

Synthesis and photophysical study of 4-(N-monoaza-15-crown-5) stilbenes forming TICT* states and their complexation with cations

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Abstract: Three new 4-(N-monoaza-15-crown-5)Stilbene derivatives (DS-Crown, DCS-Crown and PDS-Crown) were synthesized in order to study their spectroscopic properties in connection with the complexation of cations. The three fluoroionophores had almost identical photophysical properties as their counterparts, with a dimethylamino group instead of the macrocycle, but upon complexation by alkali and alkaline-earth metal ions, they showed hypso and hypochromic shifts of the absorption spectrum and a solvent-dependence of the fluorescence: particularly the p-phenyl derivative (PDS-crown) complexed with Ca^{2+} in n-BuCN led to a dual fluorescence ascribed to an equilibrium, in the excited state, between the complexed ligand involving the nitrogen of the chromophore, as in the ground state, and the cation-ligand separated by the solvent where an additional molecule of n-BuCN entered into the coordination sphere of Ca^{2+} substituting for the aromatic nitrogen-cation interaction.

INTRODUCTION

The discovery that cations and anions form stable complexes with macrocyclic polyethers and polyamines (ref.1) has opened the door to several broad and fruitful areas of chemical investigation. Particularly, there is considerable interest for compounds where insertion of a cation into the ligand cavity can change the photophysical properties i.e. variation of fluorescence intensity and/ or wavelength upon formation of metal complexes. The recognized high sensibility of the absorption and fluorescence spectroscopies led to the design of Chromo- and Fluoroionophores (ref.2).

Although the precise structure of macro-(poly)cyclic receptors such as crown ethers are felt to be essential for controlling their ionophoric properties, little is known in solution; i.e. in the conditions where complexation and transport take place. The solvent affects not only the complex stabilities and selectivities (ref.3,4), but also the nature of the complex (ref. 6-8). In some cases it has been observed, depending on the nature of the solvent and of the counterion, an "inclusive" or "exclusive" type of complexation (ref 5).

In the present paper, we report the synthesis and the photophysical properties of p-(N-monoaza-1-tetraoxa 4,7,10,13-cyclopentadecane) stilbene (DS-Crown, (1)) linked to various substituents (Fig. 1) and the effect of alkali and alkaline-earth-metal cations. The series analysed is DS-Crown (1), DCS-Crown (2), (p-cyano substituent), and PDS-Crown (3), (p-phenyl substituent). The substituent effect on the complexing ability is examined in light of possible correlations between the ease of the TICT state formation and the possible release of the cation in the excited state.

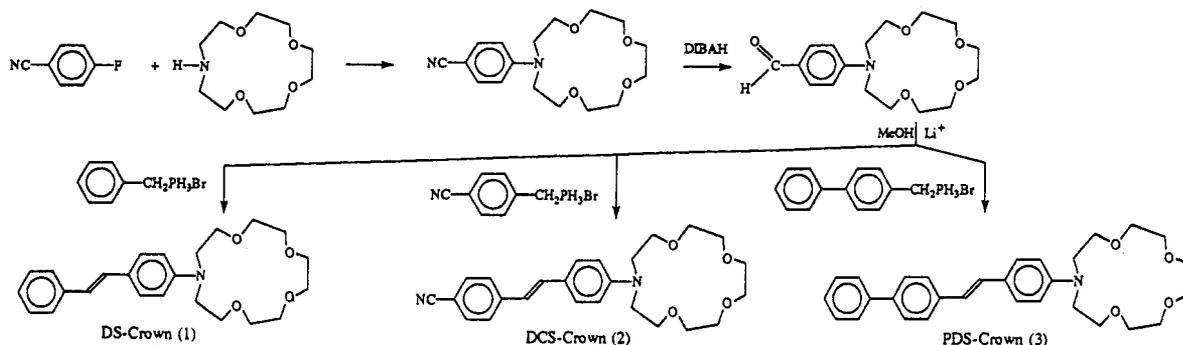
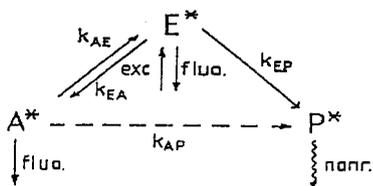


Fig. 1: Synthesis and molecular structure of DS-Crown and model compounds.

* TICT = Twisted Intramolecular Charge Transfer

A previous study of DCS (4) (ref.8,9) and DS (5) (ref.10,11), which can be considered as the model compounds without complexing properties of DCS-Crown and DS-Crown, where the crown has been replaced by the dimethylamino group, led us to propose a three-state kinetic scheme (scheme I), which in addition to state E* (planar geometry) and P* (double bond twist) contains a third state, A* (single bond twist, TICT state) which is the state responsible for the main part of the emission.



