luminescence properties of the studied species would be strongly influenced by the presence of substrates capable of interaction with the basic sites. The following experimental results confirmed this assumption. For the sake of simplicity protonation effects will be discussed first. In all the cases, we shall refer to the absorption and emission spectra of fully protonated receptors, which require an excess of acid.

Whereas the absorption spectra of **2** and **3** are not affected by the presence of trifluoroacetic acid, the absorption spectrum of **1** is significantly modified. The structured band assigned to the transition populating the ^1L_a level is slightly displayed to the red (Table 1) and the absorption tail at lower energies tends to disappear upon acid addition. Furthermore, several isosbestic points are maintained during the titration process. The spectral changes may be justified by the proposal that, upon protonation, the CT band is raised to very high energies; furthermore, the positive charges localized on the nitrogens closest to the chromophores in **1** induce a perturbation of the orbitals of anthracene, and decrease the ^1L_a energy (the π^* orbital is more stabilized than the π orbital by the added positive charge because the former is more polarizable). The latter effect is not observed for **2** and **3** probably because: (i) there is a larger separation (and smaller electronic coupling) between the nitrogen and anthracene orbitals in **2**, and (ii) the naphthalene orbitals of **3** are less polarizable than the anthracene orbitals of **1**.

The addition of trifluoroacetic acid causes strong modifications in the luminescence properties of all three receptors. For **1**, the red tail of the luminescence spectrum, attributed to the emission from the CT excited state, disappears and the maximum of the structured band is slightly displaced to a lower energy (Figure 4). Even more interestingly, the quantum yield is increased by a factor of 200 (Table 1).[10]

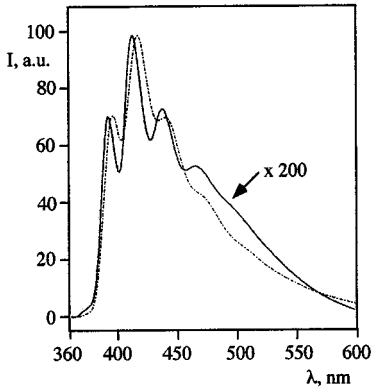


Figure 4. Normalized emission spectra of unprotonated (solid line) and protonated (dashed line) **1**

We assign this behavior to the disappearance of the CT level from the energy level scheme in Figure 3 (such a CT state is now at very high potentials). So, the emission of the protonated form of **1** can be assigned to a (unquenched) pure $\pi\rightarrow\pi^*$ fluorescence and, as a result, the quantum yield is enhanced. The close proximity of the positive charge perturbs the anthracene orbitals, and the ^1L_a state responsible for the emission is lowered, as discussed for the absorption spectral changes.

As far as **2** is concerned, protonation has no effect on the shape of the luminescence spectrum, but the quantum yield is increased by a factor of four. Also, in this case this effect is assigned to the disappearance of the electron-transfer quenching by the nitrogen lone pairs.

Significant changes also occur in the luminescence spectrum of **3** upon protonation (Figure 5, Table 1). In this case, the luminescence quantum yield is enhanced by a factor of 26, and, more interestingly, the luminescence is blue-shifted by 2300 cm^{-1}.

The disappearance upon protonation of the CT state, responsible for the high-energy emission of the nonprotonated compound, makes the $\pi\rightarrow\pi^*$ states of the naphthalene subunits the lowest-energy levels in the protonated species, and explains the changes in the luminescence properties. Excimer-type emission is also reduced, probably because, in the protonated form, the two naphthalene subunits are kept apart by electrostatic interactions of the (protonated) nitrogens.

