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The charge transfer state of excited bianthryl and a derivative: solvatochromism, emission CT spectra broadening in homogeneous solvents¹

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Abstract

The photophysical properties of a recently synthesized molecule, the bis-9,9'-(2-ethyl-10-hexyl)anthryl (BOA), have been studied with the parent molecule, the 9,9'-bianthryl (BA), in solvents of various polarity. The comparative analysis of the photophysical behaviour of these two probes has been achieved in order to emphasise environmental effects of the alkyl substituent on the aromatic chromophore. The results obtained in perfluoroalkane, reported for the first time in this paper, suggest that the charge transfer state (CT) of BA or BOA contributes to the fluorescence emission even in non polar solvents like cyclohexane. The fluorescence spectra of these two probes in perfluoroalkane have been introduced as standard spectra of the locally excited state form (LE) and used to obtain a new decomposition of the other overall fluorescence spectra into two emission components: one coming from the CT state and the second from the initial excited singlet state (LE). We have analysed the solute–solvent interactions not only in term of Stokes shift but also using the inhomogeneous band broadening parameter. The vibrational band decomposition found its validation in the agreement observed between the thermodynamic and spectroscopic properties of both excited states. A correlation between the inhomogeneous broadening and the Stokes shift of the charge transfer spectrum is exhibited. The existence of up to 50% of the CT state even in non polar solvents like cyclohexane has been shown. The dipole moment of the CT state of BA and of BOA can be estimated in the range of 6.2 to 10.3 D depending on the solvatochromic model used. It has been shown that the alkyl substituent of BOA destabilises the CT state and only four methylene groups of each lateral chain of BOA contribute to the local environment of the aromatic chromophore.

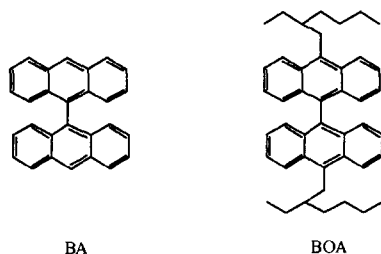
1. Introduction

Since the discovery of the dual fluorescence emission of 9,9'-bianthryl (BA) in 1968 by Lippert and Schneider [1], its photophysical properties have been intensively studied.

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¹ This study forms part of the PhD Thesis of H. Laguitton-Pasquier, Ecole Normale Supérieure de Cachan, Cachan (1995).

The fluorescence emission spectrum of BA depends strongly on the nature of the surrounding media [1–4]. The fluorescence is emitted from two distinct excited states: a locally excited state (LE) and an intramolecular charge transfer state [3] (CT). It is usually assumed that, in non polar solvents, only the LE state is emitting [3,5,6]. In polar solvents, a new band appears which is assigned to the CT state. The most recent models [2,3,5,7] present the CT state originating from the LE state and the exchange process between LE and CT states is attributed to an equilibrium at the picosecond scale [2,7,8] depending on the solvent polarity. An increase of polarity enhances the formation of the CT excited form.



We report for the first time the fluorescence spectroscopy of BA in 1,3-dimethylperfluorocyclohexane (DMPFC) which is less polar [9] ($\epsilon = 1.863$) and less polarisable [9] ($n = 1.2898$) than typical alkane solvents like cyclohexane (Table 1). We have shown that both BOA (bis 9,9'-(2-ethyl-10-hexyl)anthryl) in alkane and BA in DMPFC exhibit fluorescence spectra of which vibrational bands are better defined than those of the fluorescence spectrum of BA in cyclohexane. These results imply a new decomposition of BA emission spectra. We have used a constrained multi-Gaussian fit of the overall spectrum to isolate the emission of respectively LE and CT states.

The width of absorption bands of charge transfer states depends also on polarity [11–16], Marcus has shown that the fluctuation of the solvent reaction field dominates the electron transfer processes. In the same way as the reaction field induces a red shift on the CT fluorescence emission spectrum, the fluctuation of the reaction field induces a broadening of the vibrational and electronic bands [11–16]. We pro-

pose to assign the broadening of the CT state emission in polar solvents not to a change in the Franck–Condon factor [5,3] but simply to the inhomogeneous band broadening of dipolar state induced by polar solvents. In this work, we describe the CT emission spectra as the sum of three vibronic bands of which the width is an adjustable parameter. For the first time, we have been able to check with a reasonable success the Born–Oppenheimer cycle which relates the fluorescence emission energy to the excited states equilibrium.

In this work, we compare BA and BOA in order to analyse the effect of alkyl substituent on the chromophore photophysical properties. Electronic effects (inductive effects) can stabilise the LE state with respect to the CT state. By their volume and their hydrophobicity, the octyl substituents can provide a particular solvation of the chromophore that reduces the solvatochromic effect. The stationary fluorescence emission spectra of BA and of BOA in various solvents are reported. We have determined the fluorescence quantum yields and the fluorescence decay times of these two compounds. We have observed that BOA and BA present similar photophysical properties. However, the alkyl chains of BOA induce a less polar environment around the BOA chromophore with respect to the BA.

Table 1
Refractive index n , relative dielectric constant ϵ_r [10] and polarity scale E_T^N [10] of the different solvents used

Solvents	n	ϵ_r	E_T^N
DMPFC	1.2898 [9]	1.863 [9]	
cyclohexane	1.4247	2.02	0.006
CCl ₄	1.4581	2.238	0.052
1,4-dioxane	1.405	2.21	0.164
THF	1.4055	7.58	0.207
CHCl ₃	1.4486	4.81	0.259
CH ₂ Cl ₂	1.422	9.08	0.309
acetone	1.3572	21.0	0.355
DMSO	1.4779	46.45	0.444
acetonitrile	1.3421	35.94	0.460
methanol	1.33	32.63	0.762

DMPFC: 1,3-dimethylperfluorocyclohexane; CCl₄: tetrachloromethane; THF: tetrahydrofuran; CHCl₃: chloroform; CH₂Cl₂: dichloromethane; DMSO: dimethoxysulfoxide.

2. Experimental procedure

BOA was synthesised by R. Lapouyade and BA was kindly supplied by C. Bied-Charreton. The purity of the samples (BA and BOA in each solvent) was checked by HPLC. Spectroscopic grade solvents were used. DMSO was dried on activated molecular sieves (4 Å). In Table 1, we report the physical constants of the different solvents involved in the comparative analysis of the photophysical behaviour of BA and BOA.

Probe (BA and BOA) concentrations were 5×10^{-6} mol dm⁻³ for steady-state and time-resolved fluorescence measurements.

The stationary fluorescence spectra have been recorded with a SPEX spectrofluorimeter.

Fluorescence quantum yields and lifetimes of aerated solutions of BA and BOA were measured at room temperature. For quantum yield determination, a degassed solution of 9,10-diphenylanthracene in cyclohexane ($\Phi_F = 0.91 \pm 0.02$) [17] was used as a standard. The quantum yield of the sample S (Φ_F^S) is determined using the following equation [17]:

$$\Phi_F^S = \frac{I_F^S}{I_F^{\text{ref}}} \frac{1 - 10^{-\text{OD}^{\text{ref}}}}{1 - 10^{-\text{OD}^S}} \left(\frac{n^S}{n^{\text{ref}}} \right)^2 \Phi_F^{\text{ref}},$$

where I_F , the emission intensity, was calculated from the spectrum area $\int I(\bar{\nu}) d\bar{\nu}$, OD represents the optical density at the excitation wavelength and n the refractive index, measured at 25°C, of the sample solution. The superscripts S and ref refer respectively to the sample and to the standard. Optical density at the excitation wavelength never exceed 0.1.

Time-resolved fluorescence studies have been investigated with the time correlated photon counting method [18]. The photon source was a Spectra-Physics set-up composed of a Titanium Sapphire Tsunami laser pumped by an argon ion laser, a pulse selector, doubling (LBO) and tripling (BBO) crystals. Light pulses were 1.2 ps long and selected by an opto-acoustic crystal at a repetition rate of 4 MHz. Fluorescent photons were detected with a Hamamatsu MCP photomultiplier R3809U. We used a constant fraction discriminator optimised for the output of MCP directly behind the photomultiplier. They are sold by the Institut of Nuclear Physics in Orsay (France). The time to amplitude converter is

provided by TENNELEC. With this set-up, we achieved 37 ps fwhm instrument response.

3. Experimental results

The absorption and the fluorescence excitation spectra of BOA and BA are anthracene like (Fig. 1 and Fig. 2). The vibronic progression of these three compounds are close: 1430 cm⁻¹ for BOA, 1411 cm⁻¹ for BA and 1419.7 cm⁻¹ for anthracene. The absorption and the excitation spectra of BOA as those of BA are independent on the emission wavelength and on the solvent polarity. We observed no particular correlation between the wavelength position of the intensity maximum in the BA or BOA excitation spectra and the polarity of solvents.

As seen in Fig. 2 and Fig. 3, the emission spectra of BA and BOA in cyclohexane and in DMPFC and their excitation spectra are anthracene like. This means that the electronic interactions in the ground and the Franck–Condon states of the two anthracenic moieties are weak for these two probes.

