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Electronic spectroscopy of pyrromethene 546

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Abstract

UV–Vis absorption and fluorescence (steady state and time-correlated) spectroscopies are applied to study the photophysics of pyrromethene 546 in a multitude of apolar, polar, and protic solvents, including water/ethanol mixtures. The solvent effect on the absorption and fluorescence bands is analysed in terms of the stabilization of several resonance structures of the π-system of the chromophore by general and specific H-bond solute/solvent interactions. Highest and lowest values for the rate constant of radiative and radiationless deactivation of PM546 are observed in high polar and H-bond donor solvents, respectively, and they are recommended as the best media to obtain the highest laser efficiency of PM546 in liquid solutions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Pyrromethene 546; UV–Vis absorption; Fluorescence; Photophysics; Solvent effect

1. Introduction

Pyrromethenes (PM) are a new laser dye family with interesting photophysical and lasing properties [1,2]. They are a serious rival to rhodamine dyes as active media of sintonizable lasers in the visible region of the electromagnetic spectrum, since pyrromethenes may have a higher lasing efficiency [3,4]. Both dye families have similar photophysical properties, with molar absorption coefficient at the absorption maximum around $10^5\ M^{-1}\ cm^{-1}$ and fluorescence quantum yield close to one, and the higher lasing efficiency for pyrromethenes is attributed to a lower triplet-triplet absorption coefficient at the lasing spectral region [1], decreasing the losses at the resonator cavity. Moreover, the higher photostability of pyrromethene dyes with respect to rhodamines [5] increases the lifetime of the laser signal for the former dye family.

Pyrromethene dyes as active media in dye lasers are mainly used in solid state matrixes such as polymers, silica, etc. [6–8]. However, active media in liquid solutions are of great interest because of the multitude of different environments that can be used. Good correlations between the photophysical properties and the lasing characteristics of PM dyes were proven in liquid solutions [9,10]. Thus, the evolutions of the fluorescence band and the fluorescence quantum yield of PM567 with the solvent are, respectively, similar to those observed in the lasing band and the lasing efficiency [9]. Moreover, similar correlations were reported by changing the molecular structure of the PM dyes (i.e. PM546, PM556, and PM567) in common solvents [10]. Therefore, the understanding of the solvent effect on the photophysics of PM dyes can be used to predict the most recommended media to obtain the highest lasing power of these dyes. However, there is an important lack of bibliographic data on the photophysics of bipyrromethene-BF_2 complexes [11].

In previous papers [9,12], the effect of the solvent on the photophysics of PM556 and PM567 was studies. In the present paper, the photophysical properties of PM546 (Fig. 1) are obtained in several apolar, polar and protic solvents, including water/ethanol. PM546 is not soluble in pure water or in very water-rich water/ethanol mixtures. The solvent effects on the absorption and fluorescence bands are studied by a multicomponent linear regression in which several solvent parameters are simultaneously analysed. The paper discusses, from a photophysical point of view, which is the most adequate environment to obtain the highest laser efficiency of PM546 in liquid solutions.

2. Experimental

Pyrromethene 546 (laser grade) was supplied by Exciton and was used as received. All the solvents were of spectroscopic grade and were used without further purification. Water was distilled and deionized. Samples with different

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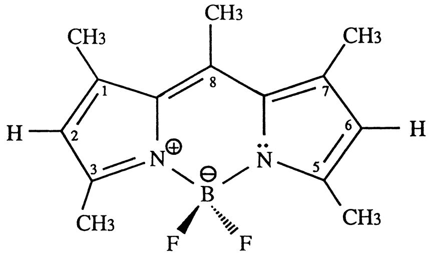

Fig. 1. Molecular structure of PM546. Other PM dyes are PM556 and PM567 with sulfonate and ethyl groups at two and six positions, respectively, of the chromophore.

concentrations of PM546 in methanol were obtained by dilution of a concentrated stock PM546/methanol solution. Diluted samples of PM546 in several solvents were prepared by diluting a stock PM556/acetone solution in which the acetone was eliminated by vacuum evaporation before adding the corresponding solvent.

