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Journal of Photochemistry and Photobiology A: Chemistry 181 (2006) 142–146

Journal of Photochemistry and Photobiology A:Chemistry

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# Triplet-state spectroscopy of dipyrromethene·$BF_2$ laser dyes

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Received 18 October 2005; received in revised form 15 November 2005; accepted 17 November 2005
Available online 27 December 2005

## Abstract

The substituents at positions 2, 6 and 8 in the commercial dye PM567 have been changed and their influence on the triplet state of each dye has been studied in terms of the absorption spectra, lifetimes, quantum yields and triplet–triplet extinction coefficients. The dyes have in position 8 the groups *p*-acetoxypolymethylene, *p*-(acetoxypropyl)phenyl or *p*-(acetoxymethyl)polyphenylene, or in positions 2 and 6 the groups *tert*-butyl (commercial dye PM597) or 3′-acetoxypropyl. The triplet-state spectroscopy results nearly independent on the molecular structure for the mono- and di-substituted aliphatic derivatives. However, the 8-aryl substitution increases both the triplet absorption over the fluorescence spectral region and the triplet-state quantum yield, but reduces the triplet absorption coefficient.

*Keywords:* Laser dyes; Dipyrromethene; Fluorescence; Triplet-state properties

## 1. Introduction

From the mid-1960s, dye lasers have been attractive sources of coherent tunable visible radiation because of their unique operational flexibility [1]. As a result of the continuous effort to improve dyes for laser applications, Boyer et al. studied a new class of laser dyes: the dipyrromethene·$BF_2$ (PM or BODIPY) dyes, with reduced triplet–triplet absorption, high fluorescence quantum yields and emission covering the spectral region from green/yellow to the red, outperforming the most widely employed laser dye, Rhodamine 6G, considered as the benchmark in both efficiency and photostability [2–7].

Special attention has been paid to the dye 4,4-difluoro-1,3,5,7,8-pentamethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene (PM567; Scheme 1) because of the simplicity of its chemical structure and its good laser performance in both liquid and solid states [8,9]. However, when reviewing the spectroscopic and photochemical parameters of the PM chromophore, one concludes that it is not yet the ultimate high efficiency and photostable laser dye because it is not enough stable for the required uses, being particularly sensitive to photoreactions with oxygen [10].

Since the photophysical behavior and the photochemical stability of this dye can be modulated by changes in the substitution pattern on the tricyclic ring system [11], over the last few years our group have studied the effect of changing the 8-methyl group in PM567 by the substituent *p*-acetoxypolymethylene, *p*-(acetoxypropyl)phenyl or *p*-(acetoxymethyl)polyphenylene, named as PnAc, P1Ar3Ac and PmAr1Ac (Scheme 1), or the ethyl groups of PM567 in positions 2 and 6 by the 3′-acetoxypropyl substituent (PDiAc; Scheme 1), in order to study the influence that both the position and the type of substituent in the chromophore core of PM567 have on the photophysical properties and lasing behavior [12–14].

These new dyes, when dissolved in a variety of organic solvents as well as in poly(methyl methacrylate), lased more efficiently than PM567 under otherwise identical experimental conditions, and demonstrated improved photostability under continuous UV irradiation [13,15–18]. However, the presence of substituents in the chromophore does not significantly modify

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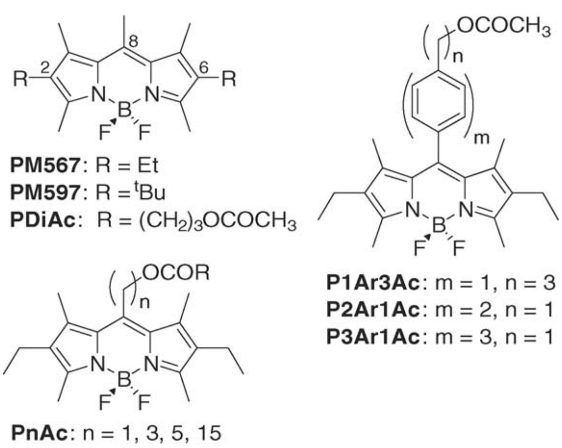
doi:10.1016/j.jphotochem.2005.11.016



Scheme 1. Molecular structures of the herein studies dyes.

the singlet-state photophysics of the chromophore (absorption and emission wavelengths, fluorescence quantum yields and fluorescence decay time) with regard to that of PM567, especially if the linear polymethylene chain has five or more methylene groups [13,16,18–22].

