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Cation-triggered photoinduced intramolecular charge transfer and fluorescence red-shift in fluorescence probes

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Abstract. – We report the synthesis of two new nonpolar fluorescence cation probes (DDS-crown, **5** and DDB-crown, **6**) designed from stilbene and 1,4-diphenyl 1,3-butadiene, respectively, by substitution at the two ends with two electron-donor groups (D) (dimethylamino and monoaza-15-crown-5), one of which is able to chelate a cation. The absorption and fluorescence spectra in several solvents of different polarity and the picosecond transient absorption spectra give an estimate of the Intramolecular Charge Transfer (ICT) strength in the excited state. When a cation (Ca^{2+}) is chelated by the macrocycle, the ICT process is increased and the fluorescence is red-shifted. These spectroscopic effects of cation-chelation are enhanced in a third probe (DDCS-crown, **7**) derived from DDS-crown by inserting an electron-acceptor (A) group (CN) at the *ortho* position of the macrocycle in order to increase the ICT.

Key words : Fluorescent cation probes, sub-picosecond transient absorption, photoinduced intramolecular charge transfer.

Résumé. – **Transfert de charge intramoléculaire et déplacement bathochrome du spectre d'émission, induits par un cation, dans les sondes fluorescentes.** Nous décrivons la synthèse de deux sondes fluorescentes apolaires (DDS-couronne, DDB-couronne) constituées respectivement des chromophores stilbène et 1,4-diphényl 1,3-butadiène, substitués aux deux extrémités par des groupes donneurs d'électrons (D = diméthylamino et monoaza-15-couronne-5) dont l'un est capable de complexer un cation. Les spectres d'absorption et de fluorescence dans plusieurs solvants de polarité différente et l'étude des spectres d'absorption transitoire (résolution temporelle picoseconde) permettent d'évaluer le taux de transfert de charge à l'état excité. Quand un cation est complexé par le macrocycle un transfert de charge intramoléculaire (TCI) apparaît, ou est accru, à l'état excité et la fluorescence est déplacée vers le rouge. Les effets spectroscopiques de la complexation du cation sont accentués dans une troisième sonde dérivée de DDS-couronne par introduction d'un groupe accepteur d'électron (CN) en position *ortho* du macrocycle.

Introduction

For a long time dipolar conjugated molecules, with a large dipole moment difference in the ground and excited electronic states, have been the most efficient organic compounds for obtaining large second-order hyperpolarizabilities for nonlinear optics (NLO) applications. They have also provided interesting intrinsic fluorescent ion probes when an ionophore maintains a cation in the vicinity of the electron-donor end of the polar molecule. Unfortunately, their dipolar property

in the ground state presents some drawbacks for these two applications, which could be avoided if the dipolar enhancement upon electronic excitation was achieved from apolar molecules. The purpose of this work was thus to trigger a highly polar excited state from nonpolar or slightly polar ground state molecules through cation-interaction.

To be more specific, the simplest theoretical description of the molecular quadratic hyperpolarizability β is a two-level model¹, which suggests that molecules for second-order NLO applications² must possess a

strong charge-transfer electronic transition characterized by a large oscillator strength and a great difference between the ground and the excited state dipole moments. Such requirements have best been met by dipolar, highly polarizable, donor- π -acceptor systems, showing strong charge transfer between the electron-donating and the electron-withdrawing groups upon electronic excitation. But the intermolecular dipole-dipole interactions favor anti-parallel molecular arrangements that cancel their second-order NLO effects in condensed media. Several methods are widely used to artificially achieve noncentrosymmetry but often lead to a thermodynamically unstable alignment. A growing trend is the rational approach to structurally-controlled multimolecular assemblies^{3,4}.

Polar molecules, as those defined above, have also been used as fluorescent cation probes, after chemical modification of one substituent, to get ion recognition⁵⁻⁸. We recently showed that from these molecules, namely the 4-*N,N*-dimethylamino 4'-*A*- (electron acceptor) stilbenes **1** (Fig. 1), we could design fluorescent cation probes **2** by replacing the donor group (NMe₂) with an electronically equivalent *N*-monoaza-15-crown-5 macrocycle that has cation-complexing ability^{9,10}. These fluorescence probes are models of a very popular family of calcium indicators, the fluorescent conjugates of BAPTA¹¹ **3** (BAPTA = 1,2-(bis)2'-amino-phenoxyethane-*N,N,N',N'*-tetraacetic acid), because of the same chromophore-binding site relationship: they are intrinsic fluorescence probes with a nitrogen atom of the fluorophore π system also acting as a ligand for the complexed cation⁵. Upon calcium complexation (**4**) the electron lone pair on nitrogen is stabilized and the absorption spectrum blue-shifted¹², but in the excited state the electron density on the nitrogen atom is lowered, the cation is driven away and, as a result, the fluorescence is hardly changed¹⁰. Therefore, measurement of calcium concentrations from the intensity ratio at two emission wavelengths is still rare¹¹ and a red-shift of the emission, upon calcium complexation, is highly desirable in order to allow relative intensity measurements at two wavelengths outside the endogeneous molecule emission domain.

