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Journal of Photochemistry and Photobiology A: Chemistry 184 (2006) 298–305

Journal of Photochemistry and Photobiology A:Chemistry

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Concerning the color change of pyrromethene 650 dye in electron-donor solvents

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Received 12 December 2005; received in revised form 27 April 2006; accepted 28 April 2006

Abstract

This paper studies the change in the color from violet to green of pyrromethene 650 (PM650) dye observed in certain *N*,*N*′-dialkyl-amides characterized by their high electron-donor ability and low proton-donor capacity. For this purpose, the photophysical properties of PM650 are registered in diluted solutions of several amides, including dimethylformamide/dioxane mixtures. The color change of PM650 is discussed on the basis of the formation of new hypsochromic absorption and fluorescence bands, which are assigned to the formation of new chromophoric species as consequence of a specific reaction between PM650 and the amide solvents. The influence of the ageing time of the sample and the temperature on the color change is also discussed. In some cases the ageing leads to the bleaching of the dye.

Keywords: Photophysics; Pyrromethene PM650 dye; Solvent interactions; Color change; Electron-donor media

1. Introduction

The study of the photophysical properties of laser dyes is of great scientific and technological interest because of the important implications in photonics (active media of tunable lasers), in optics (mainly in the design of new non-linear optical devices) and in the development of new fluorescence probes and sensors [1–4]. Dye lasers are widely used in spectroscopic research and in technology because of their unique characteristics, such as ultrashort pulse laser signal, tunable availability, energy efficiency, etc. [5,6]. With the aim of improving the photophysical and lasing properties of laser dyes, Boyer et al. studied a new class of dyes, the dipyrromethene-BF_2 complexes (PM), synthesized by means of the fluoroboration of two pyrrol units linked by a methylene group [7].

PM dyes have demonstrated excellent photophysical and lasing characteristics [8–16]. They exhibit strong absorption and fluorescence bands from the yellow to the near-red region of the visible spectral region, with high fluorescence quantum yields and lasing efficiencies. This is in part due to their quasi-aromatic character of the chromophoric system [17], which decreases the intersystem-crossing probability, reducing the ability for the triplet–triplet absorption, one of the most important reasons for the losses in the resonator cavity. Moreover, PM dyes are also characterized by a high photostability improving the operative lifetime of the photoresponse signal of these dyes [18,19]. PM dyes have been also successfully applied as fluorescent probes of several biological systems [20–23].

The application of dyes as fluorescent molecular probes and sensors are based on the changes in the photophysical properties of the chromophoric system with the physicochemical properties of the environment and/or with the presence of any specific molecule [24–31]. The photophysics of alkyl-, aryl- or acetoxymethylene derivatives of PM dyes do not shown an important dependence on the nature of the solvent [8,16,32]. However, important bathochromic shifts in the absorption and fluorescence bands are observed for the PM650 dye when the environment was changed from apolar solvents to polar/protic media [33]. This derivative is characterized by a strong electron-withdrawing cyano group at the 8-position of the PM chromophoric π-system (Fig. 1). The bathochromic spectral band shift was assigned to an intramolecular electron transfer (ICT) process from the aromatic ring to the cyano group, which is favored in polar media. The formation of ICT from the fluo-

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doi:10.1016/j.jphotochem.2006.04.043

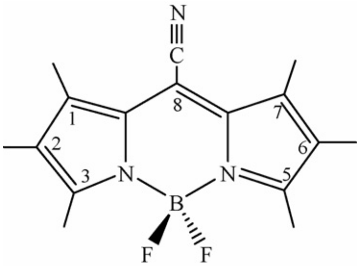

Fig. 1. Molecular structure of pyrromethene 650.

rescent excited state of PM650 also reduces the fluorescence quantum yield and lifetime of the dye in polar/protic environments. This study was conducted in multitude of apolar, polar/aprotic and polar/protic solvents [33]. During this study, it was observed a change in the color of PM650 after the preparation of the samples in certain solvents, mainly in amides, which can be characterized by their high electron-donor capacity and their low proton-donor ability.

The object of the present work is to characterize the nature of the color change of PM650 in electron-donor solvents. For this purpose the absorption and fluorescence spectra of PM650 are recorded as a function of the ageing time of the samples in those solvents in which the change in the color of the dye was observed by the naked eye, mainly in polar basic amides.

2. Experimental

Pyrromethene 650 (8-cyano-1,2,3,5,6,7-hexamethyl-4,4′-difluoro-4-bora-3a,4a-diaza-*s*-indacene) was purchased from Exciton (laser grade) and used as received. Dilute solutions (2×10^{-6} M) in different media were prepared by adding the corresponding solvent (25 cm^3) to an adequate amount of a stock solution of PM650 in acetone ($\sim 10^{-3}$ M) after vacuum evaporation of acetone. All solvents were of spectroscopy grade and were used without further purifications.

