

Photophysical properties of safranin and phenosafranin A comparative study by laser flash photolysis and laser induced optoacoustic spectroscopy

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Abstract

The triplet quantum yield of the dyes safranin and phenosafranin was determined in methanol and acetonitrile by laser flash photolysis (LFP) and laser induced opto-acoustic spectroscopy (LIOAS). The excited singlet properties of both dyes were also determined in the two solvents. The LFP determination of the triplet yield was carried out by actinometric determination of the product $\Phi_T \varepsilon_T$ and independent estimation of ε_T by the singlet depletion method and by energy transfer using anthracene as energy donor. The results of the three methodologies coincide within the experimental error. The values of Φ_T are in the range 0.21–0.50, and in the case of phenosafranin are considerably higher than those previously reported in the literature. An interesting outcome is that the results of LIOAS determination agree with those of LFP within the confidence interval.

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1. Introduction

In the last few years, the photochemistry of the cationic dyes safranin (3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride, SF⁺) and phenosafranin (3,7-diamino-5-phenylphenazinium chloride, PS⁺) has received considerable attention because of the photoredox properties of the dyes [1,2]. In particular SF⁺ was investigated for applications in some areas of research such as, analytical [3,4], biological [5], solar energy [6,7] and initiation of photopolymerization [8–12]. The related dye PS⁺ has been extensively employed as a sensitizer in energy and electron transfer reactions in homogeneous media [13–16] and in semiconductors [17] and polymeric media [18]. The dye was also employed as a probe in reverse micellar systems [19] and its photostability in polymer-coated semiconductors was investigated [20].

The electrochemistry of these dyes was investigated long time ago by Clark and co-workers [21] and more recently the electrochromic properties of PS⁺ were reported [22]. In a pioneering work, Baumgartner et al. [23] have studied the triplet state properties of SF⁺ as a function of pH in aqueous media using conventional flash photolysis.

However, although the two dyes have very similar absorption and fluorescence emission spectra, and redox properties, some photophysical properties of interest for the sensitizing applications present contradictory reports in the literature. In particular large discrepancies are apparent in the values of the triplet yield. Thus the intersystem crossing quantum yield of PS⁺ was reported as 0.1 and 0.06 in acetonitrile and water, respectively [13]. Also a value of 0.10 was given for the dye in methanol [24]. However, these values seem rather low by comparison with the closely similar dye SF⁺, for which triplet quantum yields of 0.5 and 0.34 [25,26] were reported in ethanol. These values were determined by dif-

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ferent techniques and it was of interest to investigate if the discrepancies might arise in the experimental design. Here we present results on the excited states parameters of SF⁺ and PS⁺ in methanol and acetonitrile. In particular the triplet yield was determined by laser flash photolysis (LFP) and by time resolved laser induced optoacoustic spectroscopy (LIOAS). From this point of view one of the objectives of this paper is to explore the suitability of LIOAS measurements to determine photophysical parameters of dyes in excited state.

2. Experimental

Safranine and phenosafranine were from Aldrich (Milwaukee, USA) and Evans Blue (EB) and cresyl violet were from Sigma Chemical Co. (St. Louis, USA). All the dyes were used as received. Acetonitrile (MeCN) and methanol (MeOH) both HPLC grade, were from Sintorgan (Buenos Aires, Argentina).

Absorption spectra were determined on a Hewlett-Packard 6453E diode array spectrophotometer. Steady-state fluorescence measurements were made using a Spex Spectrofluorometer. Fluorescence quantum yields were determined using cresyl violet in MeOH as a standard ($\Phi_F = 0.54 \pm 0.03$) [27]. Fluorescence lifetime measurements were performed with an Edinburgh Instruments OB 900 time-correlated single-photon counting fluorometer. Transient absorption spectra were determined with a Spectron SL400 Nd:YAG laser generating 532 nm pulses (~18 ns pulse width). The laser beam was defocused in order to cover all the path length (10 mm) of the analyzing beam from a 150 W Xe lamp. The experiments were performed with rectangular quartz cells with right angle geometry. The cell holder was thermostated by water circu-

lation. The detection system comprises a Photon Technology International (PTI) monochromator coupled to a Hamamatsu R666 PM tube. The signal was acquired by a digitizing scope (Hewlett-Packard 54504) where it was averaged and then transferred to a computer. The solutions were purged with argon for 30 min before their use. The results were the same irrespective of argon or nitrogen purging. Irradiated solutions do not present any evidence of a photochemical reactions after tens of laser pulses.

