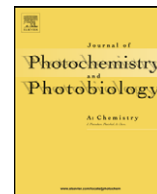




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## New laser dye based on the 3-styryl analog of the BODIPY dye PM567

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### ABSTRACT

We report the synthesis, photophysical properties and evaluation of laser dye of a new BODIPY dye with a 3-styryl substituent, PMS, and with the rest of the substituents as in the commercial dye PM567. PMS shows an emission band at 584 nm in methanol, i.e. displaced ca. 50 nm to longer wavelengths with regard to the green-emission band of PM567, as well as a high-fluorescence quantum yield (0.82) and also a high-molar absorption coefficient ( $10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) in the same solvent. The laser action of the new dye has been analyzed under transversal pumping at 532 nm,  $5.5 \text{ mJ pulse}^{-1}$  and up to 10 Hz repetition rate, in both liquid phase and incorporated into solid polymeric matrices of methyl methacrylate copolymerized with crosslinking or fluorinated monomers. Lasing emission at 602–610 nm, with maximum efficiencies of 18%, were reached in these media. In solid-fluorinated matrices, good lasing photostabilities were established, with 30% of the initial laser output remaining after 100,000 pump pulses at 10 Hz.

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### 1. Introduction

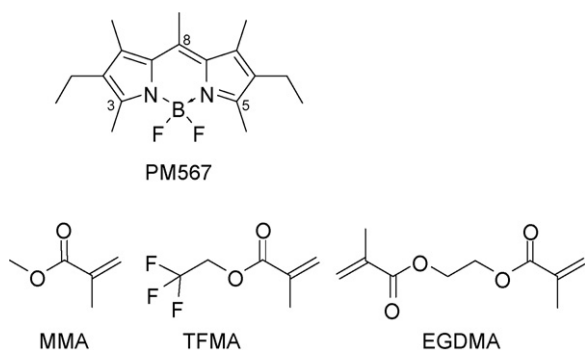
Some modern biotechnological and electronic applications require new fluorophores with predetermined properties such as high-fluorescence quantum yield, large Stokes shift and optimized absorption profile, so as to meet the demands for more sensitive analytical protocols, sensors and light-emitting devices [1,2]. A particularly nowadays popular family of such dyes is that with the chromophore 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, known as BODIPY or BDP [3]. The photonic and photophysical properties of many of these dyes are characterized by high-fluorescence quantum yields, low rates of intersystem crossing (ca. one-fifth of their rhodamine counterparts), large molar absorption coefficients, excellent photostabilities, and emission spectral profiles covering a wide wavelength range [4,5]. These properties have led to emerging applications as light harvesting systems [6], chemosensors [7], biological labels [8,9], laser dyes in liquid solutions [10] and in solid-state materials [11], among others.

In recent years, several reports have demonstrated that structural modifications in these BDP dyes can give rise to large changes in their photophysical and optical properties [12,13]. In particular,

some efforts have been focused on displacing the emission band of green-emitting dyes to longer wavelengths by attaching to the BDP core electron-donating groups [5a], by rigidifying the structure [5b,14], and by extending the conjugation of the chromophore [15] but it is not known whether their fluorescence emission is of utility for the generation of laser emission [8b,16]. Moreover, these structural modifications can lead some times to molecules with undesired properties. For example, the photophysical properties of structures substituted with electron-donating groups can be influenced by the solvent polarity, as a consequence of the appearance of electron-transfer processes in polar environments, leading to low fluorescence quantum yield values [15b], and thus their utility is far from clear [16].

With the aim of converting the structure of the green-emitting laser dye 2,6-diethyl-1,3,5,7,8-pentamethyl-BDP, commercially known as Pyrromethene 567 (PM567, Fig. 1), into another one with wavelengths of fluorescence and laser emissions shifted to the red, we report here on a newly synthesized dye, PMS (Scheme 1), with the same structure as PM567 but substituted at position 3 by an (*E*)-styryl group, instead of a methyl group. This structure was selected because PM567 has demonstrated good laser performance in both liquid and solid media [11,13]. Several substituted 3-styryl and 3,5-distyryl BDP dyes have been previously synthesized with the purpose of shifting the fluorescence emission to the red. In the particular case of (*E*)-*p*-(*N*-dimethylamino)styryl-BDP dyes, their

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**Fig. 1.** Molecular structures of commercial dye PM567 and of the monomers used in this work.