UV–vis absorption and fluorescence spectra were recorded on a Cary 4E spectrophotometer and on a Shimadzu RF-5000 spectrofluorimeter, respectively, with 1-cm quartz cells. Fluorescence spectra were corrected from the monochromator wavelength dependence and the photomultiplier sensibility. Fluorescence quantum yield (ϕ) was evaluated using a diluted solution of PM650 (after excitation at 540 nm) or PM567 (after excitation at 470 nm) in methanol as reference ($\phi = 0.06$ and 0.91, respectively [33,34]) and by taking into account the solvent refractive index.

Radiative decay curves were registered with the time correlated single-photon counting technique (Edinburgh Instruments, model FL920). Emission was monitored at the maximum of the fluorescence band, after excitation at 410 nm by means of a diode laser with 150 ps FWHM pulses, 10 MHz repetition rate and a power supply of 0.65 mW (PicoQuant, model LDH410). The fluorescence decay curves, after the deconvolution of the instrument response function detected by a Ludox scatter, were analyzed as monoexponentials (statistical parameter $\chi^2 < 1.2$), except in the mentioned cases, and the fluorescence lifetime (τ) was obtained from the slope. The experimental errors in the ϕ and τ values are estimated to be 5 and 1%, respectively. The temperature of the samples was controlled by an external flow of thermostatized water.

^{1}H NMR spectra were taken on an INOVA-300 spectrometer. Mass spectra were recorded by electron impact (70 eV) in a Hewlett-Packard 5973 spectrometer in the direct injection mode and by electrospray positive mode in a Hewlett-Packard 1100 spectrometer. HPLC analysis were registered with Agilent Tech. Series 1100 apparatus with C18 reverse phase column, acetonitrile/water 9:1 as eluent and the flow was fixed at 2 mL min^{-1}.

3. Results and discussion

The general photophysical properties of PM650 dye in several media have been already discussed in a previous paper [33]. However, it was observed that in some solvents (e.g. *N*,*N*-dimethylformamide, DMF, or *N*,*N*-dimethylacetamide, DMA) the color of the solution changes from violet, the normal tonality of PM650 dye, to green just after sample preparation. Both *N*,*N*′-dialkylamide solvents are characterized by their polar and basic characters, as is reflected by the corresponding Taft parameters [35] of polarity ($\pi^* = 0.88$ for both solvents) and basicity ($\beta = 0.69$ and 0.76 for DMF and DMA, respectively) [36]. On the other hand, when PM650 was dissolved in other *N*-alkyl or non-alkyl amides, such as *N*-methylformamide (MF) and formamide (F), the change in the color of the dye was observed to be much slow and it took place over a few days after sample preparation. With respect to *N*,*N*′-dialkyl-amides, these last solvents are characterized by a slightly higher polar character ($\pi^* = 0.90$ and 0.97 for MF and F, respectively) and a similar or lower basicity ($\beta = 0.80$ and 0.48, respectively), but these solvents are more acid (Taft parameters: $\alpha = 0.62$ and 0.71, for MF and F, respectively) than DMF or DMA (with $\alpha = 0$) [36]. From these observations, it can be concluded that the environmental acidity/basicity affects the change in the color of PM650, slowing down the process by increasing/decreasing the acidity/basicity of the solvent. Consequently, PM650 dye can be used as a molecular probe to characterize the acid/base character of the surrounding.

In other non-amide solvents with high electron-donor ability (such as acetone, 2-pentanone, ethyl acetate and diethyl ether), the change of the PM50 color was not observed. However, the samples became nearly transparent after several days. In apolar (*c*-hexane), low-basic (dioxane) and polar/protic (methanol) solvents the PM650 color remained unaltered for several weeks. Such effects, to our knowledge, have never been reported before in any PM dyes, and should be related with the presence of the cyano group in the chromophoric π-system of PM dyes and the nature of the solvents (polar and basic environments).

Fig. 2 compares the absorption and fluorescence spectra of PM650 in DMF and in acetone, solvents with similar polarity and basicity, just after sample preparation. The absorption and fluorescence bands of PM650 in acetone are centred at 588 and 606 nm, respectively, which are the responsible for the violet color of PM650. These spectral bands are red-shifted with