The details of our LIOAS set-up have been reported elsewhere [28]. The same laser used for LFP was employed with the beam width shaped to a rectangular slit (0.5 mm w × 5 mm h), allowing a time resolution of the LIOAS experiments from ca. 20 ns up to 3 μ s using deconvolution techniques [29]. The total laser energy after the slit was <150 μ J per pulse, measured with a piezoelectric energy meter Melles-Griot model 13PEM001. The dye EB was used as calorimetric reference [30,31]. In all cases the plots of the amplitude of the opto-acoustic signal versus the laser energy were linear with zero intercepts, indicating that bi-photon processes or signal saturation do not take place.

3. Results and discussion

3.1. Fluorescence

The results for the photophysical parameter of the excited singlet state for both dyes in MeCN and MeOH are collected in Table 1. The singlet energy level, E_s , was determined by the interception of normalized absorption and emission spectra plotted in energy scale. On going from MeOH to MeCN a

Table 1
Photophysical parameters of the dyes in methanol and acetonitrile

	MeOH		MeCN	
	Safranine	Phenosafranine	Safranine	Phenosafranine
$\lambda_{\max} (\epsilon_G)^a$	529 (54100 ± 550)	527 (48000 ± 300)	518 (45700 ± 300)	517 (43800 ± 100)
$\lambda_{\text{em}} / \text{nm}$	568	567	557	556
E_S / cm^{-1}	18310	18390	18710	18720
Φ_F	0.21	0.20	0.24	0.23
τ_f^b / ns	2.6	2.1	3.8	3.5
$\lambda_{\max}(\text{T-T})^c / \text{nm}$	822	800	845	830
$\Phi_T \epsilon_T^d / \text{M}^{-1} \text{cm}^{-1}$	6200	3200	6500	9700
$\epsilon_T^{\max} (\text{GSD})^e / \text{M}^{-1} \text{cm}^{-1}$	19700	21000	22200	20400
$\epsilon_T^{825} (\text{GSD})^f / \text{M}^{-1} \text{cm}^{-1}$	19200	11300	17100	19100
$\epsilon_T^{825} (\text{Etr})^f / \text{M}^{-1} \text{cm}^{-1}$	23400	15500	22600	27900
$\Phi_T E_T / \text{cm}^{-1}$ (LIOAS)	2930 ± 600	3090 ± 600	7350 ± 500	7500 ± 600
Φ_T (GSD)	0.31	0.28	0.38	0.50
Φ_T (Etr)	0.26	0.21	0.29	0.35
Φ_T (LIOAS)	0.20 ± 0.04	0.22 ± 0.04	0.51 ± 0.06	0.53 ± 0.07

^a Maximum of ground state spectrum in nm and absorption coefficient in units of $\text{M}^{-1} \text{cm}^{-1}$.

^b Fluorescence lifetime in air equilibrated solution.

^c Maximum of the T–T absorption spectrum.

^d Measured at 825 nm.

^e Measured at the maximum of the T–T absorption spectrum.

^f Measured at 825 nm.

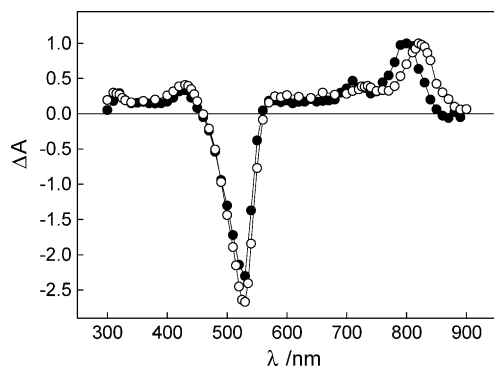


Fig. 1. Transient absorption spectrum of SF⁺ (○) and PS⁺ (●) in MeOH taken at 1 μs after the laser pulse. The absorbances are normalized at the maximum.

blue shift of ca. 10 nm is observed in both the absorption and fluorescence emission spectra. At the same time the quantum yield increases and the lifetime becomes longer. However, both dyes present similar fluorescence parameters when they are compared in the same solvent.

3.2. LFP determination of triplet state properties

The larger differences between the dyes reside in the photophysical parameters of the triplet state. Fig. 1 shows the transient absorption spectra of SF⁺ and PS⁺ in MeOH obtained 1 μs after 532 nm laser pulse excitation. The spectrum of SF⁺ presents a relatively intense maximum band at 822 nm with less intense maxima at 730 and 430 nm. The latter is an apparent maximum, produced by the onset of the ground state absorption. Negative absorbance was observed in the 460–550 nm region, which corresponds to the depletion of the SF⁺ ground state absorption ($\lambda_{\text{max}} = 529$ nm). These spectral features may be ascribed to the T–T absorption of the dye. The temporal decay over the whole spectral range (including the negative absorption region) follows a first-order law and takes place over several tens of microseconds. Similarly, the T–T spectrum of PS⁺ shows maxima at 800 and 710 nm, and a less intense maximum at 430 nm.