In the excited state, the excitation remains on its anthracenic parent ring or jumps to the second one. The first electronic configuration of the excited state gives rise to a non polar state that can be compared to the ¹L_a state of an anthracene molecule. The emission observed in alkane is generally assigned to this locally excited state (LE).

As a general rule, the emission spectra of BOA are similar to those of BA. A progressive red-shift and a loss of the structure of the fluorescence emission spectra of BOA like those of BA are observed as the solvent polarity increases (Fig. 4 and Fig. 5). These observations are characteristic of a dipolar excited state (CT) emission. The persistence of the vibronic structure in the blue edge of the emission spectra in polar solvents like DMSO suggests the existence of two weakly coupled excited states [3,5,19,20], LE and CT. We note that the BOA emission spectra are more structured than those of BA at the blue edge of the spectra.

The fluorescence excitation and emission spectra in 1,3-dimethyl-perfluorocyclohexane (DMPFC) are blue shifted with respect to the corresponding spectra in cyclohexane, 8 nm for BA and 6 nm for BOA.

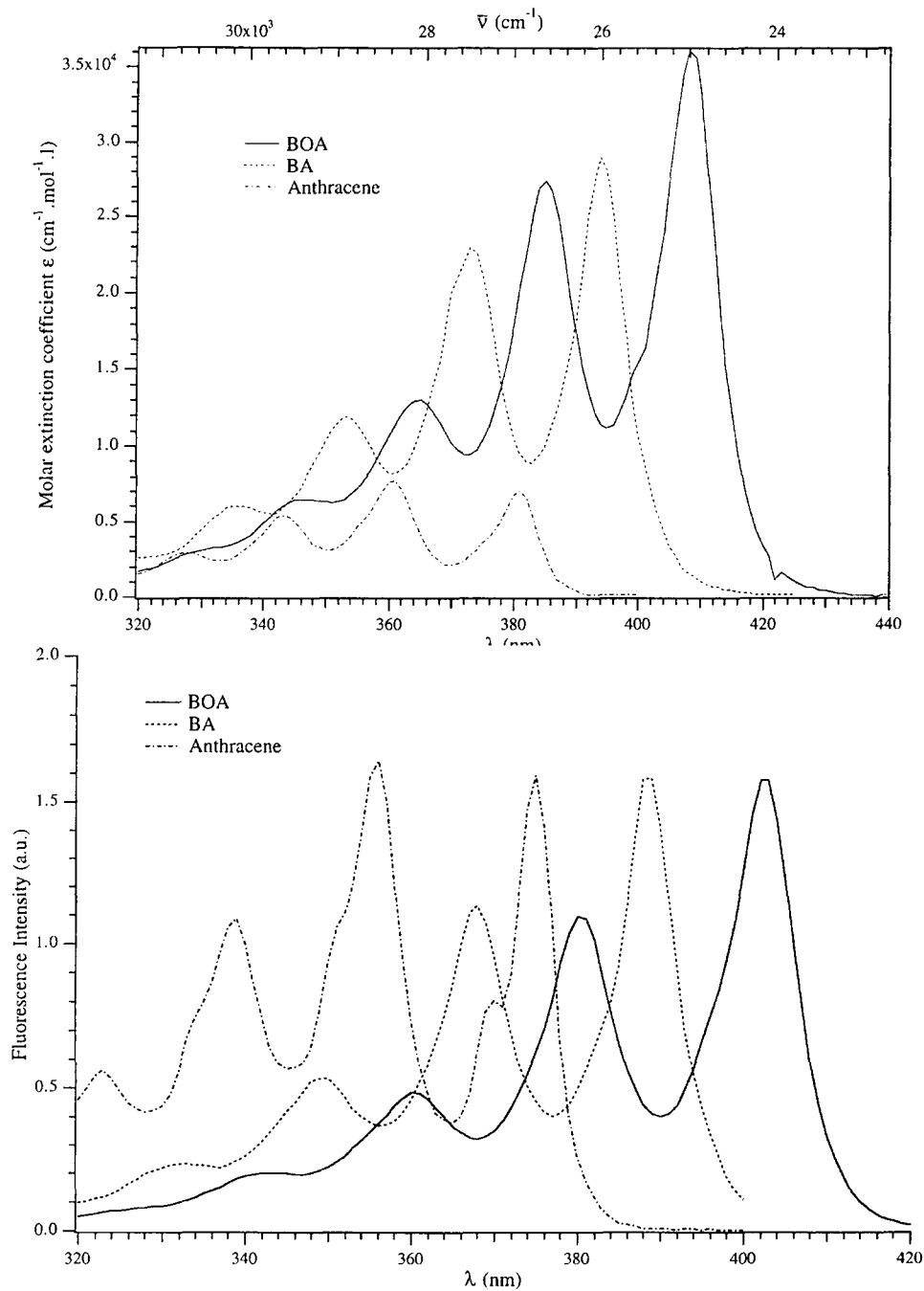


Fig. 2. Fluorescence excitation spectra of BA, BOA and anthracene in CHCl_3 at room temperature ($\lambda_{\text{em}} = 450 \text{ nm}$).

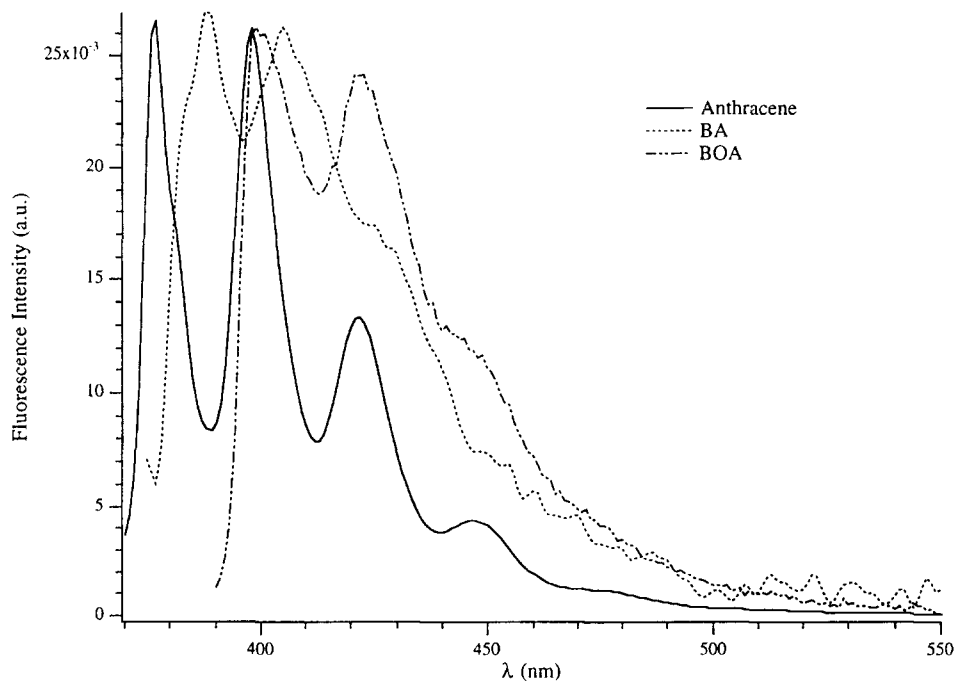


Fig. 3. Fluorescence emission spectra of BA, BOA and anthracene in DMPFC at room temperature and upon excitation at 370 nm for BA, at 380 nm for BOA and at 360 nm for anthracene.

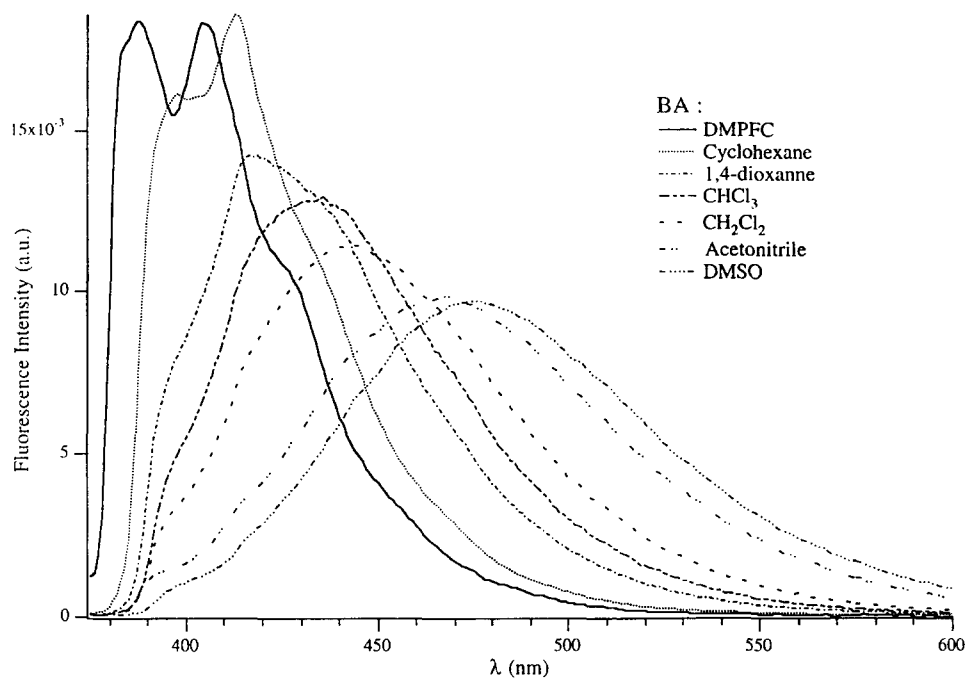


Fig. 4. Fluorescence emission spectra of BA in various solvents at room temperature ($\lambda_{\text{exc}} = 370$ nm). Spectra are normalised to the same area.