UV–V is absorption and fluorescence (after excitation at $\lambda = 465$ nm) spectra were recorded on a Cary 4E spectrophotometer and on a Shimadzu RF-5000 spectrofluorimeter, respectively. Fluorescence spectra were corrected for the wavelength dependence of the monochromator and photomultiplier sensitivity. Fluorescence quantum yields (ϕ) were evaluated by the means of corrected fluorescence spectra using a diluted PM567 solution in ethanol as reference ($\phi^\circ = 0.91$ at 20°C [9]) and taking into account the effect of the refractive index of the solvent. Radiative decay curves were recorded by the time-correlated single-photon counting technique (Edinburgh Instruments model ηF900). The emission was monitored at about $\lambda \approx 505$ nm after excitation at 340 nm by means of a hydrogen flash-lamp with 1.5 ns FWMH pulses and 40 kHz repetition rate. For diluted dye solutions, the fluorescence decay curves were analysed as a one-exponential decay ($\chi^2 < 1.2$) and the fluorescence decay time (τ) was obtained from the slope. The estimated errors in the determination of ϕ and τ values are 5% and 1%, respectively. The rate constant for the radiative (k_{fl}) and non-radiative (k_{nr}) deactivation processes were calculated by: $k_{\text{fl}} = \phi/\tau$ and $k_{\text{nr}} = (1-\phi)/\tau$. The temperature was always 20 (±0.2)°C and all the measurements were performed in aired samples.

The photophysical properties were studied in diluted dye solutions (2×10^{-6} M) in 1 cm optical pathlength quartz cuvettes. The fluorescence spectra and decay curves of more concentrated solutions (upto 2×10^{-3} M) were recorded in 0.1 and 0.01 cm optical path quartz-cuvettes using the front-face configuration, orientating the cuvettes 30° and 60° with respect to the excitation and the emission-detection beams, respectively, in order to reduce the reabsorption and reemission effects [13].

3. Results and discussion

The Vis-absorption and fluorescence spectra of a diluted solution of PM546 in methanol are shown in Fig. 2. This green/yellow dye has absorption and emission bands centred at $\lambda_{\text{ab}} \approx 492$ and $\lambda_{\text{fl}} \approx 504$ nm, respectively, with a fluorescence quantum yield close to one ($\phi = 0.95$). The fluor-

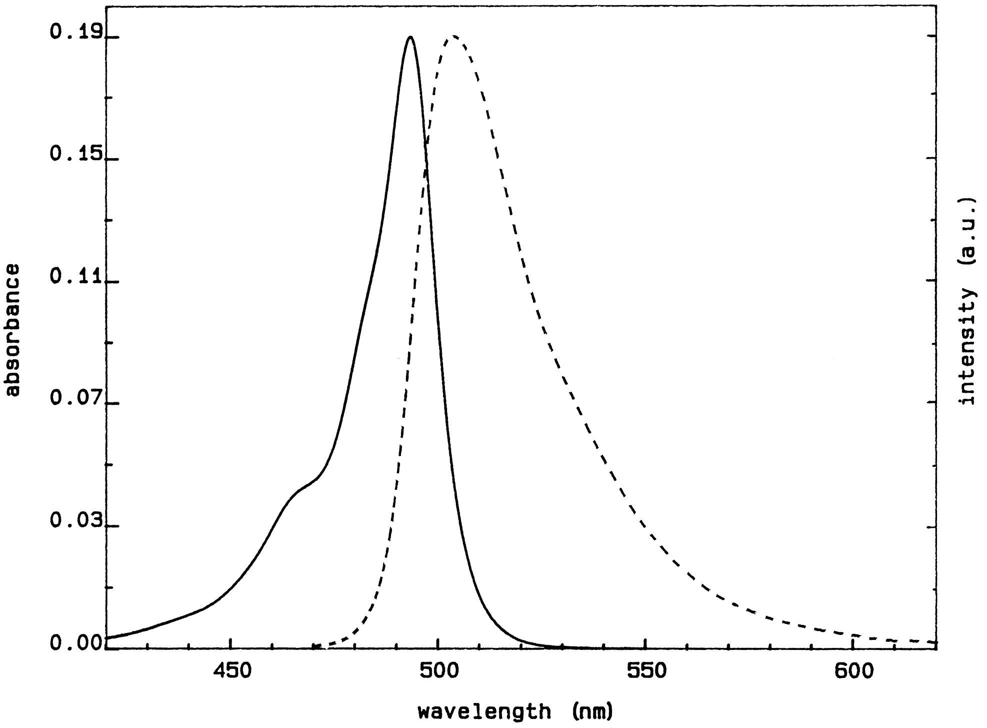

Fig. 2. Absorption (left and solid curve) and fluorescence (right and dashed curve) spectra of PM546 (2×10^{-6} M) in methanol.