A negative absorbance was observed in the 460–550 nm region, corresponding to the ground state depletion of the dye. In both cases the negative absorption in the region of 500–550 nm of the difference transient spectra matched the ground-state absorption band of the dyes. This is consistent with the lack of photoproduct formation under our conditions of laser experiments.

The transient absorption spectra in MeCN are shown in Fig. 2. The maxima are shifted with respect to MeOH and are now at 845, 750 and 440 nm for SF⁺, and at 830, 740 and 440 nm for PS⁺.

In order to obtain the triplet quantum yields Φ_T , three independent techniques were employed. The first two are based on measurements by the LFP technique of the product of the triplet quantum yield and its absorption coefficient at a working analysis wavelength, $\Phi_T \varepsilon_T$, and independent mea-

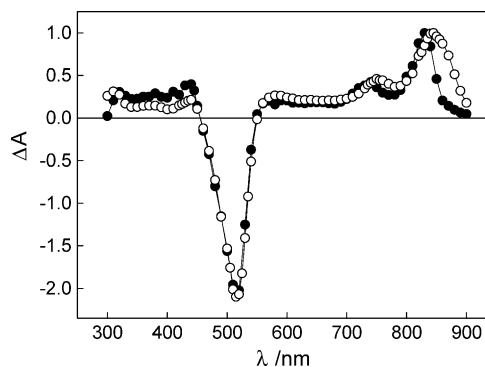


Fig. 2. Transient absorption spectrum of SF⁺ (○) and PS⁺ (●) in MeCN taken at 1 μs after the laser pulse. The absorbances are normalized at the maximum.

surements of ε_T by two non-related methodologies. The other way of obtaining the intersystem crossing quantum yield is by means of LIOAS determinations.

To obtain $\Phi_T \varepsilon_T$ the actinometry was carried out with ZnTPP (zinc tetraphenyl porphyrin) in benzene. The triplet yield of ZnTPP was measured at 470 nm immediately after the laser pulse. Values of $7.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and 0.83 were used for ε_T and ϕ_T of ZnTPP, respectively [32]. The initial absorbance change extrapolated at zero laser pulse energy was measured at 470 nm for ZnTPP triplet and at 825 nm for the dyes triplet with solutions of matched absorbance at 532 nm. The observation wavelength for the dye was chosen in order to match a high-energy line of the analyzing light.

The product $\Phi_T \varepsilon_T$ for the dyes was obtained from Eq. (1):

$$(\Phi_T \varepsilon_T)_D = \frac{\text{slope}_D}{\text{slope}_{\text{ZnTPP}}} (\Phi_T \varepsilon_T)_{\text{ZnTPP}} \quad (1)$$

where slope_D and $\text{slope}_{\text{ZnTPP}}$ are the initial slopes of the plots of T–T absorption versus laser energy for the dye and the reference, respectively.

In order to determine Φ_T by means of Eq. (1) the absorption coefficients of the triplet dyes are necessary. They were determined by two independent techniques, the ground state depletion (GSD) and the energy transfer (Etr) methods [33]. In the first one, the transient negative difference absorbance at the maximum wavelength of the ground absorption ΔA_G was compared with the absorption at the maximum of the T–T spectrum of the dye ΔA_T with the aid of Eq. (2). In Eq. (2) ε_T and ε_G are the molar absorption coefficients of the triplet and ground state, respectively, at the wavelengths of maximum absorbance. Since the bleaching in the narrow region near to the ground state maximum is very similar, but not matching exactly, to the ground state absorption, the values of ε_T determined in this way should be considered as upper-limit values, since there could be a small positive contribution of the triplet state to the absorption in the 500–550 nm region:

$$\varepsilon_T = \left(\frac{\Delta A_T}{\Delta A_G} \right) \varepsilon_G \quad (2)$$

An extra source of error, although in the opposite direction, might be an underestimation of the ground state absorption coefficient due to some impurities in the sample. The triplet absorption coefficients at 825 nm to be used in conjunction with Eq. (1) were obtained from the value at the maximum and the spectra in Figs. 1 and 2. With these the triplet yield were determined and are collected in Table 1.