Table 2

Oscillator strength (f) of the $LE \rightarrow S_0$ transition, rate constant ($k_{f,LE}^0$) and lifetime ($\tau_{f,LE} = 1/k_{f,LE}^0$) of the radiative fluorescence emission of the LE state

	f	$k_{f,LE}^0$ (s^{-1})	$\tau_{f,LE}$ (ns)
BOA	0.36	2.21×10^8	4.5
BA	0.294	1.91×10^8	5.2
anthracene	0.101	7.79×10^7	12.8

Such a blue shift has been also observed for DPA in perfluoro-*n*-hexane [9]. This is the expected positive solvatochromic effect on both absorption and emission spectra due to the small refractive index value of DMPFC. The fluorescence emission spectra of BOA and BA in DMPFC are the most structured and exhibit a vibronic progression closer to that of anthracene. Furthermore, the intensity at the red edge of the emission spectra is lower than in cyclohexane whereas the intensity at the blue edge is more important. This result means that even in cyclohexane the CT state presents a contribution to the fluorescence emission and consequently suggests the formation of the CT state in apolar solvent like cyclohexane (see below).

We calculated the oscillator strength f and the rate constant of radiative fluorescence emission of

the LE state, $k_{f,LE}^0$ (Table 2), by the following equations [21]:

$$f = 4.3 \times 10^{-9} \int \varepsilon(\bar{\nu}) d\bar{\nu},$$

$$k_{f,LE}^0 = \bar{\nu}_0^2 f,$$

where $\varepsilon(\bar{\nu})$ represents the molar extinction coefficient at a given wavenumber $\bar{\nu}$, and $\bar{\nu}_0$ denotes the wavenumber corresponding to the absorption spectrum maximum. We use for BA $\bar{\nu}_0 = 25654 \text{ cm}^{-1}$, for BOA, $\bar{\nu}_0 = 24783 \text{ cm}^{-1}$ and for anthracene, $\bar{\nu}_0 = 27777 \text{ cm}^{-1}$. The increase of the oscillator strength can be correlated to the progressive loss of the molecular symmetry from anthracene to BOA.

For BOA and BA, the fluorescence emission decay was monoexponential at all the emission wavelength studied (from 500 to 410 nm). The deviation from monoexponentiality observed once in DMSO disappeared after further solvent purification. No rise was observed at the scale of the time response function of our instrument (37 ps fwhm), specially in the initial part of the decay. This observation is a consequence of an equilibrium rapidly achieved between the LE and the CT states [2,7,8].

The fluorescence quantum yields and decay times of BOA were similar to those of BA. The same behaviour for these two probes has been observed as

Table 3

Fluorescence quantum yields and decay times of BA and of BOA in various aerated solutions (*: degassed solutions); comparison with the results reported in the literature (degassed solutions)

Solvents	Quantum yield			Lifetime τ (ns)		
	Φ_{BOA}	Φ_{BA}	Φ_{BA}^{lit}	τ_{BOA}	τ_{BA}	τ_{BA}^{lit}
DMPFC	0.006	0.014		4.6	3.5	
	0.026 *	0.037 *				
cyclohexane	0.61	0.55	0.55 [15,16,22]	5.2	5	5.7 [2]–8 [22]
CCl_4	0.09	0.106		1.1	1.3	
1,4-dioxane	0.61	0.50	0.51 [2,3]	9.8	11	15.5 [2]
	0.72 *	0.63 *				
THF	0.62	0.51			10.2	
$CHCl_3$	0.57	0.60		11.44	11.4	
CH_2Cl_2	0.51	0.58		17	15.7	
acetone	0.23	0.22	0.39 [22]		11.4	32 [22]
DMSO	0.26	0.38		30	28	
	0.33 *	0.48 *				
acetonitrile	0.15	0.16	0.23 [2,3]	12	13	35 [3]–45 [2]
methanol	0.24	0.27	0.33 [22]	12.2	13.5	

the solvent polarity increases: in agreement with the literature [2,3,22], a reduction of the fluorescence quantum yields and an increase of the fluorescence decay times are reported on Table 3. The experimental values obtained in this work are lower than those given in the literature [2,3,22]. This is mainly due to the experimental conditions, data in the literature have been obtained with degassed solutions.

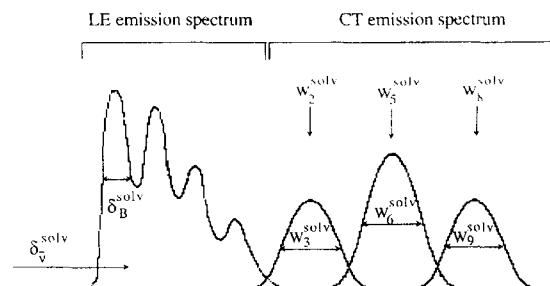
In agreement with the quenching capacity of CCl_4 [23], we obtained weak values of the fluorescence quantum yields and fluorescence decay times in this solvent.

In DMPFC, 1,4-dioxane and DMSO, we make sure that the emission spectrum shape is independent of the oxygen concentration in solution. The emission spectra of solutions with or without O_2 are homologous.

4. Data analysis

The persistence of the vibronic structure at the blue edge of the emission spectrum in the most polar solvents suggests that the fluorescence spectrum is the sum of a LE and a CT emission spectra. In order to estimate the proportion of the CT state formed in cyclohexane and the dipole moment of the LE and the CT states, the determination of each individual contribution is required.

The spectral properties of the excited states of BA and BOA are strongly dependent on the solvent polarity and spectral shifts or spectral broadening represent a direct consequence of this dependence. The inhomogeneous broadening of electronic and vibrational bands [11–16] results from the statistical positions of solvent molecules around the solute at a given time. The random movement of solvent molecules induces a fluctuation of the energy of the vibrational and electronic states of the solute molecule. The absorption or emission band observed in condensed phase can be assimilated to the envelope of the narrow transition of individual solute molecules in the various environments created by the statistical arrangements of solvent cages. This broadening is most important for polar states. We have used a multi-Gaussian fit which takes into account this broadening of the vibrational bands. By choosing a multi-Gaussian fit, we take the risk of an



Scheme 1. Experimental fluorescence emission spectrum decomposition: the LE spectrum is allowed to shift (δ_B^{solv}) and broaden (δ_v^{solv}) with the solvent polarity. This broadening is the same for each vibrational band of the LE spectrum. In the CT spectrum, described by three Gaussians, each band is allowed to shift and broaden independently of each other.

overdetermination of our model, leading to a cross correlation between the adjustable parameters and erratic values of the fit results. The success of the fit will have to be estimated not only from the quality of the fit (χ^2 parameter) but also from the consistence between the parameter values of the different vibrational components.

4.1. Method of decomposition²

The fluorescence emission decay was monoexponential in all solvents as a consequence of an equilibrium rapidly achieved between the LE and the CT states [2,7,8]. This equilibrium is assumed to be solvent polarity dependent and the fluorescence emission spectra reproduces the relative weight of LE and CT states in the dynamic exchange process. We have described the decomposition of the emission spectrum of BA and BOA in a given solvent by the following equation:

$$S_{\text{tot}}^{\text{solv}}(\bar{\nu}) = K^{\text{solv}} S_{\text{LE}}^{\text{solv}}(\bar{\nu}) + S_{\text{CT}}^{\text{solv}}(\bar{\nu}), \quad (1)$$

where $S_{\text{tot}}^{\text{solv}}(\bar{\nu})$ represents the experimental normalised fluorescence emission spectrum, $S_{\text{LE}}^{\text{solv}}(\bar{\nu})$ the LE normalised spectrum, $S_{\text{CT}}^{\text{solv}}(\bar{\nu})$ the unknown CT spectrum and K^{solv} the relative proportion of the normalised LE spectrum. The abscissa scale of emission spectra has been converted in cm^{-1} .

² We first proposed this method of decomposition few years ago: two TICT molecules in solvents and micelles [24].