escence emission of PM546 in viscous solvents is polarised and it is attributed to the low rotational diffusion of the dye molecules during the lifetime of the excited state in viscous solvents, which affects the radiative and radiationless deactivation processes from the S_1 excited state. This effect is avoided by recording the fluorescence intensity with an emission polariser at the magic angle 54.7° and a vertical polariser in the excitation beam [14].

The shape of the absorption band is nearly independent of the dye concentration. Only a slight increase in the absorbance at the shoulder ($\lambda \approx 465$ nm) over that at the absorption maximum (A_{465}/A_{492} in Table 1) by increasing the dye concentration (upto the solubility limit 4.6×10^{-4} M) would indicate a slight tendency of the PM546 molecules to aggregate. Using the method described in reference [15], the proportion of aggregates for the highest concentrated solution (4.6×10^{-4} M) of PM546 in methanol is lower than 1% of the total molecules, suggesting the poor tendency of PM dyes to aggregate in liquid solutions. This result implies a great advantage of PM dyes with respect to rhodamine dyes, since the rhodamine aggregates are efficient quenchers of the fluorescence emission from monomers [16,17], reducing the quantum lasing efficiency (number of lasing photons per number of pumping photons) for concentrated rhodamine solutions in which the laser signal is obtained. Moreover, rhodamine aggregates absorb light at the laser spectral region which is inactive in fluorescence emission, increasing the losses of the resonator cavity.

On the other hand, the dye concentration affects the fluorescence emission. The fluorescence band shifts to higher wavelengths, the fluorescence quantum yield decreases and the lifetime of the S_1 excited state increases when the dye concentration is augmented (Table 1). These effects can be assigned to the reabsorption/reemission phenomena (probability of absorbing a previously emitted photon), since they are reduced by decreasing the penetration of the excitation and the analysis emission beams through the sample by means of the front-face configuration (Table 1). Reabsorption and reemission effect depend on the overlap between the absorption and the emission bands and although they can be corrected by mathematical methods [13,18], diluted solutions, where these effects are minimised, are recommended to evaluated the fluorescence parameters. Reabsorption/reemission effects also negatively affect the lasing efficiency, since they increase the losses in the resonator cavity.

The photophysical properties of PM546 are effected by the solvent (Table 2). PM546 is soluble in apolar, polar, and protic organic solvents, but is not soluble in water or in water/ethanol mixtures with very poor content in ethanol ($x_{\mathrm{EtOH}} < 0.05$). Generally, the absorption and fluorescence bands shift to higher energies and the fluorescence quantum yield decreases from apolar to protic solvents (Table 2). The solvent effect on the photophysics of PM dyes is better treated by considering several solvent parameters, rather than by one solvent parameter which includes several solvent properties [19–22]. A chemical–physical property (XYZ) is linearly correlated with several solvent parameters (A, B, C, etc.) by means of Eq. (1)

$$(\mathrm{XYZ}) = (\mathrm{XYZ})_0 + aA + bB + cC + \cdots \qquad (1)$$

where $(\mathrm{XYZ})_0$ is the chemical–physical property in an inert solvent and *a, b, c*, etc. are the adjusted coefficients which are indicative of the dependence of the chemical–physical property (XYZ) with the respective solvent properties *A, B, C*, etc. The spectral bands can be mainly affected by the dipolarity/polarizability, the H-bond donor capacity, and the electron donation ability of the solvent. These solvent properties are bibliographically identified with several solvent parameter scales, most of them interconnected [23–27]. Taft et al. [28–30] proposed the π^*-, α-, and β-scales to, respectively, quantify the above-mentioned solvent properties, whereas Catalan et al. [31–33] suggest the $\mathrm{SPP^N}$-, SA-, and SB-scales, respectively. In this paper both sets of solvent scales are used and compared.