It should be noted that the enhancement of the emission quantum yields of **1**−**3** is not paralleled by a similar increase in lifetimes upon protonation (Table 1). Indeed, pro-

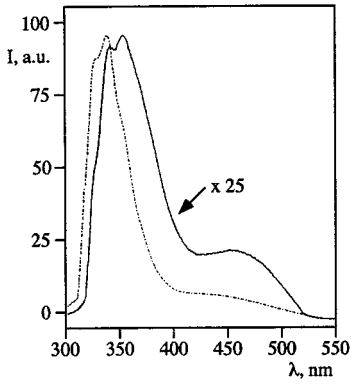


Figure 5. Normalized emission spectra of unprotonated (solid line) and protonated (dashed line) **3**

tonation may also cause changes in compound conformation and in chromophore excited-state dynamics, so modification of both radiationless and radiative rate constants could occur.

The trend of the acid titration, common to all the three compounds, deserves a final comment. The first equivalent of added acid has a very small or negligible effect on the emission intensity; only the successive acid addition significantly modifies the luminescence response . It can be reasonably assumed that the first acid equivalent is complexed by the "inner" nitrogens of the azacrown, which are far from the chromophore, thus the luminescence properties are affected to a lower extent.[11]

Successive protonations involve the nitrogens closest to the chromophores, and the effect is much larger. It should also be noted that, in all the cases, the end of titration is achieved upon addition of a number of proton equivalents larger than the number of protonable nitrogen sites. Indeed, the partially protonated species behaves as a weak base and this makes the complete protonation of the receptor more difficult.

Behavior in the Presence of Cations

Fluorimetric titration of **1**−**3** with Na^+, K^+, Mg^{2+} and Ca^{2+} cations as their perchlorate salts has been carried out. Titration curves have been analyzed with the nonlinear Equation (1) developed by Valeur and co-workers for 1:1 adducts.[13]

$$X = X_0 + \frac{X_{lim} - X_0}{2C_0}\left[C_0 + C_M + \frac{1}{Ka} - \sqrt{\left(C_0 + C_M + \frac{1}{Ka}\right)^2 - 4C_0C_M}\right]$$

In this Equation, C_o is the concentration of the ligand, C_m is the concentration of the added salt, and X_o and X are the fluorescence intensities in the absence and presence of the added salt, respectively. For better calculations, X_{lim} was left as a floating parameter.

The effects of the cations in solution, at the end of the titration, on the spectroscopic and photophysical properties of **1**−**3** are similar to those obtained by protonation (which was expected because protons and cations have the effect of "removing" the CT levels from the energy level schemes in Figure 3), so it will not be discussed in detail.

The titration results are shown in Table 2**.** An example of the titration curves and fittings are shown in Figure 6. It is interesting to note that the very good fit with Equation (1) indicates that the stoichiometry of the adducts is 1:1. This is as expected because the macrobicycles have a cleft in which cations may be accommodated and complexed, while each single ring is too small to host metal ions efficiently in acetonitrile.[3,14]

Table 2. Association constants in acetonitrile for 1:1 adducts

[a]	**1**	**2**	**3**
K^+	$< 100\ M^{-1}$	$< 100\ M^{-1}$	$< 100\ M^{-1}$
Na^+	$< 100\ M^{-1}$	$< 100\ M^{-1}$	$< 100\ M^{-1}$
Mg^{2+}	$200\ M^{-1}$	$21000\ M^{-1}$	$17000\ M^{-1}$
Ca^{2+}	$780\ M^{-1}$	$425000\ M^{-1}$	$736000\ M^{-1}$

[a] The concentrations of the compounds were 5×10^{-5} M. The correlation coefficients were in all cases ≥ 0.994. The salts used were perchlorates.

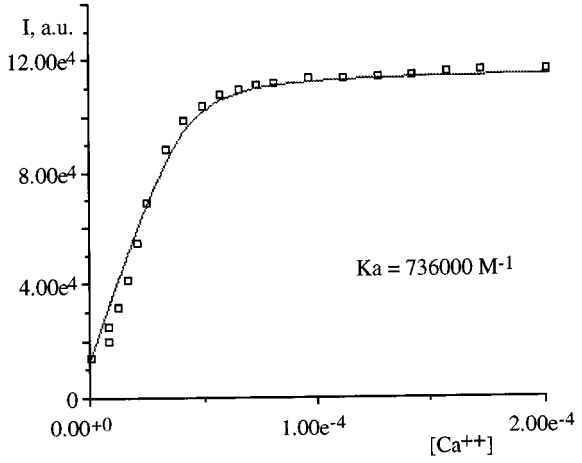


Figure 6. Luminescence output changes and best fitting of the data for **3** and Ca^{2+}; the fitting was obtained from Equation (1) (see text)

