Linear Molecular Recognition: Spectroscopic, Photophysical, and Complexation Studies on α,ω-Alkanediyldiammonium Ions Binding to a Bisanthracenyl Macrotricyclic Receptor

Frédéric Fages,*,† Jean-Pierre Desvergne,† Kathrin Kampke,† Henri Bouas-Laurent,*,† Jean-Marie Lehn,‡ Michel Meyer,§ and Anne-Marie Albrecht-Gary§

Contribution from the Laboratoire de Photochimie Organique, CNRS URA 348, 351 Cours de la Libération, 33405 Talence Cedex, France, Chimie Supramoléculaire, CNRS URA 422, Institut Le Bel, 4 rue Blaise Pascal, 67000 Strasbourg, France, and Laboratoire de Physico-Chimie Bioinorganique, CNRS URA 405, EHICS, 67000 Strasbourg, France

Received June 15, 1992

Abstract: The new macrotricyclic ditopic bisanthracenyl receptor **1** displays monomer and excimer type fluorescence, the latter resulting from manifold intramolecular interactions between the anthracene and amino chromophores. This receptor, of cylindrical shape, also presents a geometrical recognition ability toward linear dications $H_3N^+-(CH_2)_n-NH_3^+$ (S_n^{2+}). ^1H NMR complexation studies of $\mathbf{1},S_n^{2+}$ (n = 6–10, 12) indicate the formation of mononuclear dihapto cryptates. The UV–visible absorption and fluorescence properties of **1** undergo important changes upon complexation of S_n^{2+}, but S_5^{2+} does not significantly alter the spectra. Addition of S_n^{2+} (n = 6–10, 12) produces an enhancement of the monomer-like emission with complete disappearance of the excimer part. The spectrum is then similar to that displayed by the monochromophoric reference compound **2**. The amplitude of the effect, dependent upon the chain length n, is maximum for n = 6 and 7 and slightly decreases when n increases. The stability constants of the complexes have been determined by spectrophotometry. High values of the constants, ranging between 10^4 and 10^7 M^{-1}, were obtained for the 1/1 inclusion complexes $\mathbf{1}S_n^{2+}$ with n = 6–10 and 12. S_5^{2+} forms both 1/1 and 1/2 complexes in solution. In agreement with the other data, the complexation ability was found to be maximum for n = 6 and 7 (stability constant ca. 10^7 M^{-1}). This behavior can be interpreted in terms of adaptability of the structurally flexible ligand toward the substrates S_n^{2+}.

In the past few years, there has been an increasing interest in the photochemistry and photophysics of supramolecular assemblies.[1] Investigation of the interplay between complexation and photochemical and/or luminescent properties in host–guest chromophoric systems has led to the conception of new molecular and supramolecular devices displaying photoactivity features.[2-4] In that connection, fluorescent molecules that respond to metal cations have been synthesized recently[5-9] and such systems are of considerable interest especially for their application to trace metal detection.[10]

Besides, organic cations do represent attractive targets for both molecular recognition and optical detection studies. While crown-ether-containing cyclophanes are being developed for better recognition of molecular guest cations,[11-14] there are only few examples of hosts capable of detecting organic substrates by absorption and emission spectroscopies.[12a,15] Furthermore, artificial receptors, in which the complexing ability could be affected by light-induced conformational or structural changes, might be used for the conception of light-to-ion devices, i.e., systems generating photoinduced ionic pulses by release or uptake of shape-defined molecular ionic species upon illumination.[16,17]

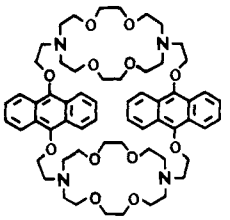
We recently reported[18] a preliminary study of the bisanthracenyl macrotricyclic receptor **1** (Chart I) that combines the photophysical properties of the anthracene ring and the complexing ability of two face-to-face N_2O_4 macrocycles toward bisalkylammonium cations. It was shown to encapsulate the α,ω-heptamethylenediammonium cation $H_3N^+(CH_2)_7NH_3^+$, and this was the first example of optical detection of a linear molecular cation.

† Photochimie Organique.
‡ Chimie Supramoléculaire.
§ Physico-Chimie Bioinorganique.

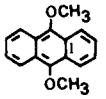
(1) Balzani, V. Ed. *Supramolecular Photochemistry*; Reidel: Dordrecht, 1987.
(2) *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H. J., Dürr, H., Eds.; VCH: Weinheim, 1991.
(3) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *25*, 1304.
(4) Löhr, H.-G.; Vögtle, F. *Acc. Chem. Res.* **1985**, *18*, 65.
(5) (a) Fages, F.; Desvergne, J.-P; Bouas-Laurent, H.; Marsau, P.; Lehn, J.-M.; Kotzyba-Hibert, F.; Albrecht-Gary, A.-M.; Al Joubbeh, M. *J. Am. Chem. Soc.* **1989**, *111*, 8672. (b) Bouas-Laurent, H.; Desvergne, J.-P.; Fages, F.; Marsau, P. in ref 2 p 265. (c) Desvergne, J.-P.; Fages, F.; Bouas-Laurent, H.; Marsau, P. *Pure Appl. Chem.* **1992**, *64*, 1231.
(6) (a) Bourson, J.; Valeur, B. *J. Phys. Chem.* **1989**, *93*, 3871. (b) Fery-Forgues, S.; Le Bris, M. T.; Guetté, J.-P.; Valeur, B. *J. Phys. Chem.* **1988**, *52*, 6233.
(7) (a) Huston, M. E.; Engleman, C.; Czarnik, A. W. *J. Am. Chem. Soc.* **1990**, *112*, 7054. (b) Czarnik, A. W. in ref 2 p 109.
(8) (a) De Silva, A. P.; De Silva, S. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1709. (b) De Silva, A. P.; Gunaratne, H. Q. N.; Sandanayake, K. R. A. S. *Tetrahedron Lett.* **1990**, 5193. (c) De Silva, A. P.; Gunaratne, H. Q. N. *J. Chem. Soc., Chem. Commun.* **1990**, 186.
(9) For fluorescent systems bearing calix[4]arenes units, see, for example: (a) Jin, T.; Ichikawa, K.; Koyama, T. *J. Chem. Soc., Chem. Commun.* **1992**, 499. (b) Deng, G.; Sakaki, T.; Kawahara, Y.; Shinkai, S. *Tetrahedron Lett.* **1992**, 2163.
(10) *Fiber Optic Chemical Sensors and Biosensors*; Wolfbeis, O. S., Ed.; CRC Press: 1991; Vol. I and II.
(11) (a) Schneider, H. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1417. (b) Smidtchen, F. P.; Leich, A. G.; Schummer, A. *Pure Appl. Chem.* **1989**, *61*, 1535.
(12) (a) Sutherland, I. O. *Pure Appl. Chem.* **1990**, *62*, 499. (b) Sutherland, I. O. *Chem. Soc. Rev.* **1986**, *15*, 63.
(13) (a) *Cyclophan-Chemie*; Vögtle, F.; Ed.; Teubner: Stuttgart, 1990. (b) Diederich, F. *Cyclophanes, Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, 1991.
(14) Lehn, J.-M. *Science* **1985**, *227*, 849.
(15) (a) Misumi, S. *Pure Appl. Chem.* **1990**, *62*, 493. (b) Aoyama, Y.; Asakawa, M.; Yamagishi, A.; Toi, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1990**, *112*, 3145. (c) Chang, S. K.; Van Engen, D.; Fan, E.; Hamilton, A. *J. Am. Chem. Soc.* **1991**, *113*, 7640. (d) Minato, S.; Osa, T.; Ueno, A. *J. Chem. Soc., Chem. Commun.* **1991**, 107. (e) Ueno, A.; Kuwabara, T.; Nakamura, A.; Toda, F. *Nature* **1992**, *356*, 136.
(16) Bouas-Laurent, H.; Castellan, A.; Daney, M.; Desvergne, J.-P.; Guinand, G.; Marsau, P.; Riffaud, M.-H. *J. Am. Chem. Soc.* **1986**, *108*, 315.
(17) Warmuth, R.; Grell, E.; Lehn, J.-M.; Bats, J. W.; Quinkert, G. *Helv. Chim. Acta* **1991**, *74*. 671.
(18) Fages, F.; Desvergne, J.-P.; Bouas-Laurent, H.; Lehn, J.-M.; Konopelski, J.-P.; Marsau, P.; Barrans, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 655.