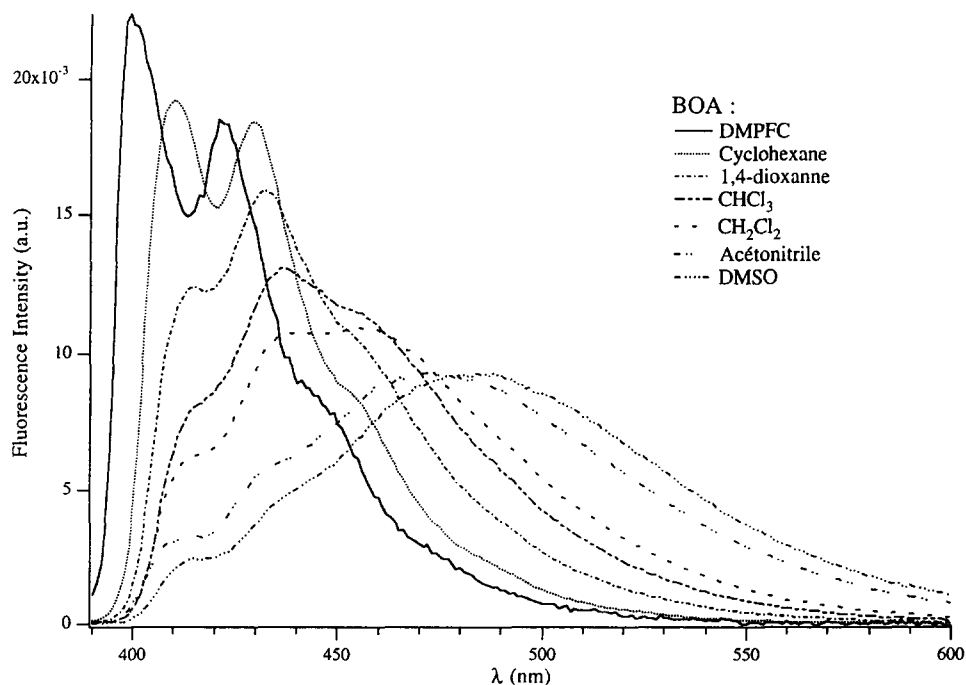


Fig. 5. Fluorescence emission spectra of BOA in various solvents at room temperature ($\lambda_{\text{exc}} = 380$ nm). Spectra are normalised to the same area.

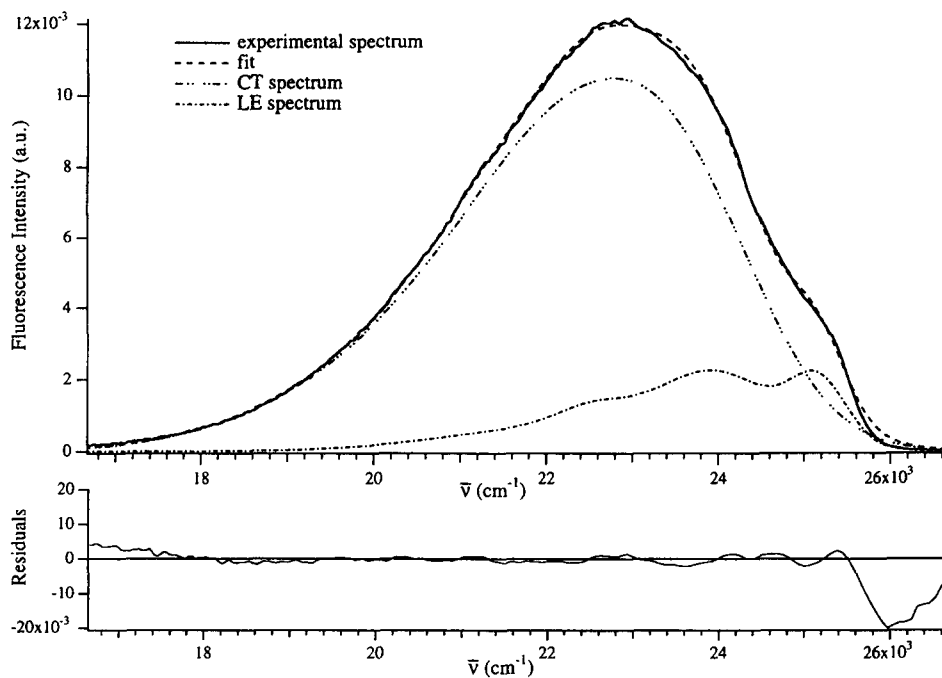


Fig. 6. Decomposition of the experimental BA emission spectrum in CHCl_3 into a LE spectrum and a CT spectrum. The LE spectrum corresponds to $K^{\text{sol}}_{\text{LE}}(\bar{\nu}, \delta_p^{\text{sol}}, \delta_B^{\text{sol}})$.

We have used the emission spectrum in DMPFC as a representative model of the pure LE emission spectrum. The solute–solvent interactions in the perfluoroalkane solvents (PFA) are weak and of the same order as those in noble gas [9]. Then, we assume that in DMPFC, the CT state is not present in a significant amount at the equilibrium. The emission spectrum in DMPFC is composed of four well defined vibronic bands (Fig. 4 and Fig. 5). The upper part of each experimental vibrational band presents a Gaussian profile [6,11]. Thus, we have decomposed the fluorescence emission spectrum of BA and of BOA solubilized in DMPFC in four basic Gaussian components.

In order to describe the LE state emission spectrum in the various solvents, we had to rectify the blue shift of the emission spectrum in DMPFC and to take into account the broadening of the vibrational band enhanced by the solvent polarity. We have described the LE emission spectrum,

$S_{LE}^{solv}(\bar{\nu}, \delta_v^{solv}, \delta_B^{solv})$, as the sum of four Gaussian components of fixed amplitudes where δ_v^{solv} and δ_B^{solv} were two adjustable parameters: δ_v^{solv} and δ_B^{solv} correcting parameters of respectively the blue shift of the emission spectrum in DMPFC and the broadening of the vibrational band. It appeared after the fit that the induced broadening δ_B^{solv} of the LE spectrum by the solvent was very small and was not dependent on the solvent polarity. Only δ_v^{solv} behaved as an adjustable parameter.

Concerning the emission spectrum of the CT state, the best fits have been obtained when the CT emission spectrum was described by three Gaussian components. The initial purpose of this decomposition was simply to define the main characteristics of the CT spectrum and the presence of three Gaussian components were in agreement with Visser's observations [2] (see discussion).

In short, we resolve the experimental fluorescence emission spectrum of BA and of BOA in a given

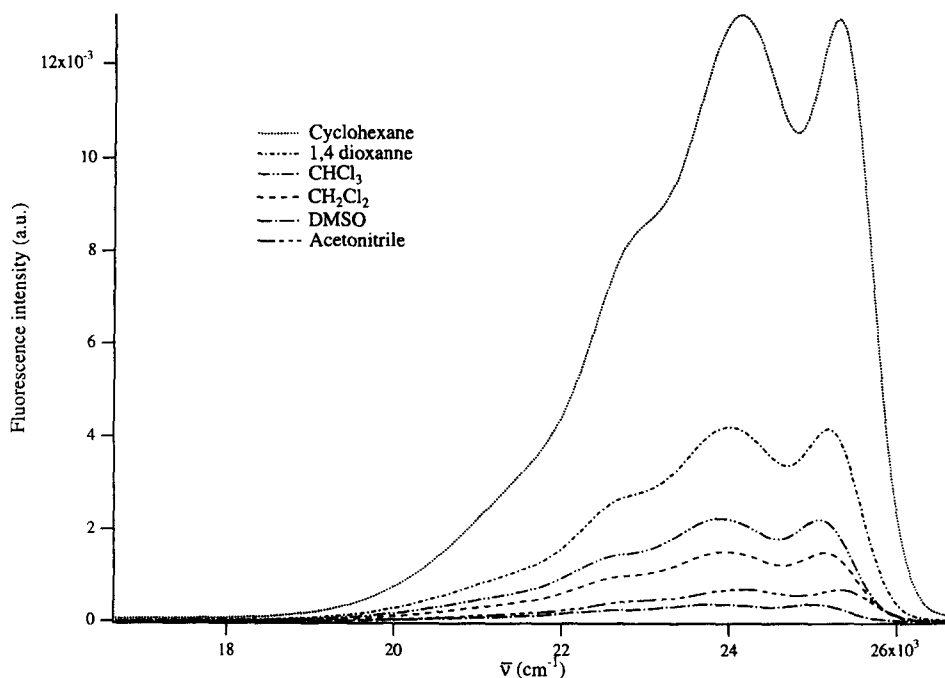


Fig. 7. Fluorescence emission spectra of the LE state of BA in various solvents. The actual contribution of LE to the fluorescence is shown. This explains the progressive decrease of the emission intensity as the solvent polarity is increasing.

solvent (Scheme 1) by the sum of a contribution of the LE spectrum deduced from the spectrum in DMPFC and of three Gaussian components representative of the CT spectrum:

$$S_{\text{tot}}^{\text{solv}}(\bar{\nu}) = K^{\text{solv}} S_{\text{LE}}^{\text{solv}}(\bar{\nu}, \delta_{\text{v}}^{\text{solv}}, \delta_{\text{B}}^{\text{solv}}) + \sum_{j=0}^2 W_{1+3j}^{\text{solv}} \times \exp\left\{-\left[(\bar{\nu} - W_{2+3j}^{\text{solv}})/W_{3+3j}^{\text{solv}}\right]^2\right\}. \quad (2)$$

The calculations have been achieved using a specific computer program and the final parameter values were defined by the minimisation of the χ^2 parameter.