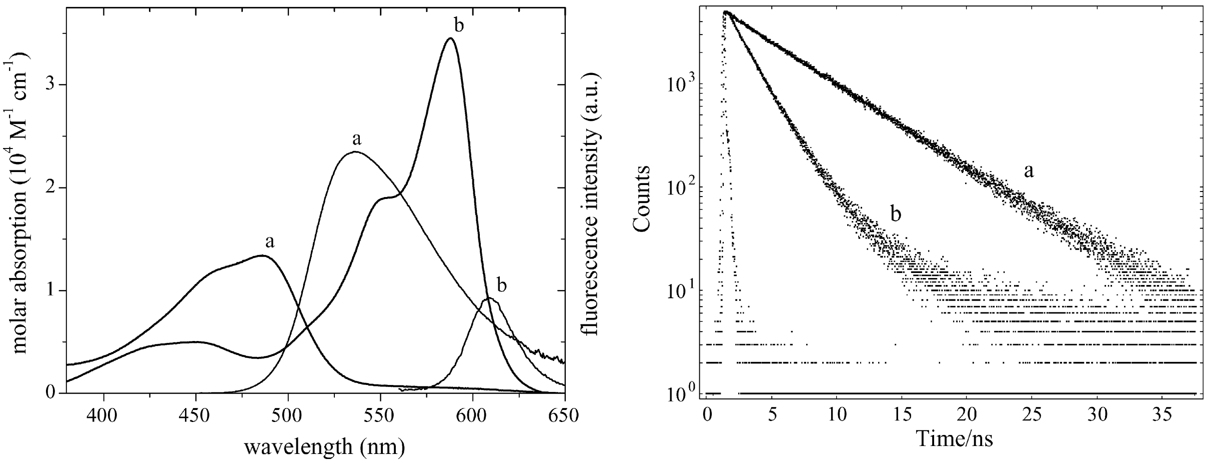

Fig. 2. Absorption and fluorescence spectra (scaled to its ϕ value), and fluorescence decay curves of PM650 (2×10^{-6} M) in DMF (a) and acetone (b).

respect to other PM dyes with alkyl- and/or acetoxy-substituents, with typical absorption and fluorescence bands at around 480–550 nm [16]. The absorption and fluorescence bands of PM650 in DMF are drastically shifted to higher energies (100 nm in absorption and 70 nm in fluorescence) with respect to those in acetone, leading to an important Stokes shift (up to 2000 cm^{-1}) in the former solvent, probably one of the highest values reported for PM dyes. The spectral bands of PM650 in DMF remind to those observed for other PM alkyl-derivatives [16].

The absorption and fluorescence intensities of PM650 in DMF decrease and increase, respectively, with respect to the values in acetone (Fig. 2), leading to a significant improvement in the fluorescence quantum yield (ϕ) of PM650 in the former solvent. The ϕ value of PM650 in acetone (~0.1, Table 1) is much lower than any other values reported for other PM dyes ($\phi \geq 0.5$), which was previously assigned to an extra non-radiative deactivation via an intramolecular charge transfer (ICT) state of PM650 in polar solvent [33]. Indeed, the fluorescence lifetime of PM650 in acetone ($\tau \sim 1$ ns, Table 1) is also much lower than other PM dyes ($\tau \geq 4$ ns). However, the ϕ and τ values of PM650 in DMF and in DMA (Table 1) do not correspond to those expected for the polarity of these solvents, suggesting the absence of this extra non-radiative deactivation of PM650 in DMF and DMA. Furthermore, the hypsochromic absorption and fluorescence bands of PM650 in amides tend to disappear after ageing the samples during several weeks.

To get a deeper understanding of this change in the color and posterior degradation of PM650 dye in amides, the photophysical properties of the dye have been registered at several ageing times in DMF/dioxane mixtures with different DMF contents (4, 8, 16, 32 and 64%, v/v). Dioxane can be considered as an "chemically inert" solvent for PM650, since the photophysical properties of this dye do not show any time evolution in this solvent at least during 1 month. Fig. 3 shows the evolution of the absorption and fluorescence spectra with the DMF concentration for three ageing times: after sample preparation ($t = 0$, left), 1 day (middle) and 1 week (right).

For $t = 0$, no changes are observed in absorption spectra for low DMF content mixtures (<16%), with absorption centered at around 590 nm (Fig. 3, left-top, curves a–d). However the fluorescence intensity (at $\lambda = 605$ nm) progressively decreases with the DMF content (Fig. 3, left-bottom, curves a–d). These results indicate that the fluorescent spectroscopy is a more sensitive technique than the absorption one and suggest that the changes in the photophysics of PM650 is observed just after sample preparation, even for low DMF contents. The freshly prepared sample with moderated DMF content (32%, curves e) shows a slight decrease in the absorption intensity, while for samples with higher DMF content (>64%, curves f and g) a new absorption band appears at higher energies (~480 nm) in detriment of the normal absorption band of PM650. The excitation at this hypsochromic band provides a new fluorescence

Table 1

Photophysical properties (absorption and fluorescence wavelength, λ_{ab} and λ_{ab}, and fluorescence quantum yield and lifetime, ϕ and τ) of PM650 dye just after sample preparation ($t = 0$) and for 1 week ageing in amide solvents (DMF: *N*,*N*-dimethylformamide; DMA: *N*,*N*-dimethylacetamide; MF: methylformamide; F: formamide)