Fig. 3(A) shows the correlation between the absorption wavenumber predicted by the multicomponent linear regression with the π^*-, α-, and β-scale and the experimental value for all the solvents listed in Table 2. The corresponding adjusted coefficients are listed in Table 3. The linear correlation is not good (correlation coefficient $r = 0.71$) and important deviations are observed in water/ethanol mixtures, in 2,2,2-trifluoroethanol, and in ethylenglycol (high polar and H-bond donor solvents). If data obtained in water/ethanol mixtures are not considered in the multicomponent linear relation, the correlation coefficient does not ameliorate and the adjusted coefficients are similar to those listed in Table 3. The absorption wavenumber of PM546 shows a

Table 1
Evolution of the photophysics of PM546 with the dye concentration and optical length of the cuvette in methanol

[PM546] (M)	Optical path (cm)	λ_{ab} (nm)	A_{465}/A_{492}	λ_{fl} (nm)	ϕ	τ (ns)	$\lambda_{fl}{}^b$ (nm)	ϕ^b	τ^b (ns)
2.0×10^{-6}	1	492.3	0.263	503.6	0.95	5.58	–	–	–
2.8×10^{-5}	1	492.3	0.264	511.2	0.78	6.95	506.4	0.92	5.79
	0.1[a]	492.3	0.265	504.0	0.95	5.60	–	–	–
4.6×10^{-4}	0.1[a]	492.3	0.266	513.6	0.72	7.25	506.8	0.91	5.93
	0.01[a]	492.3	0.267	504.0	0.93	5.75	503.6	0.94	5.63

[a] Fluorescence beams recorded in the front-face configuration.

[b] Corrected for reabsorption/reemission effects [14,18].

Table 2
Photophysics of PM546 (2×10^{-6} M) in several solvents (including water/ethanol mixtures) at 20°C

1	Solvent	λ_{ab} (nm)	ε (10^4 M^{-1} cm^{-1})	λ_{fl} (nm)	ϕ	τ (ns)	k_{fl} (10^8 M^{-1} s^{-1})	k_{nr} (10^7 M^{-1} s^{-1})
1	2-methylbutane	497.5	9.83	506.8	0.93	5.84	1.60	1.2
2	Hexane	498.2	9.79	507.2	0.90	5.51	1.64	1.8
3	Cyclohexane	499.4	9.74	509.6	0.77	5.23	1.47	4.5
4	2-methylheptane	498.1	9.72	507.2	0.84	5.41	1.55	3.0
5	Benzene	499.9	8.70	510.4	0.63	4.72	1.33	7.9
6	Toluene	500.0	8.63	510.4	0.62	4.92	1.27	7.6
7	Diethyl ether	495.7	8.71	505.6	0.91	5.45	1.68	1.6
8	1,4-dioxane	496.0	8.47	506.8	0.87	5.06	1.73	2.5
9	THF[a]	496.1	8.43	506.4	0.78	4.97	1.57	4.4
10	NMP[a]	496.5	5.32	506.4	0.68	5.02	1.36	6.3
11	Ethyl acetate	494.1	8.13	504.0	0.85	5.58	1.52	2.7
12	DMF[a]	497.6	6.88	504.8	0.67	4.92	1.36	6.8
13	Acetone	493.0	7.86	503.6	0.93	5.55	1.68	1.3
14	Acetonitrile	491.7	7.88	502.0	0.93	5.39	1.72	1.4
15	Ethylenglycol	495.4	7.99	505.6	0.78	5.03	1.54	4.4
16	F_3-ethanol[a]	490.1	8.47	502.8	0.99	6.22	1.59	0.2
17	2-phenox yethanol	499.6	7.89	510.8	0.76	5.09	1.49	4.8
18	1-decanol	499.6	8.74	507.6	0.85	5.10	1.67	2.9
19	1-octanol	498.5	8.69	507.6	0.87	5.12	1.70	2.5
20	1-hexanol	497.8	8.53	507.2	0.85	5.21	1.63	2.9
21	1-butanol	496.9	8.35	506.8	0.87	5.27	1.66	2.4
22	2-propanol	495.6	8.30	505.6	0.88	5.31	1.67	2.2
23	1-propanol	496.0	8.73	506.4	0.86	5.31	1.62	2.7
24	Ethanol	494.8	8.10	504.8	0.89	5.52	1.61	2.0
25	Methanol	492.3	8.21	503.6	0.95	5.58	1.71	0.9
Water/ethanol mixture:[c]								
26	95% (0.85)	494.7	8.21	504.8	0.88	5.46	1.61	2.3
27	90% (0.74)	494.6	8.12	504.8	0.89	5.50	1.62	2.0
28	80% (0.55)	494.6	8.04	504.4	0.87	5.53	1.57	2.4
29	70% (0.42)	494.5	7.97	504.4	0.88	5.59	1.58	2.1
30	60% (0.32)	494.3	7.85	504.8	0.89	5.69	1.57	1.9
31	50% (0.24)	494.2	7.87	504.4	0.94	5.61	1.67	1.1
32	40% (0.17)	493.9	7.70	504.0	0.92	5.53	1.66	1.5
33	30% (0.12)	493.5	7.56	503.6	0.96	5.45	1.76	0.7
34	20% (0.07)	492.5	7.48	502.0	0.95	5.38	1.76	0.9
35	10% (0.03)	491.6	[b]	500.0	0.96	[b]	–	–