0002-7863/93/1515-3658$04.00/0

Chart I. Bisanthracenyl macrotricyclic receptor **1**, Its Monochromophoric Reference Compound **2**, and the Ammonium Substrates Investigated in this Study: N^+, Neopentylammonium; S_n^{2+}, α,ω-Alkanediyldiammonium



1



2

$(CH_3)_3CCH_2 - NH_3^+ , Cl^-$

N^+ , Cl^-

$^+H_3N - (CH_2)_n - NH_3^+ , X^-$

S_n^{2+} , X^-
n = 5 - 10, 12
X^- = Cl^- , picrate

During the course of our work, fluorescent enhancements were also observed[19] with a bicyclic diazacrown-ether-conjugated anthracene derivative related to **1** but more flexible, designed as a fluorescent sensor for α,ω-diammoniumalkane salts. Other examples of fluorescent polytopic macrotricyclic ligands are reported, but they were used for different purposes.[20-22]

We describe herein the spectroscopic and complexation properties of the synthetic receptor **1** in the presence of a range of different-sized bisalkylammonium salts S_n^{2+} (with n = 5–10 and 12) in solution at room temperature (Chart I). The receptor **1** has been designed in view of its potential capacities (i) to provide complexation selectivity toward linear dications due to its macrotricyclic structure, (ii) to display "monomeric" and intramolecular excimer fluorescence sensitive to structural factors. Therefore the spectroscopic properties of **1** have been investigated in the presence of these diammonium substrates. The detailed description of the synthesis of **1** will be reported in a forthcoming paper, together with structural studies.[23]

Experimental Section

Reagents and Solvents. All reagents and solvents (spectrophotometric grade) were used directly as received. The reference compound, **2** (9,10-dimethoxyanthracene), was synthesized according to a known procedure.[24] The diammonium substrates $H_3N^+(CH_2)_nNH_3^+$ were obtained after treatment of the corresponding commercial diamines with picric acid in water[25] (S_n^{2+}, dipicrates; n = 5–9) or hydrochloric acid in methanol (S_n^{2+}, dichlorides; n = 5–10, 12). The diammonium salts were crystallized twice in water (dipicrates) or in methanol (dichlorides) and vacuum dried overnight over P_2O_5 at 80 °C.

Spectroscopic Methods. Proton NMR spectra were recorded on a Bruker AC 250 (250 MHz). Chemical shifts are reported in ppm vs Me_4Si. In the diammonium substrates complexation experiments, 5 mg (or 2.5 mg) of the receptor **1** were dissolved in ca. 0.7 mL of $CD_3OD/CDCl_3$ 1:9 (or $CD_3OD/CDCl_3$ 8:2) (v/v) and slightly over 1 equiv of the diammonium dipicrate (or dichloride) was directly added to the NMR tube. UV–vis spectra were recorded on a Cary 219 spectrophotometer. Fluorescence spectra were obtained with a Hitachi Perkin Elmer MPF 44 or a Spex Fluorolog, corrected for emission. The fluorescence quantum yields (average from three independent experiments) were determined on degassed samples by comparison with quinine sulfate in 1 N sulfuric acid;[26] the experimental error on the quantum yield values is estimated to be ±5%. Degassing was carried out on a high-vacuum line using repeated freeze–pump–thaw cycles. All the spectroscopic measurements were performed at 25 °C in chloroform-containing solvent mixtures because of solubility restrictions.

Table I. ^1H NMR Chemical Shifts[a,c] of the Bound S_n^{2+} Substrates in the Molecular Cryptates of Receptor **1** and Chemical Shifts for Reference Systems[b]

	substrate chemical shifts[a]				
substrate	α	β	γ	δ	ε
S_6^{2+}	2.09	–0.10	–2.04		
(8.72[e])	2.72[b]	1.53[b]	1.34[b]		
S_7^{2+}	2.39	0.41	–1.19	–2.12	
(9.96[e])	2.73[b]	1.57[b]	1.40[b]	1.40[b]	
S_8^{2+}	2.50	0.78	–1.08	–1.22	
(11.21[e])	2.78[b]	1.50[b]	1.34[b]	1.34[b]	
S_9^{2+}	2.56	1.08	–0.75	–1.09	–0.95
(12.45[e])	2.74[b]	1.55[b]	1.26[b]	1.26[b]	1.26[b]
S_9^{2+} [c]	2.55	1.02	–0.87	–1.18	–1.05
(12.45[e])					
S_{10}^{2+}, S_{12}^{2+} [c]	2.5; 1.2; 0.5; –0.4[d]				
(13.69, 16.18[e])					

[a] 250-MHz ^1H NMR spectra in $CD_3OD/CDCl_3$ 1:9 (v/v) at 20 °C. Shifts given vs Me_4Si. Picrates are used as counteranions. [b] 250-MHz ^1H NMR spectra in $CD_3OD/CDCl_3$ 1:9 (v/v) at 20 °C. Shifts δ given vs Me_4Si. Chemical shifts of the methylenic protons of S_n^{2+} bound to two $[18]N_2O_4$-Me_2 macrocycles **3** (from ref 25). [c] Solvent mixture: $CD_3OD/CDCl_3$ 8:2 (v/v). Chlorides of S_n^{2+} are used. [d] Not assigned. Peaks are not resolved. [e] Separation (Å) of nitrogen atoms in the extended (all anti-conformation) diammonium substrates S_n^{2+} calculated with $1.245x(n+1)$ (see ref 12a).