In this paper we present a photophysical study – absorption, steady-state fluorescence and sub-picosecond transient absorption – of the electronically symmetrical molecules **5** and **6**, and of a slightly polar one **7**, able to interact at one end with an ion (proton or cation), with the aim to direct and increase the intramolecular charge transfer in the excited state of the chromophore. As a result, the fluorescence of these probes should be red-shifted upon cation (proton) interaction, while variation of the cation, particularly towards those that form complexes with two crown-ethers^{13,14}, could lead to acentric materials with a large second-order susceptibility¹⁵ (χ^2).

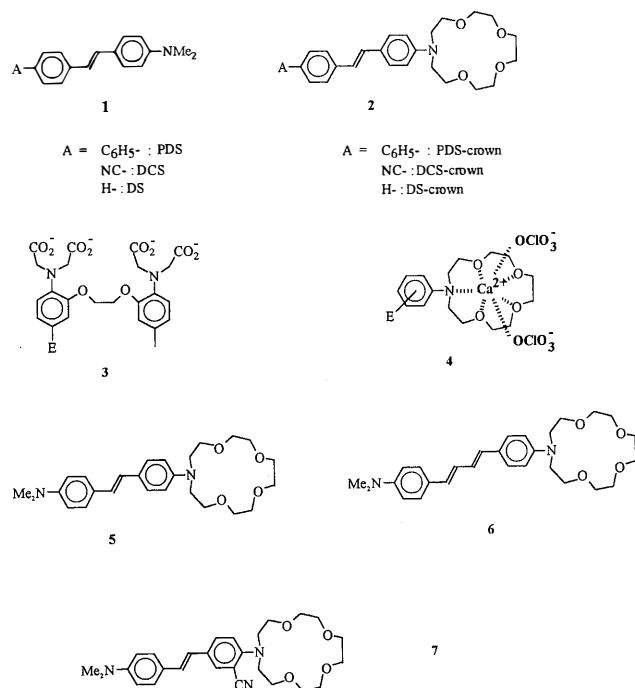


Figure 1. – Structural formula of the compounds.