[a] THF – tetrahydrofurane; NMP – 1-methylpyrrolidin-2-one; DMF – N,N-dimethylformamide; F_3-ethanol – 2,2,2–trifluoroethanol.
[b] Partially soluble.
[c] Percentage (in volume) of ethanol and molar fraction of ethanol (x_{EtOH}) in parentheses.

Table 3
Adjusted coefficients ($(\nu_x)_o$, a, b, and c). (See Eq. (1)) and correlation coefficient (r) for the multilinear regression analysis of a photophysical property (ν_x) of PM546 with π^*-, α-, and β-solvent scales [28–30] and with the SPP^N-, SA-, and SB-solvent parameters [31–33]

(ν_x) (cm^{-1})	$(\nu_x)_o$	a (π^*-scale)	b (α-scale)	c (β-scale)	r
ν_{ab}	20080 (±30)	160 (±50)	90 (±30)	−100 (±50)	0.71
ν_{fl}	19690 (±30)	120 (±50)	70 (±30)	−50 (±50)	0.66
$\Delta\nu_{St} = \nu_{ab} - \nu_{fl}$	400 (±50)	40 (±20)	20 (±10)	−50 (±20)	0.65
(ν_x) (cm^{-1})	$(\nu_x)_o$	a (SPP^N-scale)	b (SA-scale)	c (SB-scale)	r
ν_{ab}	19720 (±90)	660 (±150)	70 (±50)	−190 (±60)	0.77
ν_{fl}	19440 (±90)	450 (±140)	60 (±50)	−90 (±60)	0.68
$\Delta\nu_{St} = \nu_{ab} - \nu_{fl}$	280 (±30)	210 (±50)	10 (±50)	−100 (±20)	0.80

To improve to correlation coefficient see the text.

better multicomponent linear correlation with the SPP^N, SA, and SB solvent parameters (Fig. 3(B)). In this case, deviations are observed in aromatic solvents (benzene, toluene, and 1-methylpyrrolidin-2-one), in dimethylformamide, and in ethylenglycol. If these solvents are excluded from the multicomponent regression then a correlation coefficient