	$t = 0$				$t = 1$ week			
	λ_{ab} (nm)	λ_{fl} (nm)	ϕ	τ (ns)	λ_{ab} (nm)	λ_{fl} (nm)	ϕ	τ (ns)
DMF	481	536	0.40	5.15	484	535	0.44	5.13
DMA	479	535	0.38	5.25	477	532	0.42	5.19
MF	592	611	0.08	1.59	455	535	0.31	5.06
F	594	616	0.05	1.41	451	540	0.16	4.59
Dioxane	590	607	0.19	2.89	589	606	0.18	2.85
Acetone	588	606	0.11	1.81	588	605	0.07	1.55

The photophysics of PM650 in dioxane and acetone are also included for comparison [33].

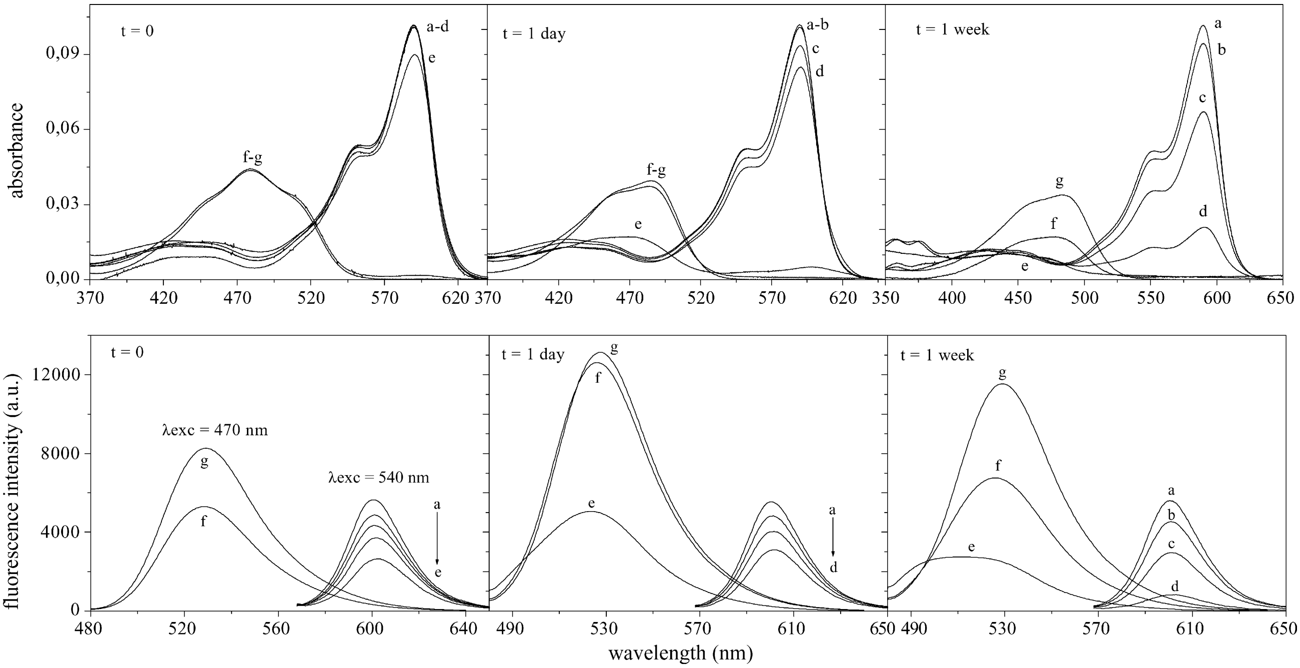

Fig. 3. Absorption (top) and fluorescence (bottom) spectra of PM650 (3 × 10^{-6} M) in several DMF/dioxane mixtures: 0% (a), 4% (b), 8% (c), 16% (d), 32% (e), 64% (f) and 100% (g) of DMF at three ageing times [$t = 0$ h (left), $t = 1$ h (middle) and $t = 1$ week (right)].

band placed at 538 nm with a higher ϕ value than that in pure dioxane.

The decay curves of PM650 in DMF/dioxane mixtures, exciting at 410 nm and monitoring the emission at 605 nm, can be adequately analyzed as a single exponential, except in the sample of 32%, where the evolution of one fluorescent band to the other begins to be observed. In this case the fluorescence decay is analyzed as a biexponential, with a short lifetime of 1.64 ns (and a preexponential factor of 77%), which is shorter than that normally observed for PM650 in pure dioxane ($\tau = 2.8$ ns). The long lifetime component (4.95 ns) matches that observed in pure DMF (5.15 ns), registered at 540 nm. For low DMF content mixtures (0–16%), the fluorescence lifetime observed at 605 nm as a monoexponential decay decreases with the DMF content. For the 64% mixture the fluorescence lifetime recorded at 535 nm is the same as that observed in pure DMF. Consequently, the presence of DMF in dioxane leads to an extra non-radiative deactivation of the 605 nm emission by a bimolecular mechanism.