Experimental section

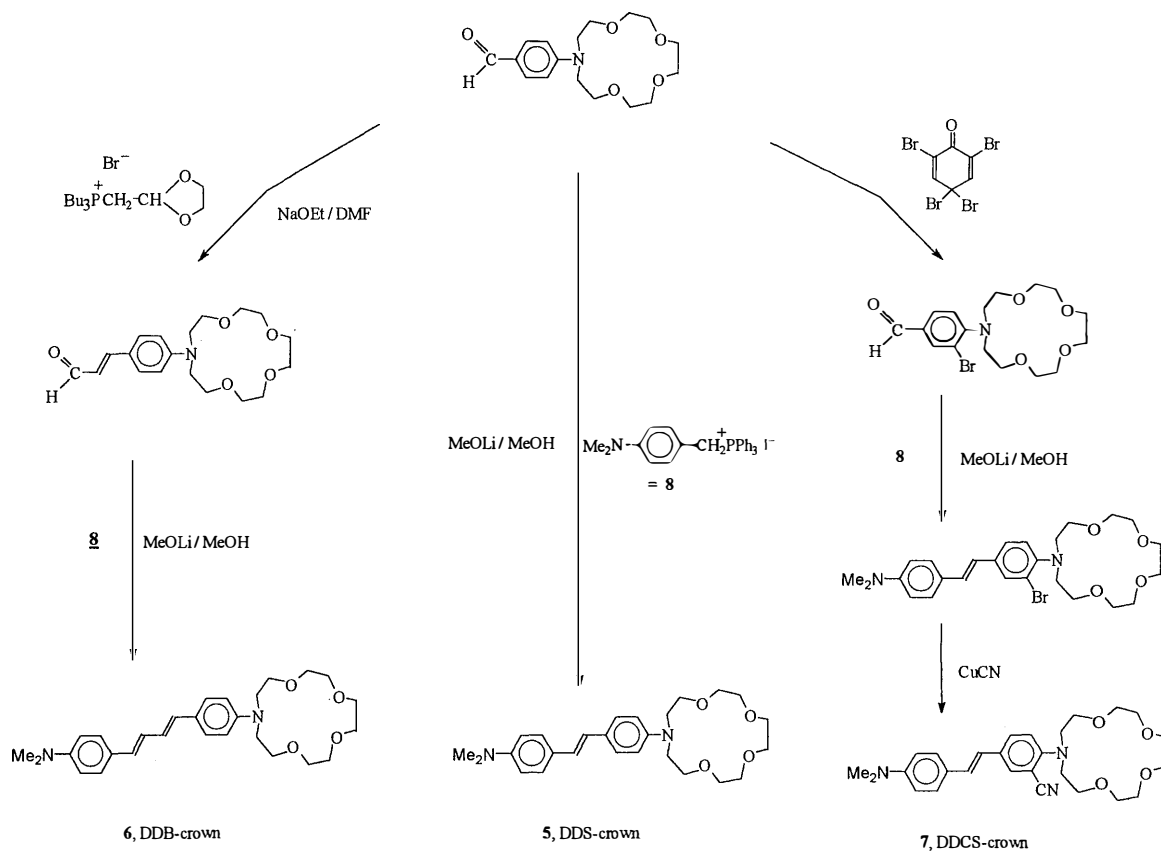
Synthesis

4-*N,N*-dimethylamino 4'-*A* stilbenes and 4-*N*-(1-monoaza-4,7,10,13-tetraoxacyclopentadecane) 4'-*A* stilbenes were prepared as reported earlier^{9,16}. 4-*N*-(1-monoaza-4,7,10,13-tetraoxacyclopentadecane) 4'-*N,N*-dimethylaminostilbene (**5**, DDS-crown), 3-cyano 4-*N*-(1-monoaza-4,7,10,13-tetraoxacyclopentadecane) 4'-*N,N*-dimethylaminostilbene (**7**, DDCS-crown), and 1-(*p*-*N*-(1-monoaza-4,7,10,13-tetraoxacyclopentadecane)phenyl)4-(*p*-*N,N*-dimethylaminophenyl) 1,3-butadiene (**6**, DDB-crown) were synthesized by the route outlined in Scheme 1.

The three new compounds **5**, **6** and **7** were prepared by a Wittig reaction of (*p*-dimethylaminobenzyl)triphenylphosphonium iodide¹⁷ with 4-*N*-(1-monoaza-4,7,10,13-tetraoxacyclopentadecane) benzaldehyde¹⁸, 4-*N*-(1-monoaza-4,7,10,13-tetraoxacyclopentadecane)cinnamaldehyde¹⁹ and 3-bromo 4-*N*-(1-monoaza-4,7,10,13-tetraoxacyclopentadecane) benzaldehyde²⁰, respectively followed by cyanation of the brominated stilbene.

Typical procedure for the Wittig reactions

In a two-neck flask equipped with a refluxing condenser and a dropping funnel, lithium (70 mg) was added to methanol (25 mL) under argon. After dissolution of the metal, the phosphonium salt (1.05 g, 2 mmol) and the aldehyde solutions in methanol (2 mmol)



Scheme 1.

were successively added at room temperature. The solution was stirred at room temperature for 24 h and refluxed for an additional 2 h. After cooling (0 °C), water (100 mL) was added and the resulting solution extracted three times with methylene chloride. The organic phases were dried over Na₂SO₄, filtered and evaporated to dryness. The yellow residue, dissolved in methylene chloride, was eluted through a short silica gel column, the eluent was concentrated and, after addition of methanol, yellow crystals of the *trans* derivatives were obtained (≈ 30%).

DDS-crown, **5**

m.p. = 132 °C; ¹H NMR (CDCl₃, 250 MHz): δ (ppm): 2.96 (6H, s, -CH₃), 3.55–3.66 (16H, m, -CH₂-O-), 3.74–3.79 (4H, t, -N-CH₂-), 6.62–6.74 (4H, 2d, H_{ar}), 6.84 (2H, s, -CH=CH-), 7.32–7.39 (4H, pseudo t, H_{ar}); ¹³C NMR (CDCl₃) δ (ppm): 40.8 (N-CH₃), 52.6 (-CH₂-N<), 68.6, 70.2, 71.4 (-CH₂-O-), 111.6, 112.9, 124.4, 127.0, 127.3 (C_{ar}H), 146.6, 150.0 (Cq); MS (*m/z*): 440 (100%, M⁺•), 308 (13%), 264 (17%), 250 (15%).

DDB-crown, **6**

m.p. = 142 °C; ¹H NMR (CDCl₃, 250 MHz): δ (ppm): 2.89 (6H, s, -CH₃), 3.53–3.58 (16H, m, -CH₂-O-), 3.66–3.71 (4H, m, -N-CH₂-),

6.36–6.76 (7H, m), 7.19–7.31 (5H, m); ¹³C NMR (CDCl₃) δ (ppm): 41.0 (N-CH₃), 54.2 (-CH₂-N<), 70.3, 70.7, 71.4 (-CH₂-O-), 118.0, 131.2, 133.3 (C_{ar}H), 151.0 (Cq); MS (*m/z*): 466 (100%, M⁺•).

DDCS-crown, **7**

m.p. = 84 °C; ¹H NMR (CDCl₃, 250 MHz): δ (ppm): 2.98 (6H, s, -CH₃), 3.66–3.78 (20H, m, -CH₂-O- and -CH₂-N), 6.71–6.97 (2H+3H, m, -CH=CH- and H_{ar}), 7.36–7.50 (4H, m, H_{ar}); ¹³C NMR (CDCl₃) δ (ppm): 41.0 (N-CH₃), 53.8 (-CH₂-N<), 70.0, 70.4, 70.5 (-CH₂-O-), 117.5, 127.4, 132.0, 134.0 (C_{ar}H), 100, 115.0, 120, 130, 150.0 (Cq); IR (KBr) $\bar{\nu}$ (cm⁻¹): 2880, 1620, 1540, 1520, 1350, 1140, 850; MS (*m/z*): 465 (100%, M⁺•), 275 (13%).

Instrumentation

¹H and ¹³C NMR spectra were recorded in CDCl₃ solution on a Bruker AC 250 MHz at the Centre d'étude structurale et d'analyse des molécules organiques de l'Université de Bordeaux I.