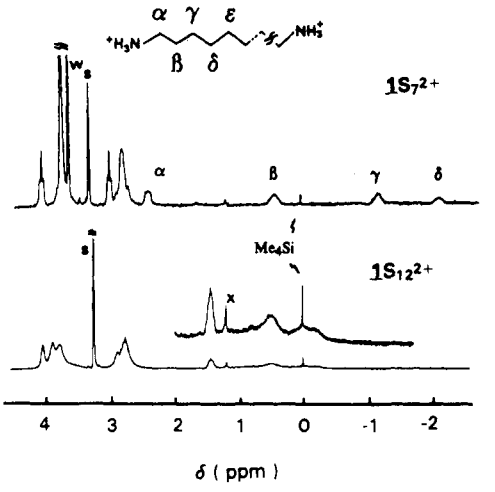


Figure 1. Aliphatic part of the 250 MHz proton NMR spectra of the complexes of **1** with $S_7^{2+}(picrate)_2$ (in $CD_3OD/CDCl_3$ 1:9 (v/v) and with $S_{12}^{2+}(chloride)_2$ (in $CD_3OD/CDCl_3$ 8:2 (v/v)). Peaks marked with W, S, and X are due to residual water, solvent, and some impurity, respectively.

Results and Discussion

^1H NMR Spectroscopy. The formation of bisammonium complexes (n = 5–10 and 12) with receptor **1** has been studied by proton NMR spectroscopy at 250 MHz.

Except for S_5^{2+}, substrate binding was indicated by the presence in the spectra of peaks ascribable to the CH_2 signals of the substrate located at high field, usually upfield of Me_4Si. The 1/1 stoichiometry of the complexes was established by integration studies. Precipitation of a pale yellow material occurred in the NMR tube upon addition of S_5^{2+} to the solution, and only very weak and broad proton resonances of the free ligand were recorded. The results are collected in Table I, and Figure 1 shows the ^1H NMR spectra of the complexes formed by the binding of S_7^{2+} and S_{12}^{2+} to receptor **1**.

As already observed for the diammonium cryptates of aromatic group-containing macrotricycles,[27,28] the protons of the substrates experience an intense shielding effect due to the proximity of the anthracenic π-clouds in the bridges. The substrates S_n^{2+} (n =

(19) De Silva, A. P.; Sandanayake, K. R. A. S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1173.
(20) Prodi, L.; Ballardini, R.; Gandolfi, M. T.; Balzani, V.; Desvergne, J.-P.; Bouas-Laurent, H. *J. Phys. Chem.* **1991**, *95*, 2080.
(21) Herrmann, U.; Tümmler, B.; Maass, G.; Mew, P. K. T.; Vögtle, F. *Biochemistry* **1984**, *23*, 4059.
(22) Gubelmann, M.; Harriman, A.; Lehn, J.-M.; Sessler, J. L. *J. Chem. Soc., Chem. Commun.* **1988**, 77; *J. Phys. Chem.* **1990**, *94*, 308.
(23) An outline of the synthesis of **1** is given in ref 18.
(24) Meyer, K. H. *Ann.* **1911**, *370*, 70.
(25) Kotzyba-Hibert, F. Thèse d'Etat, Strasbourg, 1983.
(26) Hanai, S.; Hirayama, F. *J. Phys. Chem.* **1983**, *87*, 83 and references therein.
(27) Hamilton, A.; Lehn, J.-M.; Sessler, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5158.
(28) Kotzyba-Hibert, F.; Lehn, J.-M.; Vierling, P. *Tetrahedron Lett.* **1980**, 941.

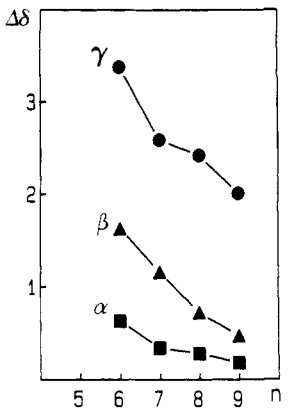


Figure 2. Upfield shift ($\Delta\delta$ in ppm) observed for the α, β, and γ protons of the substrates S_n^{2+} (picrate)$_2$ (n = 5–9) in the proton NMR spectrum ($CD_3OD/CDCl_3$ 1:9 (v/v), 250 MHz) of their complexes with the receptor **1**, plotted against the chain length n. $\Delta\delta$ is the chemical shift difference between a given CH_2 signal in the complex and the reference value obtained for the same substrate bound to two [18]-N_2O_4-Me_2 macrocycles **3** (see Table I and ref 25).

6–12) must therefore be contained in the molecular cavity of the ligand, with each $-NH_3^+$ groups bound to either of the N_2O_4 macrocycles. In contrast, S_5^{2+}, at the high concentration required for the NMR experiments and used in equimolar amount, is likely to preferably form insoluble external complexes.[19,29]

The largest upfield chemical shifts are observed with S_6^{2+} and S_7^{2+} (Table I, Figure 2) indicating that these cations provide the best fit, in agreement with examination of CPK molecular models of **1** and with published experimental data[30] on a dibenzo analog of receptor **1**. This also correlates well with the comparison between the complexation sites separation (9.73 Å) obtained from the X-ray structure analysis[18,23] of the rubidium binuclear complex of **1**, and the N···N separations calculated[12a] for the totally extended conformation of α,ω-alkanediammonium cations (Table I).

In contrast to other macrotricycles,[25,31,32] receptor **1** is able to accommodate inside the molecular cavity the longest dicationic species (n = 9–12) and still high values of the upfield shifts for the CH_2 protons of the substrate chain are noticed. Nevertheless in these cases, one notes that the signals of the CH_2 protons of both the host and the guest broaden, presumably because the fit between **1** and these long substrates is not ideal allowing more degrees of freedom in the complexes. The most pronounced effect is observed with the S_{12}^{2+} dication (Figure 1), the spectrum being then indicative of the occurrence of several species in relative slow exchange on the NMR time scale as demonstrated in analogous cases.[12b] Finally, it should be pointed out that the receptor **1** forms an inclusion complex with S_9^{2+} in two different solvent systems and with two kinds of counteranions, thus exhibiting the same behavior under different experimental conditions. Only slight differences in the chemical shifts of the complex are thus noted (Table I).