The effect of the DMF content on the absorption and fluorescence bands of PM650 is more prominent after 1 day of sample preparation (Fig. 3, middle). The sample with a moderate DMF content (32%, curves e) clearly presents the spectral bands at higher energies and the spectral changes are observed for low DMF contents (<16%, curves a–d). The fluorescence band of PM650 in high contents of DMF (>64%, curves f and g) presents an important increase in its intensity. In this case, the biexponential decay curve is recorded for the 16% DMF sample. These spectral changes are even more pronounced for sample ageing for 1 week (Fig. 3, right).

Besides all these changes in the normal bathochromic absorption and fluorescence bands of PM650, the intensity of the hypsochromic absorption (around 480 nm) and fluorescence (around 530 nm) bands progressively decreases with respect to those bands observed after 1 day of ageing. Thus, after 1 month (data not shown), the PM650 samples in moderated-high DMF content (>16%) are completely bleached and only the sample in pure DMF presents the PM650 spectral bands. These observations indicate that the bleaching process of PM650 becomes slower as the basicity of the solvent increases (i.e., in pure DMF).

In order to carry out a more profound study of the color change and bleaching of PM650 in amides, other factors affecting these processes are now analyzed. For instance, and as is quantitatively discussed later, the increase in the temperature favors the loss of the bathochromic absorption (590 nm) and fluorescence (605 nm) bands of PM650 in DMF/dioxane mixtures. The reversibility of this process has been experimentally tested by suddenly increasing and decreasing the temperature of the sample in order to check if the bathochromic bands are recovered. This was performed for the 32% DMF mixture. After 1 h of ageing at room temperature, the sample was abruptly heated at 60 °C for a short time (∼3 min), for which a decrease in the 590 nm absorption band was observed (∼55% of the original band). After a fast cooling (∼5 min) of the sample to achieve 25 °C, the absorption spectrum did not reach the original band. During the time used for this experimental procedure (∼10 min), the absorption spectrum of PM650 in 32% DMF kept at room temperature did not significantly change (the loss in the absorption intensity was <5% of its original value). So, from these results, it can be concluded that the loss in the 590 nm absorption band and 605 nm fluorescence band of PM650 with the DMF content is an irreversible process. Indeed, it is ascribed to a chemical reaction between PM650 and DMF molecules, with an associated activation energy (see below). Since these changes

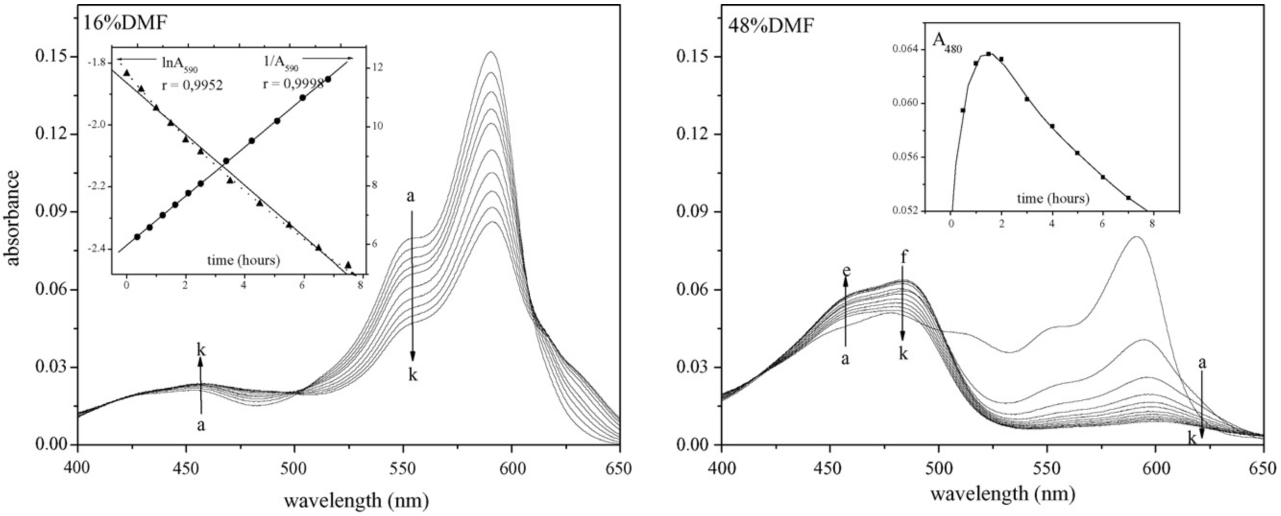

Fig. 4. Absorption spectra of PM650 (4×10^{-6} M) for different ageing times: 1/2 h (a), 1 h (b), 3/2 h (c), 2 h (d), 5/2 h (e), 3 h (f), 4 h (g), 5 h (h), 6 h (i), 7 h (j) and 8 h (k) in two DMF/dioxane mixtures [16% (left) and 48% (right)]. The inset of both the figures include the evolution of the absorbance at 590 nm (left, following a first- and second-order kinetics) and 480 nm (right) with the ageing time of the corresponding samples.