For the Etr method an energy donor was employed to sensitize the triplet formation. Anthracene was selected as sensitizer due to its triplet energy (177.6 kJ/mol) [34], which is higher than the triplet energy of SF⁺ (171.8 kJ/mol) [35] and PS⁺ (170.8 kJ/mol) [35], respectively. The anthracene initial triplet transient absorption ΔA_A was measured at 419 nm. The long time absorbance of the triplet state of the dyes ΔA_T was measured at 825 nm in all cases, and the absorption coefficient was determined by Eq. (3):

$$\varepsilon_T = \varepsilon_A \frac{\Delta A_T}{\Delta A_A} f^{-1} \quad (3)$$

where ε_T and ε_A are the absorption coefficient of the triplet dye at 825 nm and that of anthracene at 419 nm, respectively. A value of 61,000 M⁻¹ cm⁻¹ was employed for ε_A in both solvents [33]. In Eq. (3) f is the fraction of anthracene triplets intercepted by the dye, and is given by

$$f = \frac{k_{et}[D]}{k_{et}[D] + \tau_0^{-1}} \quad (4)$$

where k_{et} is the energy transfer rate constant, $[D]$ is the concentration of the dye and τ_0 is the triplet lifetime of anthracene in the absence of D . The rate constant k_{et} was measured by the triplet decay of anthracene as a function of the dye concentration.

The use of Eq. (3) is based on the assumption that the only process leading to the quenching of anthracene triplet by the dye is energy transfer. One secondary quenching channel might be the electron transfer reaction either from or to the anthracene triplet state, however it can be disregarded due to the positive values of the driving force of these reactions.

The error of Φ_T as determined by the LFP methods is difficult to assert, however, considering the various assumptions involved and the experimental errors of the measured quantities used in Eq. (1)–(3) the uncertainty in the values would be at least of 20%.

The results are presented in Table 1 where it can be seen that the agreement between the GSD and Etr methods is fairly good. The triplet yields obtained by the GSD method combined with ZnTPP actinometry are higher in all cases, but the trend is similar to those afforded by the Etr measurements. The triplet yield of both dyes is similar and higher in the non-protic solvent.

3.3. LIOAS measurements

Time-resolved laser-induced optoacoustic spectroscopy (LIOAS) is a sensitive photobaric method for non-destructive

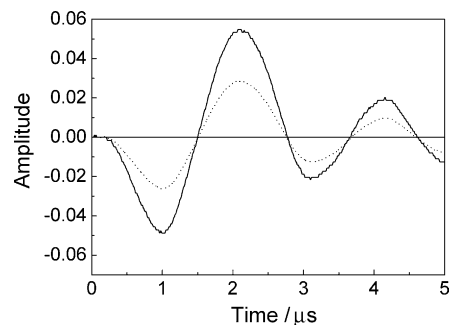


Fig. 3. Optoacoustic signal for EB (—) and PS⁺ (---) in MeCN.

probing of materials that monitors the pressure changes induced in a liquid sample after photoexcitation with a laser pulse. LIOAS delivers information generally not available from optical studies, and therefore complements other methods. After the laser pulse the time evolution of the pressure wave is monitored by a fast piezoelectric transducer located in a plane parallel to the direction of the laser beam (right-angle arrangement). In this way the heat evolved in the non-radiative processes can be determined. These measurements can be used for determination of energy levels of intermediates (including the energy associated with chromophore-solvent interactions), provided that the quantum yield of the reaction is known. Conversely, if the energy level of the intermediates is known from other spectroscopic techniques, the determination of quantum yields is possible.

In the present case we applied the LIOAS technique to estimate the triplet quantum yield of the dyes. The analysis of the time-resolved acoustic signals was performed using a deconvolution procedure that has been described elsewhere [28,30,31]. In LIOAS measurements the signal function $S(t)$ is the convolution of the instrumental function $R(t)$ (the signal of the calorimetric reference EB) with the sample function $H(t)$ [Eqs. (5) and (6)] [29,31]:

$$S(t) = R(t) \otimes H(t) \quad (5)$$

with

$$H(t) = \sum \frac{\varphi_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right) \quad (6)$$

where φ_i and τ_i are the amplitude factor and lifetime for the i th component of the acoustic signal, respectively.

