Anthraceno-Cryptands: A New Class of Cation-Complexing Macrobicyclic Fluorophores

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Abstract: A new class of macrobicyclic and cation photosensitive compounds, the anthraceno-cryptands A_{nn} is described. In these ligands, the nitrogen lone pairs form intramolecular exciplexes with the anthracene ring, inducing a dual fluorescence emission (monomer type and exciplex) sensitive to the nature of the solvent. Thus, although A_{22} displays an intense triple exciplex emission in aprotic solvents, only a strong monomer-type emission is observed in methanol; this behavior is ascribed to hydrogen bonds between the solvent and the nitrogen lone pairs, which maintain an out–out conformation preventing exciplex formation. For A_{33}, the two nitrogens do not appear to be simultaneously involved in the solvation as a dual emission is recorded in methanol. Anthraceno-cryptands A_{nn} present drastic changes in fluorescence emission upon complexation by alkali-metal cations and protons; the fluorescence spectrum displays a hypsochromic shift and the quantum yield is enhanced. Comparison with the reference molecules, i.e., the macrocyclic "crowned" molecules (M_n) and 9,10-di-*n*-propylanthracene (R), shows that the spectroscopic response is related (i) to the ability of the cation to suppress the nitrogen–anthracene interaction (ii) to the distance separating the aromatic π cloud and the cation. Unusual interactions between heavy-metal cations (Tl^+ and Ag^+) and anthracene have been revealed: a novel complex with Tl^+ and an exciplex with Ag^+ have been described. The stoichiometry and the stability constants of the complexes with protons and metal cations (Tl^+ and Ag^+) have been determined by spectrometric titrations.

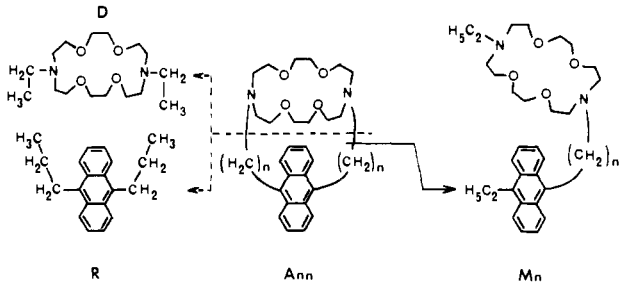
A number of new compounds whose electronic absorption and emission spectra and photochemical reactivity are markedly affected by the presence of cations or, conversely, whose complexing ability can be significantly changed by photochemical reactions have been synthesized and investigated during the last decade.[1a-q] This may lead to the conception of light-driven ionic molecular devices[2] that release or take up ionic species under irradiation; one may thus envisage the generation of reversible photoinduced ion pulses.

The fluorescence of aromatic hydrocarbons is most often quenched by inorganic salts,[3] but moderate fluorescence enhancements have been observed with the macrocyclic polyethers dibenzo-18-crown-6 and 1,8-naphtho-21-crown-6 in the presence of alkali-metal cations.[1c,e,f] Aromatic chromophores incorporated into ligands stronger than monocyclic ethers, such as cryptands, were expected to exhibit more pronounced photophysical responses in the presence of salt,[1q] and some of us reported a preliminary study[4] of two anthraceno-cryptands A_{nn} (n = 2, 3) (Scheme I) that combine the complexing ability of the cryptands[5] and the photophysical properties of the anthracene ring,[6] in particular an intense fluorescence emission; the latter can be quenched by formation of intramolecular exciplexes[7] between the aromatic ring and the nitrogen lone pairs and restored by protonation or metal cation complexation by the [18]-N_2O_4 macrocyclic moiety of compounds A_{nn}. In parallel, anthracenoyl cryptands were used as fluorescence probes for membrane studies.[8]

Along these lines, strong fluorescence enhancements were observed with 9-anthrylmethyl-substituted monoazacrown ethers[1j] and with 9,10-$(TMEDA)_2$-substituted anthracenes.[1o] Important modifications of fluorescence emission with heterocycles linked to azacrown ethers have been noted.[1m,n]

Another advantage of the anthraceno-cryptands is that they appear well suited to examination of the interaction of the nitrogen lone pairs with the aromatic ring in a given arrangement. Moreover, they were also designed to bring new insights into oriented proximity interactions between metal cations and π systems. Similar molecules appeared recently,[2] which can be used

Scheme I. Anthraceno-cryptands A_{nn} (n = 2, 3) and Their Monochromophoric R and Trichromophoric M_n Reference Compounds[a]



[a] The 1,10-diaza crown ether D is the complement to R.

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[∥] Chimie Physique et Electroanalyse.

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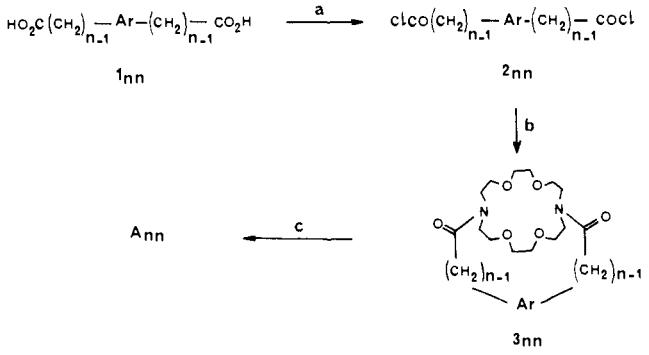
Scheme II. Synthesis of Anthraceno-cryptands A_{nn} (n = 2, 3; Ar ≡ 9,10-anthrylidene)[a]



[a] (a) $SOCl_2$; (b) [18]-N_2O_4 macrocycle, Et_3N, benzene; (c) (i) B_2H_6/THF, (ii) 6 N, HCl, (iii) $Et_4N^+OH^-$.

as light conversion systems (in the presence of lanthanoid cations) or as light-to-electron conversion devices (in a zinc porphyrin macrotricyclic skeleton).

We report here the results obtained on compounds A_{nn} since the preliminary communication;[4] some related work has been published separately.[7,9] We describe the synthesis, the structure determination, and the complexing ability of the ligands and the photophysical study in the absence and the presence of protons as well as of light- and heavy-metal cations. To characterize the rigid bicyclic skeleton effect of A_{nn}, several flexible reference compounds were also synthesized and studied: 9,10-di-*n*-propylanthracene (R), a monochromophoric model, 9,10-disubstituted anthracenes with a pendant [18]-N_2O_4 unit (M_n), and the *N,N'*-diethyl-[18]-N_2O_4 macrocycle (D) (Scheme I).

Results

Syntheses. (1) Cryptands A_{nn}. The generalized synthetic strategy for compounds A_{nn} is outlined in Scheme II. It follows a route that allows introduction of the two different bridges n = 2, n = 3 between the [18]-N_2O_4 unit and the anthracene ring.

The anthracenedicarboxylic acids $\mathbf{1}_{nn}$ were prepared according to published procedures[10] and subsequently transformed into the corresponding dichlorides $\mathbf{2}_{nn}$ with thionyl chloride[11] (75% yield). High dilution condensation of $\mathbf{2}_{nn}$ with the [18]-N_2O_4 macrocycle[12] affords the macrobicyclic diamides respectively $\mathbf{3}_{22}$ (mp >260 °C; 61% yield) and $\mathbf{3}_{33}$ (mp >260 °C; 65% yield). By reduction with diborane, the diamides give the anthraceno-cryptands as yellow solid materials A_{22} (mp >260 °C; 65% yield) and A_{33} (mp 215 °C; 77% yield).

(2) Reference Compounds. The preparation of 9,10-di-*n*-propylanthracene (R) is described in the literature.[13]

The synthesis of the new compounds M_n (n = 2, 3) is outlined in Scheme III.

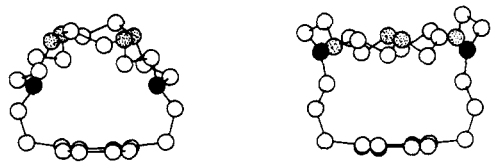


Figure 1. Crystal structures of the anthraceno-cryptands A_{22} (left) and A_{33} (right).

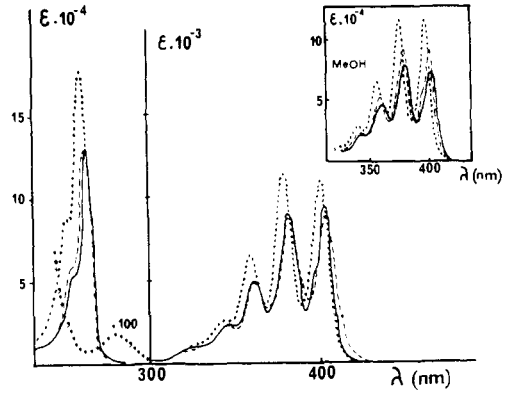


Figure 2. Electronic absorption spectra of A_{nn}, R, and of the *N,N'*-diethyl-diaza-18-crown-6 in methylcyclohexane (concentration, $<10^{-4}$) at room temperature. The latter has ϵ = 210 M^{-1} cm^{-1} at 285 nm. A_{22}, —; A_{33}, - - -; R, ···, D, +. Inset: spectra of A_{22}, A_{33}, and R in CH_3OH.