Scheme I: Three-state kinetic scheme proposed for the interpretation of the photophysical behaviour of donor-acceptor stilbenes

In the azacrown compounds the nitrogen atom simultaneously acts as an electron donor to complexed cations as well as to the chromophore. When the complexed crowns are excited, the electron flow from the nitrogen to the chromophore weakens the interaction with the cation, which can eventually be expelled. This ejection capacity should follow the magnitude of the electron delocalization in the E* state and /or the TICT state if reached.

1. EXPERIMENTAL SECTION

Synthesis: 4-(N-monoaza-1-tetraoxa-4,7,10,13-cyclopentadecane)benzotrile (6) was prepared by nucleophilic aromatic substitution of 4-fluorobenzotrile with monoaza-15-crown-5 according to the general procedure given by Suhr for secondary amines (ref.12); reaction with DIBAH and then with the relevant phosphonium salts led to DS-Crown (1), DCS-Crown (2) and PDS-Crown (3). All the compounds were purified by column chromatography on silica gel.

Materials and Apparatus: Solvents used were of spectrometric grade either from SDS, or from Merck. Butyronitrile (Fluka) was successively stirred with active carbon, K₂CO₃, KMnO₄, P₂O₅ and distilled after filtration. Alkali-metal and alkaline-earth-metal perchlorates purchased from Janssen and Alfa were of the highest quality available and vacuum dried over 24 hours at 140°C, and kept anhydrous over P₂O₅ in a dessicator.

The absorption spectra were recorded on a Varian Cary 219 spectrometer. The corrected emission spectra were obtained on a Fluorolog Spex 212. The fluorescence quantum yields were measured by using quinine bisulfate in 1N H₂SO₄ ($\Phi_f = 0.55$) as a standard. The optical density was lower than 0.1 and the solutions were not degassed. The temperature effect was carried out with solutions degassed by the freeze-pump-thaw method, with an optical density around 0.08 (fluorescence) and 1 for absorption. Fluorescence lifetime measurements were performed with a single photon counting (SPC) equipment described elsewhere (ref.13) using synchrotron radiation from Bessy (single bunch mode) as excitation source. The decay times were fitted using the iterative reconvolution procedure, which allowed a time resolution down to 0.1 ns and a relative precision of better than 0.1 ns.

2. SPECTROSCOPIC STUDY OF THE AZACROWN PROBES

2.1 Solvatochromism: The main characteristics of ultraviolet-visible and fluorescence spectra of DS-Crown, DCS-Crown and PDS-Crown are reported in table 1. For the three compounds the absorption maxima are weakly affected by an increase of the polarity while fluorescence maxima are strongly redshifted indicating a larger dipole moment in the excited state. The dipole moment of the excited state (μ_e) can be determined by the solvatochromic method. The equations relevant for calculating μ_e have been first derived by Ooshika, Lippert and Mataga (ref.14-16). All these equations are based on the Onsager description of a solute-induced reaction field inside a spherical solvent cavity of radius "a" (ref.17). With the usual assumptions (ref.18-19) the solvatochromic equation (1) can be used:

$$hc\nu(F) = -2\mu_e(\mu_g - \mu_e)\Delta f'/a^3 + \text{Const}' \quad (1)$$

The polarity parameter $\Delta f'$ is defined by $((\epsilon - 1) / (2\epsilon + 1) - 0.5(n^2 + 1) / (2n^2 + 1))$ and the indices e and g denote ground and electronically excited state respectively. The solvatochromic slopes were determined by the plot of fluorescence maxima versus the solvent polarity parameter $\Delta f'$ and gathered in table 2. For the Onsager parameter "a" we took the value obtained for 40% of the long axis of the model compounds (the long ethylene oxide chain, which is not part of the auxochromic group, is neglected); i.e. 4.36 Å, 5.43 Å and 5.5 Å for DS-Crown, DCS-Crown (ref.9) and PDS-Crown respectively. The dipole moments of the ground state have been