From the data in Table 2, it is clear that alkali ions are hardly complexed, while alkaline earth cations like Mg^{2+}, and especially Ca^{2+}, are suitable guests. The selectivity dependence of the complexation constants on the charge of the guests suggests that a major factor in adduct formation is the electrostatic interactions: nitrogen and oxygen lone pairs coordinate strongly to divalent cations. The magnesium ion is too small to take full advantage of multiple electrostatic interactions, and its association constants are much smaller than the corresponding ones for the larger calcium cation, which fits the cleft better. Different contact areas[15] between substrate and receptor in calcium and magnesium adducts are therefore responsible for the different association constants of the adducts. However, different solvation of Mg^{2+} and Ca^{2+} by acetonitrile could also contribute to the different values of the association constants.

The association constants of analogous adducts involving different hosts are also significantly different (Table 2), although the receptor subunit is identical for all the three species. In particular, association constants for **1** and **2**,

which also have the same chromophores, are quite different. This is a strong indication that for **1**−**3** the spacer between the photo-active and the receptor subunits also influences the formation of the adduct. Several factors could explain this: (i) when the spacer is a simple methylene group, as in **1**, the two anthracene subunits could sterically hinder each other from the ideal receptor conformation for adduct formation and destabilize the adduct; the propylene chains in **2** reduce such a steric crowding and therefore, enhance the association constants; (ii) the propylene chains in **2** may also reduce the electron-withdrawing effect of the anthracene on the nitrogens, and allow a stronger interaction between nitrogen lone pairs in **2** and substrate compared with **1**; (iii) intramolecular hydrogen bonding in **1** between the fluorophore(s) and the polyazacrowns may possibly be present, as demonstrated recently in a similar luminescent receptor containing an anthracene subunit as the photoactive site.[1p] This hydrogen bonding significantly reduces the cation complexation strength by making some oxygen lone pairs unavailable (or available at the cost of a significant nuclear reorganization energy), and should be much more effective in **1** than in **2** because of the close proximity of the partners in the former compound. This confirms that the excellent luminescent potential of the aromatic hydrocarbons could be negatively counterbalanced by their potential to interfere with complexation, and this effect should be considered in the design of luminescent sensors.

Significantly higher association constants for alkaline-earth cations are also found for **3** than for **1**, in which the same spacer is present (Table 2, Scheme 1). Steric constrains and hydrogen bonding are significantly reduced in **3**, and therefore this luminophore/receptor species resembles **2** rather than **1** as far as its complexation ability is concerned. The balance of: (i) the entity of the luminescent output changes upon complexation/protonation, and (ii) the association constants, indicate that **3** is the most efficient luminescence sensor for Ca^{2+} ions among the three systems studied here. Interestingly, **3** is also the receptor for which the highest selectivity for Ca^{2+} versus Mg^{2+} is found. In the light of the interest of fluorescent indicators for Ca^{2+} detection in vivo,[16] compound **3** looks quite promising for possible application upon suitable functionalization of the remote phenyl ring for solubilization in aqueous solution.[17]

Conclusion

Three luminescent receptors **1**−**3** have been synthesized and their absorption and photophysical properties in acetonitrile solution and in the presence of protons and some alkali and alkaline-earth metal cations have been investigated. In spite of the similarity in the structural formulas, compounds **1**−**3** show quite interesting differences in their photophysical properties. In all the cases, protonation strongly affects the luminescence properties by the removal from the excited-state energy level of charge-transfer states which dominate the photophysics of the unprotonated species. Alkaline-earth metal ions are selectively complexed by **1**−**3**. The differences in the association constants of the adducts indicate that the spacer between the luminescent and receptor subunits may play an active role, not only in transmitting the information from the receptor to the luminophore, but also in the stabilization of the adduct. The potential of the luminophores to interfere with the complexation process may reduce the complexation ability of the species.