Could this change of substituents in the PM567 core enhance the lasing performance without modifying the photophysical properties? Although both the lasing and the photophysical properties of PM laser dyes have been studied with some detail in liquid and solid solutions, to our knowledge no systematic study of their triplet-state characterization in relation with both their structure and laser action has been carried out. The lack of these photophysical data makes it difficult to rationalize the improved lasing properties of PM567 analogues and the relationship with their molecular structure. In fact, previous studies have demonstrated significant effects of the substituents at different positions of the PM core on the electronic spectra of several derivatives [3].

Furthermore, the generation of triplet-state dye molecules on excitation always reduces the laser emission because of their long lifetime. They influence both by reducing the number of excited singlet-state molecules with stimulated emission and, more important, absorbing laser radiation. Consequently, the reduction in laser emission depends on the value of the triplet extinction coefficient over the laser action spectral region and on the concentration of triplet-state molecules.

In order to elucidate the above points and, at the same time, to obtain a clearer understanding of the photophysics of these PM dyes, in the present work we have properly characterized the triplet state of the dye molecules by recording their T–T absorption spectra and determining their photophysical properties.

## 2. Experimental

### 2.1. Materials

The synthesis of the new dyes was carried out following previously described procedures [12–14]. PM567 and PM597 (both laser grade from Exciton) were used as received. The purity of the dyes was found to be >99%, as determined by spectroscopic and chromatographic methods. Acetonitrile was HPLC grade from Sintorgan and was used without further purification.

### 2.2. Methods

The transient absorption spectra were recorded using laser-flash photolysis (LPF) equipment. A Spectron SL400 Nd:YAG laser (532 nm, ∼18 ns pulse width) was used as excitation source. 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 detection system comprised a monochromator (Photon Technology International) coupled to a photomultiplier (Hamamatzu R666). The signal, acquired by a digitizing scope (Hewlett-Packard 54504) was averaged and then transferred to a computer.

The experiments were carried out in diluted acetonitrile solution, with the dye concentration ranging from $6 \times 10^{-6}$ M to $8 \times 10^{-5}$ M, depending on the dye. Solutions were deaerated by purging with argon for 20 min without using triplet energy transfer to increase the initial concentration of triplet states.

The triplet–triplet molar absorption coefficients at the wavelength of triplet maximum were determined by the Ground State Depletion (GSD) technique [23]. The transient negative absorbance at the maximum wavelength of the ground absorption ($\Delta A_G$) was compared with the absorption at the maximum of the T–T spectrum of the dye ($\Delta A_T$) following the equation:

$$\varepsilon_T = \left(\frac{\Delta A_T}{\Delta A_G}\right)\varepsilon_G \tag{1}$$

where $\varepsilon_G$ and $\varepsilon_T$ are the molar absorption coefficients of ground and triplet states, respectively, at the wavelengths of maximum absorbance. Taking into account that the bleaching in the narrow region near to the ground state maximum is very similar, but not matching exactly the ground state absorption, the values of $\varepsilon_T$ determined in this way should be considered as upper limit values, since a small positive contribution of the triplet state to the absorption in the transient negative absorbance region could be present.

LFP technique allows determine the product of the triplet quantum yield ($\Phi_T$) by the absorption coefficient ($\varepsilon_T$) of each dye at the analytical wavelength. Zinc(II) tetraphenylporphine (ZnTPP) in benzene was used as reference for the determination of absolute $\Phi_T$ values in the following way: the product $\Phi_T\varepsilon_T$ for the dyes was obtained from the equation:

$$(\Phi_T\varepsilon_T)_D = \frac{\mathrm{slope}_D}{\mathrm{slope}_{ZnTPP}}(\Phi_T\varepsilon_T)_{ZnTPP} \tag{2}$$

where $\mathrm{slope}_D$ and $\mathrm{slope}_{ZnTPP}$ are the initial slopes in the plots of T–T absorption versus laser energy for the dye (at $\lambda_{max}$) and the reference ZnTPP (at 470 nm), respectively. Values of $7.3 \times 10^4\ M^{-1}\ cm^{-1}$ and 0.83 were used, respectively, for $\varepsilon_T$ and $\Phi_T$ of ZnTPP [24]. The dye and the reference solutions were matched in absorbance at 532 nm.