UV–Visible Absorption Spectroscopy. The electronic absorption spectrum of **1** in diluted solution (CH_3OH) at room temperature is characteristic of a 9,10-disubstituted alkyloxyanthracene[33] but presents significant modifications in comparison with that of 9,10-dimethoxyanthracene **2** (Figure 3). Indeed, the $^1L_a \leftarrow A_1$ transition shows marked hypochromic and

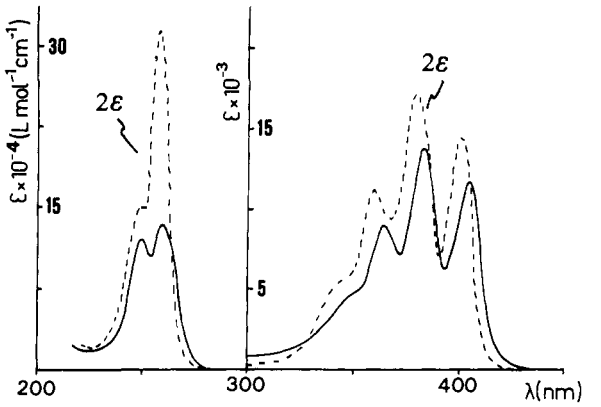


Figure 3. UV absorption spectra in methanol at room temperature of compound **1** (—) (concentration ca. 10^{-5} M) compared with that of reference compound **2** (– –; ε ×2) (concentration ca. 10^{-4} M).

Table II. UV Spectral Modification of **1** (Concentration ca. 10^{-5} M, $CH_3OH/CHCl_3$ 9:1 (v/v), 25 °C) in the Presence of Ammonium Substrates (Concentration ca. 10^{-3} M)[a]

	^1B_b band				^1L_a band	
	252 nm		260 nm		405 nm	
substrate	Δε	Δλ	Δε	Δλ	Δε	Δλ
N^+	↑18	–	↑14	–	↑6	←0.5
S_5^{2+}	↑18	–	↑12	–	↑5	←0.5
S_6^{2+}	↑29	–	↑45	←1.0	↑12	←0.5
S_7^{2+}	↑34	–	↑43	←1.0	↑16	←1.0
S_8^{2+}	↑38	←0.5	↑13	←1.0	↑13	←1.0
S_9^{2+}	↑55	←1.0	↓13	←0.5	↑18	←1.0
S_{10}^{2+}	↑18	←1.5	↓22	←0.5	↑14	←1.0
S_{12}^{2+}	↑18	←1.0	↓9	←1.0	↑13	←1.0

[a] Δε represents the variation (%) of the molar absorption intensity and Δλ the shift (nm). Arrows ↑ and ↓ denote hyper- and hypochromism, respectively. Arrows → and ← indicate batho- and hypsochromism, respectively. (–) no effect. N^+ = neopentylammonium.

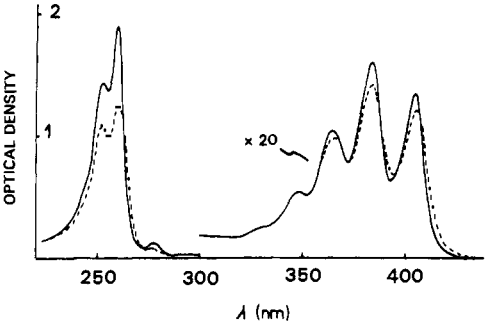


Figure 4. Electronic absorption spectra of **1** in $CH_3OH/CHCl_3$ 9:1 (v/v) (25 °C, concentration < 10^{-5} M):(– –) without salt; (—) with S_6^{2+}, $2Cl^-$ (ca. 10^{-3} M).

bathochromic shifts whereas the $^1B_b \leftarrow A_1$ transition is still more perturbed and appears to be split in two, roughly equally intense, bands. Taking into account our results on cation-complexing anthracenophanes,[16,34] these spectral changes indicate some degree of parallelism between the long axes of the two aromatic rings.

Addition of diammonium chloride substrates (S_n^{2+}, $2Cl^-$; n = 5–10, 12, large excess) into solutions of receptor **1** in the mixed solvent $CH_3OH/CHCl_3$ 9:1 (v/v) markedly alters the spectrum (Figure 4), the perturbation depending on the length of the added species (Table II). Whereas hyperchromic and hypsochromic moderate shifts are observed for the ^1L_a band, more significant spectral changes of the ^1B_b band are recorded (Figures 4 and 5).

(29) (a) Johnson, M. R.; Sutherland, I. O.; Newton, R. F. *J. Chem. Soc., Chem. Commun.* **1979**, 306. (b) *J. Chem. Soc., Perkin Trans. I* **1980**, 586.
(30) Chapoteau, E.; Czerch, B. P.; Kumar, A.; Pose, A. *J. Incl. Phenom.* **1988**, *6*, 41.
(31) Kotzyba-Hibert, F.; Lehn, J.-M.; Saigo, K. *J. Am. Chem. Soc.* **1981**, *103*, 4266.
(32) Pascard, C.; Riche, C.; Césario, M.; Kotzyba-Hibert, F.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1982**, 557.
(33) (a) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New-York, 1965. (b) Brotin, T.; Waluk, J.; Desvergne, J.-P.; Bouas-Laurent, H.; Michl, J. *Photochem. Photobiol.* **1992**, *55*, 335.
(34) Hinschberger, J.; Desvergne, J.-P.; Bouas-Laurent, H.; Marsau, P. *J. Chem. Soc., Perkin Trans. 2* **1990**, 993.