Experimental Section

General Remarks: Solvents were purified by standard methods and dried if necessary. All commercially available reagents were used as received. TLC was carried out on silica gel 60-F_{254}. Column chromatography was carried out on silica gel Si 60, mesh size 0.040−0.063 mm (Merck, Darmstadt, Germany). − ^{1}H NMR (300 MHz) spectra were recorded with a Bruker AC 300 spectrometer. − Elemental analyses were performed by the Departmental Service of Microanalysis (University of Milan). − Melting points (uncorrected) were determined with a capillary melting point apparatus Buchi SMP-20. − Absorption spectra were obtained with a Kontron Uvikon 860 spectrophotometer. − For luminescence spectra and lifetimes, a Jobin-Yvon/Spex Fluoromax 2 spectrofluorimeter and an Edinburgh FL-900 single-photon-counting spectrometer, respectively, were used. Luminescence quantum yields were obtained by the optically dilute method[18] with anthracene in deoxygenated ethanol as standard ($\Phi = 0.27$).[19] Experimental uncertainties are as follows: absorption spectra: ±2 nm; extinction coefficients: 10%; luminescence maxima: ±2 nm; luminescence lifetimes: 10%; quantum yields: 20%.

7,19-Bis(anthracenylmethyl)-1,7,13,19-tetraaza-26-Benzyl-4,10,16,22-tetraoxabicyclo[12.12.3]heptacosane (1): Solid Na_2CO_3 (0.5 g, 4.7 mmol) was added to a solution of the bisamine **4** (0.45 g, 0.94 mmol) and 9-chloromethylanthracene (0.43 g, 1.88 mmol) in CH_3CN (60 mL), and the resulting suspension was stirred at reflux for 6 days. The reaction mixture was allowed to cool to room temp., filtered through Celite and the solvent evaporated to afford 0.85 g of the crude product, as a yellow viscous oil. Purification by column chromatography (SiO_2, CH_2Cl_2/CH_3OH = 90:10 v/v) afforded 0.42 g (52%) of pure **1** as a yellow solid. − M.p. 120−122 °C (dec.) − ^{1}H NMR ($CDCl_3$): δ = 1.80−2.00 (m, 1 H, C*H*), 2.10−3.15 (m, 20 H, CH_2N), 3.15−3.90 (m, 18 H, CH_2O and CH_2Ph), 4.60 (s, 4 H, CH_2-Anthr.), 7.12−7.39 (m, 5 H, C_6H_5), 7.39−7.60 (m, 8 H, H^2, H^3, H^6, H^7-Anthr.), 8.00 (d, J = 8.5 Hz, 4 H, H^4, H^5-Anthr.), 8.41 (s, 2 H, H^{10}-Anthr.), 8.43−8.65 (m, 4 H, H^1, H^8-Anthr.). − MS-FAB(+); *m*/*z*: 882 [M + Na^+], 859 [M^+] calcd. for $C_{56}H_{66}N_4O_4$ 859. − $C_{56}H_{66}N_4O_4$ (859.16): calcd. C 78.28, H 7.76, N 6.52; found C 78.60, H 7.90, N 6.45.