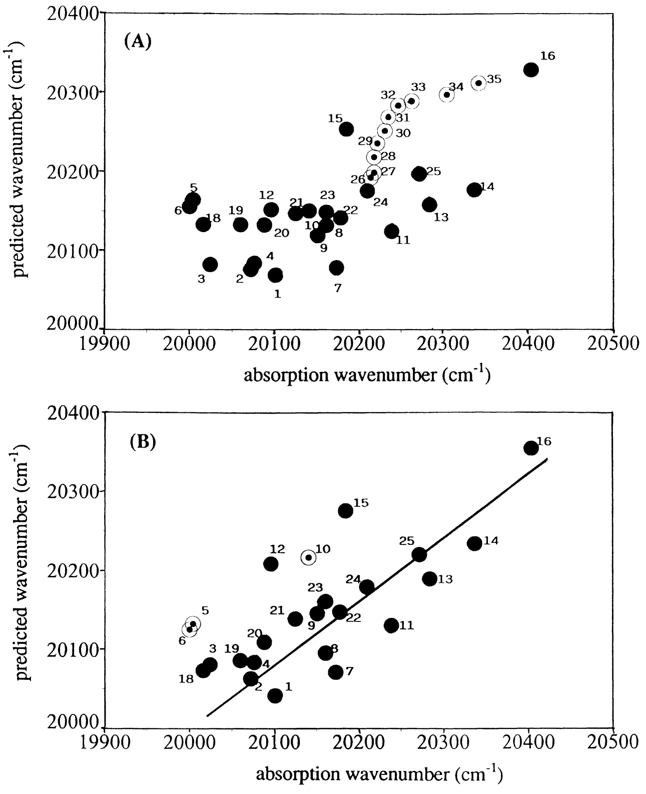

Fig. 3. Correlation between the predicted values by the multicomponent linear regression and the experimental absorption wavenumber (in cm^{-1}) of PM546: with the solvent parameters: (A) π^*-, α-, and β-scales; and (B) with the SPP^N-, SA-, and SB-scales. (the solvent numbers correspond to those in Table 2 and the π^*, α, and β data for water/ethanol mixture are obtained from extrapolating the data reported in [34].).

$r = 0.92$ is obtained. Indeed, aromatic solvents can give rise to deviations in the photophysics of π-systems because of the high polarizability of the π-system of the solvent or/and because of an extra π–π interaction between the aromatic systems of the solute and the solvent. This extra effect is considered in the π^*-scale by introducing a correction factor for aromatic solvents [25] but is not taken into account in the SPP^N parameter. On the other hand, ethylenglycol is a special solvent since it has two hydroxyl groups which can specifically interact with the solute to a different extent. Similar qualitative results to those observed in Fig. 3 are obtained for the wavenumber of the fluorescence band and the Stokes shift. The respective adjusted coefficients are also listed in Table 3.

The adjusted coefficients obtained by the two sets of solvent parameters are qualitatively similar, Table 3, corroborating that these solvent parameters are interconnected [23–27]. Thus, the coefficient '*a*' and '*b*' controlling, respectively, the dipolarity/polarizability and the H-bond donor capacity (acidity) of the solvents get positive values, whereas coefficient '*c*' controlling the electron donor ability (basicity) of the solvents takes negative values in both sets of solvent parameters (Table 3). Therefore, the absorption and fluorescence bands shift to higher energies and the Stokes shift increases in solvents with high polarity and H-bond donor capacity (the coefficients '*a*' and '*b*' > 0), and in solvents with low electron donating ability, coefficient '*c*' < 0.

The hypsochromic shift observed in the absorption and fluorescence bands by increasing the solvent polarity suggests that the dipole moment in the S_1 excited state is lower than that in the S_0 ground state. Fig. 4 shows some representative resonance structures for the π-system of the dipyrromethene-BF_2 chromophore. The resonance structure '*a*' is characterised by the participation of the electron lone pair of a N-atom in the π-system, whereas the positive charge of the chromophore is delocalized throughout the π-system in the mesomeric structure '*b*', with a higher dipole moment. Therefore, the participation of structure '*b*' would be more important in the S_0 ground state than in the S_1 excited state.

These resonance structures can also explain the effect of the solvent acidity and basicity in the spectral bands. Thus, a H-bond donor solvent will stabilize the resonance structure '*b*' (with respect to structure '*a*') by specifically interacting between the H-atom of protic solvents and the electron lone pair of the N-atoms of the pyrromethene chromophore, reducing the participation of these electron pairs in the conjugated π-system and justifying the observed hypsochromic shift in the absorption and fluorescence bands (adjusted coefficient $b > 0$, Table 3). On the other hand, a basic (electron donor) solvent will stabilize the positive charge of the chromophore localized at a N-atom (stabilization of the resonance structure '*a*') leading to the observed bathochromic shift in the absorption and fluorescence bands (adjusted coefficient $c < 0$, Table 3).