Table I. Electronic Absorption Spectral Data [λ (nm) Wavelength of the Maximum of the Lowest Energy Vibronic Band of the ^1L_a Electronic Transition] for Compounds A_{nn}, M_n, and R in Toluene and Methanol at Room Temperature[a]

	λ, nm (ε, M^{-1} cm^{-1})	
	toluene	methanol
A_{22}	406 (9200)	402 (7800)
A_{33}	406 (8300)	400 (9300)
M_2	402 (9200)	398 (9500)
M_3	402 (9300)	398 (9700)
R	402 (11300)	398 (11500)

[a] The intensity (ε, M^{-1} cm^{-1}) is given in parentheses.

The ester $\mathbf{7}_2$ (mp 88–89 °C), obtained (80% yield) from 10-ethylanthrone[14] (**4**) by the Reformatsky reaction, was readily transformed into the acid $\mathbf{8}_2$ (mp 258 °C; 84% yield). In a similar way, $\mathbf{8}_3$ was obtained (mp 146 °C; 93% yield) from the ester $\mathbf{7}_3$ (mp 74–75 °C) prepared (79% yield) by catalytic hydrogenation of ester **6** (mp 110–111 °C). The latter was obtained (77% yield) by treating compound[15] **5** with triethyl phosphonoacetate[16] (Horner–Emmons reaction). The carboxylic acids $\mathbf{8}_n$ were quantitatively converted into the corresponding chlorides $\mathbf{9}_n$ with oxalyl chloride in refluxing benzene ($\mathbf{9}_2$, mp 162 °C; $\mathbf{9}_3$, waxy compound). These acid chlorides were condensed without purification with the *N*-acetyl-[18]-N_2O_4 derivative[17] to give the corresponding diamides $\mathbf{10}_n$ (waxy compounds; 83% yields). Reduction with diborane and subsequent treatment with concentrated HCl gave M_n (M_2, oil, 92% yield; M_3, oil, 88% yield).

The *N,N'*-diethyl-[18]-N_2O_4 macrocycle D (mp 48 °C) was obtained by reduction with diborane of the diacetyl derivative (mp 98 °C) resulting from the condensation (90% yield) of acetyl chloride with the [18]-N_2O_4 macrocycle.

Characterization of the Free Ligands. (1) Structure of the Anthraceno-Cryptands (A_{nn}). (a) X-ray Structure Analysis. The crystal structures[9b] of the cryptands A_{22} and A_{33} show that a preformed cavity exists which should allow internal cation complexation (Figure 1). In the crystalline state, the nitrogen lone

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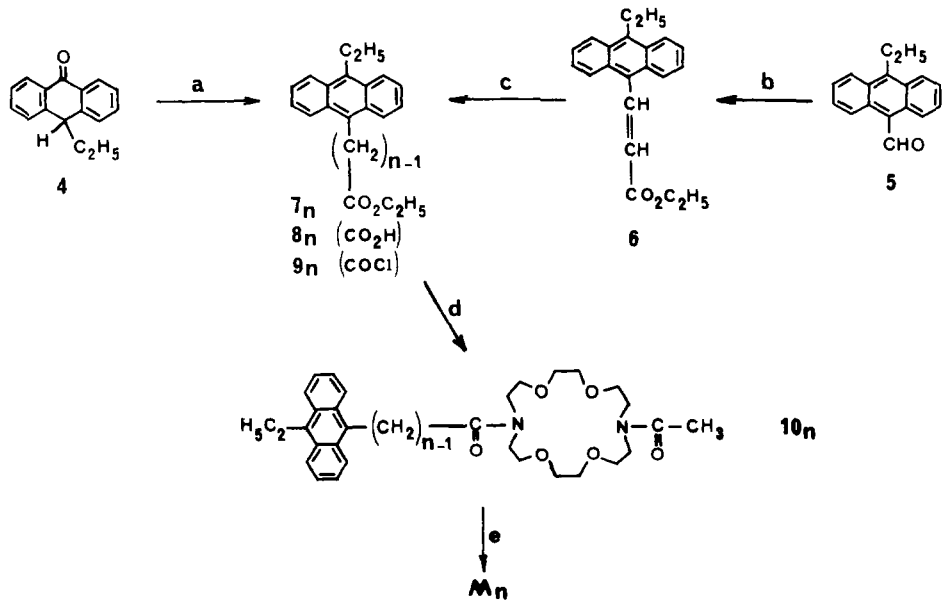
Scheme III. Synthesis of the Reference Compounds M_n[a]



[a] (a) Zn, $BrCH_2CO_2Et$, toluene/THF, (b) $(EtO)_2POCH_2CO_2Et$, NaH, 1,2-dimethoxyethane; (c) H_2, Pd/C, ethanol; (d) *N*-acetyl-"N_2O_4", Et_3N, benzene; (e) (i) B_2H_6/THF, (ii) HCl/H_2O, (iii) LiOH/H_2O.

pairs of A_{22} are oriented, inside the cavity, toward the aromatic ring whereas they point outside for A_{33}.

(b) NMR Spectrometry. The NMR spectra (^1H and ^{13}C) in solution (methylene chloride, chloroform[9a] and toluene[7]) show that the structure of the free ligands is symmetrical on the NMR time scale and resembles that determined previously by X-ray structure analysis.[9b] In particular, the ^{13}C NMR spectra indicate that the carbon skeleton of the two cryptands exhibits C_{2v} symmetry.

(c) UV–Visible Absorption Spectra. UV absorption spectra of A_{nn} in diluted solutions (MCH, MeOH, toluene) are characteristic of 9,10-disubstituted alkylanthracenes. However, they present slight but significant bathochromic and hypochromic shifts in comparison with 9,10-di-*n*-propylanthracene (R) (Figure 2). The UV absorption of the [18]-N_2O_4 chromophore is located at high energy (<300 nm) and its spectral contribution is negligible compared to the ^1B_b transition of the aromatic moiety. The spectra of the molecules M_n have the same positions as the reference compound R and no important interactions between the nitrogen lone pairs and the anthracene ring in the ground state are detected by this technique; nevertheless, a hypochromic effect of M_n compared to R suggests that, on average, the amine and anthracene ^1L_a transition moments tend to be parallel and superimposed,[18] in a way similar to that in A_{nn}.

The molar extinction coefficients of compounds M_n and R are not significantly affected by the nature of the solvent in contrast to those recorded for the macrobicyclic derivatives A_{nn}, which exhibit a weak but clear variation from toluene to methanol (12–14%) (Table I).

This solvent dependence could be correlated with the well-known ability of cryptands to display several sets of conformers differing by the orientation of the nitrogen lone pairs.[12,19] Indeed we have demonstrated in previous papers[7,9a] that A_{22} is present as two main conformers in the ground state: an endo–endo form, prevailing in the crystal,[9b] which is in rapid interconversion in fluid solution with an exo–exo form where the lone pairs do not interact with the aromatic π cloud. The relative populations of these two conformers are temperature and solvent dependent; in aprotic solvents, the endo–endo conformer is largely favored (6/1),[7] whereas in a protic solvent such as methanol, the exo–exo species could be predominant due to specific solvation of the nitrogens by the solvent. As a consequence, the UV spectrum is shifted toward higher energy. Although the conformational distribution in A_{33} has not been established, a similar trend may be expected. This interpretation is consistent with the modification of the UV spectra observed in presence of protons. Indeed, the addition of trifluoroacetic acid in excess to the solutions exactly restores the absorption spectrum of the reference compound R by quaternization of the nitrogens.

The constants K_i (i = 1, 2) associated to the equilibria

$$H^+ + (H_{i-1}A_{nn})^{(i-1)+} \rightleftharpoons (H_iA_{nn})^{i+}$$

and corresponding to the protonation of one of the two nitrogen sites of the cryptands have been determined (Table II; Figure 3).

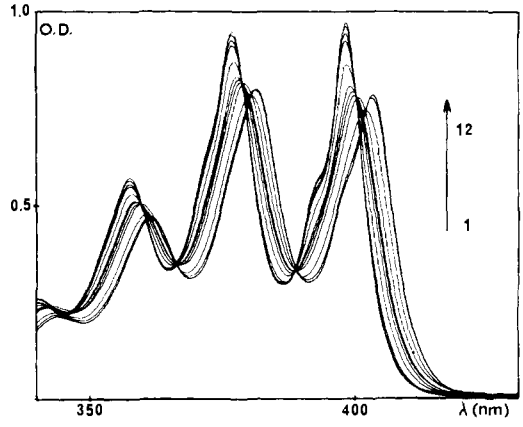


Figure 3. Electronic absorption spectra of A_{22} in methanol versus –log [H^+] (25 °C). [A_{22}] = 1.8 × 10^{-4} M; I = 0.1 (TBA-ClO_4) (TBA, tetrabutylammonium). –log [H^+]: 1, 3.57; 2, 5.49; 3, 7.16; 4, 7.54; 5, 8.12; 6, 8.52; 7, 8.71; 8, 8.90; 9, 9.29; 10, 10.02; 11, 11.08; 12, 12.09.