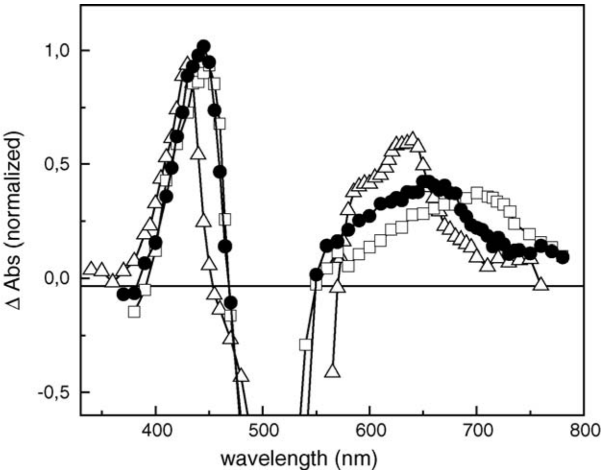


Fig. 1. Normalized T–T absorption spectra extrapolated at zero time of different PM dyes in deaerated acetonitrile solution: PM567 (□), P1Ac (△) and P2Ar1Ac (●).

## 3. Results and discussion

The triplet–triplet absorption spectra of selected PM dyes are given in Fig. 1. They show large negative peaks caused by depletion of the ground state. In all cases, the negative absorption of the difference transient spectra is very similar to the ground state absorption band of the corresponding dye, revealing the lack of photoproduct generation under the selected laser experimental conditions.

The difference spectra obtained by laser flash photolysis for the PM dyes show absorptions in the 350–800 nm range. They can be divided in three spectral regions, two with positive bands at each side of the negative band corresponding to the bleaching in the region around the maximum of the ground state absorption (in the 470–560 nm range). In a similar way to the previous reports for PM567, the region corresponding to the more energetic transitions (350–470 nm) can be assigned to the combined absorption of triplet state and the redox products of triplet self-quenching, and on the other side (560–800 nm) the absorption bands are assigned exclusively to the triplet–triplet absorption [25,26].

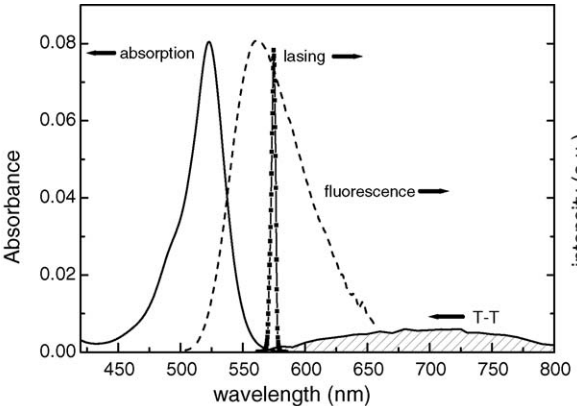


Fig. 2. UV–vis absorption, normalized fluorescence, stimulated emission and T–T absorption spectra of PM597 in diluted acetonitrile solution.

The spectral profile of the T–T absorption band, together with the absorption and fluorescence spectra and laser emission of PM597, are shown in Fig. 2. Similar spectra were obtained for all the other materials studied in this work. Table 1 summarizes the T–T absorption wavelengths of all the studied dipyrromethene derivatives in deaerated acetonitrile solution. In this table are also included the absorption, fluorescence and laser wavelength in order to determine the corresponding spectral Stokes shifts that could affect in a significant way the laser action of these dyes.

All the studied dyes exhibit low T–T absorption and large Stokes shifts with respect to both the fluorescence and the laser emissions, with the substituents affecting the photophysical properties in the following way. The presence at position 8 of an acetoxypolymethylene linear chain with three or more methylenes (dyes PnAc), as well as the presence of acetoxypropyl or *t*-butyl groups at positions 2 and 6 (PDiAc and PM597, respectively), left T–T absorption unaffected, ruling out any possible intramolecular interaction between the *p*-acetoxy group of the analogues with linear substituents and the PM core, favored by the length and flexibility of the polymethylene chain. On the other hand, as previously observed [3], the 8-aryl substitution in PM567 causes an increase in the T–T absorption over the fluorescence spectral region, although the most drastic