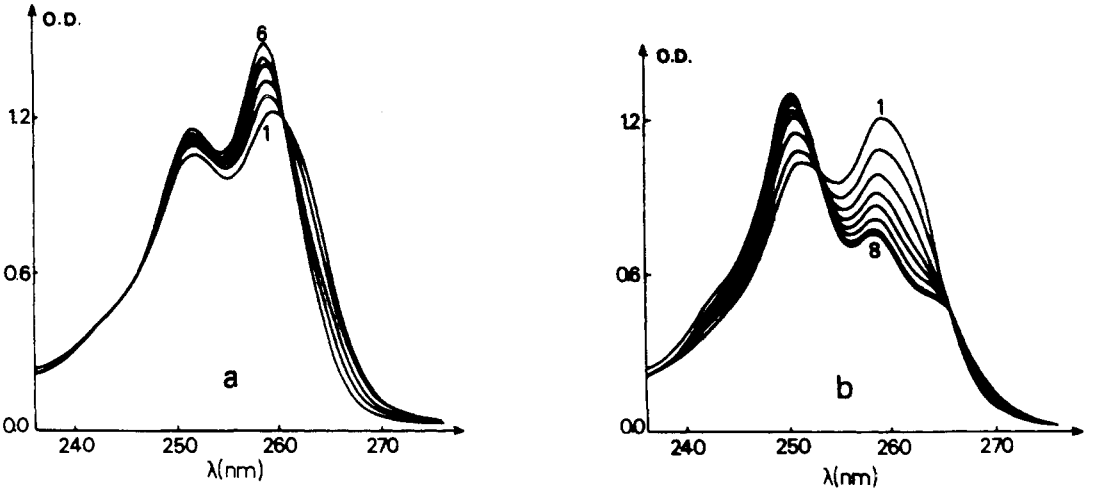


Figure 5. Spectrophotometric titrations of ligand **1** by the diammonium substrates S_6^{2+}, $2Cl^-$ (a) and S_9^{2+}, $2Cl^-$ (b) (25 °C; $CH_3OH/CHCl_3$ 9:1 (v/v)). (a) [**1**] = 8.4 × 10^{-6} M, [S_6^{2+}] × 10^6 M: 1, 0.0; 2, 2.1; 3, 4.2; 4, 6.3; 5, 8.4; 6, 21.0. (b) [**1**] = 8.3 × 10^{-6} M, [S_9^{2+}] × 10^6 M: 1, 0.0; 2, 2.1; 3, 4.1; 4, 6.2; 5, 8.3; 6, 12.4; 7, 33.2; 8, 58.1.

Table III. Stability Constants (β) of S_n^{2+}, $2Cl^-$ Complexes with Receptor **1** ($CH_3OH/CHCl_3$ 9:1 (v/v); 25 °C)[a]

complexes	log β	complexes	log β
1 S_5^{2+}	6.5 ± 0.4	**1** S_8^{2+}	6.0 ± 0.5
1 $(S_5^{2+})_2$	10.8 ± 0.8	**1** S_9^{2+}	6.3 ± 0.5
1 S_6^{2+}	6.8 ± 0.5	**1** S_{10}^{2+}	5.2 ± 0.5
1 S_7^{2+}	7.2 ± 0.5	**1** S_{12}^{2+}	4.6 ± 0.7

[a] The uncertainties correspond to the estimated experimental errors.

Table IV. Fluorescence Quantum Yields (Experimental Error ±5%) of **1** in $CH_3OH/CHCl_3$ 9:1 (v/v) (Degassed Solvent Mixture, Concentration < 10^{-5} M, 25 °C, λ_{exc} = 380 nm) in the Presence of the Ammonium Substrates (Concentration ca. 10^{-3} M)[b]

substrate	N^+	S_5^{2+}	S_6^{2+}	S_7^{2+}	S_8^{2+}	S_9^{2+}	S_{10}^{2+}	S_{12}^{2+}
Φ_F	0.10[a]	0.11[a]	0.61	0.55	0.42	0.51	0.51	0.21

[a] Dual fluorescence emission. [b] N^+ = neopentylammonium.

These effects were assigned to the formation of complexes between the receptor **1** and the linear diammonium substrates and this was confirmed by spectrophotometric titration experiments (vide infra). Complexation involves conformational reorganizations of the cyclophane structure,[16,32] which subsequently implies modifications of the degree of overlap between the anthracenic chromophores and this directly affects the UV absorption patterns as depicted with a series of [2.2]anthracenophanes.[35]

Spectrophotometric titrations were carried out by gradual addition of the different diammonium substrates to a solution of the ligand **1** (10^{-6} mol L^{-1}) in $CH_3OH/CHCl_3$ 9:1 (v/v). After each addition, the absorption spectrum was recorded between 200 and 300 nm (^1B_b band). The spectrophotometric data recorded for the complexation of the diammonium substrates S_n^{2+} (n = 6 and 9) by the receptor **1** are presented in Figure 5.

The data were processed by the nonlinear regression program[36] LETAGROP-SPEFO. The values of the stability constants and the electronic spectra corresponding to the various species formed at equilibrium are presented in Table III and in Figure 6a–d, respectively.

With the substrates S_n^{2+} (n = 6–12), the best statistical fit has been obtained for the formation of a 1 receptor/1 substrate species, and this is in agreement with proton NMR data. The formation of the most stable 1/1 complexes **1**S_6^{2+} and **1**S_7^{2+} gives rise to an increase of the intensity of the low-energy (ca. 260 nm) vs high-energy (ca. 250 nm) component (Figure 6a,b). These spectral modifications are consistent with the inclusion of these substrates into the hydrophobic cavity of the ligand, the polymethylene chain keeping apart the two anthracene nuclei and decreasing their mutual interaction. The resulting spectrum then tends to resemble that of the monochromophoric compound **2**.

Besides, internal 1/1 complexation of the long dications (S_n^{2+}, n = 9–12) produces in the spectra an unexpected opposite intensity modification and the buildup of shoulders at 250 and 268 nm (Figure 6c,d). For S_8^{2+}, similar but less pronounced spectral features are observed (Table II). In these cryptates, the aromatic groups might be forced to experience new interactions, involving the lateral ring of the anthracene nuclei, which are not present in the free ligand. This could account for the complex spectral patterns exhibited by the ^1B_b band which are reminiscent of that recorded for [2.2](1,4)anthracenophanes.[35] As inferred from the titration experiments, the substrate S_5^{2+} could generate both 1 receptor/1 substrate and 1 receptor/2 substrates complexes, the latter being the main species at large S_5^{2+} concentrations (ca. 100-fold excess). Indeed, S_5^{2+} gives rise to weak spectral perturbations, similar to that recorded with neopentyl ammonium chloride. The latter is a bulky group-bearing primary ammonium cation which binds preferably to the external faces of the N_2O_4 ring.

Fluorescence Emission Spectroscopy. The fluorescence emission spectrum of **1** in neat methanol is dual and relatively weak in intensity compared with that of the reference monochromophoric compound **2** (Figure 7). Two emissions can be characterized: e.g., a structured monomeric emission with Φ_{FM} = 0.03 (similar in shape to that of **2**) and a broad red-shifted band peaking at 530 nm (Φ_{FE} = 0.03) ascribable to the formation of an intramolecular complex ("excimer") involving one anthracene unit in the singlet excited state and the other chromophore in the ground state.[5a,37]

Addition of a large excess of cadaverine dication into a solution of **1** in $CH_3OH/CHCl_3$, 9:1 (v/v) did not significantly alter the fluorescence emission properties of the ligand (Figure 8), and the effect was identical to that obtained upon addition of neopentyl ammonium. In contrast, addition of the same amount of S_n^{2+} (n = 6–12) produced enhancements of the monomer-like emission accompanied by the total disappearance of the excimer part, the spectrum being similar in shape to that of **2** (Figure 8). In all cases the fluorescence excitation spectra were found to be identical to the corresponding UV–vis absorption spectra.