Table II. Protonation Constants of Anthraceno-Cryptands A_{22} and A_{33} in Methanol[a]

	ligands			
	[2.2][b] (r = 1.4 Å)	[2.2.2][b] (r = 1.4 Å)	A_{22} (r = 1.1 Å)[c]	A_{33} (r = 1.6 Å)[c]
log K_1	10.64 ± 0.01	10.72 ± 0.03	9.97 ± 0.03	10.79 ± 0.17
log K_2	9.14 ± 0.01	9.03 ± 0.01	8.42 ± 0.05	9.52 ± 0.27
log K_1 – log K_2	1.20 ± 0.01	1.69 ± 0.01	1.55 ± 0.06	1.27 ± 0.32

[a] T = 25.0 ± 0.1 °C; I = 0.1 (tetrabutylammonium perchlorate). [b] From ref 20a. [c] Radius of the free cavity of A_{nn} estimated from the crystallographic data.[9b]

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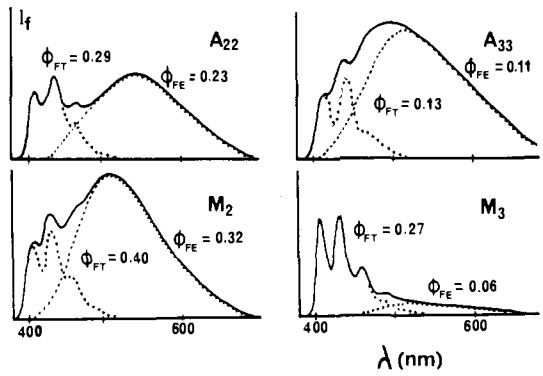


Figure 4. Corrected fluorescence emission spectra of R, A_{nn}, and M_n in degassed tetrahydrofuran (concentration, $<10^{-5}$ M) at 20 °C. The exciplex contribution (···) is obtained from difference spectra between A_{nn} or M_n (—) and R (+); λ_{exc} = 380 nm. $\phi_{FT} = \phi_{FM} + \phi_{FE}$; ϕ_{FT}, ϕ_{FM} and ϕ_{FE} are total, monomer-like, and exciplex fluorescence emission quantum yields, respectively.

The K_1 values of the [2.1.1]-, [2.2.1]-, and [2.2.2]cryptands decrease when the cavity size increases; this has been explained by the formation of an in–in monoprotonated species.[20] In the present case, the reverse is observed from A_{22} to A_{33} (Table II): monoprotonation of the smaller anthraceno-cryptand A_{22} is more difficult by ~1 order of magnitude as compared to A_{33}. This may be due to the fact that inside protonation requires a change in bridgehead orientation for A_{22}, which is preferentially out–out in methanol solution, but not for A_{33}, which contains at least one *in* site[21] (vide infra).

The $\Delta \log K = \log K_1 - \log K_2$ values are known to increase[20] when the cavity size of the cryptand decreases, indicating relative destabilization of the diprotonated species. In agreement with these observed trends, $\Delta \log K$ is higher for the smaller anthraceno-cryptand A_{22}. Similarities clearly appear in table II for A_{33} and [2.2], suggesting a weak participation of the aromatic ring in the protonated species of A_{33}.

According to the conformational dynamics of the cryptand A_{22}, it is reasonable to postulate an out–out geometry for the diprotonated species and infer it for A_{33}. Moreover, this could explain the ^1H NMR spectra of A_{22} in methanol (CD_3OD) in the presence of trifluoroacetic acid. Since the NMR data are consistent with a symmetrical structure of the molecular framework (implying the same conformation at the nitrogen sites), they indicate that this structure differs from metal cations to protons. In the presence of metal cations, it has already been demonstrated[9a] that both the nitrogen lone pairs present an "in–in" orientation, and consequently, an "out–out" geometry for the diprotonated A_{nn} is likely.

(2) Fluorescence Emission Spectra. Whereas 9,10-di-*n*-propylanthracene (R) displays the expected emission fluorescence for the anthracenic chromophore (Figure 4), anthracenes bridging an [18]-N_2O_4 ring (A_{nn} and M_n) exhibit a dual fluorescence, which can be analyzed as follows: a structured part similar to the emission spectrum of the reference compound R ascribable to the locally excited state and a red-shifted structureless band attributed to an intramolecular exciplex involving nitrogen lone pairs and the aromatic ring[4,7,21] (the fluorescence excitation spectra scanned on the structured and the nonstructured bands are identical). The relatively weak intensity of A_{33} fluorescence emission in methanol is ascribable to the fast formation of the exciplex (in less than 50 ps) and to the easy formation of nonemitting ion pairs.

For compounds A_{nn} and M_n, the charge-transfer character of the excited complex has been demonstrated by the red shift of the maximum for exciplex emission as a function of the polarity of the solvent.

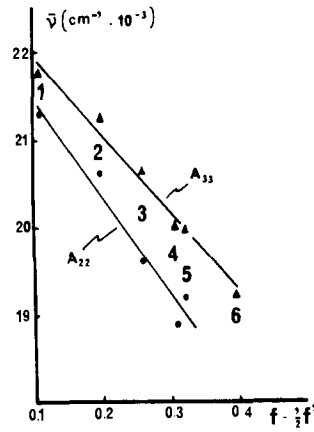


Figure 5. Wavenumber of the exciplex emission maximum of A_{nn} at 20 °C as a function of solvent polarity parameter. $f - {}^1/_2f'$; $f = (\epsilon - 1)/(2\epsilon + 1)$; $f' = (n^2 - 1)/(2n^2 + 1)$. Solvent ($f - {}^1/_2f'$). (1) methylcyclohexane (0.106); (2) trichloroethylene (0.197); (3) diethyl ether (0.256); (4) tetrahydrofuran (0.306); (5) methylene chloride (0.319); (6) methanol (0.391).

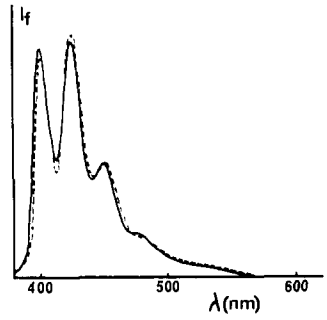


Figure 6. Corrected fluorescence emission spectrum of A_{22} in degassed methanol (–) (concentration $<10^{-5}$ M) at 20 °C. λ_{exc} = 380 nm (ϕ_F, 0.68). The major conformer in this solvent is likely to exhibit an exo–exo geometry for the nitrogen lone pairs. The other (minor) conformer (endo–endo) presumably leads directly to an ion pair stabilized by methanol, which does not emit fluorescence. In the presence of an excess of CF_3CO_2H, ϕ_F, 0.80 (- - -).

It was argued[7] that the two nitrogens are simultaneously involved in exciplex formation in A_{22}. A similar geometry should also apply to A_{33}, as shown by solvatochromic experiments (Figure 5) and supported by the detection of only one exciplex by picosecond time resolved spectroscopy.[21]

In the flexible reference molecules M_n, the formation of an intramolecular exciplex involving the two nitrogens seems rather unlikely according to the high fluorescence exciplex quantum yields observed [for example in degassed toluene at 20 °C ($C < 10^{-5}$ M), ϕ_{FE} = 0.39 for M_2 and 0.12 for M_3], which do not compare well to known data concerning triple exciplexes in flexible systems.[22] However it cannot be completely discounted.

In methanol, no exciplex is observed with A_{22}, only a relatively strong monomeric type fluorescence is recorded (ϕ_F = 0.68). This effect does not appear with the other compounds except to some extent with M_3, which displays only a weak monomeric emission. The occurrence of a specific solvation of the nitrogen lone pairs of A_{22} by methanol is assumed to maintain an exo–exo geometry in the excited state, hindering the exciplex formation (Figure 6). The minor conformer (endo–endo) presumably leads, in this protic solvent, to an ion pair that does not emit light.[23]

Complexation of Cations by Anthraceno-Cryptands A_{nn} in the Ground State. The spectroscopic properties of the anthraceno-cryptands are strongly modified in the presence of protons and

(20) (a) Spiess, B.; Arnau-Neu, F.; Schwing-Weill, M. J. *Helv. Chim. Acta* **1979**, *62*, 1531. (b) Lehn, J.-M.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1975**, *97*, 6700.

(21) Fages, F. Thèse d'Etat, Université de Bordeaux I, Talence, France, 1988.

(22) (a) Larson, J. R.; Petrich, J. W.; Yang, N. C. *J. Am. Chem. Soc.* **1982**, *104*, 5000. (b) Yang., N. C.; Gerald, R., II; Wasielewski, M. R. *Ibid.* **1985**, *107*, 5531.

(23) Beens, H.; Weller, A. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: London, 1975; Vol. 2, p 159.

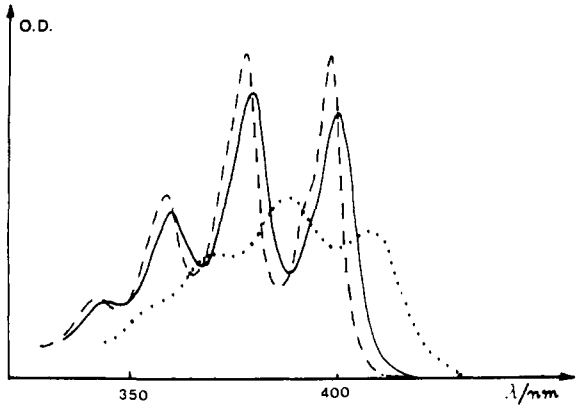


Figure 7. Electronic absorption spectrum (^1L_a band, 20 °C) of A_{22} in methanol (concentration, $<10^{-4}$ M): —, without salt; - - -, with $KClO_4$ (10^{-1} M); ···, with $AgNO_3$ (10^{-1} M).