Compounds	Solvents	λ_{abs}	λ_{flu}	$\Delta\nu_{\text{st}}$	Φ_f
DCS-Crown (I)	n-Hexane	384	420	2232	0.014
	Bu ₂ O	388	451	3600	
	Et ₂ O	387	473	4698	
	THF	394	486	4805	0.030
	CH ₂ Cl ₂	390	504	5800	
	BuCN	395	513	5823	0.063
	DMF	398	517	5783	
CH ₃ CN	395	502	5396		
DS-Crown (II)	n-Hexane	353	382	2151	0.011
	Bu ₂ O	354	397	3060	
	Et ₂ O	354	415	4268	
	THF	356	417	4109	0.011
	CH ₂ Cl ₂	358	430	4677	
	BuCN	356	434	5048	0.013
	DMF	360	437	4894	
CH ₃ CN	356	438	5259		
PDS-Crown (III)	n-Hexane	367	408	2738	0.164
	Bu ₂ O	369	435	4112	
	Et ₂ O	370	444	4505	
	THF	374	470	5461	0.199
	CH ₂ Cl ₂	372	467	5468	
	BuCN	374	478	6034	0.220
	DMF	375	490	6259	
CH ₃ CN	373	482	6063	0.274	

Table 1: Absorption and fluorescence maxima in nm, Stokes shift $\Delta\nu_{\text{st}}$ (cm⁻¹) and fluorescence quantum yields (Φ_f) of the three azacrowns in different polarity (Δf), at room temperature.

Compounds	Slopes ($\Delta\nu_{\text{st}}$)	a (Å)	μ_g (D)	μ_e (D)
DS-Crown	11224	4.36	2.41	11.35
DS	12335			11.77
DCS-Crown	13880	5.43	6.95	18.5
DCS				21.5
PDS-Crown	13289	5.5	2.41	15.84

Table 2: Dipole moment (Debye units) of the three azacrowns and their model molecules from solvatochromic slopes obtained according equation (1) taking into account n-hexane, Bu₂O, Et₂O, THF, DMF and CH₃CN.

taken equal to 2.41 D for DS (ref.21), 6.45 D for DCS (ref.20) and for PDS-Crown, in first approximation, equal to DS-Crown (2.41 D). Then the derived excited state dipole moment for the three dyes were: $\mu_{\text{e DS-Crown}} = 10.77$ D, $\mu_{\text{e DCS-Crown}} = 18.50$ D and $\mu_{\text{e PDS-Crown}} = 15.84$ D. The values of the first two are similar to those of the model compounds DS ($\mu_{\text{e}} = 11.77$ D (ref.11)), DCS ($\mu_{\text{e}} = 21.5$ D (ref.9)) and show that the introduction of the azacrown instead of the dimethylamino group doesn't affect notably the polarity of the excited state.

2.2 Quantum yields: The quantum yield of fluorescence (Φ_f) of the three azacrowns in different solvents are collected in table 1. The variations of Φ_f with solvent polarity are interpreted within the three-state model presented above (scheme 1). The fluorescence quantum yield of DS-Crown is not significantly affected in highly polar solvents, whereas Φ_f of DCS-Crown and PDS-Crown increase (table 1). For DCS-Crown we can propose that, as for DCS (ref.8,9), the relaxation $E^* \rightarrow A^*$ acts as a trap preventing the excited E^* molecules from the fast photoreaction towards P^* and thus immediate fluorescence quenching. In PDS-Crown the energy of E^* has been lowered by conjugation of the additional phenyl group. In polar solvents the activation barrier for P^* formation is increased by the high polarity of the E^* and A^* states versus the weakly polar state P^* , and leads to an increasing of Φ_f . A quantum chemical calculation of DS showed an increased polarity of the P^* state relative to that of DCS (10 D versus 3 D), which could explain the less efficient quenching of the non emitting channel in polar solvents for DS-Crown.

2.3 Time-resolved measurements: The room temperature fluorescence lifetime of PDS-Crown raises with the polarity of the solvent from 0.49 ns (CH₂Cl₂) to 0.56 ns (CH₃CN) attributed to an increased energy barrier between A^* or E^* and P^* . In ethanol the three dyes show an increase of the lifetime from 77 K to intermediate temperature (Fig. 2). Such behaviour has been previously observed for DCS (increase by 0.5 ns from 77 K to 190 K (ref.8,9) and DS (0.2 ns from 77 K to 156 K (ref.10,11)) and was assigned to the formation of an emitting TICT state. The increases for DCS-Crown (0.25 ns) and DS-Crown (0.1 ns) are lower than for the model compounds but still clearly present. For higher temperatures the lifetimes shorten as usual, due to the twisting of the double bond. The resulting fluorescence lifetime maxima occur at different temperature for DS-Crown (160 K), PDS-Crown (172 K) and DCS-Crown (175 K). From the temperature dependence of τ_f , the non-radiative decay rate constant k_{nr} was derived using equation (2);

$$k_{\text{nr}}(T) = \tau_f^{-1}(T) - \tau_{f,\text{ref}}^{-1}(T) \quad (2) \quad \text{with } \tau_f^{-1} = 1/(k_f + k_{\text{nr}}) \text{ and } \tau_{f,\text{ref}}^{-1} = 1/\tau_f.$$