are only observed in the PM650 derivative, the chemical reaction has to be related with the cyano group of this dye.

Several techniques (^{1}H NMR, mass spectrometry, HPLC) have been applied to confirm and to characterize the chemical structure of the products. HPLC analysis indicates the appearance of several products, the main of which (with an absorption band at around 470 nm) shows a lower retention time (1.4 min in a C18 reverse phase column and using acetonitrile/water 9:1 as eluent) than that of PM650 (2.0 min). This compound should be the responsible for the new green color of the samples. The structure of this decomposition product is still unknown, but preliminary ^{1}H NMR data of a minimum amount of this compound seem to indicate the disappearance of the methyl groups at positions 2 and 6 in PM650 and their substitution by hydrogen atoms, with a non-hydrogen substituent at the 8-position. Therefore the cyano group is not exchanged by a proton but probably it is reconverted into a carboxylic group. The absence of the BF_2 group in the molecule cannot be discarded. Other analytical data, such as MS spectra under different conditions, did not help in the structure elucidation. Work in progress will try to clarify this structure. A second minority compound (detected in the HPLC at a retention time of 1.5 min, with an absorption band centered at around 520 nm) could be related with the loss of the cyano group from the aromatic π-system of the PM650 core.

Quantum mechanics calculations at the TD-B3LYP level with the valence double-zeta 6-31G basis set confirm that both chemical structures would lead to a hypsochromic shift of the S_0–S_1 transition with respect to that of PM650, as it is experimentally observed. Concretely, the absorption band of the PM650 derivative without methyl groups at positions 2 and 6 and a carboxylic group at position 8 should be shifted around 3100 cm^{-1} to lower energies with respect to the PM650 dye, whereas a lower hypsochromic shift of 2370 cm^{-1} should be expected for the PM650 derivative without the cyano group at position 8. Although these theoretical shifts do not exactly match the experimental results (for instance, 3880 and 2280 cm^{-1} for the 480 and 520 nm absorption band with respect to the 590 nm band of PM650), they can semiquantitatively explain the general evolutions.

The kinetics of the chemical reaction between PM650 and DMF is now analyzed from the time-evolution of the disappearance and appearance for the bathochromic (at 590 nm) and hypsochromic (at 480 nm) absorption bands observed for PM650 in DMF/dioxane mixtures. Fig. 4 shows the time-evolution absorption spectra of solution 4×10^{-6} M of PM650 in two mixtures of DMF/dioxane with 16 and 48% (v/v) in DMF during the eight first hours after sample preparation under continuous irradiation at 650 nm. The former mixture illustrates the loss in the 590 nm absorbance giving rise to isobestic points at 500 and 610 nm (Fig. 4, left), whereas the more concentrated DMF mixture mainly reflects the time-evolution of the 480 nm absorption band (Fig. 4, right). Taking into account the precedent spectra for the 16% DMF content for $t = 0$ and 1 day (Fig. 3, top, left and middle), the continuous irradiation of the sample at 650 nm could favor the chemical reaction between PM650 and DMF.

Taking into account that DMF is in excess with respect to PM650, the [DMF] can be considered constant during the reaction and the rate for the disappearance of PM650 can be expressed by

$$-\frac{d[\text{PM650}]}{dt} = k[\text{PM650}]^a[\text{DMF}]^b = kc_0^b[\text{PM650}]^a \qquad (1)$$

where a and b are the kinetic order for PM650 and DMF, respectively, and c_0 is the analytical concentration of DMF in the mixture. The integrated equations for the pseudo-first order ($a = 1$) and the pseudo-second order ($a = 2$) with respect to PM650 are given by Eqs. (2) and (3), respectively:

$$\ln[\text{PM650}]_t = \ln[\text{PM650}]_0 - kc_0^b t \qquad (2)$$

$$\frac{1}{[\text{PM650}]_t} - \frac{1}{[\text{PM650}]_0} = kc_0^b t \qquad (3)$$

The concentration of PM650 at any time, $[\mathrm{PM650}]_t$, is proportional to the absorbance of the sample at 590, A_{590}. The evolution of $\ln A_{590}$ and $1/A_{590}$ versus time for the 16% DMF mixture is shown in the graphic inset in Fig. 4 (left). From this graphic it is clear that the reaction of PM650 with DMF follows a pseudo-second-order kinetic with respect to PM650 ($1/A_{590}$ versus t, $r = 0.9998$), rather than a pseudo-first-order kinetic ($\ln(A_{590})$ versus t, $r = 0.9952$) where a non-linear distribution is actually observed. For higher DMF content mixtures, the kinetic order for the loss of the 590 nm absorption band is not so clear.