Table 1

Photophysical properties of different substituted PM laser dyes in diluted acetonitrile solution: singlet absorption, fluorescence and laser emission, and T–T absorption wavelengths ($\lambda_{abs}$, $\lambda_{flu}$, $\lambda_{la}$ and $\lambda_{T\text{–}T}$), spectral Stokes shift of the fluorescence band and the onset of the triplet state ($\Delta\upsilon_{flu\text{-}T}$), triplet-state molar absorption coefficient ($\varepsilon_T$), triplet quantum yield ($\Phi_T$), triplet lifetime ($\tau_T$) and self-quenching constant ($k_q$)

| Dye | $\lambda_{abs}$ (nm) | $\lambda_{flu}$ (nm) | $\lambda_{la}$ (nm) | $\lambda_{T\text{–}T}$ (nm) | $\Delta\upsilon_{flu\text{-}T}$ (cm$^{-1}$) | $\Phi_T\varepsilon_T$ (M$^{-1}$ cm$^{-1}$) | $\varepsilon_T$ (M$^{-1}$ cm$^{-1}$) | $\Phi_T$ | $\tau_T$ (μs) | $k_q$[a] (10$^7$ M$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| PM567 | 514.8 | 530.4 | 560 | 700 | 4568 | 122 | 8840 | 0.014 | 46 | NCO |
| PM597 | 522.9 | 561.2 | 579 | 710 | 3734 | 90 | 10300 | 0.009 | 84 | 23.0 |
| P1Ac | 543.2 | 559.0 | 580 | 640 | 2264 | 210 | 8200 | 0.026 | 115 | 9.8 |
| P3Ac | 520.0 | 532.0 | 562 | 690 | 4304 | 130 | 8760 | 0.013 | 170 | 8.0 |
| P5Ac | 519.1 | 530.5 | 564 | 695 | 4462 | 96 | 8930 | 0.011 | 120 | NCO |
| P15Ac | 518.7 | 530.0 | 562 | 690 | 4375 | 125 | 10300 | 0.012 | 108 | 1.7 |
| P1Ar3Ac | 521.3 | 534.8 | 547 | 659 | 3523 | 164 | 8400 | 0.020 | 43 | NCO |
| P2Ar1Ac | 522.4 | 535.4 | 565 | 650 | 3293 | 190 | 5630 | 0.034 | 106 | NCO |
| P3Ar1Ac | 522.8 | 535.5 | 566 | 650 | 3289 | 135 | 4900 | 0.028 | 140 | 7.2 |
| PDiAc | 515.3 | 533.2 | 554 | 698 | 4428 | 140 | 8320 | 0.017 | 33 | NCO |

[a] NCO: no changes observed in triplet lifetime on the concentration range explored.

change is observed for P1Ac dye, since its T–T absorption band is blue-shifted around 1350 $\text{cm}^{-1}$ with respect to the PM567 dye.

The $\varepsilon_T$ value of 8840 $\text{M}^{-1}\,\text{cm}^{-1}$ determined in this work for PM567 in acetonitrile is in good agreement with previous results [26], although it is higher than that reported by Gorman et al. [25] for the same dye in benzene (6600 $\text{M}^{-1}\,\text{cm}^{-1}$). The value of $\varepsilon_T$ becomes almost independent of the molecular structure of PM dyes with the exception of PmArnAc derivatives, where the T–T absorption is lower than those of 8-alkyl substituted, since the presence of the out of the plane aryl groups sterically restricts ($\pi$, $\pi^*$) electronic transition and, consequently, the intercoupling probability of electron spin and orbital moment [28].

All the selected dyes show a low triplet quantum yield, $\Phi_T$. Again, with the exception of the P1Ac dye, $\Phi_T$ results nearly independent on the molecular structure for the PM dyes with aliphatic substituents at position 8 or at 2 and 6, respectively. The presence of one or more 8-phenylene groups enhances the triplet quantum yield with respect to that of PM567, while the lowest value of $\Phi_T$ was found for PM597. With the exception of PM597, the fluorescence quantum yield ($\Phi_f$) of these dyes depends linearly on the triplet quantum yield (Fig. 3): the higher the value of $\Phi_f$, the lower the value of $\Phi_T$. The observed relationship indicates that the non-radiative deactivation mechanism of these dyes is not mainly governed by the intersystem crossing process. However, the presence of the bulky *t*-butyl groups in the chromophoric core likely originates torsions in the pyrrol units, mainly in the excited state, leading to an increase in the rate of non-radiative deactivation process, without enhancing the triplet-state generation [27].