4.2. Results of the decomposition

4.2.1. Example of decomposition

An example of the decomposition of the total fluorescence emission spectrum is presented in Fig.

6. The values of the χ^2 parameter range from 1.1 to 1.6 depending on the solvent. The main variation of the weighting residuals are localised at the beginning and the end of the spectrum (Fig. 6) and the used of a Gaussian profile introduces only an approximate fit at the bottom of each vibrational band.

4.2.2. LE and CT emission spectra

Typical LE and CT emission spectra of BA obtained by this decomposition method are presented in Fig. 7 and Fig. 8, respectively. The LE and CT emission spectra of BOA are similar to those of BA.

The LE spectrum remains structured even in the most polar solvents. The $\delta_{\text{B}}^{\text{solv}}$ parameter presents meaningless values with respect to the broadening parameter of CT spectrum. Moreover, the change in the Stokes shift deduced from the $\delta_{\text{v}}^{\text{solv}}$ values is not correlated to the solvent polarity. All these observations are in agreement with a weak dependence of the LE state on the solvent polarity.

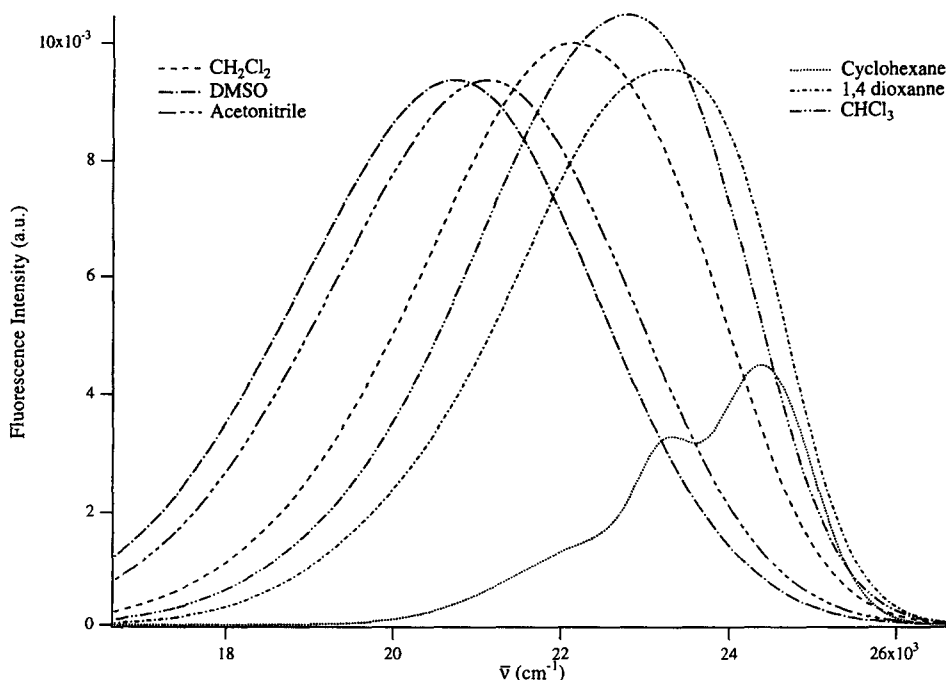


Fig. 8. Fluorescence emission spectra of the CT state of BA in various solvents. A progressive red shift and a loss of the structure of the CT emission spectra as the solvent polarity is increasing are observed.

Unlike the LE spectra, the CT spectra undergo a strong solvatochromism but remain structured in non polar solvents. The overlap of the vibrational band inhomogeneously broadened by the solute–solvent interactions leads to the loss of the structure of the CT emission spectrum which is observed with the increase of the solvent polarity. These observations are characteristic of a dipolar state.

4.2.3. LE / CT equilibrium constant

The proportion of the LE spectrum (K^{solv}) decreases as the solvent polarity increases. This behaviour is in agreement with the hypothesis of an equilibrium between the LE and the CT states depending on the solvent polarity. The equilibrium constant K_{eq} can be determined from the relative intensity of the emission spectra of the LE and the CT states described by K^{solv} . According to Eq. (1), the K^{solv} expression, function of the quantum yields of the LE (Φ_{LE}) and CT (Φ_{CT}) states, is

$$\frac{1}{K^{\text{solv}}} = 1 + \frac{\Phi_{\text{CT}}}{\Phi_{\text{LE}}} \quad (3)$$

The equilibrium constant K_{eq} is defined by the following relation:

$$K_{\text{eq}} = \frac{1 - \alpha}{\alpha} = \frac{[\text{CT}]}{[\text{LE}]} \quad (4)$$

The equilibrium between the LE and the CT states is achieved before the fluorescence deactivation of both excited states occurs [2,7,8]. Then, the expression of Φ_{LE} , Φ_{CT} and the total fluorescence quantum yield (Φ_{tot}) are

$$\Phi_{\text{LE}} = \alpha k_{\text{fLE}}^0 \tau_{\text{f}} \quad (5)$$

$$\Phi_{\text{CT}} = (1 - \alpha) k_{\text{fCT}}^0 \tau_{\text{f}} \quad (6)$$

$$\Phi_{\text{tot}} = [\alpha k_{\text{fLE}}^0 + (1 - \alpha) k_{\text{fCT}}^0] \tau_{\text{f}} \quad (7)$$

with

$$\frac{1}{\tau_{\text{f}}} = \alpha \frac{1}{\tau_{\text{LE}}} + (1 - \alpha) \frac{1}{\tau_{\text{CT}}}.$$

k_{fLE}^0 and k_{fCT}^0 represent the radiative rates of the fluorescence emission of respectively the LE and the CT states, τ_{f} is the experimental fluorescence decay time of BA and of BOA, τ_{LE} and τ_{CT} are the fluorescence lifetimes of respectively the LE and the

Table 4

Equilibrium constant (K_{eq}) and radiative rate constant (k_{fCT}^0) of the fluorescence emission of the CT state of BA and of BOA in different solvents

Solvents	K_{eq}		k_{fCT}^0 (10^7 s^{-1})	
	BA	BOA	BA	BOA
cyclohexane	1.32	1.27	4.84	3.57
CCl_4	4.71	3.66	5.83	4.37
1,4-dioxane	16.51 (2.1 ^a)	6.9	3.66 (1.6 ^a)	3.92
THF	21.47	11.54	4.34	4.68
CHCl_3	26.92	18.22	4.75	4.06
CH_2Cl_2	57.75	37.77	3.43	2.49
acetone	115.44	63.06	1.78	1.59
DMSO	702.68	438.66	1.33	0.82
acetonitrile	386.97 (97 ^a)	177.59	1.19 (0.6 ^a)	1.13
methanol	137.41	69.21	1.88	1.67

^a Results reported in the literature [3].

CT states. Eqs. (5), (6) and (7) are easily deduced from a combination between the general kinetic equations proposed by Zachariasse [25] and Eq. (4), a way to introduce the parametric conditions of the LE/CT equilibrium.

According to Eqs. (3), (4), (5) and (6), we obtain

$$K_{\text{eq}} = \left(\frac{1}{K^{\text{solv}}} - 1 \right) \frac{k_{\text{fLE}}^0}{k_{\text{fCT}}^0} \quad (8)$$

where only k_{fLE}^0 and K^{solv} are known. Combination of Eqs. (7) and (8) leads to the appropriate expressions of the unknown parameters K_{eq} and k_{fCT}^0 :

$$K_{\text{eq}} = \left(\frac{k_{\text{fLE}}^0 \tau_{\text{f}}}{\Phi_{\text{tot}}} \frac{1}{K^{\text{solv}}} - 1 \right), \quad (9)$$

$$k_{\text{fCT}}^0 = \frac{k_{\text{fLE}}^0}{K_{\text{eq}}} \left(\frac{1}{K^{\text{solv}}} - 1 \right). \quad (10)$$

The K_{eq} values depend strongly on the solvent polarity (Table 4). We note that in cyclohexane, the proportion of the CT state reaches the value of 60%. The equilibrium constant values determined for BOA are lower than for BA. This result is in agreement with the observation of the fluorescence emission spectra of BOA more structured than those of BA at the blue edge of the spectra corresponding to the LE emission.

The very long radiative lifetimes of the CT state are in agreement with the forbidden character ex-

pected for the CT–ground state transition. The oscillator strength of the CT state originates from the LE–CT mixing [3,5,19,20]. The decrease of the radiative lifetime of the CT state and, consequently, the decrease of the corresponding oscillator strength illustrate a decrease of the LE–CT mixing degree as the solvent polarity increases.

The assumption previously presented [3,5–7,19,20] that the CT state is not formed at the equilibrium in non polar solvents in a significant amount corresponds to values of K_{eq} and $k_{f_{CT}}^0$ reported in the literature weaker than those obtained in the present work. This assumption automatically implies an underdetermination of the CT state amount at the LE/CT equilibrium in the different solvents studied.

5. Discussion

5.1. Decomposition of the total fluorescence emission spectra – validity of the decomposition method

The total fluorescence is decomposed as the sum of two emission spectra which are allowed to shift and to broaden. We observed that, unlike the CT emission spectra, the LE emission spectra are independent on the solvent polarity.