Table III. UV Spectral Modification (on the ^1L_a Band) of A_{nn} and M_n ($\leq 10^{-4}$ M, Methanol, 20 °C) in the Presence of Salts or CF_3COOH (ca. 10^{-1}–10^{-2} M)[a]

	$LiClO_4$	$NaClO_4$	$KClO_4$	$AgClO_4$	$TlNO_3$	CF_3COOH
$\Delta\epsilon$ } A_{22}	–	↑9	↑12	↓30	↓19	↑15
$\Delta\lambda$ } A_{22}		→2	←1	→10	→7	–
$\Delta\epsilon$ } A_{33}	–	↓13	↓2	↓28	↓4	↑16
$\Delta\lambda$ } A_{33}		→1	→1	→4	→2	←1
$\Delta\epsilon$ } M_2	*	*	↑5	↑1	↑2	↑6
$\Delta\lambda$ } M_2			→1	→1	→3	←2
$\Delta\epsilon$ } M_3	*	*	–	↑7	↑2	–
$\Delta\lambda$ } M_3				→1	→1	

[a] $\Delta\epsilon$ represents the variation (%) of the absorption intensity and $\Delta\lambda$ the shift (nm). Arrows ↑ and ↓ denote hyper- and hypochromism, respectively. Arrows → and ← indicate batho- and hypsochromism respectively. (–) no effect; (*) not recorded.

of the metal cations examined (Li^+, Na^+, and K^+ perchlorates and Ag^+ and Tl^+ nitrates).

(1) UV–Visible Absorption Spectroscopy. The absorption spectra of A_{nn} but not of R are affected by the addition of CF_3COOH or of salts (except $LiClO_4$), the perturbation depending on the nature of the added species (Figure 7). Under the same experimental conditions, the spectra of the flexible compounds are only little altered (Table III).

Indeed, with M_n only weak hyperchromic effects are observed while some hypochromic effects are noticed with A_{nn}, depending on the nature of the added cation. Moreover, heavy cations, i.e., Ag^+ and Tl^+, produce hypochromic and bathochromic shifts (larger with A_{22}).

These data are consistent with the formation of complexes between A_{nn} and the cations (except Li^+, probably too small to be well complexed) in which the ion is bound to the [18]-N_2O_4 ring and held in the vicinity of the π system. This probably explains the red shift of the spectra with Ag^+ and Tl^+, which points to a ground-state complex between the ions and the aromatic ring.

(2) Stoichiometry and Stability Constants of the Complexes. The electronic spectra and the stability constants of the Tl(I) and Ag(I) (1:1) complexes formed with A_{22} (Figure 8) and A_{33} (Table IV) in methanol have been determined by simultaneous potentiometric and spectrophotometric measurements. The data have been processed by the LETAGROP–SPEFO program.[24]

Though the cavity size of the cryptand A_{22} seems compatible with the ionic radius of the Ag(I) cation, the stability constant of the $[Ag^+\subset A_{22}]$ cryptate decreases as compared to $[Ag^+\subset 2.2]$

(24) Sillen, L. G.; Warnquist, B. *Ark. Kemi* **1968**, *31*, 315, 377.

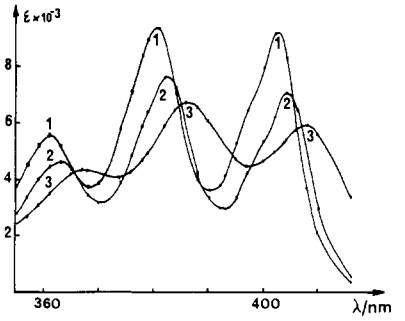


Figure 8. Calculated electronic absorption spectra of A_{22} and its Tl(I) and Ag(I) complexes in methanol. 1, A_{22}; 2, $[Tl^+\subset A_{22}]$; 3, $[Ag^+\subset A_{22}]$.

Table IV. Stability Constants of Thallium(I) and Silver(I) Complexes Formed with the Anthraceno-Cryptands A_{22} and A_{33} in Methanol[a]

	log K_s			
ligands	[2.2] (r = 1.4 Å)	[2.2.2] (r = 1.4 Å)	A_{22} (r = 1.1 Å)	A_{33} (r = 1.6 Å)
Tl^+ (r_i = 1.49 Å)	3.54[b]	10.10[c] 9.10[d] 12.20[e,f]	8.52	7.07
Ag^+ (r_i = 1.13 Å)	10.02[g] 10.18[b]	12.30[h] 12.22[g]	9.51	9.36

[a] T = 25.0 ± 0.1 °C; I = 0.1 (tetrabutylammonium perchlorate). The accuracy of our results is 0.05 for log K_s and is equal to 2σ. r_i, ionic radius of cations;[31] r, radius of the cavity of the coronand or cryptand; the latter was estimated from crystallographic data.[9b] [b] Cox, B. G.; Firman, P.; Horst, H.; Schneider, H. *Tetrahedron* **1983**, *39*, 343. [c] Yee, E. L.; Tabib, J.; Weaver, M. J. *J. Electroanal. Chem.* **1979**, *96*, 241. [d] Spiess, B., Thèse de doctorat d'Etat, Université Louis Pasteur, Strasbourg, France, 1981. [e] Cox, B. C.; Schneider, H.; Schulz, H.; Stroka, J. *J. Am. Chem. Soc.* **1978**, *100*, 4746. [f] Gutknecht, H.; Schneider, H.; Stroka, H. *Inorg. Chem.* **1978**, *17*, 3327. [g] Buschmann, H. J. *Inorg. Chim. Acta* **1985**, *102*, 95. [h] Lejaille, M. F.; Livertoux, M.; Guidon, C.; Bessierre, J. *Bull. Soc. Chim. Fr.* **1978**, 373.

and $[Ag^+\subset 2.2.2]$ cryptates (Table IV). The loss of two coordination sites in [2.2], A_{22}, and A_{33} silver(I) complexes induces a decrease in stability constants of at least 2 orders of magnitude, as compared to $[Ag^+\subset 2.2.2]$ in the same solvent. In addition, the deformation of the cavity by the aromatic groups may also contribute in particular by increasing the distance between the bridgehead nitrogens, which are expected to be the preferred coordination sites of the Ag^+ ions.

Similarly, for the A_{22} and A_{33} thallium(I) cryptates compared to $[Tl^+\subset 2.2.2]$, a decrease of at least 1 order of magnitude of the stability constant is found (Table IV). In order to analyze the above trend, it is appropriate to compare the stability of K^+ complexes with two macrobicyclic ligands [2.2.2] (log K_s = 8.7; Table IV, footnote *h*) and [2.2.C_8] (log K_s = 5.2[20b]) in methanol. In the latter case, the loss of stability is ~3 orders of magnitude for the complex formed with the cryptand with the hydrocarbon chain [2.2.C_8]. It appears that the loss in stability of the A_{22} thallium(I) complex compared to $[Tl^+\subset 2.2.2]$ is substantially smaller than the stability decreases between [2.2.2] and [2.2.C_8] K^+ complexes, in spite of the deformation of the cavity of A_{22}. A stabilization effect by the anthracene moiety of the thallium(I) A_{22} complex is observed here, in agreement with NMR emission fluorescence and X-ray structure data,[9a,b] which have shown that the cation Tl^+ is inside the cavity, coordinated by the oxygen and nitrogen atoms of the ligand and in interaction with the aromatic ring.

(3) ^1H and ^{13}C NMR Spectroscopy. NMR spectra (D_2Cl_2, $DCCl_3$, toluene) were recorded for cryptands A_{nn} in the absence and in the presence of cations (K^+, Tl^+, Ag^+). The detailed analysis of the spectra was reported elsewhere.[7,9a]

From this study, it emerges that the addition of an excess of salts (K^+, Ag^+, Tl^+) to the solutions of A_{nn} is followed by a marked modification of the spectra (Figure 9) indicative of an important conformation reorganization showing that the cation is inside the cavity.

All the ^1H NMR patterns appear to be affected in a similar way by the three cations, which induce a deshielding of the

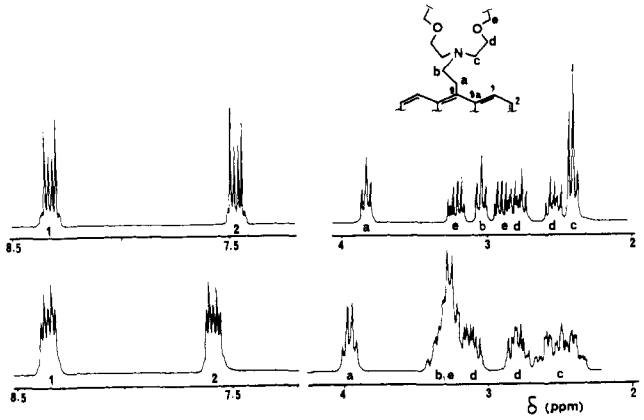


Figure 9. 200-MHz ^1H NMR spectra of A_{22} in $CDCl_3$ at room temperature. Top: without salt. Bottom: with $TlNO_3$ (saturated solution).