The absorption spectra were recorded on a Hitachi U-3300 spectrometer. The corrected emission spectra were measured on a Hitachi F-4500. The standard for the fluorescence quantum yields was quinine bisulfate in 1N H₂SO₄ (φ_F = 0.55). The experimental error for small φ_F values is ± 10%.

The solvents were of the highest quality commercially available from Merck or SDS. Butyronitrile (BuCN) from Flucka was successively stirred with active carbon, K_2CO_3 , $KMnO_4$, P_2O_5 and distilled after filtration. Calcium perchlorate was a commercial product and vacuum dried for 24 h at 140 °C and kept anhydrous over P_2O_5 in a dessicator. No fluorescent contaminants were detected upon excitation in the wavelength region of experimental interest.

Sub-picosecond “pump-probe” experiments

The experimental set-up has been described in detail elsewhere²¹. The laser system delivers a typical sub-picosecond output pulse of $\Delta t \approx 500$ fs duration, centered at 600 nm with an energy of 1.5 mJ at a 10 Hz repetition rate. The 300 nm second harmonic is used as a pump pulse to excite the molecules to be studied. The 600 nm pulse, after passing through an optical delay line (60 fs steps) is focused on a rotating quartz plate to generate a light continuum extending from 330 nm to 780 nm. This continuum is sent through the sample as the probe beam. Changing the position of the optical delay line allows observation of the transient spectra (spectral shape and optical density as a function of time) on a picosecond time-scale. The angle between the polarizations of the probe and pump beams was adjusted to 54°7 (the “magic angle”) to ensure kinetics free from reorientation effects.

Results and discussion

Absorption and steady-state fluorescence

Excited state polarity of the three probes

The absorption and fluorescence maxima, and the fluorescence quantum yields for the three probes in several solvents are collected in Table I. The position of the absorption is only slightly changed by the solvent polarity, which indicates nonpolar ground and Franck-Condon excited states. In contrast, the fluorescence is red-shifted in polar solvents, particularly for DDCS-crown, as a result of an increased dipole moment in the relaxed, fluorescing state. If we assume that the contribution of the change of polarizability $\Delta\alpha_{g-e}$ between ground and excited states is negligible, an estimate of the dipole moment from fluorescence solvatochromism can be obtained by the Lippert-Mataga equation^{22, 23}

$$\bar{\nu}_{flu0} = -2\mu_e(\mu_e - \mu_g) \frac{\Delta f'}{hc\rho^3} + \text{Const}' \quad (1)$$

where h is Planck’s constant, c the speed of light, $\bar{\nu}_{flu0}$ the fluorescence maximum in a solvent of dielectric constant ϵ and refractive index n , and $\Delta f' = [(\epsilon - 1)/(2\epsilon + 1)] - 0.5[(n^2 - 1)/(2n^2 + 1)]$ is the solvent polarity parameter. The slope of a plot of $\bar{\nu}_{flu0}$ versus $\Delta f'$ gives the value of $\mu_e(\mu_e - \mu_g)/\rho^3$, which allows the estimation of the excited state dipole moment (μ_e) from the effective radius of the solvent shell (ρ) around the molecule and from the ground

state dipole moment (μ_g), provided that the dipole moment direction does not change from ground to excited states (Table II). The Onsager radius ρ of the model compounds were estimated from the molecular weight of the compounds and a density of 1, which is very close to that of benzonitrile ($d=1.01$ g.cm⁻³)²⁴ and *N,N*-dimethylaniline ($d=0.95$ g.cm⁻³)²⁴. The Onsager radii of the crown derivatives have been taken equal to that of the dimethylamine derivatives (the model compounds) because we have previously shown, in the DMABN series that the long ethylene oxide chain, which is not part of the chromophore, can be neglected²⁵. In spite of the symmetry of the molecule, the dipole moment of the DDS-crown excited state is appreciable and can be assigned, as shown with the model compound (DDS)²⁶, to a TICT state involving the dimethylanilino or the phenyl azacrown group as the electron-donor moiety. DDB-crown appears slightly less polar than DDS-crown in the excited state. We remark, nevertheless, that the fluorescence spectra are vibrationally resolved in nonpolar solvents while an unresolved band grows in on the long-wavelength side in *n*-butyronitrile, and the whole spectrum is unresolved in acetonitrile. DDCS-crown, already slightly polar in the ground state, has the largest dipole moment of the three probes in the excited state, however it is still smaller than in D-A stilbene-crowns like DCS-crown (Table II).

Table I. – Absorption and fluorescence maxima (in nm) and fluorescence quantum yields (ϕ_f) of DDS-crown, DDB-crown and DDCS-crown in solvents of different polarity at room temperature.