On the other hand, for the mixture of 48% in DMF, the formation of the new hypsochromic absorption band of PM650 at 480 nm is favored up to an ageing time of 90 min, after which the absorbance decreases progressively (see inset graphic in Fig. 4, right). This observation confirms the presence of two consecutive mechanisms for the PM650 in electron-donor solvents: a first process involved with the formation of the hypsochromic 480 nm absorption band, due to the PM650-DMF chemical reaction in detriment of the 590 nm absorption band owing to free PM650; and a second slower process related with the degradation (bleaching) of the dye.

To assess if the bleaching of PM650 is due to an oxidation process, the absorption spectra of the dye were recorded as a function of the ageing time in an inert atmosphere by flowing N_2 gas through the sample. The experiment was performed for the DMF/dioxane mixture with a DMF content of 25%. Experimental results reveal that similar time-evolutions for the detriment of the 590 nm absorption band were detected with and without the presence of O_2. The formation of the 480 nm absorption band and its posterior degradation are slightly slowed down when O_2 is removed from the sample. In any case, the PM650 dye is completely bleached after 24 h of ageing, and it can be concluded that degradation of PM650 is not an oxidative process. Indeed, Jones et al. [37] reported a high oxidation potential (1.17 eV) for PM650, the highest value among several PM dyes, probably due to the withdrawing effect of the cyano group. At this moment, the nature of the PM650 bleaching due to the presence of DMF in dioxane is not clear.

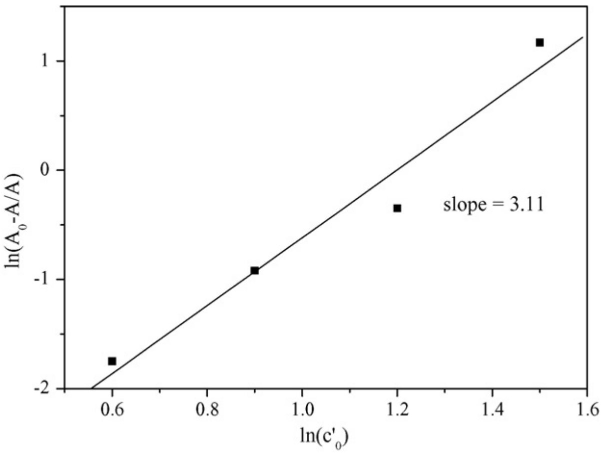

Fig. 5. Linear relationship fit of Eq. (4) for the absorbance at 590 nm of PM650 with different contents of DMF in DMF/dioxane mixtures after 1 day of sample ageing.

The kinetic order with respect to DMF can be obtained from the evolution of the [PM650] (proportional to A_{590}) with the analytical concentration of DMF (c_0) for a given time. Taking into account the second-order kinetics with respect to PM650, Eq. (3) can be transformed in

$$\ln\left(\frac{[\mathrm{PM650}]_0 - [\mathrm{PM650}]}{[\mathrm{PM650}]}\right) = \ln\left(\frac{A^0_{590} - A_{590}}{A_{590}}\right) = \ln(ktA^0_{590}) + b\ln(c_0) \qquad (4)$$

where A^0_{590} is the absorbance at 590 nm of PM650 in pure dioxane. From Eq. (4), the kinetic order of DMF can be evaluated from the slope of the linear relationship between $\ln\left(\frac{A^0_{590}-A_{590}}{A_{590}}\right)$ and $\ln(c_0)$ for a constant time after sample preparation. The validity of Eq. (4) in the present system is checked for samples ageing during 1 day (Fig. 5). The relative good linear correlation ($r = 0.987$) suggests the validity of both Eqs. (3) and (4) equations and, from the slope = 3.11, a $b \approx 3$ value is obtained.