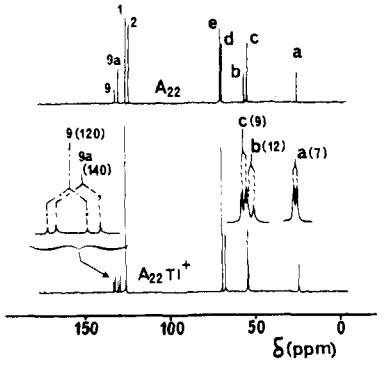


Figure 10. 50-MHz ^{13}C NMR spectra of A_{22} in $CDCl_3$ at room temperature. Top: without salt. Bottom: with $TlNO_3$ (saturated solution). The coupling constants (J_{Tl-C}) (hertz) are given in parentheses.

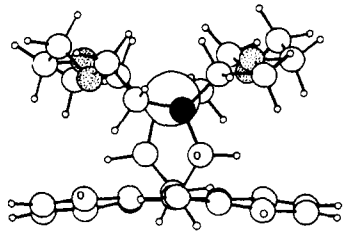


Figure 11. Molecular structure of Tl^+–A_{22} complex along the short axis of the anthracene ring. Note the deformation of the aromatic nucleus. The distance between Tl^+ and the average plane of the aromatic ring is 3.2 Å.

aromatic and benzylic signals. Analogous trends were noted[9a] in the ^{13}C NMR spectra.

The results obtained with Tl^+ must be emphasized; indeed coupling constants between the cation and H and C nuclei of the aliphatic part (3–14 Hz) of the ligand A_{22} appear in line with earlier data reported[25] for [2]cryptates. Moreover, coupling constants (120–140 Hz) between Tl^+ and aromatic carbons of the central ring were observed for the first time; they are evidence of some bonding between the cation and the anthracene ring and thus of the insertion of the cation inside the cavity (Figure 10). No perturbation of the spectra of R was detected in the presence of Tl^+.

With A_{33}, the coupling constants are not easy to determine (at room temperature the signals broaden); probably the size of the cavity is too large to keep the cation tightly in a definite position. Further, for the flexible opened molecule (M_2), no coupling was observed between the protons and the Tl^+ nucleus; only a deshielding of the signals of the aliphatic protons was detected when adding a large excess of $TlNO_3$ to the solutions.

(25) Lehn, J.-M.; Sauvage, J.-P.; Dietrich, B. *J. Am. Chem. Soc.* **1970**, *92*, 2916.

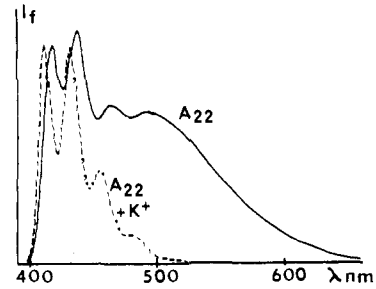


Figure 12. Corrected fluorescence emission spectra of A_{22} in degassed CH_2Cl_2 (concentration, $<10^{-6}$ M, λ_{exc}, 380 nm, 20 °C). —, without salt; ---, with $KClO_4$ (saturated solution).

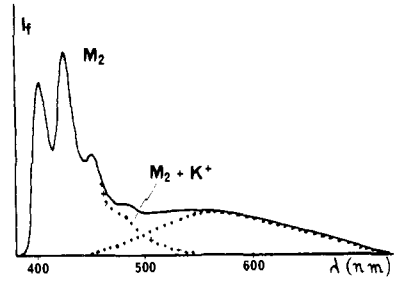


Figure 13. Corrected fluorescence emission spectra of M_2 in nondegassed methanol (10^{-6} M, λ_{exc}, 380 nm, 20 °C). —, without salt; + with $KClO_4$ (saturated solution); ···, the fluorescence exciplex spectrum.

Table V. Fluorescence Quantum Yields of A_{nn}, M_n, and R in Methanol (concentration, $<10^{-5}$ M, 20 °C, λ_{exc}, 380 nm) in the Absence and the Presence of Salts or CF_3CO_2H ($<10^{-2}$ M)

	none	$LiClO_4$	$NaClO_4$	$KClO_4$	$AgClO_4$	$TlNO_3$	CF_3CO_2H
A_{22}	0.68	0.70	0.57	0.64	0.05	0.05	0.80
A_{33}	0.04[a]	0.05[a]	0.17	0.30	0.23[a]	0.07	0.70
M_2[d]	0.10[a]	*c*	*c*	0.31	0.31	0.29	0.50
M_3[d]	0.26	*c*	*c*	0.50	0.26	0.46	0.53
R	0.76	*b*	*b*	*b*	0.39	0.67	*b*

[a] Dual fluorescence emission. [b] No effect observed. [c] Not measured. [d] Nondegassed.

(4) Structure of the $TlNO_3$–A_{22} Complex ($[Tl^+ \subset A_{22}]$, NO_3^-). Monocrystals of Tl^+, A_{22} complex were obtained from chloroformic solution of A_{22} saturated with $TlNO_3$ and the structure was determined by X-ray crystallography.[9a] As expected from spectroscopic measurements, Tl^+ is encaged inside the cryptand (Figure 11) and coordinated with the oxygen and nitrogen atoms as well as the aromatic ring[9a,c] (Tl^+···anthracene = 3.2 Å). From examination of the NMR and UV spectra of the 1:1 complexes of A_{nn} with the other cations, it is deduced that they are also inclusion complexes.

(5) Fluorescence Emission Spectra. (a) Light-Metal Cations. Addition of complexable cations (Na^+, K^+) to the solution of A_{nn} (protic or aprotic solvents) strongly reduces the red-shifted emission (exciplex component) and increases distinctly the intensity of the structured spectral part (Figure 12); no effect was detected with Li^+ (Table V). Thus involvement of the nitrogen sites in complexation is beyond doubt, since complexation prevents or strongly reduces the amine–anthracene exciplex formation.

Similar trends are observed with the flexible models M_n (Figure 13) where the cation is expected to be crowned by the [18]-N_2O_4 macrocycle and so hinders the intramolecular exciplex formation. Under the same experimental conditions, no spectral modifications were detected with R. Gradual addition of cations to A_{nn} solutions results in a progressive increase of the fluorescence intensity as shown in Figure 14. The resulting titration curves point to a 1:1 stoichiometry for the complex. Thus, compounds A_{nn}, especially A_{33} whose fluorescence emission was of low intensity, undergo a spectacular increase of light emission by addition of salts in the manner of a lamp that rekindles by addition of oil. These observations are in line with other recent results.[1]

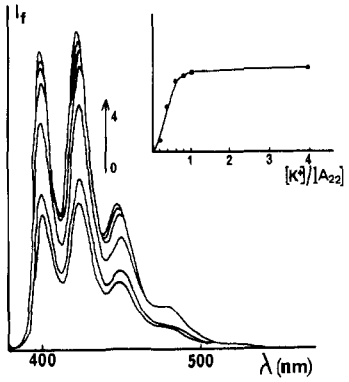


Figure 14. Fluorescence emission intensity of compound A_{22} (10^{-5} M) in nondegassed methanol as a function of added $KClO_4$ (20 °C, λ_{exc}, 380 nm). $KClO_4$ (10^{-5} M): 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, and 4.0. The titration curve $I_f \propto [K^+]$ points to a 1:1 stoichiometry for $[K^+ \subset A_{22}]$ (Inset).

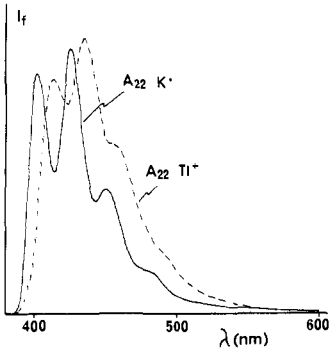


Figure 15. Corrected fluorescence emission spectra of A_{22} in degassed methanol (concentration, $<10^{-5}$ M, λ_{exc}, 380 nm, 20 °C) in the presence of K^+ (10^{-2} M) (—) and Tl^+ (---).

(b) Heavy-Metal Cations. In contrast to protons and alkali-metal cations, Ag^+ and Tl^+ behave as fluorescence quenchers, especially for A_{22} (Table V) (cation concentration ~1000 fold in excess). If the reference compound R also undergoes a fluorescence quenching by the classical heavy-atom effect, which increases intersystem crossing ($S_1 \rightarrow T_2$), the effect is not so important under the same experimental conditions (Table V). The flexible reference compounds M_n exhibit a fluorescence quenching intermediate between that of A_{nn} and R; this is accompanied by the disappearance of exciplex emission, in connection to the complexation of Ag^+ and Tl^+ by the [18]-N_2O_4 unit; the quenching is less intense than for A_{nn} as the average distance between the cation and the anthracene ring is greater.

The fluorescence emission spectra of A_{nn} in the presence of these two heavy cations was given special attention.

(c) Thallium Cations (Tl^+). If the fluorescence spectrum of A_{22} with Tl^+ is a structured anthracene monomer type emission,[9a,c] it is not superimposable to the spectra displayed by the light-cation cryptates (i.e., $[K^+ \subset A_{22}]$) since a red shift of ~730 cm^{-1} was measured (Figure 15). As the excitation fluorescence spectrum well matches the absorption spectrum of the species $[Tl^+ \subset A_{22}]$, it was concluded[9a,21] that the emission originates from an excited [Tl(I):anthracene] complex preformed in the ground state. Interestingly, only a few weak complexes between Tl^+ and arenes[26] are known in the crystalline state; this anthraceno-cryptand A_{22} appears well suited for revealing and studying this kind of faint interaction even in fluid solutions. With A_{33}, the fluorescence emission is close to that observed with light cations, probably as a consequence of the larger size of the cavity, in agreement with NMR measurements and UV spectroscopy.[9a] The anthraceno crown ethers M_n behave as A_{33} in presence of Tl^+.