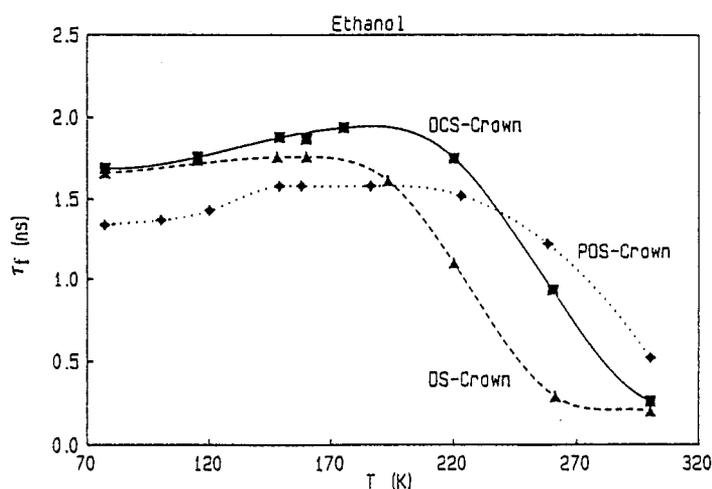


Fig. 2: Plot of the fluorescence lifetimes τ_f (ns) versus temperature (K) in ethanol for (—) DCS-Crown, (- - -) DS-Crown, and (.....) PDS-Crown.

The longest lifetimes ($\tau_{f,ref}$) are reported in table 3 and are assumed to correspond to the reverse of the emitting rate constant, when $k_{nr} \approx 0$. For comparison of the nonradiative decay step of all three dyes, we choose $\tau_f(T)$ at 260 K (where a large decrease of τ_f due to k_{nr} is already reached). Calculated values of k_{nr} at 260 K are listed in table 3.

Table 3: Fluorescence decay times (ns) at 260 K and at the reference temperature (T_{ref}), derived radiationless decay rate constants k_{nr} ($10^7 s^{-1}$), slopes, correlation coefficient, and activation energies ($kJ \cdot mol^{-1}$) of DCS-Crown, DS-Crown and PDS-Crown in ethanol.

Compounds	T_{ref} (K)	$\tau_{f,ref}$	$\tau_{f,260K}$	k_{nr}	Slope	r	E_a
DCS-Crown	175	1.94	0.93	56	3.32	0.99	27.6
DS-Crown	160	1.76	0.29	288	2.51	0.98	20.9
PDS-Crown	172	1.60	1.22	19	2.48	0.98	20.6

From the lifetimes obtained at 220 K, 260 K and 300 K we calculated similarly k_{nr} and a plot of $\ln(k_{nr})$ versus $1/T$ leads to the activation energy (E_a) for the non-radiative step to the funnel P^* (table 3). The higher activation energy E_a for DCS-Crown ($27.6 kJ \cdot mol^{-1}$) relative to DS-Crown ($20.9 kJ \cdot mol^{-1}$) can be attributed to a greater lowering of the TICT state versus the P^* state for DCS-Crown in EtOH. The same activation energy is calculated for PDS-Crown and DS-Crown but the preexponential terms are markedly different ($3.4 \times 10^{12} s^{-1}$ for PDS-Crown versus $2.7 \times 10^{13} s^{-1}$ for DS-Crown) which could indicate two different ways of deactivation; i.e. $A^* \rightleftharpoons E^*$ to P^* for DS-Crown and a possible direct transition $A^* \rightarrow P^*$ for PDS-Crown.

3. SPECTROSCOPIC STUDY OF THE COMPLEXATION IN THE GROUND AND THE EXCITED STATES PROBES

3.1 Absorption spectra: Addition of alkaline and alkaline-earth perchlorates to solutions of the azacrowns shifts the long wavelength band hypsochromically (table 4). Alkaline-earth-metal perchlorates lead to stronger shifts than alkali-metal perchlorates and the position of the spectra are different and reminiscent of the spectrum of the model molecules without donor substituent such as p-phenylstilbene (PS, Fig. 3). This change in the absorption spectra upon complexation by cations has been previously reported for closely related compounds (ref.22), and attributed to the interaction of the lone pair of the nitrogen atom with the complexed cation. The strength of the interaction between the cation and the nitrogen lone pair depends; i) on the charge density of the cation: stronger effect for divalent cations (table 4). ii) on the cation size over cavity size of the azacrown ($1.7-2.2 \text{ \AA}$ (ref.23,24)): the change on the absorption spectra is higher for cations whose ionic diameter is closest to the cavity size; i.e. stronger effect for Na^+ in the serie of monovalent cation and Ca^{2+} for divalent cations. iii) on the solvent (see below).