Compound	Solvent	λ_{abs}	λ_{flu} ^a	ϕ_f
DDS-crown	<i>n</i> -hexane	362	395 (418)	0.62
	Bu ₂ O	365	400 (424)	0.70
	Et ₂ O	364	402 (424)	
	THF	368	409 (431)	0.78
	BuCN	368	414 (434)	0.28
	PrCN	369	415 (434)	0.62
	CH ₃ CN	367	416 (434)	0.83
DDB-crown	<i>n</i> -hexane	380	(413) 437	
	Bu ₂ O	383	(420) 444	0.71
	Et ₂ O	382	(421) 445	0.48
	THF	387	(430) 454	0.55
	BuCN	388	457	0.32
	PrCN	388	458	0.41
	CH ₃ CN	385	458	0.25
DDCS-crown	<i>n</i> -hexane	353	416 (438)	0.38
	Bu ₂ O	357	428	0.35
	Et ₂ O	356	439	0.33
	THF	360	455	0.28
	BuCN	360	475	0.24
	PrCN	360	482	0.25
	CH ₃ CN	359	493	0.21

^a The number in brackets corresponds to an additional maximum of lower intensity.

Table II. – Solvatochromism slopes m (cm^{-1}) and dipole moments (D) of the D,D-stilbene-crown derivatives and of the DDB-crown (L) and their calcium complexes (L- Ca^{2+}), compared with 4-*N,N*-dimethylaminostilbene (DS) and 4-*N,N*-dimethylamino 4'-cyanostilbene (DCS), and their crown derivatives.

Compound	ρ (Å)	μ_g (D)	m (L)	μ'_e (L) ^e	m (L- Ca^{2+})	μ'_e (L- Ca^{2+}) ^e
DS	4.53	2.41 ^a	12 335	11.8	/	/
DS-crown	4.53	2.41 ^b	11 035	11.2	d	d
DCS	4.69	6.95 ^c	18 508	17.5	/	/
DCS-crown	4.69	6.95 ^b	15 507	16.4	d	d
DDS	4.81	0	6 497	8.3	/	/
DDS-crown	4.81	0 ^b	4 410	6.9	5 145	7.4
DDB-crown	4.87	0	3 640	6.4	23 380	16.1
DDCS-crown	4.86	4.12 ^{a, b}	12 260	13.9	42 410	23.8

^a ref. 34; ^b the ground state dipole moments of DS-crown and DCS-crown have been assumed to be equal to that of DS and DCS, respectively, and that of DDCS-crown equal to that of 3-cyanostilbene 34; ^c ref. 35; ^d not measured for D,A-stilbene-crowns complexed with calcium because there is a decoordination of the cation in the excited state 27; ^e the dipole moment directions are assumed to be the same in the ground and excited states.

Cation complexation effects

In previous studies we showed that stilbene-crowns with an electron-acceptor group in the *para* position (D-A stilbene-crowns) exhibited a strong intramolecular charge-transfer band as the first electronic transition and chelation of the nitrogen electron pair with a cation led to the disappearance of this band and, as a result, a blue-shift of the whole absorption spectrum occurred 9, 27. 4,4'-*N,N*-dimethylamino stilbene (DDS) shows several π - π^* transitions of lower energy than the first transition having noticeable charge-transfer character 26. When the corresponding azacrown derivatives complex a cation the nitrogen lone pair is stabilized and no longer couples with the other π -electrons. The corresponding π - π^* transitions are blue-shifted while the proximity of the cation assists the ICT transitions. Accordingly, cation complexation of DDS-crown leads to a blue-shift of the absorption spectra and the first band is now structureless as in D-A stilbenes. Furthermore, its wavelength maximum (360 nm in acetonitrile) is close to that of DS-crown (356 nm in CH_3CN). The same effect is observed in the complexation of DDB-crown, while in DDCS-crown the first electronic transition has already charge-transfer character before complexation.

The complexation constant (K_s) has been determined from the solution absorbance at various concentrations of calcium perchlorate (DDS-crown/ Ca^{2+} , Fig. 3). We have assumed a 1:1 stoichiometry and obtained K_s from the following relation derived by Valeur 6.

$$X = X_0 + \frac{X_{\text{Lim}} - X_0}{2C_0} \cdot \left[C_0 + C_M + \frac{1}{K_S} - \sqrt{\left(C_0 + C_M + \frac{1}{K_S} \right)^2 - 4 \cdot C_0 \cdot C_M} \right] \quad (2)$$

The complexation constant of calcium with DDS-crown is the highest while with DDCS-crown it is close to the values found with other D-A stilbene-crowns (Table IV). If we consider the fluorescence spectra, all three probes lead to the anticipated red-shifted emission upon calcium complexation (Fig. 2, Table III) as expected for an