Spectral parameters can affect lasing efficiency. Thus, the induced emission coefficient, responsible for the laser power, is proportional to λ^{-3}. The lowest λ_{fl} value of PM546 is observed in 2,2,2-trifluoroethanol (Table 2) and the lasing efficiency of PM546 would augment in polar solvent with high H-bond donor capacity. Moreover, extra cavity losses due to reabsorption/reemission phenomena in concentrated solutions, which depend on the absorption and fluorescence bands overlapping, would be diminished in systems with high Stokes shift ($\Delta\nu_{St} = \nu_{ab} - \nu_{fl}$). From the results listed in Table 3, the highest Stokes shift for PM546 will be observed in polar solvent with high H-bond donor capacity and high electron donating ability, such us

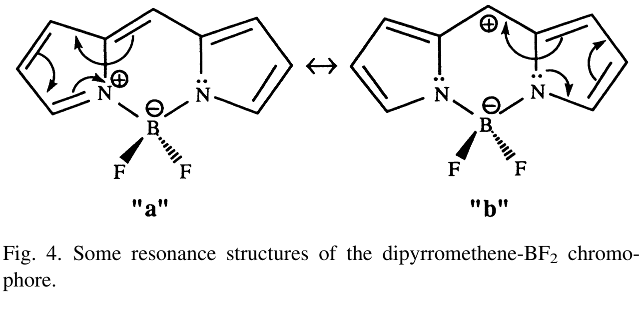

Fig. 4. Some resonance structures of the dipyrromethene-BF_2 chromophore.

2,2,2-trifluoroethanol and methanol (Table 2). However, the lasing efficiency will be governed, in the last analysis, by the rate constant of the radiative (k_{fl}) and non-radiative (k_{nr}) deactivation processes of the S_1 excited state. Systems with high k_{fl} values, in which the induced emission probability is directly proportional to the spontaneous emission probability and then to the k_{fl} value, and low k_{nr} values (reducing the competitive deactivation probability from the lasing state) are of interest.

The k_{fl} and k_{nr} values PM546 (Table 2) do not linearly correlate with any solvent parameters ($r < 0.6$), which may be due to the accumulative errors in both experimental ϕ and τ values. Highest k_{fl} values of PM546 are observed in methanol and in water-rich water/ethanol mixtures, and lowest k_{nr} value of PM546 are obtained in 2,2,2-trifluoroethanol, methanol and rich water water/ethanol mixtures (Table 2). These results suggest once again the recommendation of polar solvent with high H-bond donor capacity to obtain the highest lasing efficiencies of PM546 in liquid solution.

All these photophysical arguments (low λ_{fl} value, high stokes shift, high k_{fl} value and low k_{nr} value) favouring the laser power of PM546 in polar solvents with high H-bond donor ability are experimentally corroborated since the highest lasing efficiency of PM546 in some apolar, polar and protic solvents was previously observed in 2,2,2-trifluoroethanol [10].

4. Conclusions

The wavenumber of the absorption and fluorescence maxima of PM546 in liquid solutions depends not only on the general solvent effect (relative stalibization of the dipole moment in the S_1 and S_0 states by solvent dipolarity/polarizability), but also on specific H-bond solute/solvent interactions which stablize several resonances of the dipyrromethene-BF_2 chromophore. Thus, the participation of the electron lone pair of the N-atoms will be favoured in basic electron donating solvents, whereas the delocalization of the positive charge throught the π-system of the chromophore is favoured in H-bond donor solvents. 2,2,2-trifluoroethanol or polar solvents with high H-bond donor capacity are, from a photophysical point of view, the most recommended solvents to obtain the most efficient laser signal of PM546 in liquid solution since the lowest k_{fl} value, the highest Stokes shift,the highest k_{fl} value and the lowest k_{nr} values are observed in these solvents. Previous experimental results corroborate this conclusion [10], showing the good correlation between the photophysical properties and the lasing characteristics of PM dyes in liquid solutions.

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