(26) (a) Strauss, S. H.; Noirot, M. D.; Anderson, O. P. *Inorg. Chem.* **1986**, *25*, 3851. (b) Schmidbaur, H.; Hager, R.; Huben, B.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 338 and references therein.

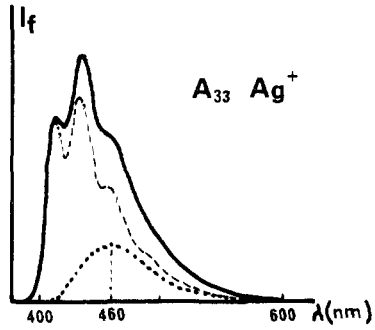
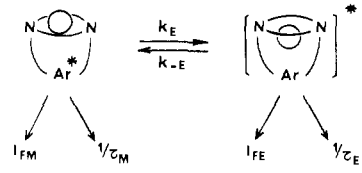


Figure 16. Corrected fluorescence emission spectra of A_{33} in degassed methanol (concentration, $<10^{-5}$ M, λ_{exc}, 380 nm, 20 °C) in the presence (10^{-2} M) of $AgNO_3$ (—) and $NaClO_4$ (---). (···) represents the fluorescence exciplex spectrum.

Scheme IV[a]



[a] k_E and k_{-E} are the rate constants for exciplex formation and dissociation, respectively. τ_M and τ_E are the fluorescence lifetimes of locally excited $^1A^*$ (without any interaction with the nitrogen lone pairs or Ag^+) denoted "monomer" and of the exciplex (Ag^+:A_{33}), respectively. At 20 °C, $k_E = 1.9 \times 10^8$ s^{-1}; $1/\tau_E = 2.1 \times 10^8$ s^{-1}; $\Delta G°(M \rightarrow E) = -0.37$ kcal mol^{-1}.

(d) Silver Cations (Ag^+). The solutions of A_{22} containing Ag^+ only display a pure monomeric type fluorescence emission spectrum as with the reference compound R or A_{22} with light cations. The excitation spectrum (scanned at all the wavelengths) fits well with the absorption spectrum of the reference compound R and not with that of a solution of A_{22} with $AgNO_3$. This means that the ground-state charge-transfer complex [Ag(I):anthracene] does not emit light and that emission originates from a nonperturbed anthracene chromophore. These results are presumably ascribable to the presence of two ground-state complexes: the major one with Ag^+ inside the cavity, forming a nonfluorescent charge-transfer complex, and the minor one with Ag^+ externally bound to the diaza-crown and also partially solvated by NO_3 or CH_3OH; because the silver cation is remote from the anthracene ring, the latter complex emits a fluorescence similar to that of R.

$$(A_{22},Ag^+)_{out} \rightleftarrows Ag^+ \subset A_{22}$$

In contrast, the fluorescence emission spectrum of A_{33},Ag^+ solutions is not superposable with those recorded with light cations (i.e., Na^+ and K^+) (Figure 16). By subtraction of the degassed methanol solution spectrum of A_{33},Na^+ from that of A_{22},Ag^+, a nonstructured band peaking at 460 nm emerges. The excitation spectra independent of the wavelength of observation match the absorption spectrum of A_{33},Ag^+, underlining the common origin of both emissions. The nonstructured emission band (which disappears in the presence of O_2) is postulated to arise from an exciplex between Ag^+ and anthracene. Up to now, only perylene has been reported[27] to form an exciplex with Ag^+.

The occurrence of an exciplex is fully confirmed by the analysis of the fluorescence emission decays, provided the classical Birks' scheme applies[28] (Scheme IV).

The experimental time dependence of the monomer $I_M(t)$ and exciplex (I_E)(t) fluorescence intensity is found to be given by the following expressions:

(27) (a) Läufer, A. G. E.; Dreeskamp, H.; Zachariasse, K. A. *Chem. Phys. Lett.* **1985**, *121*, 523. (b) Läufer, A. G. E.; Dreeskamp, H. *Ber. Bunsen-Ges. Phys. Chem.* **1986**, *90*, 1195.

(28) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970.

λ_{obs}(405 nm) $I_M(t) \propto 0.26 \exp(-t/2.36\ \text{ns}) + 0.40 \exp(-t/6.82\ \text{ns})$

λ_{obs}(510 nm) $I_E(t) \propto -0.25 \exp(-t/2.23\ \text{ns}) + 0.77 \exp(-t/6.46\ \text{ns})$

The exciplex fluorescence response function (at 510 nm) clearly grows from zero, as shown by the negative value of the first preexponential term. The fact that the sum of preexponential terms of the exciplex decay has a positive value (+0.52) and is not equal to zero, as required within the context of the proposed kinetic scheme, is caused by the presence of "monomer" emission at the observation wavelength (510 nm; see Figure 16). It should be noted that the lifetime values are similar for both monomer and exciplex decays. These observations confirm that the kinetic scheme correctly describes the proposed mechanism of the fluorescent properties of A_{33} with Ag^+.

From the values of the decay parameters and the monomer amplitude ratio, the rate constants appearing in the proposed scheme can be calculated (taking τ_M = 14 ns, the lifetime of A* obtained with A_{33} in the presence of Na^+ or K^+). The following rate parameters were obtained at 20 °C:

$$k_E = 1.9 \times 10^8\ s^{-1} \qquad k_{-E} = 1.0 \times 10^8\ s^{-1}$$
$$1/\tau_E = 2.1 \times 10^8\ s^{-1}$$

leading to

$$\Delta G^\circ = -0.37\ \text{kcal/mol}$$

A more detailed study of the thermodynamics and kinetics of the exciplex formation is under investigation.

Conclusion

We have prepared a new class of macrobicyclic photoactive ligands, the anthraceno-cryptands A_{nn}, in which the anthracenic nucleus bridges an [18]-N_2O_4 macrocycle. These molecules display a dual fluorescence (monomer and exciplex) resulting from the intramolecular interaction between the nitrogen lone pairs and the π system. The fluorescence of these compounds was shown to be very sensitive to the solvent and the presence of metal cations. Protic solvents, such as methanol, can induce hydrogen bonds with the nitrogens, relieving the intramolecular nitrogen–anthracene interaction; the solvation is followed by a net enhancement of the monomer emission. Cations that enter into the cavity of A_{nn} form stable 1:1 cryptates, the cations being held near the aromatic ring. The nitrogen lone pairs, found to quench the singlet excited state of the free ligands, are involved in the complexation of the cation inducing a strong increase of the fluorescence intensity (light cations) with the disappearance of the exciplex component. *These phenomena are dependent on the nature of the cation.* Unusual interactions between heavy-metal cations and the central ring of anthracene have been discovered with these chelators, Tl^+ leading with A_{22} to a complex presenting novel interactions and Ag^+ to a fluorescent exciplex with A_{33}.

Experimental Section

Chemicals and solvents (spectrometric grade) were used directly as received. Proton magnetic resonance spectra were recorded on a Bruker AC200 (200 MHz) spectrometer in $CDCl_3$, CD_2Cl_2, CD_3OD, and toluene-d_8 and on a Perkin-Elmer R24B spectrometer in $CDCl_3$ and CCl_4. The chemical shifts are given in δ values from Me_4Si. UV absorption spectra were recorded on a Cary 219 spectrophotometer at 25 °C. The IR spectrometer was a Perkin-Elmer 1420, and the mass spectrometer an VG Micromass Model 70-70. Fluorescence spectra were obtained with a Hitachi Perkin Elmer MPF44 fluorometer, corrected for emission. The fluorescence quantum yields were determined by comparison with quinine sulfate in 1 N sulfuric acid,[29] and the fluorescence lifetimes were measured by single-photon counting using an Applied Photophysics apparatus as already described.[30] The purity of all new compounds was checked by TLC (silica gel). Ionic cation radii (Å) were taken from ref 31: Li^+ (0.78), Na^+ (0.98), K^+ (1.33), Tl^+ (1.49), Ag^+ (1.13).

The thermodynamic constants and the electronic spectra of the different species were determined by simultaneous potentiometric and spectrophotometric measurements. Anthraceno-cryptands solutions (10^{-4} M), in the presence or absence of Ag(I) and Tl(I), were acidified with $HClO_4$ (Merck, per anal., 70%) up to 3×10^{-3} M and tetrabutylammonium methoxide (Merck, 25% in methanol) was added progressively. A small sample (500 μL) was taken after each addition in order to record the absorption spectrum on a Kontron Uvikon 860 spectrophotometer. The –log [H^+] values were measured with a combined glass electrode (Tacussel, High Alcalinity), in which the reference electrode (Ag/AgCl) was filled with tetrabutylammonium chloride (5×10^{-2} M) and tetrabutylammonium perchlorate (5×10^{-2} M) in methanol. Potential differences were measured with a Tacussel Isis 20 000 millivoltmeter. The spectrophotometric and potentiometric data were processed by the program LETAGROP-SPEFO.[24] The range of –log [H^+] used in the experiments was from 3 to 14 for the free ligands and for the thallium complexes and from 3 to 10 for the silver complexes. The metal ($TlNO_3$ and $AgNO_3$, Merck per anal.) concentrations were 3-fold in excess with respect to the anthraceno-cryptands concentrations. The ionic strength was maintained constant with tetrabutylammonium perchlorate, 0.1 M.