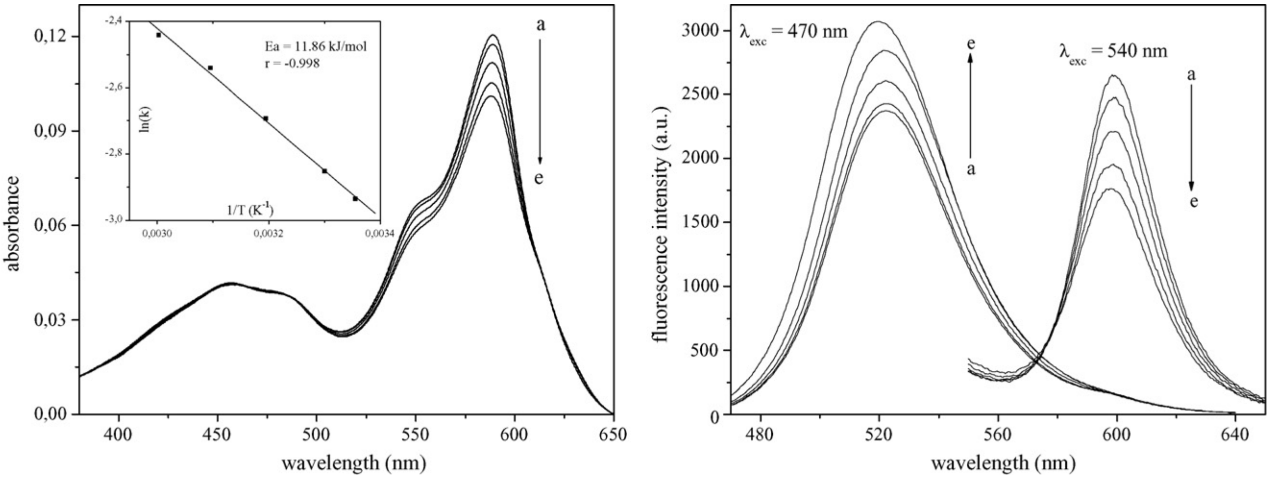

Fig. 6. Evolution of the absorption (left) and fluorescence (right) spectra of PM650 with the temperature: 25 °C (a), 30 °C (b), 40 °C (c), 50 °C (d) and 60 °C (e) for the 32% DMF/dioxane mixture. The corresponding Arrhenius plot is included in the absorption spectra.

Similar results are obtained for other ageing times, confirming a third-order kinetics with respect to DMF.

Finally, the activation energy for the chemical reaction can be evaluated from the evolution of the absorption band with the temperature. Fig. 6 shows the absorption and fluorescence spectra of PM650 in a 32% DMF content amide/dioxane mixture at 25, 30, 40, 50 and 60 °C registered after 1 h of sample preparation. Under these experimental conditions the two hypso- and batho-chromic bands are clearly observed in both absorption and fluorescence spectra, and the thermostatization times of the sample were reduced as far as possible in order to reduce the influence of the ageing time in the recorded spectra (around 7 min for thermostatization and recording at each temperature). The total time used in this temperature-dependence study was lower than 30 min. The 590 nm absorption band decreases when the temperature is raised, whereas that at 480 nm reminds unaltered. The temperature effect induces a decrease in the fluorescence band at lower energies ($\lambda \sim 605$ nm) while that at higher energies ($\lambda \sim 535$ nm) increases. Thus, the temperature favors the change in the PM650 color observed in electron-donor solvents, confirming that the chemical reaction requires an activation energy. The energy barrier for this process can be estimated from the evolution of the intercept of Eq. (4) with the temperature, which is identified with the evolution of the rate constant with the temperature. The corresponding Arrhenius plot is inset Fig. 6 (left) and, from the corresponding slope, an activation energy of $\sim$12 kJ mol^{-1} is obtained for the present system.

4. Conclusions

The presence of a cyano group at the position 8 of the pyrromethene–BF$_2$ chromophoric system induces important changes in the photophysical properties of PM dyes. The absorption and fluorescence bands of PM650 are bathochromically shifted with respect to other alkyl-, aryl- and methylene-acetoxy-PM analogs, mainly in polar solvents, and these environments favor the non-radiative deactivation of PM650 via an intramolecular charge transfer state formed between the cyano group and the chromophoric core of the dye [16]. However, PM650 in polar solvents with high electron-donor ability, such as amides, presents new absorption and fluorescence bands shifted towards higher energies, giving rise to new spectral bands close to those observed in alkyl-PMs. This behavior is attributed to a chemical reaction between the PM650 dye and the amide molecules of the solvent. The chemical structure of the products are uncertain, although they should be related with a loss of the cyano group at position 8 and/or the methyl group at positions 2 and 6 of the chromophoric ring of the dye. The drastic changes in the photophysical properties of PM650 in electron-donor solvents observed in the present work suggest that PM650 could be used as a molecular probe to characterize the electron-release ability of surrounding molecules.

Acknowledgements

This work was supported by the Spanish MEC Ministry (research project: MAT2004-04643-C03-02). V.M.M. thanks the MECD Ministry for a research grant. M.L. thanks the MED Ministry for a Juan de la Cierva contract.

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