3.2 Determination of the stability constant: Complexation constants (K_s) of various salts complex in anhydrous acetonitrile were measured by gradual addition of salt. The resulting spectra of one typical experiment ($10^{-5} M$ of DCS-Crown titrated with various amounts of $Ca(ClO_4)_2$) are shown in Fig. 4. The isosbestic points observed in this case and in all the other experiments with Li^+ , Na^+ , K^+ and Ba^{2+} seem to warrant the formation of a single complex which can be represented by the equilibrium (3).

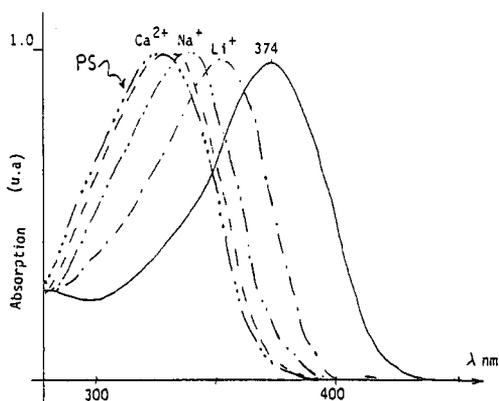


Fig. 3: Absorption spectra of (---) free PDS-Crown (3), (-.-) 3-Li⁺, (-.-.-) 3-Na⁺, (- -) 3-Ca²⁺ and (.....) PS at room temperature.

Table 4: Absorption and fluorescence maxima, quantum yields of fluorescence, in BuCN, of complexed PDS-Crown (LM) relative to the free PDS-Crown (FL).

Salts	Radius (Å)	λ_{Abs} (nm)	$\Delta\nu(Abs)_{LM,FL}$ (cm ⁻¹)	λ_F (nm)	$\Delta\nu(F)_{LM,FL}$ (cm ⁻¹)	Φ_f
None	/	374	0	478	0	0.220
LiClO ₄	1.36	350	1833	467	493	0.164
NaClO ₄	1.94	335	3113	470	356	0.149
KClO ₄	2.66	370	2891	476	88	0.145
Ca(ClO ₄) ₂	1.98	328	3750	387 461	4920 771	0.092
Ba(ClO ₄) ₂	2.68	331	3474	464	631	0.123
CF ₃ COOH	/	327	3843	393	4525	0.049

Assuming 1:1 complexation, K_s of various complexes were calculated using equation (4) (ref.22c).



$$L_o/L = K_s \cdot [M] + 1 \quad (4)$$

Where L and L_o represent the "free" and initial ligand concentration, M the total metal ion concentration. Complexation constants were derived from the slope of a plot of L_o/L versus [M]. The results of all the titration experiments in acetonitrile are compiled in table 5. The highest value is obtained with calcium (log K_s = 4.20), followed by the other divalent cations Ba²⁺ (log K_s = 3.74) and Mg²⁺ (log K_s = 2.47). The monovalent cations are better complexed when their sizes are similar to that of the azacrown; i.e. K_s (Na⁺) > K_s (Li⁺) ≈ K_s (K⁺). The uneffectiveness of silver perchlorate to change the absorption spectra of the azacrowns in acetonitrile points out the operating limitation of these probes (ref.23), but also their sensitivity to the specificity of the process of complexation. Each cation interacts with a specific number of heteroatoms (N,O) (table 5) and with a different strength according to particularly their softness, for example Ag⁺ has a strong affinity for N and the "hard" Li⁺ for O, which explains that although favoured by the preorganisation in the azacrown we don't observe the complexation of Ag⁺ in acetonitrile nor the perturbation of the absorption spectra by Li⁺ in MeOH.

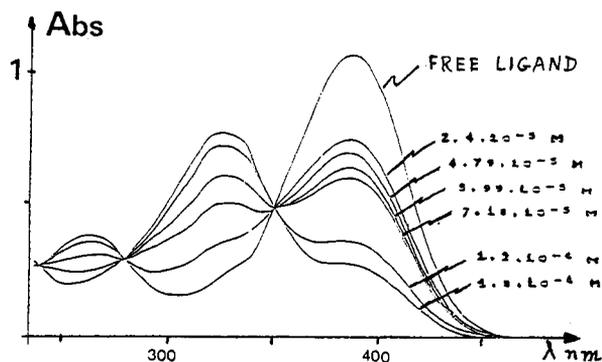


Fig. 4: Absorption spectra of DCS-Crown in acetonitrile obtained during the addition of Ca(ClO₄)₂.