The description of the emission spectra of the CT state by three Gaussian components is in agreement with the Visser's results [2]. Visser presents the fluorescence emission spectrum of the CT state of BA in 2-methylbutane at 298 K ($S_{CT}^{Visser}(\bar{\nu})$) obtained by the subtraction of the fluorescence emission spectrum at 131 K to the corresponding one at 298 K. The authors assumed that below 131 K only the LE state emits. The resultant spectrum $S_{CT}^{Visser}(\bar{\nu})$ is structured and composed of three vibrational bands. The emission spectrum of the CT state obtained either by Visser in 2-methylbutane or by our decomposition method in cyclohexane are similar (Fig. 9). The three Gaussian components used as a convenient fitting tool appear to have some physical meanings, i.e. each Gaussian component represents one vibrational band.

The significative proportion of the CT state in cyclohexane for BA and for BOA refutes the assumption that the CT state is not formed in non polar

solvents [3,5–7,19,20]. Nevertheless, Visser has shown that the excited state of BA presents a large dipole moment in the non polar solvents [2]. In order to interpret his results, Visser has suggested that the LE state is rather a charge transfer state. According to our results, such a statement is now not necessary. Even in non polar solvents, the fluorescence is emitted by two excited states: the locally excited state (LE) and the charge transfer state (CT) which is a polar state and presents a substantial dipole moment. Moreover, Zachariasse [25] has shown, in the case of the 4(alkylamino)benzonitrile compound, that the CT state could be also formed in non polar solvents.

The relative intensity of the vibrational band of the LE emission spectrum obtained in this work ($S_{LE}(\bar{\nu})$) and by Visser ($S_{LE}^{Visser}(\bar{\nu})$) were slightly different. This comparison concerning BA suggests that even in DMPFC, the CT state may be present in a very low amount.

The success of our decomposition method is mainly due to the inhomogeneous broadening parameters introduced in the Gaussian fit. According to the theories presented by Ulstrup [11] and Dogonadze [12], the full width at half-maximum of the CT emission spectrum (Δ_{CT}) is related to the Stokes shift of this spectrum ($\Delta\bar{\nu}_{st}$) by the following relation:

$$\Delta_{CT}^2 = 16 \ln 2 \frac{kT}{hc} \Delta\bar{\nu}_{st} + 16 \ln 2 \frac{kT}{h^2 c^2} \times (-\Delta E_{fluo} + hc\bar{\nu}_{abs}^{max}). \quad (11)$$

ΔE_{fluo} represents the energy gap between the ground state and the CT state in solution. It depends on the solvation free energy in the ground and the CT states as well as on the energy gap between these two states in gaseous phase. $\bar{\nu}_{abs}^{max}$ denotes the wavenumber corresponding to the absorption spectrum maximum. The theory developed by Sutin [13,14], based on the Marcus model, leads to Eq. (12) involving intramolecular vibrations

$$\frac{(hc\Delta_{CT})^2}{8 \ln 2} = 2\lambda_{out} kT + 2\lambda_{inl} kT + \lambda_{inh} h\nu_{inh}, \quad (12)$$

where λ_{out} , λ_{inl} and λ_{inh} are the three contributions to the reorganisation free energy around the solute. λ_{out} corresponds to the outer sphere reorganisation free energy, λ_{inl} and λ_{inh} are associated to the

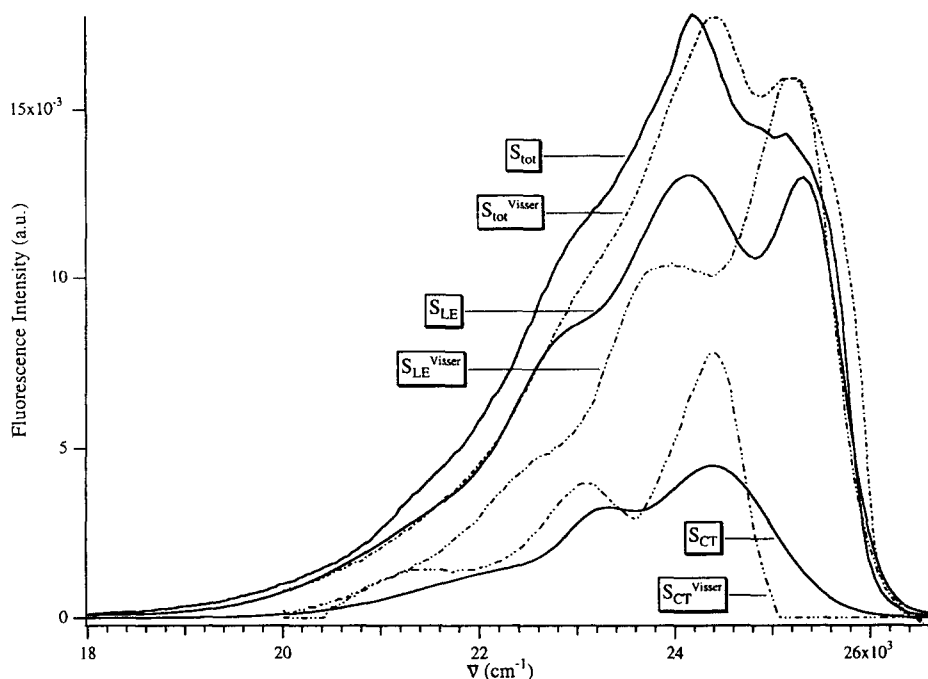


Fig. 9. Emission spectra of BA at 298 K in 2-methylbutane ($S_{\text{tot}}^{\text{Visser}}$) and in cyclohexane (S_{tot}). The superscript Visser designates the fluorescence emission spectra obtained by Visser, the other spectra have been obtained in this work.

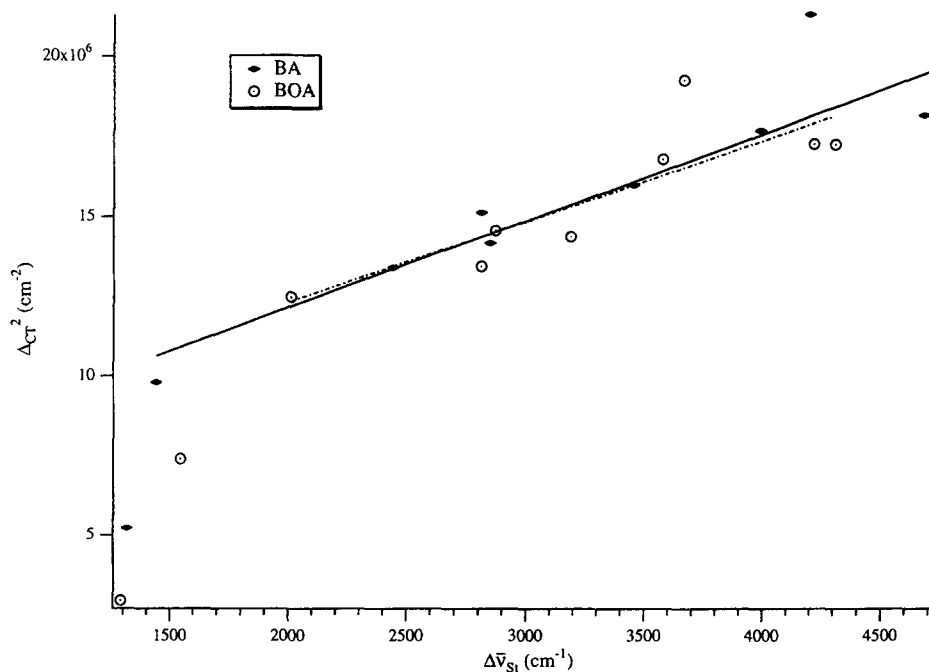


Fig. 10. Correlation between the full width at half-maximum (Δ_{CT}) and the Stokes shift ($\Delta\nu_{\text{S1}}$) of the fluorescence emission spectra of the CT state. A similar straight line is obtained using the Δ_{CT} and $\Delta\nu_{\text{S1}}$ parameters of the second or the third Gaussian of the CT emission spectrum.

structural change of the solute during the solvent relaxation. λ_{inl} and λ_{inh} represent the intramolecular reorganisation free energy associated to vibrations with respectively $h\nu < kT$ and $h\nu > kT$. λ_{out} is given by [13–16]

$$\lambda_{\text{out}} = \frac{(\mu_g - \mu_e)^2}{4\pi\epsilon_0 a^3} \left(\frac{\epsilon_r - 1}{2\epsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 1} \right), \quad (13)$$

which can be written more simply as

$$\lambda_{\text{out}} = \frac{hc}{2} \Delta \bar{\nu}_{\text{St}}. \quad (14)$$

μ_g and μ_e design the dipole moment of the ground state and of the excited state (CT). ϵ_0 , h , c and a correspond respectively to the vacuum permittivity, the Planck's constant, the velocity of light in vacuum and the Onsager radius (i.e. the radius of the solvent cavity).