The amplitude of the effects was observed to be dependent on the chain length of the substrate (Table IV). The data with S_n^{2+} (n = 6–12) are consistent with the formation of the expected dihapto cryptates, in which the anthracene rings are prevented from forming an intramolecular excimer by the polymethylene

(35) Ferguson, J. *Chem. Rev.* **1986**, *86*, 957.
(36) Sillen, L. G.; Warnquist, B. *Ark. Kemi* **1968**, *31*, 315, 377.
(37) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience, London, 1970.

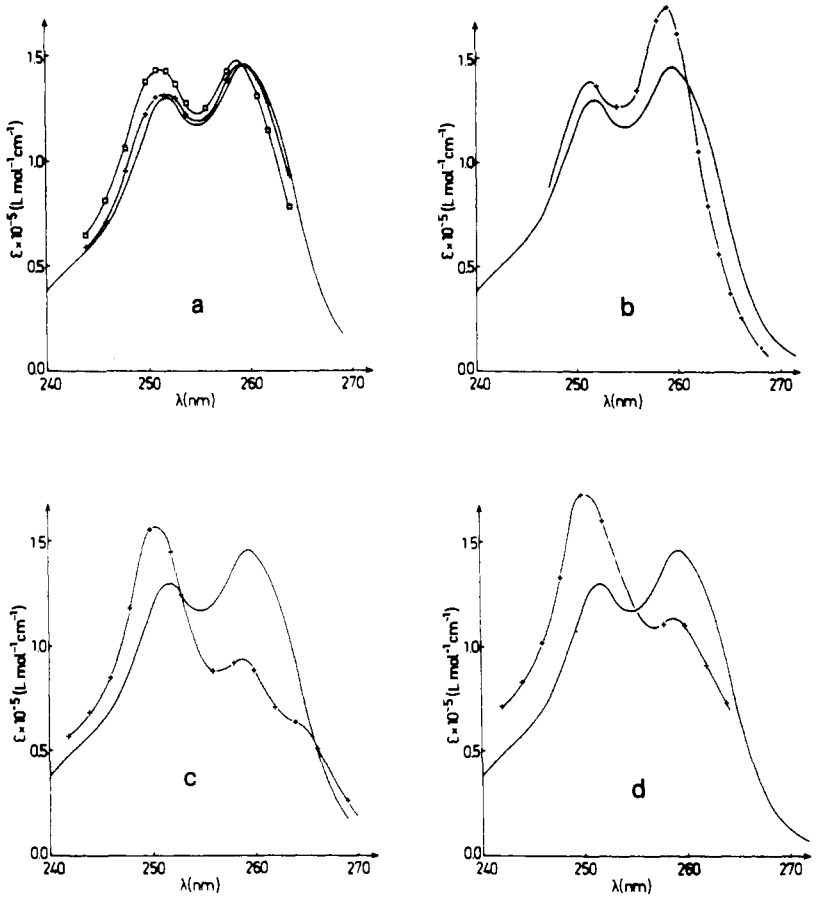


Figure 6. Calculated electronic absorption spectra of the complexes of receptor **1** with S_5^{2+} (a), S_7^{2+} (b), S_9^{2+} (c), S_{12}^{2+} (d). (—) free ligand; (– + –) $\mathbf{1}S_n^{2+}$, $2Cl^-$; (– □ –) $\mathbf{1}(S_n^{2+}, 2Cl^-)_2$ ($CH_3OH/CHCl_3$ 9:1 (v/v)).

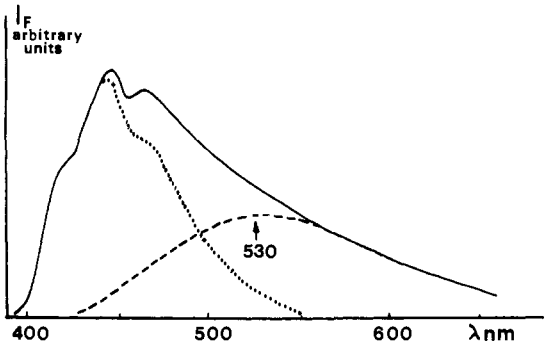


Figure 7. Corrected fluorescence emission spectra of **1** (—) and **2** (···) in degassed methanol (concentration < 10^{-5} M, 25 °C). The excimer contribution (– –) is obtained from difference spectra between **1** and **2**; λ_{exc} = 380 nm.

chain. The strongest enhancements are noted for S_6^{2+} and S_7^{2+} in agreement with the results outlined above. That the fluorescence quantum yield of the complexes is decreasing with increasing diammonium chain length suggests the occurrence, in these more flexible cryptates, of conformations where the two anthracene nuclei are not completely parted from each other. The resulting interactions, efficient enough to allow the quenching of the anthracenic chromophore fluorescence, would not lead however to the formation of excimer-type fluorescent species.

Due to the remarkable fluorescent properties of the anthracene ring, an elegant way to monitor the complexation between **1** and the diammonium substrates is provided by fluorescence titration experiments. In the case of S_6^{2+}, a binding-induced fluorescence enhancement has been recorded as a function of the concentration of salt (Figure 9).

Proposed Structures of the Complexes. In order to rationalize these experimental data, different structures can be proposed for

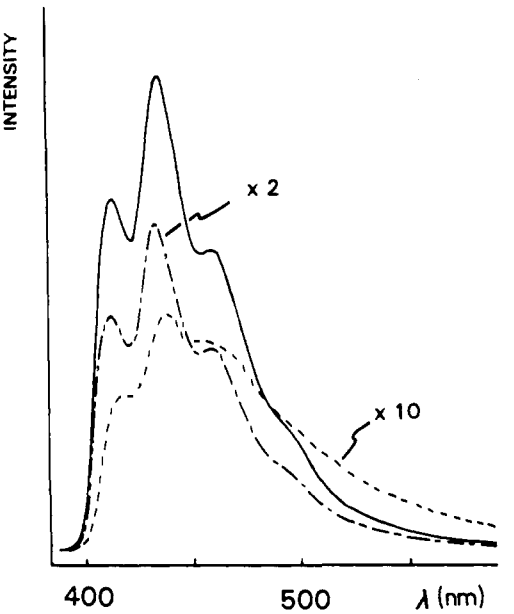


Figure 8. Corrected fluorescence emission spectra of the complexes of **1** in degassed $CH_3OH/CHCl_3$ 9:1 (v/v) (concentration < 10^{-5} M, λ_{exc} = 380 nm, 25 °C) with S_5^{2+}, $2Cl^-$ (– –), S_6^{2+}, $2Cl^-$ (—), and S_{12}^{2+}, $2Cl^-$ (— – —) (substrate concentration ca. 10^{-3} M).