Salts	Radius [26]	Coordination number [27]	Softness (σ) [28]	Solvent	Ln K _s
LiClO ₄	1.36	6	0.247	CH ₃ CN EtOH	1.71 0
NaClO ₄	1.94	6	0.211	CH ₃ CN	2.03
KClO ₄	2.66	6	0.232	CH ₃ CN	1.71
Mg(ClO ₄) ₂	1.32		0.167	CH ₃ CN	2.47
Ca(ClO ₄) ₂	1.98	7	0.180	CH ₃ CN CH ₂ Cl ₂	4.20 5.23
Ba(ClO ₄) ₂	2.68	9	0.184	CH ₃ CN	3.74
AgClO ₄		6	0.073	CH ₂ Cl ₂ MeOH Et ₂ O CH ₃ CN	5.2 3.1 4.3 0

Table 5: Ln K_s values for complexes of DCS-Crown (2) with various salts at room temperature.

3.3 Fluorescence study: In neat acetonitrile, excitation of the fully complexed probes, DS-Crowns/ Ca^{2+} , leads to the fluorescence of the free ligand, only slightly shifted by the proximity of the cation, as it was observed, in the literature, for similar probes (ref.22).

In dichloromethane at room temperature the fluorescence spectra of DCS-Crown (2) and PDS-Crown (3) fully complexed by Ca^{2+} are the mirror-image of the absorptions and remain unaltered at low temperature whereas under the same conditions, DS-Crown (1) shows dual fluorescence (Fig. 5).

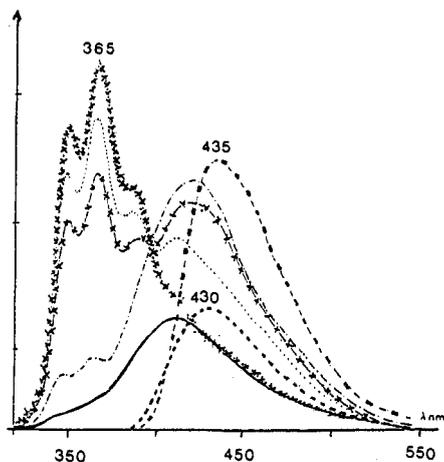
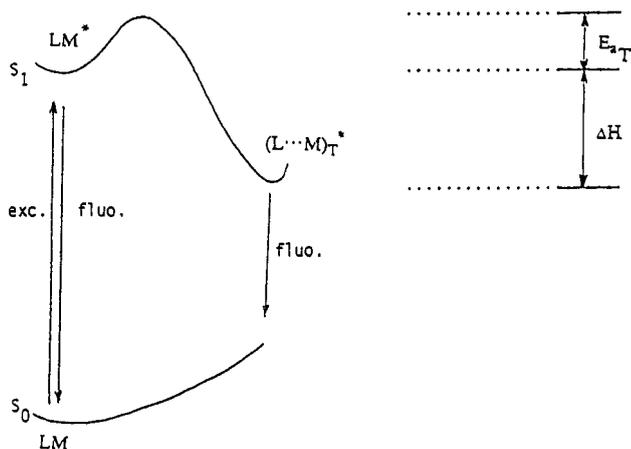


Fig. 5: Fluorescence spectrum of $3 \cdot 10^{-6}$ M solution of DS-Crown in CH_2Cl_2 function of temperature: Free ligand (---) 302 K, (-.-) 197 K and complexed ligand with $\text{Ca}(\text{ClO}_4)_2$ at (—) 300 K, (-.-.-) 239.4 K (—-—) 195 K, (....) 187.5 K and (****) 183 K.

Scheme II: Proposed two-state kinetic scheme used for the interpretation of the photophysical behaviour of DS-Crown



For 2-Ca^{2+} , 3-Ca^{2+} and for the short-wavelength band of 1-Ca^{2+} , the fluorescence band is similar to that of the protonated species of the compounds without donor group. That means that in poorly coordinating solvent the excited state keeps completely or partially (1-Ca^{2+}) its interaction with the cation.

The long-wavelength band of 1-Ca^{2+} , which resembles that of the free ligand ($\Delta\nu = 1558 \text{ cm}^{-1}$ shift to high energy), points out to the quasi disappearance of the interaction between the cation and the nitrogen of the chromophore. The breaking of the cation-nitrogen interaction is the result of the reduced electron density on the nitrogen when the chromophore is excited. The initially excited complexed ligand (LM^*) state leads to the TICT state $(\text{L}\cdots\text{M})_{\text{T}}^*$, which is more easily reached in the complexed crown if it is already partly twisted (ref.21d). A possible mechanism is sketched in scheme II, where LM^* represents the complexed ligand and $(\text{L}\cdots\text{M})_{\text{T}}^*$ the ion-perpendicular ligand.