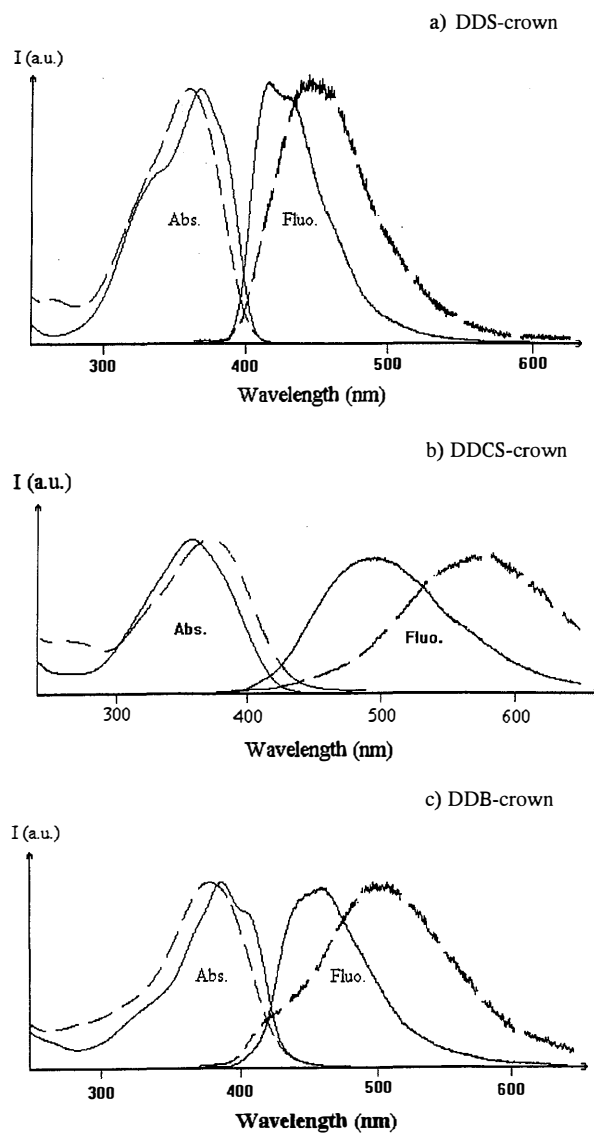


Figure 2. – Steady state absorption and emission spectra of the three probes in acetonitrile. Full line: without Ca^{2+} ; dotted line: with Ca^{2+} .

Table III. – Absorption ($\lambda_{\text{abs}}^{\text{max}}$, nm), fluorescence ($\lambda_{\text{fluo}}^{\text{max}}$, nm) maxima and fluorescence quantum yields (ϕ_f) of the three probes in the presence of $\text{Ca}(\text{ClO}_4)_2$ (conc. $\approx 10^{-3}$ mol.L $^{-1}$) in various solvents at room temperature.

Compound	Solvent	$\lambda_{\text{abs}}^{\text{max}}$	$\lambda_{\text{fluo}}^{\text{max}}$	ϕ_f
DDS-crown	CH_2Cl_2	366	445	0.08
	BuCN	360	449	0.05
	PrCN	360	452	0.11
	CH_3CN	360	452	0.08
DDB-crown	CH_2Cl_2	389	464	0.15
	BuCN	379	494	0.08
	PrCN	381	497	0.15
	CH_3CN	377	501	0.06
DDCS-crown	CH_2Cl_2	363	491	
	BuCN	361	545	0.21
	PrCN	373	565	0.10
	CH_3CN	361	573	0.10

enhanced ICT process. The fluorescence quantum yield is significantly lowered upon complexation, similar to D-A stilbenes with a cationic electron-acceptor group (pyridinium). This behavior is assigned to the formation of a TICT state with efficient radiationless deactivation in polar solvents²⁸. Although we cannot define the dipole moment of an ionic species let us assume, as a first approximation, that the cation does not interfere with the solvation of the chromophore in the ground and excited states. Applying the Lippert-Mataga equation leads to the dipole moment change $\Delta\mu_{e-g}$ upon electronic excitation: if the enhancement of the dipole moment upon calcium complexation is very small with DDS-crown, while it is around 10 Debye with DDB-crown and DDCS-crown.

Picosecond spectroscopy

Without cation

Before studying the influence of a cation on the photophysical behavior of the three probes, it is necessary to rationalize this behavior in the absence of a cation.

Let us recall that the photophysics of “push-pull” stilbenes has first been rationalized by Rettig²⁹ with a three-state model involving the Franck-Condon state (called DE for delocalized excitation) and two other states formed from the DE state: the TICT state involving a twist around a single bond and the so-called P* state related to the isomerization of the double bond. The formation of these two states is in competition and controlled by the solvent polarity. Direct evidence for DE and TICT states was given for the first time by picosecond transient absorption^{21, 27}. We directly observed the formation, in “push-pull” stilbenes, of the TICT state from the DE state in polar solvents while the route to the P* state is slowed down.

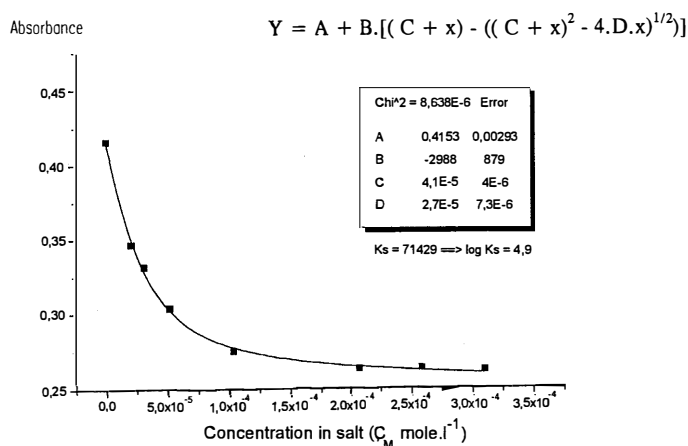
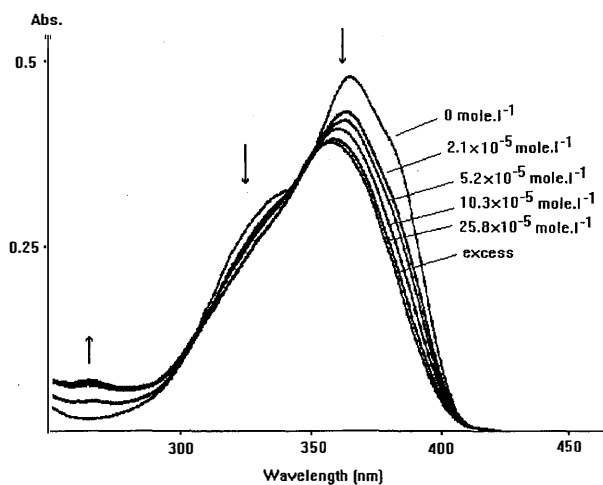