We can use the width and the Stokes shift of individual Gaussian as well as those of the whole CT spectrum³. In both cases, we obtained a good correlation between the parameters Δ_{CT}^2 and $\Delta \bar{\nu}_{\text{St}}$ in agreement to the theoretical relations (11) and (12). For example, the experimental slope obtained from the whole spectra for BA and BOA (Fig. 10) is 2410 cm^{-1} which is close to the theoretical slope $16 \ln 2 (kT/hc) = 2298 \text{ cm}^{-1}$ at 298 K.

Thus, the consistent evolution of vibrational band components with solvent polarity and the correlation obtained between the adjustable parameters and the experimental data represent two significant elements of validation of our spectral decomposition method.

5.2. Equilibrium between the LE and the CT states

The red shift of the CT emission is a direct measurement of the CT state stabilisation energy, since the ground state energy is almost solvent independent. The equilibrium constant K_{eq} is also re-

lated to this stabilisation energy. Indeed, K_{eq} depends on the energy gap (ΔE_0) between the lowest vibrational and rotational levels of the LE and the CT states [26]:

$$K_{\text{eq}} = \frac{q_{\text{CT}}}{q_{\text{LE}}} e^{-\Delta E_0/kT}, \quad (15)$$

where q_{CT} and q_{LE} design respectively the molecular partition function of the compound in the CT and the LE states. The energy gap ΔE_0 depends on the Stokes shift of the CT spectrum. The Stokes shift is usually defined as the shift of the first vibrational band of the fluorescence emission spectrum with respect to the corresponding band of the absorption spectrum. The first vibrational band of the CT spectrum, described by the first Gaussian, is probably perturbed by a contribution of the LE spectrum. In fact, whatever the solvent is, the shift of the CT spectrum can also be determined by the shift of the second or the third vibrational band. Then, we have defined the Stokes shift ($\Delta \bar{\nu}_{\text{St}}^v$) of the CT spectrum with respect to the second vibrational band and noted $\bar{\nu}_{\text{fluo}}^v$ the corresponding wavenumber of the emission intensity maximum:

$$\Delta \bar{\nu}_{\text{St}}^v = (\bar{\nu}_{\text{abs}}^{\text{max}} - \bar{\nu}_{\text{fluo}}^v). \quad (16)$$

The energy gap ΔE_0 is defined by the following relation:

$$\Delta E_0 = E_{\text{CT}} - E_{\text{LE}}, \quad (17)$$

where E_{LE} and E_{CT} represent respectively the energy of the lowest vibrational and rotational level of the LE state and the CT state after the relaxation of the solvent. Considering the Stokes shift $\Delta \bar{\nu}_{\text{St}}^v$, Eq. (17) becomes

$$\Delta E_0 = -hc\Delta \bar{\nu}_{\text{St}}^v + E_{S_0}^{\text{FC}} + E_{\text{LE}}^{\text{FC}} - E_{\text{LE}} - E_{S_0}, \quad (18)$$

where E_{S_0} denotes the energy of the lowest vibrational and rotational level of the ground state. $E_{\text{LE}}^{\text{FC}}$ and $E_{S_0}^{\text{FC}}$ represent respectively the energy of the vibrational level reached after the absorption and the emission process of one photon. The superscript FC refers to the Franck–Condon state. The emission process occurs from the relaxed CT state to a non relaxed Franck–Condon state on S_0 , so that $E_{\text{CT}} = hc\bar{\nu}_{\text{fluo}}^v + E_{S_0}^{\text{FC}}$. In this Franck–Condon state, the solvent is not relaxed, thus, a solvent reorganisation

³ We defined the Stokes shift of the whole CT spectrum or of individual Gaussian as the shift of, respectively, the maximum of the whole CT fluorescence spectrum or of individual Gaussian with respect to the first vibrational band of the absorption spectrum. The latter definition should be preferred, however, the former is usually used when there is no evidence of vibronic structure in the emission spectrum.

around this state follows. Then, $E_{S_0}^{\text{FC}} - E_{S_0} = \lambda_{\text{out}} + \lambda_{\text{inl}} + \lambda_{\text{inh}}(h\nu_{\text{inh}})/(2kT)$ where we can assume that λ_{inl} and λ_{inh} are independent of the solvent [14,15]. For the absorption process where both S_0 and LE states are non polar, the solvent relaxation can be neglected. Then, the relation between the equilibrium constant and the Stokes shift can be written as

$$\ln(K_{\text{eq}}) = p\Delta\bar{\nu}_{\text{St}}^{\text{v}} + \ln\left(\frac{q_{\text{CT}}}{q_{\text{LE}}}\right) + \frac{1}{kT}E(\text{LE}, \lambda_{\text{in}}), \quad (19)$$

with $p = (hc/2kT)$ and $E(\text{LE}, \lambda_{\text{in}}) = -E_{\text{LE}}^{\text{FC}} + E_{\text{LE}} - \lambda_{\text{inl}} - \lambda_{\text{inh}}(h\nu_{\text{inh}})/(2kT)$. The linear relation between $\ln(K_{\text{eq}})$ and $\Delta\bar{\nu}_{\text{St}}^{\text{v}}$ is verified (Fig. 11) with a slight difference between the experimental (p_e) and theoretical (p) values of the slope; we have obtained $p/p_e = 1.2$ for BA and $p/p_e = 0.75$ for BOA. These results suggest a significant correlation between the main thermodynamic parameter, K_{eq} , of the LE/CT equilibrium and the spectroscopic properties of these two probes and introduce a sort of validation of our spectroscopic model. The slight deviations observed from theoretical and experimental values indicate

that the representation of the CT emission spectrum by three Gaussian components is not perfect. This is especially the case for BA in the more polar solvents where an additional Gaussian gives best results. In fact, the induced shift of each Gaussian component by the solvent contains both the dipolar interaction and the change in the Franck–Condon factor leading to higher experimental value of the slope ($p_e < (hc/2kT)$) than the theoretical one. We shall thus prefer to measure the energy gap between LE and CT states from the K_{eq} values than to determined it from the Stokes shift values.

5.3. CT state dipole moment

Previous determinations of the dipole moment of the BA excited state have been done by Lippert and Schneider [1] from the total fluorescence emission spectra, using the simplified Lippert–Mataga relation [27,28],

$$\Delta\bar{\nu}_{\text{St}} = \frac{2(\mu_e - \mu_g)^2}{4\pi\epsilon_0 hca^3} \Delta f_{\text{Lippert}},$$

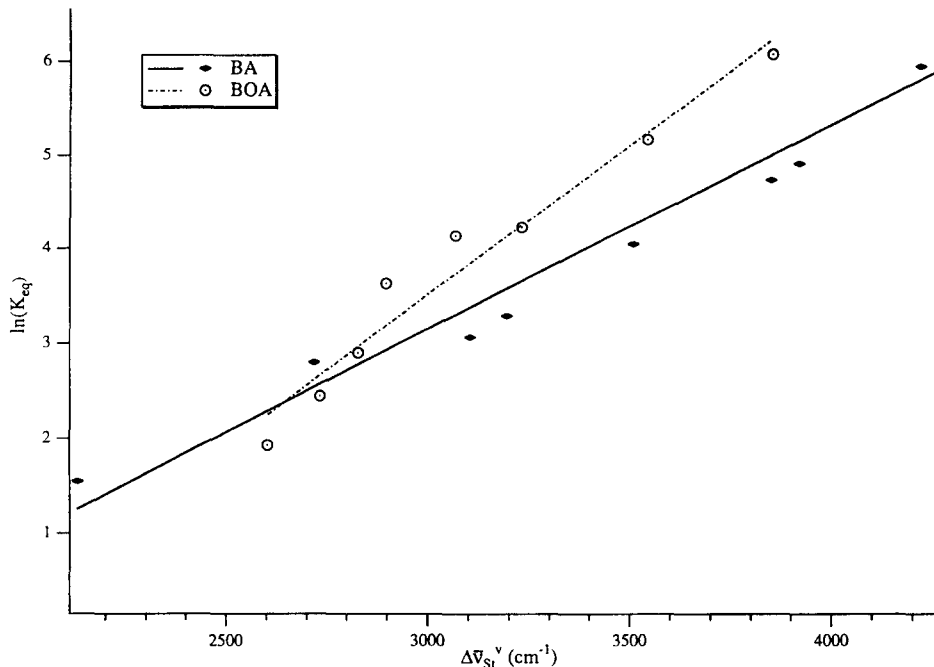


Fig. 11. Relation between the equilibrium constant K_{eq} and the Stokes shift $\Delta\bar{\nu}_{\text{St}}^{\text{v}}$. In agreement with the theoretical relation (19), a straight line is obtained.

with

$$\Delta f_{\text{Lippert}} = \left(\frac{\epsilon_r - 1}{2\epsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 2} \right). \quad (20)$$

They obtained a value of 20 D using $a = 6 \text{ \AA}$. According to this method and using the same value of a , we have found from our experimental emission spectra $\mu_e^{\text{BA}} = 17 \text{ D}$. However, the dipole moment deduced from the total fluorescence emission spectra cannot be assigned to the CT state because the overlap between LE and CT emission spectra is large: especially in non polar solvents, the solvatochromic shift of the CT spectrum is perturbed and masked by the LE spectrum. Thus, the determination of the dipole moment of the CT state requires the decomposition of the overall fluorescence emission spectra.