7,19-Bis-γ-(9-anthryl)propyl-1,7,13,19-tetraaza-26-benzyl-4,10,16,22-tetraoxabicyclo[12.12.3]heptacosane (2): Solid Na_2CO_3 (0.24 g, 2.30 mmol) was added to a solution of the bisamine **4** (0.22 g, 0.46 mmol) and 9-(3-bromopropyl)anthracene (**10**; 0.28 g, 0.92 mmol) in CH_3CN (50 mL), and the resulting suspension was stirred at reflux for six days. The reaction mixture was allowed to cool to room temp., filtered through Celite and the solvent evaporated to afford 0.48 g of the crude product, as a yellow viscous oil. Purification by column chromatography (SiO_2, CH_2Cl_2/CH_3OH = 90:10 v/v) afforded 0.23 g (54%) of pure **2** as a yellow solid. − M.p. 111−113 °C (dec.) − ^{1}H NMR ($CDCl_3$): δ = 1.80−2.00 (m, 1 H,

C*H*), 2.20−3.10 (m, 28 H, CH_2N and CH_2CH$_2$), 3.30−3.80 (m, 22 H, CH_2O, CH_2Ph and CH_2-Anthr.), 7.01−7.22 (m, 5 H, C$_6H_5$), 7.30−7.53 (m, 8 H, H^2, H^3, H^6, H^7-Anthr.), 7.96 (d, J = 8.3 Hz, 4 H, H^4, H^5-Anthr.), 8.25 (d, J = 8.6 Hz, 4 H, H^1, H^8-Anthr.), 8.30 (s, 2 H, H^{10}-Anthr.). − MS-FAB(+); *m/z*: 937 [M + Na$^+$], 915 [M + 1]$^+$ calcd. for $C_{60}H_{74}N_4O_4$ 915. − $C_{60}H_{74}N_4O_4$ (915.27): calcd. C 78.72, H 8.16, N 6.12; found C 78.10, H 8.20, N 6.00.

1,7,13,19-Tetraaza-26-benzyl-7,19-bis(naphthylmethyl)-4,10,16,22-tetraoxabicyclo[12.12.3]heptacosane (3): Solid Na_2CO_3 (0.35 g, 3.30 mmol) was added to a solution of the bisamine **4** (0.32 g, 0.66 mmol) and 1-chloromethylnaphthalene (0.26 g, 1.32 mmol) in CH_3CN (30 mL), and the resulting suspension was stirred at reflux for six days. The reaction mixture was allowed to cool to room temp., filtered through Celite and the solvent evaporated to afford 0.65 g of the crude product, as a yellow viscous oil. Purification by column chromatography (SiO_2, $CHCl_3/CH_3OH$ = 90:10 v/v) afforded 0.17 g (34%) of pure **3** as a yellow viscous oil. − ^{1}H NMR ($CDCl_3$): δ = 1.80−2.00 (m, 1 H, C*H*), 2.25−3.05 (m, 20 H, CH_2N), 3.20−3.65 (m, 18 H, CH_2O and CH_2Ph), 4.05 (s, 4 H, CH_2-Napth.), 7.14−7.31 (m, 5 H, C$_6H_5$), 7.37−7.55 (m, 8 H, H^2, H^3, H^6, H^7-Napth.), 7.76 (d, J = 8.1 Hz, 2 H, H^4-Napth.), 7.84 (d, J = 8.1 Hz, 2 H, H^5-Napth.), 8.30 (d, J = 7.8, 1 H, H^8-Napth.), 8.39 (d, J = 7.8 Hz, 1 H, ^{8}-Napth.). − MS-FAB(+); *m/z*: 781 [M + Na]$^+$, 759 [M + 1]$^+$ calcd. for $C_{48}H_{62}N_4O_4$ 758. − $C_{48}H_{62}N_4O_4$ (759.04): calcd. C 75.94, H 8.25, N 7.38; found C 75.73, H 8.05, N 7.12.