Figure 3. – a) Absorption spectra of DDS-crown (1.05×10^{-5} mol.L $^{-1}$) in acetonitrile with various amounts of $\text{Ca}(\text{ClO}_4)_2$. b) Variation of the absorbance at 380 nm as a function of the calcium perchlorate concentration. The solid line represents the best fit with equation 2. The value of X_{Lim} , which cannot be accurately determined, is left as a floating parameter in the analysis. The various parameters are defined as $A = X_0$, $B = (X_{\text{Lim}} - X_0)/2$, $C = C_0 + 1/K_S$ and $D = C_0$.

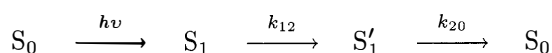
Table IV. – Stability constant ($\log K_S$) calculated according to equation (2) for various D-A and D-D stilbene-crowns with calcium salt in acetonitrile at room temperature.

	DCS-Cr.	DS-Cr.	PDS-Cr.	DDCS-Cr.	DDS-Cr.
$\log K_S$	4.1	4.4	4.8	4.5	4.9

More surprisingly, we showed that the three-state scheme (and particularly the presence of the TICT state) also applied to electron-rich symmetrical stilbenes, namely to DDS, a stilbene with two electron-donor substituents in the *para* positions²⁶.

It is then interesting to deny or confirm, by direct observation, the validity of this model and particularly

formation of the TICT state. We thus recorded the time evolution of the transient absorption spectra of the three probes in acetonitrile. Analysis of the results, using a mathematical procedure described elsewhere²¹, leads to a kinetic behavior implying the presence of two states according to Scheme 2.



Scheme 2.

From the results it was possible to obtain the spectra and kinetics of the S_1 and S'_1 states as shown in Figure 4 and Table V. The results may be summarized as follows. For DDS-crown (Fig. 4a) and DDCS-crown (Fig. 4b), excitation produces the DE state (with spectra S_1) from which a charge-transfer state is formed (with spectra S'_1). We may observe that the spectrum S'_1 of the charge-transfer state is blue-shifted with respect to the DE spectrum (S_1): this blue-shift illustrates the stabilization of the charge-transfer state. The formation rate of the ICT states is $k_{12} = 5 \pm 1.5 \times 10^{10} \text{ s}^{-1}$ for DDS-crown and $k_{12} = 9 \pm 1 \times 10^{10} \text{ s}^{-1}$ for DDCS-crown (see Table V). Since the presence of the electron-acceptor group -CN in DDCS-crown enhances the charge transfer with respect to DDS-crown, it is quite normal to observe a larger formation rate constant k_{12} for the charge-transfer state in DDCS-crown compared to DDS-crown. However, we have to note that the S'_1 state of these two probes, with maxima near 550-570 nm, cannot be compared to the spectrum of the dialkyl aniline radical cation whose maximum appears at 490 nm³⁰. That supports the idea that the twist of the ICT relaxed state is far from the orthogonal, complete twisting to 90° observed for example, in the TICT model compound DMABN³¹. Vibrational coupling occurs between the CT and the DE states, which induces intensity borrowing from the oscillator strength of the $S_1 \rightarrow S_0$ transition, leading to a short radiative lifetime and large fluorescence quantum yield as was observed for biperylenyl³². With DDB-crown (Fig. 4c) we were unable to resolve the presence of two excited states. This can be explained if we admit that the formation rate of the TICT state (k_{12}) is too fast to be observed with our experimental setup. We observe however, a strong gain in the spectral range near 460 nm, which supports, as for the two other probes, a short radiative lifetime compatible with a strong coupling between the DE and TICT states.

With cation

Addition of calcium perchlorate to the three probes in acetonitrile leads to a very strong blue-shift of the