Fig. 3 shows a typical set of optoacoustic signals for PS⁺ and the calorimetric reference. By numerical deconvolution, the amplitude φ could be determined. This is related to q_i the heat released with the i th process, through Eq. (7)

$$E_\lambda \varphi_i = q_i + \Delta V_i \left(\frac{c_p \rho}{\beta} \right) \quad (7)$$

where ΔV_i is the associated reaction volume change, and E_λ is the excitation molar energy ($\equiv 225$ kJ mol⁻¹ at 532 nm) and $C_p \rho / \beta$ are the thermoelastic parameters of the solvent. In the present case the second term may be disregarded, albeit that it is difficult to measure in an organic solvent, since the

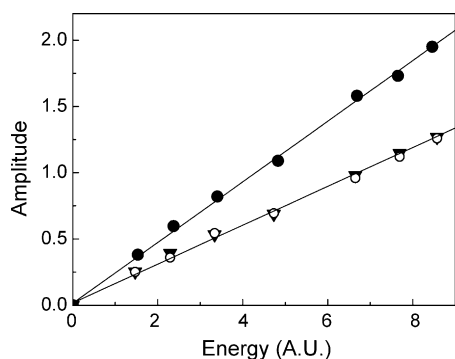


Fig. 4. Amplitude of the LIOAS signal in MeCN vs. laser pulse energy: (●) EB; (▼) SF⁺; (○) PS⁺.

volume change for the intersystem crossing process may be disregarded [36]. Moreover, in a first approximation the heat released q may be obtained from the ratio of the signal amplitude, determined as a difference between the first maximum and minimum in the prompt signal, of the reference and the sample. It was found that the results obtained using the amplitude ratio or deconvolution were practically indistinguishable. Therefore, the amplitude factors were determined from the ratio of the slopes of the acoustic wave amplitude versus laser pulse energy extrapolated to zero energy, for the sample and the reference. In all cases the plots of the amplitude of the optoacoustic signal versus the laser energy were linear with zero intercepts (Fig. 4) and safranin and phenosafranin shown the same slope indicating that both dyes store the same energy. Therefore, an average value of q was determined for this process. It corresponds to the prompt heat release and includes contributions from vibrational relaxation $S_1^n \rightarrow S_1^o$, non-radiative deactivation $S_1 \rightarrow S_0$, and $S_1 \rightarrow T_1$ transition.

In our irradiation conditions only the triplet state of the dyes was formed as an energy storage species and the energy balance may be written as

$$E_\lambda = q + \Phi_F E_S + \Phi_T E_T \quad (8)$$

In Eq. (8) $\Phi_F E_S$ is the energy lost as fluorescence from the singlet state of the dyes and $\Phi_T E_T$ is the energy stored by triplet state of the dyes. Using the values of Φ_F and E_S given in Table 1 and the triplet energies for SF⁺ and PS⁺, 14,357 and 14,277 cm⁻¹, respectively [35], the Φ_T could be determined and are included in Table 1.

It can be seen that the values for Φ_T in Table 1 differ from those previously reported for phenosafranin (0.1 in MeCN and MeOH [13,24]) and safranin (0.5 in ethanol [25]). Now, considering the similarity of the photophysical parameters for ground state and first excited singlet for both dyes, Table 1, it is most surprising a difference by a factor of 5 in the triplet yield, even taking into account the solvent diversity. Actually, on going from ethanol to MeOH the singlet properties only undergo a minor change [26]. The values in MeCN and MeOH are the results of nanosecond laser flash photolysis [13] and picosecond double pulse fluorescence excitation [24], while the figure 0.5 in ethanol was obtained by

repetitive picosecond photometry [25]. It is difficult to trace the origin of the differences, since the methods are based on a number of assumptions that are different for each experimental approach. Also the purity of the sample, especially when dealing with synthetic dyes, is an important factor to be considered when trying to assert the validity of some result. Our results are intermediate to those in the literature and they are more in line with the similarity of the rest of the photophysical parameters of the dyes. Moreover, a lower limit for triplet quantum yield can be estimated as 0.14 from the results of sensitized photooxidation of di-*n*-butyl sulfide in MeOH employing SF⁺ as sensitizer [37]. In any case the accurate determination of intersystem crossing quantum yield is a difficult task. A glance at Table 1 shows that even with the same sample differences of the order of 30% in the values are apparent depending on the technique employed for the determination. Nevertheless, from the present results it can be confidently concluded that Φ_T are higher in MeCN than in MeOH for both dyes. The reasons for this solvent effect are unclear but it may be related to hydrogen bonding interactions in alcoholic solvents that markedly affect the photophysical properties of the dyes [26,38].

4. Conclusions

The application of laser flash photolysis or LIOAS techniques for the determination of triplet yields of safranin and phenosafranin afforded results coincident within the experimental error. In general it can be said that when the triplet quantum yield is higher than 0.1 the LIOAS results are in good agreement with those obtained by laser flash photolysis or other experimental techniques. For molecules with lower triplet yield, where most of the energy is released in the prompt processes, the experimental error becomes very significant, and it is difficult to estimate the triplet state parameters by LIOAS. With regard to the particular results of the present work, we found very similar quantum yields for both dyes in contradiction with values in the literature that showed large differences.

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