2,13-Dioxo-6,9,17,20-tetraoxa-3,12-diaza[14.8^{3,12}](9,10)-anthracenophane (3_{22}). To 1.5 L of stirred and degassed benzene were added simultaneously and dropwise at room temperature (8 h) under high dilution conditions two degassed benzenic solutions (2 × 500 mL) of 9,10-anthracenediacetyl dichloride[11] (2.8 g, 9 mmol) and of the [18]-N_2O_4 macrocycle (2.0 g, 8 mmol) with triethylamine (1.9 g, 19 mmol). After the addition was completed, the mixture was filtered and the solvent removed under reduced pressure. Chromatography on alumina column (CH_2Cl_2 as eluent) of the solid brown crude product gave 3_{22} as a yellow solid (2.4 g, 61% yield): mp >260 °C; ^{1}H NMR δ 2.4–4.1 (m, 24 H, "N_2O_4" ring), 4.5–5.1 (AB, 4 H, J = 16 Hz, ArCH_2CO), 7.5–8.8 (m, 8 H, Ar); IR (KBr pellets) 2940, 2860, 1630, 1470, 1450, 1410, 1120, 1080, 780, 745 cm^{-1}; MS m/z 520 (calcd 520). Anal. Calcd for $C_{30}H_{36}N_2O_6$: C, 69.21; H, 6.97; N, 5.38; O, 18.44. Found: C, 68.15; H, 6.91; N, 5.38; O, 18.22.

3,14-Dioxo-7,10,19,22-tetraoxa-4,13-diaza[16.8^{4,13}](9,10)-anthracenophane (3_{33}). By the same procedure as above, using 1.0 g (4 mmol) of [18]-N_2O_4 macrocycle 1.0 g (20 mmol) of triethylamine, and 1.5 g (4.6 mmol) of 9,10-anthracenedipropionyl dichloride,[11] 3_{33} was obtained as a yellow solid (1.4 g, 65%): mp >260 °C; ^{1}H NMR δ 3.0–4.0 (m, 32 H, "N_2O_4" ring, ArCH_2CH_2CO), 7.2–8.3 (m, 8 H, Ar); IR (KBr pellets) 2950, 2840, 1630, 1450, 1430, 1410, 1110, 750 cm^{-1}; MS m/z 548 (calcd 548). Anal. Calcd for $C_{32}H_{40}N_2O_6$: C, 70.05; H, 7.35. Found: C, 70.13; H, 7.26.

6,9,17,20-Tetraoxa-3,12-diaza[14.8^{3,12}](9,10)anthracenophane (A_{22}). A solution of the diamide 3_{22} (0.52 g, 1 mmol) in 30 mL of anhydrous tetrahydrofuran (THF) was placed under nitrogen atmosphere in a 100-mL two-neck flask equipped with a reflux condenser and a serum cap; 5 mL of a solution of diborane (1 M in THF) was added with a syringe. The mixture was stirred and refluxed for 2 h. After cooling to room temperature, distilled water was added cautiously. The solvent was evaporated and the crude amine borane derivative (mp >260 °C, pale yellow powder) obtained was used for the next step without further purification. This solid was treated under N_2 atmosphere with 10 mL of HCl (6 N) at 100 °C for 5h, after which the solution was cooled to room temperature and 100 mL of distilled water was added. The aqueous layer was made alkaline (pH = 8–9) by addition of LiOH (30%) and extracted with 3 × 50 mL of $CHCl_3$. The combined chloroform extracts were dried ($MgSO_4$) and evaporated to give a brown solid material, which was purified by chromatography on neutral alumina (Merck II-III, eluent CH_2Cl_2). The pale yellow solid was crystallized in toluene (65%): mp > 260 °C; ^{1}H NMR δ 2.40 (m, 8 H, NCH_2CH_2O), 2.53–2.77 (m, 8 H, NCH_2CH_2O), 3.05 (m, 8 H, OCH_2CH_2O), 3.05 ("t", 4 H, NCH_2CH_2Ar), 3.83 (m, 4 H, CH_2Ar), 7.48–8.31 (m, 8 H, Ar); IR (KBr pellets) 2830, 2760, 1600, 1450, 1425, 1340, 1285, 1260, 1240, 1120, 1110, 1080, 1060, 1010, 950, 820, 750, 730, 660, 640 cm^{-1}; MS m/z 492 (calcd 492). Anal. Calcd for $C_{30}H_{40}N_2O_4$: C, 73.14; H, 8.18; N, 5.69; O, 12.99. Found: C, 72.44; H, 8.22; N, 5.63; O, 13.01.

7,10,19,22-Tetraoxa-4,13-diaza[16.8^{4,13}](9,10)anthracenophane (A_{33}). Similarly, A_{33} was prepared from the diamide 3_{33}. A_{33} was isolated by neutral alumina chromatography (CH_2Cl_2) and crystallization in toluene as a yellow solid (77%): mp 215 °C; ^{1}H NMR δ 2.09 (m, 4 H, Ar$CH_2CH_2CH_2$N), 2.38 (m, 8 H, NCH_2CH_2O), 2.41 (m, 4 H, Ar$CH_2CH_2CH_2$N), 2.85 (m, 8 H, NCH_2CH_2O), 3.08 (m, 8 H, OCH_2CH_2O), 3.77 ("t", 4 H, ArCH_2), 7.51–8.40 (m, 8 H, Ar); IR (KBr pellets) 3040, 2920, 2860, 1620, 1470, 1445, 1360, 1335, 1315, 1250,

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1140, 1110, 1010, 910, 780, 750, 660 cm^{-1}; MS m/z 520 (calcd 520). Anal. Calcd for $C_{32}H_{44}N_2O_4 \cdot {}^1/_2H_2O$: C, 72.45; H, 8.49; N, 5.28; O, 13.58. Found: C, 72.88; H, 8.32; N, 5.28; O, 13.54.

9-[(Ethoxycarbonyl)methyl]-10-ethylanthracene (7_2). To a stirred suspension of zinc powder (6.5 g, 0.1 mol) in dried THF (150 mL) was added ethyl bromoacetate (17 g, 0.1 mol) dropwise under N_2 atmosphere. After completion of the operation, a small amount of iodine was added; then the reacting medium was refluxed and 10-ethylanthrone[14] (4.5 g, 20 mmol) dissolved in THF–toluene (1/1 v/v; 100 mL) was added dropwise. Reflux was continued for 2 h; concentrated H_2SO_4 (5 mL) was added and reflux was maintained 1 h longer. After being cooled to room temperature, the mixture was hydrolyzed with acidic water (10% H_2SO_4, 500 mL). The usual workup was followed by chromatography on an SiO_2 column (eluent ligroin), and 7_2 was obtained (4.7 g, 80%) as yellow pale crystals: mp 88–89 °C; ^{1}H NMR δ 0.80–1.50 (2 t, 6 H, CH_3CH_2OCO, CH_3CH_2Ar), 3.40 (q, 2 H, CH_3CH_2Ar), 3.90 (q, 2 H, CH_3CH_2OCO), 4.30 (s, 2 H, $ArCH_2COO$), 7.0–8.30 (m, 8 H, Ar); IR (KBr pellets) 3080, 2970, 2940, 2910, 2880, 1730, 1620, 1530, 1480, 1450, 1440, 1385, 1370, 1320, 1275, 1210, 1170, 1030, 935, 800, 780, 755, 730, 640 cm^{-1}; MS m/z 292 (calcd 292). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.19; H, 6.85; O, 10.99. Found: C, 81.60; H, 6.99; O, 11.09.

9-[2-(Ethoxycarbonyl)vinylene]-10-ethylanthracene (6). To a stirred suspension of NaH (1.25 g, 52 mmol) in dried dimethoxyethane (DME, 200 mL) was added dropwise, at room temperature, triethyl phosphonoacetate[16] (12 g, 53 mmol). Stirring was continued for 1 h, and a solution of 9-ethyl-10-formylanthracene[15] (10 g, 43 mmol) in DME (100 mL) was slowly added. The reacting medium turned red. Stirring was continued for 2 h after the addition, and the solution was hydrolyzed with water (200 mL). After the usual workup and crystallization in ethanol, **6** was obtained as red plates (10 g, 76%): mp 110–111 °C; ^{1}H NMR δ 1.50 (2 t, 6 H, CH_3CH_2, CH_3CH_2OCO), 3.50 (q, 2 H, CH_3CH_2Ar), 7.20–8.40 (m, 8 H, Ar), 6.1–8.6 (AB, J = 16 Hz, HC=CH); IR (KBr pellets) 3080, 2980, 2940, 2880, 1720, 1635, 1450, 1385, 1370, 1310, 1260, 1230, 1170, 1060, 1030, 990, 930, 880, 850, 760, 720, 645 cm^{-1}; MS m/z 304 (calcd 304). Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.89; H, 6.58; O, 10.53. Found: C, 82.99; H, 6.66; O, 10.57.