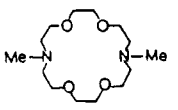
the complexes. Although direct comparison with literature data about the complexation of diammonium substrates is difficult because they were obtained under different experimental conditions (Table V), the new bisanthracenyl macrotricyclic receptor **1** appears to be a good ligand of diammonium substrates.

The most stable complexes are formed with the S_6^{2+} and S_7^{2+} cations, their length fitting well with the size of the internal cavity

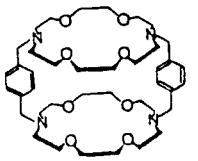
Table V. Stability Constants of Internal Diammonium S_n^{2+} Complexes with Various Macrocyclic Ligands[a]

1 : this work

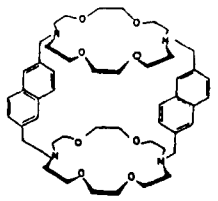
3 :



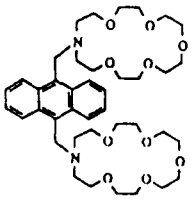
5 :



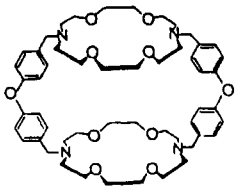
7 :



4 :



6 :



ligands	1	3	4	5	6	7
exptl conditions	$CH_3OH/CHCl_3$ (9:1) T = 25 °C absorptn spectroscopy	PC: $1,2C_2H_4Cl_2$ (2:1) T = 25 °C polarography (38)	$CH_3OH/CHCl_3$ (1:1) T = 25 °C fluorescence (19)	PC: $1,2C_2H_4Cl_2$ (2:1) T = 25 °C polarography (38)		$CDCl_3/CD_3OD$ (9:1) T = −59 °C NMR (32)
substrates	β (mol^{-1} L)					S
n = 3		(0.9 ± 0.4) × 10^3	~1.9 × 10^5	≥10^6	(5.5 ± 1.0) × 10^3	
4			~3.2 × 10^5	≥10^6	(4 ± 2) × 10^3	8
5			~3.2 × 10^5	≥10^6	(13 ± 3) × 10^3	32
6	(5.9 ± 1.2) × 10^6		~1.6 × 10^5	(1.2 ± 0.8) × 10^3	(7 ± 1) × 10^3	11
7	(1.4 ± 0.6) × 10^7		~5.3 × 10^4	(1.0 ± 0.6) × 10^3	(6 ± 2) × 10^3	6
8	(1.2 ± 0.1) × 10^6		~7.9 × 10^4			1
9	(2.0 ± 0.1) × 10^6					
10	(1.6 ± 0.1) × 10^5					
12	(3.9 ± 1.3) × 10^4					
NH_4^+		(2.1 ± 0.4) × 10^3		(4 ± 1) × 10^3 (6 ± 3) × 10^7 [b]	(4 ± 2) × 10^8 [b]	

[a] S, selectivity; PC, propylene carbonate. [b] Global thermodynamic constant for dinuclear complexes.

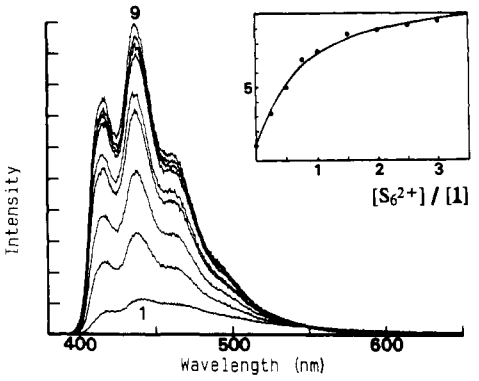


Figure 9. Fluorescence emission intensity of receptor **1** (concentration 10^{-5} M) in nondegassed $CH_3OH/CHCl_3$ 9:1 (v/v) as a function of added S_6^{2+}, $2Cl^-$ (25 °C); λ_{exc} = 369 nm (isosbestic point). S_6^{2+}, $2Cl^-$ (10^{-5} M): 1, 0.0; 2, 0.25; 3, 0.50; 4, 0.75; 5, 1.0; 6, 1.5; 7, 2.0; 8, 2.5; 9, 3.0. The titration curve $I_f \alpha$ [S_6^{2+}] is given in the inset.

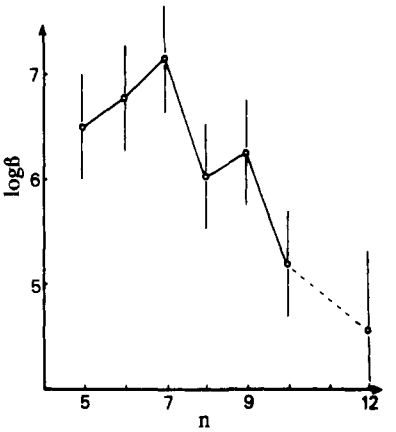


Figure 10. Stability constant of $1S_n^{2+}$ complexes plotted against the chain length n. ($CH_3OH/CHCl_3$ 9:1 (v/v); 25 °C). Error bars were drawn according to experimental error values given in Table III.

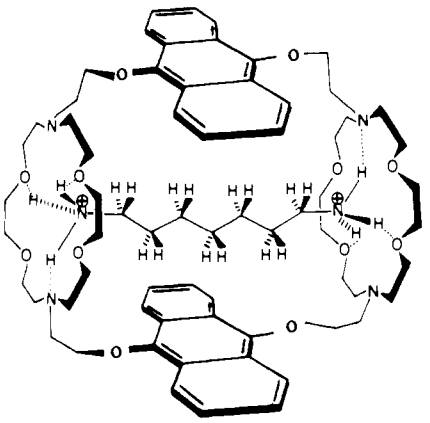
of the receptor. Their stability is about one order of magnitude higher than that of the $1S_n^{2+}$ (n = 9, 10, 12) complexes (Table III). Figure 10 shows a nonmonotonous variation of the stability constants with the length of the substrates, and similar behavior has already been reported for flexible ligands, the monoanthracene bicyclic ligand[19] **4** and the bisdiphenyl ether tricyclic receptor[38] **6**.