Diethyl 9-Anthrylmethylmalonate (5): A solution of diethyl malonate (1.42 g, 8.82 mmol) in dry THF (25 mL) was slowly added to a stirred suspension of NaH (50% in mineral oil; 0.43 g, 8.82 mmol) in dry THF (25 mL) at 0 °C under a nitrogen atmosphere. The reaction mixture was maintained at room temperature for 1 h, in order to promote the anion formation, then cooled to 0 °C and a solution of 9-chloromethylanthracene (2.00 g, 8.82 mmol) in THF (10 mL) was quickly added. The reaction mixture was kept at room temp. under magnetic stirring for 15 h. The solvent was evaporated in vacuo, the residue was taken up with H_2O (80 mL) and CH_2Cl_2 (80 mL) in a separating funnel and acidified with aqueous 10% HCl. The organic phase was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic phase was dried over $MgSO_4$ and the solvent evaporated to afford 3.00 g of an orange thick oil. Purification by column chromatography (SiO_2, CH_2Cl_2) afforded 2.23 g (72%) of pure **5** as a yellow solid. − M.p. 81−83 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.05 (t, J = 7.1 Hz, 6 H, CH_3), 3.87 (t, J = 7.4 Hz, 1 H, C*H*), 3.96−4.13 (m, 4 H, CH_2CH$_3$), 4.30 (d, J = 7.4 Hz, 2 H, CH_2CH), 7.41−7.55 (m, 4 H, H^2, H^3, H^6, H^7-Anthr.), 8.00 (d, J = 8.1 Hz, 2 H, H^4, H^5-Anthr.), 8.27 (d, J = 8.8 Hz, 2 H, H^1, H^8-Anthr.), 8.38 (s, 1 H, H^{10}-Anthr.). − $C_{22}H_{22}O_4$ (350.41): calcd. C 75.40, H 6.34; found C 75.25, H 6.28.

9-Anthrylmethylmalonic Acid (6): A solution of **5** (2.11 g, 6.02 mmol) and NaOH (0.96 g, 24.08 mmol) in 96% EtOH (50 mL) was stirred at room temp. for 30 min. The precipitated sodium salt was filtered off, washed with EtOH (20 mL) and dissolved in H_2O (10 mL) . The aqueous phase was acidified with 10% HCl, and the precipitate was filtered off and dried for 3 h (0.1 Torr, 40 °C) to afford 1.60 g (90%) of pure **6** as a yellow solid. − M.p. 209−210 °C. − ^{1}H NMR ([D$_6$]DMSO): δ = 3.66 (t, J = 7.4 Hz, 1 H, C*H*), 4.15 (d, J = 7.4 Hz, 2 H, CH_2), 7.49−7.60 (m, 4 H, H^2, H^3, H^6, H^7-Anthr.), 8.10 (d, J = 7.8 Hz, 2 H, H^4, H^5-Anthr.), 8.32 (d, J = 8.6 Hz, 2 H, H^1, H^8-Anthr.), 8.54 (s, 1 H, H^{10}-Anthr.), 12.8 (br. s, 2 H, O*H*, D$_2$O exchange). − $C_{18}H_{14}O_4$ (294.30): calcd. C 73.45, H 4.80; found C 73.60, H 4.58.

3-(9-Anthryl)propionic Acid (7): A sample of **6** (1.50 g, 5.10 mmol) was decarboxylated at 220 °C for 20 min under an inert atmosphere. After cooling to room temp. the residue was taken up as a suspension with aqueous 10% Na_2CO_3, acidified with aqueous 10% HCl and the precipitate was filtered off and dried for 3 h (0.1 Torr, 40 °C) to afford 1.14 g (89%) of pure **7** as a yellow solid. − M.p. 194−195 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.81−2.84 (m, 2 H, CH_2COOH), 3.88−4.15 (m, 2 H, CH_2-Anthr.), 7.44−7.58 (m, 4 H, H^2, H^3, H^6, H^7-Anthr.), 8.10 (d, J = 7.8 Hz, 2 H, H^4, H^5-Anthr.), 8.26 (d, J = 8.8 Hz, 2 H, H^1, H^8-Anthr.), 8.38 (s, 1 H, H^{10}-Anthr.). − $C_{17}H_{14}O_2$ (250.30): calcd. C 81.57, H 5.65; found C 81.21, H 5.52.