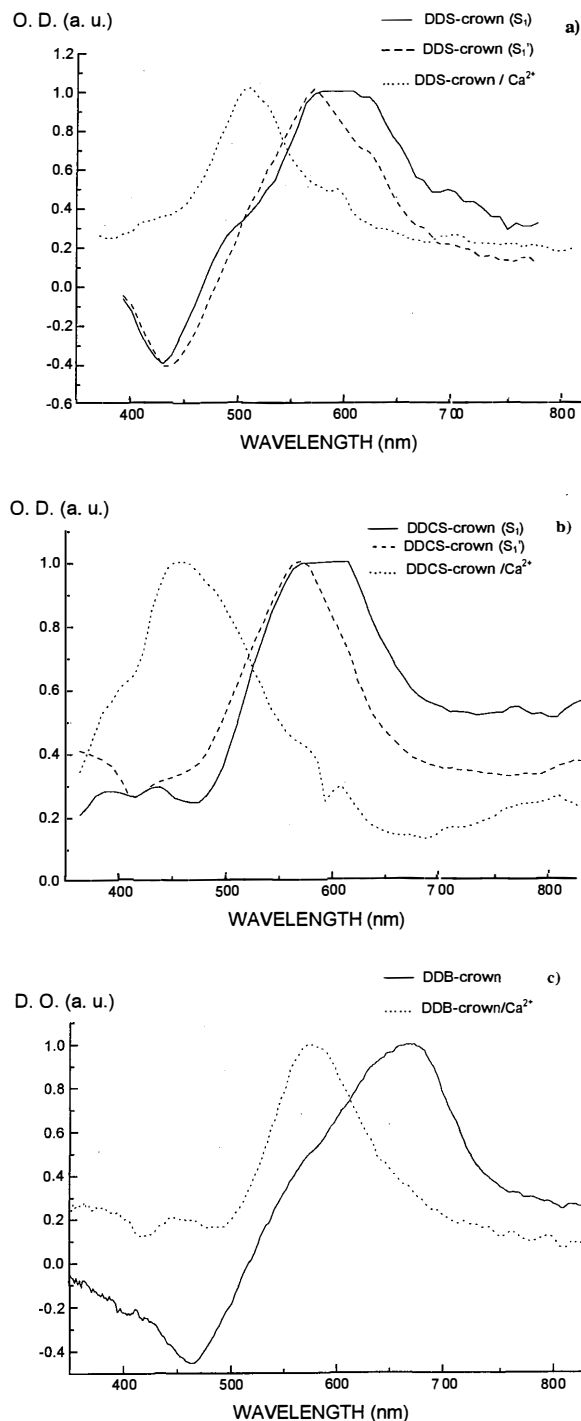


Figure 4. – Transient absorption spectra of the three probes in acetonitrile. Without Ca^{2+} : full line (first excited state S_1), dashed line (second intermediate state S'_1). With Ca^{2+} : dotted line. (a) DDS-crown, (b) DDCS-crown and (c) DDB-crown.

transient absorption compared to the spectra of the free probes. Furthermore, there is no kinetic evolution within the available time resolution (1 ps).

Table V. – Rate constants of the different processes following excitation of the three probes with and without calcium perchlorate, in acetonitrile (Scheme 2).

	k_{12} (s ⁻¹)	k_{20} (s ⁻¹)
DDS-crown	$5 \pm 1.5 \times 10^{10}$	$< 2 \times 10^9$
DDS-crown\Ca ²⁺	$> 10^{12}$	$2.9 \pm 0.1 \times 10^9$
DDCS-crown	$9 \pm 1 \times 10^{10}$	$< 2 \times 10^9$
DDCS-crown\Ca ²⁺	$> 10^{12}$	$< 1.2 \times 10^9$
DDB-crown	$> 10^{12}$	$1 \pm 0.1 \times 10^9$
DDB-crown\Ca ²⁺	$> 10^{12}$	$2 \pm 1 \times 10^9$

The two stilbene probes present a transient absorption peaking at 460 nm (DDCS-crown/Ca²⁺) and 510 nm (DDS-crown/Ca²⁺), which is more similar to the dialkylaniline radical cation. Chelation of the calcium cation by the nitrogen lone pair of the azacrown enhances and speeds up the intramolecular charge transfer and leads to a TICT state less strongly coupled to the DE states than the TICT state that is produced from the free probes. Accordingly, the fluorescence quantum yield is decreased. The same behavior, but enhanced, has already been observed when D-A stilbenes have a pyridinium²⁸ or nitrobenzene electron-acceptor group³³.

If we assume that the energy of the ground state and of the upper state reached by absorption from excited states is not altered by calcium complexation, the stabilization energy of the excited state produced on

calcium complexation can be calculated from the blue-shift of the picosecond transient absorptions: 2140 cm⁻¹ (DDS-crown), 4382 cm⁻¹ (DDCS-crown) and 2400 cm⁻¹ (DDB-crown); and from the red-shift of the fluorescence, respectively 1916 cm⁻¹, 2832 cm⁻¹ and 1874 cm⁻¹. While the probe order for increasing cation effect remains the same, DDS-crown < DDB-crown < DDCS-crown, the discrepancy between the values obtained from the transient absorption and the steady-state fluorescence are highest for the more polar probes, perhaps pointing to a difference from the rotamers contribution around the perpendicular conformation (TICT state) for the two transitions.

Conclusion

We have shown that diphenyl polyenes (stilbene and 1,4-diphenyl-1,3-butadiene) substituted at the two ends by electron-donor groups, one of which is able to chelate a cation, exhibit strong intramolecular charge transfer upon electronic excitation, in the presence of calcium cations, with a resulting bathochromic shift of the fluorescence.

This spectroscopic effect was increased when an electron-acceptor group was introduced at the *ortho* position of the macrocycle in order to increase the ICT process induced by the cation.

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