The kinetics of the triplet state was determined analyzing the dependence of the triplet decay on the dye concentration. For all the selected dyes, the triplet state follows a single-exponential decay, within experimental errors. The experimental decay rate constants of the triplet, $\tau_T^{-1}$, depend linearly on the dye concentration. From the linear-fit intercept, the triplet lifetime of the dyes, $\tau_T$, can be deduced, while the slope of the line corresponds to the self-quenching rate constant, $k_q$. In these experiments, the dye concentration was varied from $11 \times 10^{-5}$ M up to $0.6 \times 10^{-5}$ M. Further decrease of the concentration below this limit worsened drastically the signal/noise ratio, due to the low absorption coefficients of the dyes at 532 nm. As can be seen in Table 1, the first-order kinetics of these dyes results to be little dependent and even, for same of them, independent of the ground state concentration, which indicates the absence of significant self-quenching.

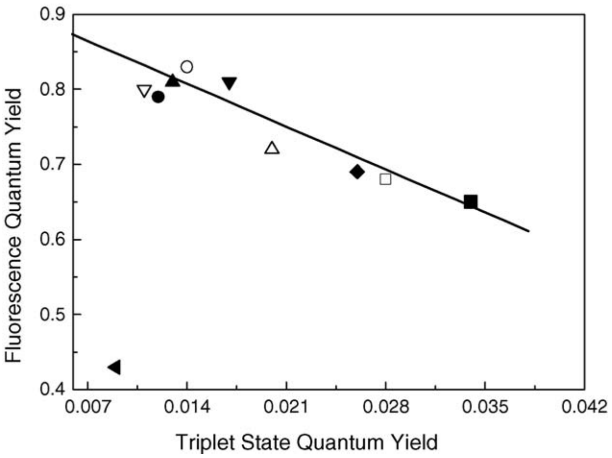


Fig. 3. Dependence on the triplet quantum yield of the fluorescence quantum yield for the different PM dyes: PM567 (○), PM597 (◄), P1Ac (◆), P3Ac (▲), P5Ac (▽), P15Ac (●), P2Ar1Ac (■), P3Ar1Ac (□), P1Ar3Ac (△) and PDiAc (▼).

The triplet-state lifetimes reported in Table 1 have to be considered as the lower limit, since they can be significantly affected by high experimental errors, leading to a systematic reduction of their absolute values. However, taking into account that the experimental conditions were kept constant during all measurements, the relative values are comparable and, thus provide relevant information on the influence of the molecular structure on the triplet-state kinetics. Although a clear dependence cannot be established, it seems that the presence of a polymethylene chain at 8 position leads to an increase of $\tau_T$ with respect to that of PM567, while the triplet lifetime decreases for the 2,6-di-substituted dye PDiAc. For the 8-aryl analogues, this trend appears less clear: while P1Ar3Ac exhibits a low $\tau_T$ value (43 $\mu$s), the triplet lifetime of P2Ar1Ac and P3Ar1Ac are much higher than that of PM567.

On the other hand, the observed values of the self-quenching rate constants are high enough as to influence on the deactivation of the triplet states under laser operation, with concentrations of ca. $10^{-3}$ M. This indicates that the triplet-state losses must be lower in these conditions; however, this process should affect the chemical stability of the dye, in view of the fact that the dye decomposition must be favored by reaction of the radical ions (produced by the self-quenching process) and any scavengers present in the dye solution.

## 4. Conclusions

The results presented in this work indicate that appropriate chemical modifications in the PM molecules can yield laser dyes with improved properties, such as low T–T absorption coefficients, low triplet quantum yields and low overlap between the fluorescence spectral region and the onset of T–T absorption. However, it cannot be established a direct relationship between the lasing efficiency and the photostability of these dyes on one hand, and the kinetics and spectroscopic characteristics of their triplet state on the other. Although it can be expected that the decrease of the value of $\Phi_T\varepsilon_T$ increases the laser action, this behavior is only followed for some dyes such as PM597, P5Ac and, even, P1Ac, a dye with higher $\Phi_T\varepsilon_T$ but lower laser photostability than PM567. However, despite having higher $\Phi_T\varepsilon_T$ values, dyes such as P3Ac, P1Ar3Ac and PDiAc lase more efficiently and with higher photostability than the dye PM567. At the present time, we cannot offer any non-speculative explanation for some of the behaviors described in the present work. Experimental studies are currently in progress to gain more insights on the influence of the $S_n$ excited state on the lasing behavior of these PM dyes.

## Acknowledgements

H.A.M. thanks to the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Secretaría de Ciencia y Técnica de la Universidad Nacional de Río Cuarto, Argentina, for financial support. This work was also supported by Project MAT2004-04643-C03-01 of the Spanish MEC, and by Project No. 7N/0100/02 of the Comunidad Autónoma de Madrid. M.L. thanks the MEC for a *Juan de la Cierva* scientific contract.

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