However, the proportion of the short wavelength fluorescence of 1-Ca^{2+} increases when the temperature is lowered. The observation of an isoemissive point reveals an equilibrium between the complexed planar state and the TICT complexed species. From a two states model for the excited state, when the ground state is not affected by the temperature, the temperature study allows the measurement of the enthalpy change (ΔH) and the activation energies (E_{aT}) involved between LM^* and $(\text{L}\cdots\text{M})_{\text{T}}^*$ states. A plot from 183 K to 239 K of $\ln [\Phi_{f(\text{L}\cdots\text{M})_{\text{T}}^*} / \Phi_{f(\text{LM}^*)}]$ versus $1/T$ leads to $E_{aT} = 5 \text{ kJ}\cdot\text{mol}^{-1}$ (Fig. 6). The reason why only DS-Crown led to the long-wavelength emission could result from the lower activation energy towards the TICT state.

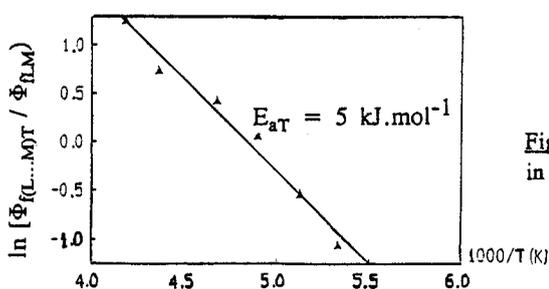


Fig. 6: Plot of $\ln [\Phi_{f(\text{L}\cdots\text{M})_{\text{T}}^*} / \Phi_{f(\text{LM}^*)}]$ versus $1/T$ of 1-Ca^{2+} in CH_2Cl_2 and determination of E_{aT} .

In moderately polar solvent (*n*-BuCN) and whatever the temperature, between 353 K to 172 K, DS-Crown and DCS-Crown led to one fluorescence band close to the fluorescence of the free ligand. At room temperature, the fluorescence of PDS-Crown presents two bands, and lowering the temperature from 353 K to 193 K, strongly affects the fluorescence spectra as represented in Fig. 7. Excitation spectra from room temperature until 193 K are not wavelength dependent. We propose that the short wavelength band derives from the complexed ligand (LM) formed in the ground state while the long wavelength band, close to the emission of the free ligand, results from the ion-ligand separated by the solvent (L/S/M) in analogy with the classical contact ion-pairs and solvent separated ion-pairs equilibrium (ref.25).

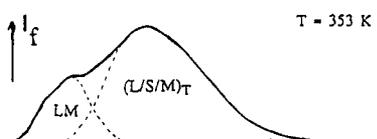
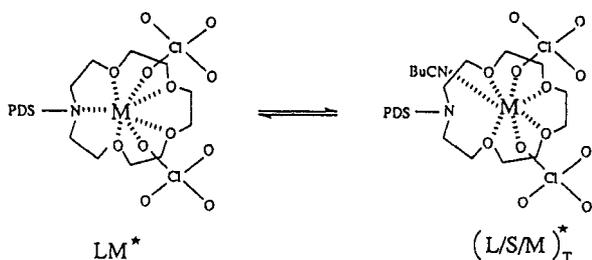


Fig.7: Variation of the dual fluorescence of 3-Ca^{2+} in BuCN versus the temperature; the short wavelength is attributed to LM^* and the long wavelength to $(\text{L/S/M})_{\text{T}}^*$.

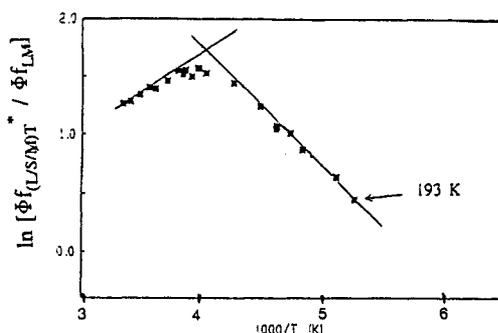
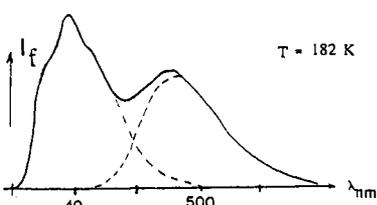
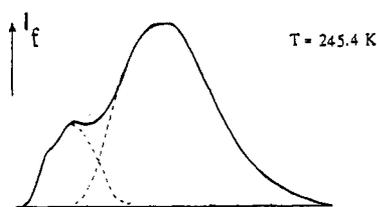


Fig.8: Determination of E_{aF} , E_{aB} and ΔH by plot of $\ln [\Phi_{\text{f(L/S/M)}_{\text{T}}}^* / \Phi_{\text{fLM}}^*]$ versus $1/T$.