Ethyl 3-(9-Anthryl)propionate (8): A solution of **7** (1.00 g, 4.00 mmol) in absolute ethanol (50 mL) with a few drops of concentrated sulfuric acid was heated at reflux for 5 h. After cooling to room temp. the solvent was evaporated, and the residue was transferred into a separating funnel with CH_2Cl_2 (50 mL) and washed with H_2O (2 × 15 mL). Evaporation of the solvent afforded a brown thick oil residue which was purified by crystallization with EtOH to afford 1.04 g (94%) of pure **8** as a yellow solid. − M.p. 64.5−65.5 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.25 (t, J = 7.1 Hz, 3 H, CH_3), 2.74−2.80 (m, 2 H, CH_2COOH), 3.91−4.00 (m, 2 H, CH$_2$-Anthr.), 4.20 (q, J = 7.1 Hz, 2 H, CH_2CH$_3$), 7.43−7.56 (m, 4 H, H^2, H^3, H^6, H^7-Anthr.), 8.00 (d, J = 8.1 Hz, 2 H, H^4, H^5-Anthr.), 8.27 (d, J = 8.8 Hz, 2 H, H^1, H^8-Anthr.), 8.37 (s, 1 H, H^{10}-Anthr.). − $C_{19}H_{18}O_2$ (278.35): calcd. C 81.97, H 6.53; found C 81.56, H 6.42.

9-(3-Hydroxypropyl)anthracene (9): A solution of **8** (0.80 g, 2.87 mmol) in dry Et_2O (25 mL) was slowly added to a stirred suspension of $LiAlH_4$ (0.54 g, 14.35 mmol) in dry Et_2O (25 mL) under an inert atmosphere. The reaction mixture was refluxed for 1 h, the excess of $LiAlH_4$ was carefully destroyed by addition of ethyl acetate, H_2O and aqueous 20% H_2SO_4 and the product was extracted with Et_2O (3 × 20 mL). The organic phase was dried over $MgSO_4$ and the solvent evaporated in vacuo to afford 0.64 g (94%) of pure **9** as a yellow solid. − M.p. 97.5−98.5 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.05−2.13 (m, 2 H, CH_2CH$_2$OH), 3.73 (t, J = 7.8 Hz, 2H, CH_2OH), 3.82 (t, J = 6.2 Hz, 2 H, CH_2-Anthr.), 4.80 (br. s, 1 H, O*H*, D$_2$O exchange), 7.42−7.53 (m, 4 H, H^2, H^3, H^6, H^7-Anthr.), 8.00 (d, J = 8.7 Hz, 2 H, H^4, H^5-Anthr.), 8.30 (d, J = 8.7 Hz, 2 H, H^1, H^8-Anthr.), 8.35 (s, 1 H, H^{10}-Anthr.). − $C_{17}H_{16}O$ (236.31): calcd. C 86.39, H 6.84; found C 86.10, H 6.68.

9-(3-Bromopropyl)anthracene (10): A solution of **9** (0.65 g, 2.75 mmol) in toluene (40 mL) was heated at reflux and stirred with aqueous 40% HBr (20 mL) for three days. The reaction mixture was cooled to room temp., transferred into a separating funnel and the organic phase separated. The aqueous phase was washed twice with toluene (20 mL). The combined organic phase was dried over $MgSO_4$ and evaporated to afford 0.9 g of dark thick oily residue. Purification by column chromatography (SiO_2, CH_2Cl_2) afforded 0.63 g (90%) of a green solid. − M.p. 87−88 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.31−2.42 (m, 2 H, CH_2CH$_2$Br), 3.60 (t, J = 6.4 Hz, 2 H, CH_2Br), 3.75−3.84 (m, 2 H, CH_2-Anthr.), 7.44−7.57 (m, 4 H, H^2, H^3, H^6, H^7-Anthr.), 8.01 (d, J = 8.2 Hz, 2 H, H^4, H^5-Anthr.), 8.30 (d, J = 8.8 Hz, 2 H, H^1, H^8-Anthr.), 8.35 (s, 1 H, H^{10}-Anthr.). − $C_{17}H_{15}Br$: calcd. C 68.23, H 5.06; found C 68.35, H 5.18.

Acknowledgments

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