9-[2-(Ethoxycarbonyl)ethyl]-10-ethylanthracene (7_3). Catalytic hydrogenation (atmospheric pressure, room temperature) of ester **6** (2.9 g, 9.5 mmol) over 10% Pd/C (0.5 g) in anhydrous ethanol (100 mL) afforded, after crystallization in aqueous ethanol, 2.3 g (79%) of ester 7_3 as a bright yellow solid: mp 74–75 °C; ^{1}H NMR δ 0.90–1.50 (2 t, 6 H, CH_3CH_2), 2.4–4.3 (m, 8 H, CH_2), 7.1–8.2 (m, 8 H, Ar); IR (KBr pellets) 3080, 2960, 1720, 1480, 1440, 1425, 1290, 1250, 1190, 1040, 740, 640 cm^{-1}; m/z 306 (calcd 306). Anal. Calcd for $C_{21}H_{22}O_2 \cdot {}^1/_2H_2O$: C, 80.00, H, 7.30; O, 12.69. Found: C, 80.35; H, 7.21; O, 12.17.

(9-Ethyl-10-anthryl)acetic Acid (8_2). A mixture of 2.0 g (6.8 mmol) of ester 7_2, 2.0 g (50 mmol) of NaOH, and 100 mL of ethanol was stirred at reflux for 2 h under N_2 atmosphere. Most of the alcohol was removed under reduced pressure and the brown residue dissolved in the minimum of water. The aqueous solution was cooled and acidified with concentrated HCl. The yellow precipitate was crystallized in benzene, which gave pure 8_2 as pale yellow needles (1.5 g, 83%): mp 258 °C; IR (KBr pellets) 3700–3100, 2950, 1685, 1615, 1440, 1420, 1320, 1270, 1220, 795, 770, 750, 630 cm^{-1}; MS m/z 264 (calcd 264). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.82; H, 6.06; O, 12.12. Found: C, 81.06; H, 6.04; O, 12.20.

β-(9-Ethyl-10-anthryl)propionic Acid (8_3). Prepared as 8_2 from the ester compound 7_3 (1 g, 3.3 mmol) as a yellow amorphous solid (0.85 g, 93%): mp 146 °C; ^{1}H NMR δ 1.40 (t, 3 H, CH_3), 2.4–4.0 (m, 6 H, CH_2), 7.2–8.4 (m, 8 H, Ar), 11.4 (s, 1 H, COOH); IR (KBr pellets) 3600–3100, 2960, 2920, 1700, 1630, 1480, 1450, 1380, 1300, 1260, 1210, 1160, 1100, 800, 750 cm^{-1}; MS m/z 278 (calcd 278). Anal. Calcd for $C_{19}H_{18}O_2 \cdot H_2O$: C, 77.02; H, 6.76. Found: C, 77.81; H, 6.71.

9-(2,13-Dioxo-6,9,17,20-tetraoxa-3,12-diaza[8^{3,12}]docosyl)-10-ethylanthracene (10_2). A benzene (50 mL) solution of 1.50 g (6 mmol) of acid chloride 9_2 prepared from acid 6_2 (1.5 g, 5.7 mmol), oxalyl chloride (3.0 g, 24 mmol), and benzene (50 mL) was added dropwise to a solution of the N-acetyl-[18]-N_2O_4 macrocycle[17] (1.5 g, 6 mmol) and triethylamine (1.0 g, 10 mmol) in benzene (100 mL). Then 20 mL of sodium hydroxide (10%) was added and the mixture was stirred for 15 min. After decantation, the benzene solution was extracted successively with (i) 30 mL of sodium hydroxide (10%), (ii) 3 × 20 mL of hydrochloric acid (10%), and (iii) distilled water up to neutral pH. The organic phase was dried ($MgSO_4$) and evaporated to give an orange waxy product (2.3 g, 84%): ^{1}H NMR δ 1.2 (t, 3 H, CH_3CH_2Ar), 1.80 (s, 3 H, CH_3CON), 3.35 (m, 26 H, CH_2), 4.40 (s, 2 H, $ArCH_2CON$), 7.10–8.20 (m, 8 H, Ar); IR (NaCl, film) 3080, 2980, 2940, 2860, 1640, 1450, 1415, 1360, 1350, 1220, 1120, 1030, 910, 780, 760, 730 cm^{-1}.

9-(3,14-Dioxo-7,10,18,21-tetraoxa-4,13-diaza[8^{4,13}]tricosanyl)-10-ethylanthracene (10_3). By the same procedure as above, using 2.0 g (7 mmol) N-acetyl-[18]-N_2O_4 macrocycle, 1.5 g (15 mmol) of triethylamine and 2.0 g (7 mmol) of acid chloride 9_3 (prepared as 9_2), 10_3 was obtained as an orange pasty product (3.1 g, 83%): ^{1}H NMR δ 1.30 (t, 3 H, CH_3CH_2Ar), 1.90 (s, 3 H, CH_3CON), 2.40–4.10 (m, 30 H, CH_2), 7.10–8.40 (m, 8 H, Ar); IR (NaCl, film) 3060, 3020, 2980, 2920, 2860, 1635, 1460, 1440, 1410, 1280, 1200, 1110, 1030, 750, 675 cm^{-1}.

Model Compounds M_n. They were obtained after reduction of the diamides 10_n with diborane in THF according to the procedure described for compounds A_{nn}.

9-(6,9,17,20-Tetraoxa-3,12-diaza[8^{3,12}]docosyl)-10-ethylanthracene (M_2). From 2.3 g, (4.2 mmol) of diamide 10_2 and 10 mL of diborane solution (1 M in THF) was obtained pure M_2 after chromatography on neutral alumina (eluent benzene) as an orange oily product (2.0 g, 92%): ^{1}H NMR δ 1.10 (t, 3 H, CH_3CH_2N), 1.40 (t, 3 H, CH_3CH_2Ar), 2.50–3.00 (m, 12 H, NCH_2), 3.50–3.70 (m, 20 H, $ArCH_2$, OCH_2, 7.50–8.50 (m, 8 H, Ar); IR (NaCl, film) 3080, 2940, 2840, 1610, 1500, 1450, 1370, 1300, 1260, 1130, 1060, 930, 750 cm^{-1}; MS m/z 522 (calcd 522). Anal. Calcd for $C_{32}H_{46}N_2O_4 \cdot H_2O$: C, 71.11; H, 8.89; N, 5.18. Found: C, 71.80; H, 8.78; N, 4.92.

9-(7,10,18,21-Tetraoxa-4,13-diaza[8^{4,13}]tricosanyl)-10-ethylanthracene (M_3). From 3.1 g (5.5 mmol) of diamide 10_3 and 15 mL of diborane solution (1 M in THF) was obtained pure M_3 after chromatography on neutral alumina (eluent benzene) as an orange oily product (2.5 g, 88%): ^{1}H NMR δ 0.90 (t, 3 H, CH_3CH_2N), 1.40 (t, 3 H, CH_3CH_2Ar), 1.80 (m, 2 H, $ArCH_2CH_2CH_2N$), 2.30–2.90 (m, 12 H, NCH_2), 3.50 (m, 20 H, $ArCH_2$, OCH_2), 7.20–8.50 (m, 8 H, Ar); IR (NaCl, film) 3080, 2950, 2840, 1620, 1450, 1350, 1260, 1130, 1060, 930, 750, 730, 700, 650 cm^{-1}; MS m/z 536 (calcd 536). Anal. Calcd for $C_{33}H_{48}N_2O_4$: C, 73.88; H, 8.96; N, 5.22. Found: C, 73.08; H, 8.98; N, 4.82.

N,N'-Diacetyl-[18]-N_2O_4 Macrocycle. To a stirred solution of [18]-N_2O_4 macrocycle (5 g, 19 mmol) and triethylamine (4 g, 41 mmol) in dried benzene (150 mL) was added dropwise acetyl chloride (3.2 g, 41 mmol) in benzene (30 mL). Following the workup used for 8_n, the expected diamide was obtained as a white solid (6 g, 90%): mp 98 °C; ^{1}H NMR δ 2.25 (s, 6 H, CH_3CO), 3.75 (m, 24 H, "N_2O_4" ring); IR (KBr pellets) 3000–2850, 1630, 1480, 1450, 1420, 1350, 1100, 1030, 900 cm^{-1}; MS m/z 346 (calcd 346). Anal. Calcd for $C_{16}H_{30}N_2O_6$: C, 55.49; H, 8.67; N, 8.09; O, 27.75. Found: C, 55.53; H, 8.78; N, 8.04; O, 27.59.

N,N'-Diethyl-[18]-N_2O_4 Macrocycle. According to the procedure described for compounds A_{nn}, the diethyl derivative was obtained after reduction of the diamide (2.5 g, 7 mmol) in THF (20 mL) with 15 mL of diborane solution (1 M in THF). After chromatography on neutral alumina (eluent benzene) a transparent oil was obtained; after standing, it gave a white solid (2.0 g, 87%): mp 48 °C; ^{1}H NMR δ 0.90 (t, 6 H, CH_3), 2.60 (m, 12 H, NCH_2), 3.40 (m, 16 H, OCH_2); IR (NaCl, film) 3000–2700, 1450, 1340, 1120, 1070, 750, 720 cm^{-1}; MS m/z 318 (calcd 318). Anal. Calcd for $C_{16}H_{34}N_2O_4$: C, 60.38; H, 10.69; N, 8.81; O, 20.13. Found: C, 60.20; H, 10.80; N, 9.13; O, 19.78.

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