If we measure the emission bands as a function of the temperature we can obtain the activation energies of the forward (E_{aF}) and the backward (E_{aB}) reactions between LM^* and $(\text{L/S/M})_{\text{T}}^*$ and also the enthalpy change (ΔH). The ratio $\Phi_{\text{f(L/S/M)}_{\text{T}}}^* / \Phi_{\text{fLM}}^*$ is given by equation (5);

$$I_{(\text{L/S/M})_{\text{T}}} / I_{\text{LM}} = \Phi_{\text{f(L/S/M)}_{\text{T}}}^* / \Phi_{\text{fLM}}^* = (k_{\text{f}} \cdot k_{\text{aF}}) / (k_{\text{f}} \cdot (k_{\text{aB}} + k_{\text{f}} + k_{\text{CI}})) \quad (5)$$

Experimentally, Fig. 8 shows high temperature (HT) and low temperature (LT) regions with a maximum at intermediate temperature ($T_{\text{max}} = 263 \text{ K}$). At sufficiently high temperature, where k_{aB} is larger than $k_{\text{f}} + k_{\text{CI}}$, the process is thermodynamically controlled, and the slope of the plot $\ln [\Phi_{\text{f(L/S/M)}_{\text{T}}}^* / \Phi_{\text{fLM}}^*]$ versus $1/T$ gives $-\Delta H/R$. In the LT region where $k_{\text{aB}} \ll k_{\text{f}} + k_{\text{CI}}$ the process is kinetically controlled and the slope leads to E_{aF}/R . The thermodynamic parameters derived are $E_{\text{aF}} = 8.56 \text{ kJ} \cdot \text{mol}^{-1}$, $E_{\text{aB}} = 13.11 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta H = -4.55 \text{ kJ} \cdot \text{mol}^{-1}$.

That PDS-Crown is the only one of the three probes from which we can detect the fluorescence of the complexed ligand. This could be ascribed to a higher strength of interaction with the cation in the Franck Condon excited state as indicated by the charge on the nitrogen for the model of the three probes calculated by CNDO/S method for the S_1 state: DS (-0.302), DCS (-0.276) and PDS (-0.319).

To ascertain the hypothesis of an ion-ligand separated by the solvent we have measured the fluorescence spectra of PDS-Crown in CH_2Cl_2 with increasing amounts of BuCN, CH_3CN and H_2O . Variation of the nature and the concentration of the polar solvent in the CH_2Cl_2 solution enables a distinction to be made between the specific

solute-solvent interactions and the macroscopic dielectric solvent effect on the fluorescence spectrum. The addition of the nitrile solvents causes a quenching of the fluorescence (F(LM)) and the appearance of a new emission at long wavelength ($\lambda_{\max} = 448$ nm) which we assigned to the ion ligand separated by the solvent (Fig.9). The wavelength of the emission, is as expected from the ion-dipole proximity, at a slightly higher energy than that of the free ligand in CH_2Cl_2 (448 nm versus 467 nm). The isoemissive point implies the formation of one new fluorescent species (or several always in the same proportion) when nitrile is added and the coordination number of Ca^{2+} lets expect that a solvent separated L/S/M might form (Fig. 9). The absorption and excitation spectra are not affected by the addition of the indicated amount of nitrile which excludes the formation of the solvent separated complex L/S/M already in the ground state. It's the shift of the charge from the nitrogen of the azacrown following the electronic excitation which allows the "insertion" of an additional solvent molecule (Fig. 7). Addition of water leads to a decomplexation of the cation already in the ground state and we have been unable to observe the specific decoordination of the nitrogen chromophore in the excited state.

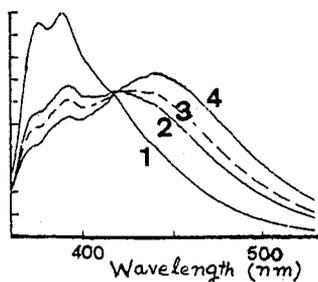


Fig. 9: Fluorescence spectra of PDS-Crown/ Ca^{2+} in CH_2Cl_2 in function of $[\text{BuCN}]$; (1) = 0 M, (2) = 0.015 M, (3) = 0.27 M and (4) = 0.42 M.

Acknowledgements This work has been supported by BMFT (project 05414 FAB1) and the EC-Large Scale Installations Program (GE1-0018-D(B)).

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