Consequently, the analysis of the Stokes shift of the CT emission spectrum allows us to determine its

dipole moment. The Bilot relation [29,27,28] can be used to link the Stokes shift of the CT emission spectrum to the dipole moment of the CT state:

$$\Delta \bar{\nu}_{\text{St}} = \frac{2(\mu_e - \mu_g)^2}{4\pi\epsilon_0 hca^3} \Delta f_{\text{Bilot}},$$

with

$$\Delta f_{\text{Bilot}} = \left(\frac{2n^2 + 1}{n^2 + 2} \right) \left(\frac{\epsilon_r - 1}{\epsilon_r + 2} - \frac{n^2 - 1}{2n^2 + 2} \right) \quad (21)$$

and combined to the Lippert–Mataga relation [30–32]:

$$\Delta \bar{\nu}_{\text{St}} = \frac{2(\mu_e - \mu_g)^2}{4\pi\epsilon_0 hca^3} \Delta f_{\text{L-M}},$$

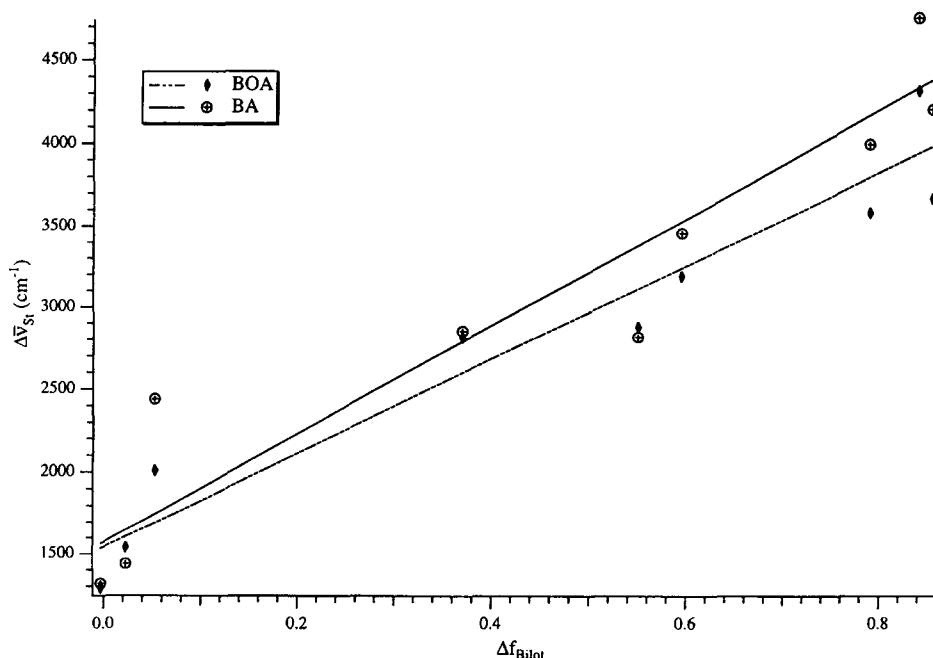


Fig. 12. Influence of the solvent polarity (Δf_{Bilot}) on the Stokes shift of the CT spectrum. From the experimental slope, the dipole moment of the CT state of BA and of BOA could be estimated (Table 5). A similar straight line is obtained using the Bilot relation (21) as well as the Lippert–Mataga relation (22).

with

$$\Delta f_{L-M} = \frac{\epsilon_r - 1}{2\epsilon_r + 1} \left(1 - \frac{\epsilon_r - 1}{3(2\epsilon_r + 1)} \right)^{-1} - \frac{n^2 - 1}{2(2n^2 + 1)} \left(1 - \frac{n^2 - 1}{3(2n^2 + 1)} \right)^{-1}. \quad (22)$$

The absence of a significant solvent dependence on the excitation spectrum is consistent with the idea that the dipole moment in the ground state of BA [2] and of BOA (μ_g) are equal to zero. We have the opportunity to measure the Stokes shift from the whole fluorescence emission spectrum of the CT state or from the shift of individual Gaussian used in the fit. Between both methods, the latter should be preferred [21]. Indeed, the dipole moment determined from the Stokes shift of the whole fluorescence spectrum is almost systematically overestimated due to the specific value of the Franck–Condon factors attributed to each vibrational component. Whatever the data used, for BA and BOA, we obtained a straight line (Fig. 12). The slopes are reported in Table 5.

The analysis of the equilibrium constant K_{eq} introduces the opportunity to estimate by another way (Eq. (19)) the Stokes shift of the CT spectrum. Using this Stokes shift, the dipole moment of the CT state has been estimated at 6.2 D for BA and 8.4 D for BOA according to the Bilot relation (21) and at

Table 5
Dipole moments of the CT state of BA and of BOA obtained from the Bilot relation (21)

	Slope (cm^{-1})	Onsager radius a (Å)	CT dipolar moment (D)
BA	3272.9	6	8.4
BOA	2796	7.75	11.4
BA ^a	2137	6	6.8
BOA ^a	1143	7.75	7.3

The values of the Onsager radius (a) are deduced from the van der Waals volume of each molecule.

For BA, the radius obtained agrees with that used by Lippert and Schneider [1].

^a Stokes shift of the second vibrational Gaussian band. The analysis using the third Gaussian band gives similar values of the dipole moment.

Table 6

Calculated dipole moment of the CT state of BA and of BOA deduced from the equilibrium constant analysis; the difference between the dipole moment values obtained using the relations (23) and (24) is usual [13–16]

	BA ($a = 6$ Å) (D)	BOA ($a = 7.75$ Å) (D)
μ_{CT} (Bilot relation (21))	6.2	8.4
μ_{CT} (Lippert–Mataga relation (22))	10.3	13.2

10.3 D for BA and 13.2 D for BOA according to the Lippert–Mataga relation (22) (Table 6). The difference between the dipole moment values obtained from the relations (21) or (22) have been previously observed for other compounds [27].

The dipole moment obtained for BA is lower than the Lippert and Schneider's value [1]. An estimation of the dipole moment of BA CT state has been determined by theoretical calculations [33] and leads to a value lower than 14 D.

5.4. Comparison between BA and BOA

The evolution of the emission spectra, the quantum yields and the lifetimes with the solvent polarity are similar for BA and BOA. As expected, BOA presents the same photophysical properties as BA.

The study of the LE/CT equilibrium shows that whatever the solvent is, the CT state of BA is more stabilised than the corresponding excited state of BOA. Moreover, the Stokes shift and the inhomogeneous broadening of the fluorescence emission spectra of the CT state of BOA are less important. The difference between BA and BOA can be assigned to a difference either in dipole moments or in molecular volumes or both. As the alkyl groups present a symmetrical position on both side of the chromophore and as they are expected to introduce a small inductive effect, we can assume a similar dipole moment value for both molecules [33]. Using this hypothesis, we have estimated the radius of the Onsager cavity of BOA at $a_{BOA} = 6.4$ Å whatever the dipole moment values used in Table 6. Using this value of a , the increase of the Onsager cavity volume from BA to BOA is 180 Å^3 ; it corresponds, in fact, to the van der Waals volume of 8 or 9 CH_2 (or CH_3)

groups. Consequently, only 4 or 5 CH₂ (or CH₃) groups, part of each alkyl substituent, seem to be involved in the Onsager cavity of BOA.

6. Conclusion

We have shown in the present work that the basic photophysical processes of BOA are identical to those of BA. BA and BOA are two fluorescence probes strongly dependent on the solvent polarity.

Our fluorescence spectroscopy results confirm that the fluorescence emission of these two probes originates from two excited states: a locally excited state (LE) which is a non polar state and a charge transfer state (CT) which is strongly dependent on the solvent polarity. In our work, we extend this mechanism to solvents of low polarity.

The decomposition of the stationary fluorescence emission spectra gives us the opportunity to determine the vibrational structure of the CT emission spectrum and the proportion of the LE and the CT states as a function of the solvent polarity. We have used the fluorescence emission in DMPFC as a reference of the LE state emission.

From the results of this vibrational band decomposition, the dipole moment of the CT state of BA and BOA have been estimated in the range of 6.2 to 10.3 D. The comparison between both molecules leads to an estimation of the Onsager radius of BOA: $a_{\text{BOA}} = 6.4 \text{ \AA}$. It seems that only 4 or 5 CH₂ groups of each lateral chain of BOA are involved in the Onsager cavity of BOA.

The consistent results obtained with our vibrational band decomposition method are mainly due to the contribution of solute–solvent interactions which lead to an inhomogeneous broadening and a shift of fluorescence spectra. A good correlation between this inhomogeneous broadening and the Stokes shift of the CT spectrum has been obtained. These results illustrate clearly the originality and the pertinence of our decomposition method.

The results of the vibrational band decomposition introduce the formation of the CT state in non polar solvents like cyclohexane. This new result suppresses the controversy concerning the polar or apolar nature of the LE state and then, the substantial dipole moment determined by Visser [2] in non polar

solvents is due to the formation of a significant amount of CT state.

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