The structure of receptor **1** should be flexible. Indeed the OCH_2CH_2 linkages in the anthracene-containing lateral bridges are likely to bring some degrees of freedom as observed in previous systems.[38]

The preferential complexation of diammoniums S_6^{2+} and S_7^{2+} results from the optimal structural complementarity between the receptor and the substrates. As demonstrated elsewhere[32] for the complex of cadaverine dication with a bisnaphthalene macrotricyclic ligand, S_6^{2+} and S_7^{2+} are expected to be held inside the cavity of **1** and fully extended, so that they form a dynamically rigid super structure in which the intramolecular formation of excited complexes involving the two anthracene units is hindered (Chart II). In these complexes, all oxygen sites at the meso positions of the anthracene rings would display an endo orientation, i.e., with their free dipole moment pointing toward the inside of the cavity and interacting with the positive-charged extremities of the guest anchored to the N_2O_4 macrocycles.

(38) Boudon, C.; Gross, M.; Kotzyba-Hilbert, R.; Lehn, J.-M. *J. Electroanal. Chem.* **1985**, *191*, 201.

Chart II. Hypothetical Structure of the Inclusion Complex $1S_7^{2+}$



Conversely, long-chain substrates might be flexible enough to fit and stabilize an opened-cavity conformation of the receptor **1** as revealed by examination of CPK molecular models. Here the phenolic-type oxygen sites would exhibit an exo orientation and part of the aliphatic chain of the substrate would be located outside the cavity. The conformational dynamics likely to prevail in these nonoptimal complexes could account for the observation of the poorly resolved ^1H NMR spectra and of residual intramolecular interactions between the anthracene nuclei in both ground and excited states. The threshold between these two hypothetical structures in solution would be reached for $n = 8$ or 9.

These interpretations lie on the assumption that conformational changes of the host molecule are associated with the molecular recognition processes and this possibility has been recently justified in terms of adaptability,[39] rather than complementarity, between a flexible biscrown ether peptidic receptor and a range of linear diammonium cations (S_n^{2+}, $n = 2$–9). Finally, it is to be mentioned that the dependence of the receptor fluorescence quantum yields with the chain length of the guest dications (Figure 11) reflects that of the stability constants (Figure 10) except in the case of S_5^{2+} (see below). This qualitative correlation in the case of **1** could allow a rough estimation of the complexation selectivity of the receptor[40] **8** toward S_n^{2+} substrates (Chart III). From the dependence of its fluorescence emission intensity with n (Figure 11), the selectivity of **8** is likely to be increased for longer dications in agreement with a larger cavity size.

The behavior of S_5^{2+} is particular as it forms a 1:2 complex in addition to the 1:1 complex (Table III); the binding constant of the 1:1 complex is of the order of magnitude as that of S_6^{2+} and S_8^{2+}, but it is observed that in the presence of a large excess of S_5^{2+}, the equilibrium is shifted toward the 1:2 complex. A tentative representation of their schematic structures is given in Scheme I. The fluorescence quantum yield (determined in the presence of a large excess of S_5^{2+}) most probably originates in the emission of the 1:2 external complex which displays a dual fluorescence similar in shape and quantum yield to that of the free ligand in contrast with the 1:1 complexes displayed by the other S_n^{2+} salts investigated. Thus, the high binding constant of the 1:1 complex ($\log\beta = 6.5$) should not necessarily parallel the rather low fluorescence quantum yield ($\Phi_F = 0.11$).

Conclusion

The macrotricyclic receptor **1** displays a complex fluorescence spectrum made of monomer- and excimer-type emission, the latter resulting from the manifold intramolecular interaction between the anthracene and amino chromophores. The fluorescence of that compound was shown to be very sensitive to the presence of α,ω-alkanediammonium ions. Those molecular cations that enter into the cavity of **1** form stable mononuclear dihapto cryptates, the methylenic chain being held between the two aromatic rings, and an inhibition of the excimer formation is observed as a main consequence. *These effects are dependent on the chain length of the diammonium substrates.* The study of the macrotricyclic receptor **1** is a first step toward the development of luminescent probes for the detection of linear diammonium aliphatic guest by fluorescent spectroscopy.

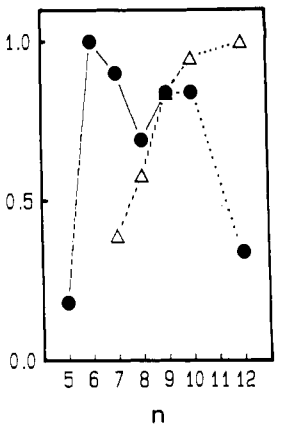
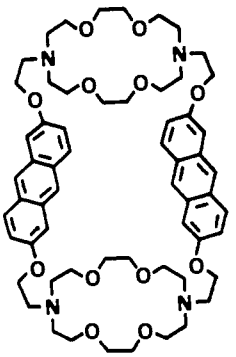


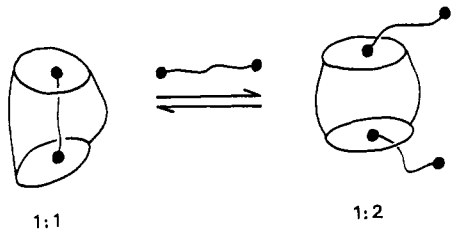
Figure 11. Ratio of the fluorescence quantum yields Φ_f^n/Φ_f^6 (●, values taken from Table IV) and Φ_f^n/Φ_f^{12} (△, unpublished data, nondegassed, $n = 5$ and 6 noninvestigated) calculated for the complexes $1S_n^{2+}$ and $8S_n^{2+}$, respectively, and plotted against the chain length n ($CH_3OH/CHCl_3$ 9:1 (v/v), 25 °C).

Chart III. Macrocyclic Receptor **8** Incorporates 2,6-(Instead of 9,10-)Disubstituted Anthracene Units in Order To Encapsulate Longer Diammonium Molecular Substrates



8

Scheme I. Schematic Representation of the Two Complexes between **1** and S_5^{2+} (1:1 Internal and 1:2 External)[a]



[a] Receptor **1** is depicted by a flexible cylinder; ~ S_5^{2+}.

Acknowledgment. La Région Aquitaine is thanked for partial support of the Centre d'Etudes de la Structure et d'Analyse des Molécules Organiques equipment. The CNRS and the University Bordeaux I are gratefully acknowledged for financial assistance.

(39) Voyer, N.; Deschênes, D.; Bernier, J.; Roby, J. *J. Chem. Soc., Chem. Commun.* **1992**, 134.

(40) Fages, F.; Bouas-Laurent, H. et al. unpublished results.