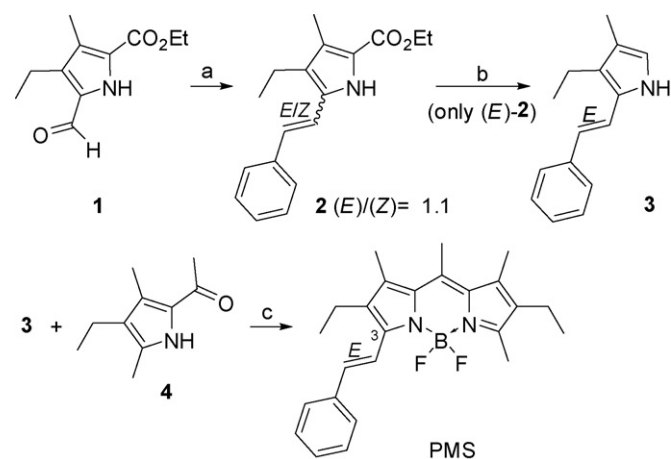
photophysical properties are strongly influenced by the solvent and the medium pH [17,18], so that these dyes have been proposed as molecular switches [15b], pH [15a], anion [19,20] and cation [5d] sensors, fluorescent labels for cholesterol and sphingolipids [21], logic circuits [12e], and, in the form of 2,6-dibromo derivatives, as sensitizers for photodynamic therapy [22].

We also report here the photophysical and lasing properties of the dye PMS in air-equilibrated liquid solutions in apolar, polar non-protic and polar protic solvents, as well as in solid solutions in linear homopolymers of methyl methacrylate (MMA) or in linear copolymers of MMA with the fluorinated monomer 2,2,2-trifluoroethyl methacrylate (TFMA). Taking into account that the rigidity of the matrix is of utmost importance in order to optimize their lasing action, we have also incorporated the new dye into a crosslinked copolymer of MMA with ethylene glycol dimethacrylate (EGDMA). The molecular structures of the monomers are shown in Fig. 1.

## 2. Experimental

### 2.1. Materials

Solvents for photophysical and laser studies were of spectroscopic grade (Merck, Aldrich or Sigma) and were used without purification. Methyl methacrylate (Aldrich) was successively washed with 5% NaOH in water and pure water, dried over  $\text{Na}_2\text{SO}_4$  and distilled under reduced pressure; TFMA and EGDMA (both Aldrich, purity >99.5%) were used as received. Chemicals for syn-



**Scheme 1.** Synthesis of the 3-styryl dye PMS. Reagents and conditions: (a)  $\text{PhCH}_2\text{PPh}_3$ ,  $\text{MeONa}$ , THF, Ar, rt, 0.5 h, then **1** in THF, 2 h, then reflux, 1 h; (b) NaOH, EtOH– $\text{H}_2\text{O}$ , pressure tube, Ar, 80 °C, 2 h; (c)  $\text{POCl}_3$ ,  $\text{CHCl}_3$ , rt, 12 h, then  $\text{Et}_3\text{N}$ ,  $\text{BF}_3\text{OEt}_2$ , rt, 3 h.

thetic work (Aldrich) were used as received. The synthesis of ethyl 4-ethyl-5-formyl-3-methylpyrrol-2-yl-carboxylate (**1**) [23] and 2-acetyl-4-ethyl-3,5-dimethylpyrrole (**4**) [24], and the synthesis and preparation of solid solutions of dyes into polymeric matrices [25] have been previously described.

### 2.2. Photophysical properties

The photophysical properties of  $2 \times 10^{-6}$  M solutions of PMS were measured in 1-cm optical path length quartz cuvettes. UV–vis absorption and fluorescence (after excitation at 540 nm) spectra were recorded on a Varian model Cary 4E and a SPEX model Fluorolog 3-22 spectrophotometers. The emission spectra were corrected for the monochromator wavelength dependence and the photomultiplier sensitivity. Fluorescence quantum yields ( $\Phi$ ) were determined using a  $2 \times 10^{-6}$  M solution of PM650 in cyclohexane as a reference ( $\Phi = 0.36$ ) [26]. Radiative decay curves were registered with the time-correlated single-photon counting technique (Edinburgh Instruments, model FL920). The emission was monitored at 590 nm, 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). After the deconvolution of the instrumental response function, the fluorescence decay curves of PMS were analyzed as a monoexponential, controlled by the chi-square ( $\chi^2$ ) and Durbin-Watson (DW) statistical parameters and by the analysis of the residuals. The fluorescence lifetime ( $\tau$ ) was obtained from the corresponding slope. The accuracy in  $\Phi$  and  $\tau$  values was estimated as ca. 2 and 1%, respectively. The radiative ( $k_{\text{fl}}$ ) and non-radiative ( $k_{\text{nr}}$ ) deactivation rate constants were calculated by the expressions  $k_{\text{fl}} = \Phi/\tau$  and  $k_{\text{nr}} = (1 - \Phi)/\tau$ , respectively. All measurements were performed at  $20 \pm 0.2$  °C.

### 2.3. Laser experiments

Liquid solutions of the dye were contained in 1-cm optical path quartz cells carefully sealed to avoid solvent evaporation during the experiments. The solid samples for laser experiments were cast in a cylindrical shape, forming rods of 10-mm diameter and 10-mm length. A cut was made parallel to the axis of the cylinder to obtain a lateral flat surface of ca.  $6 \times 10$  mm<sup>2</sup>. This surface as well as the ends of the laser rods were prepared for laser experiments by using a grinding and polishing machine (Phoenix Beta 4000, Buehler) until optical-grade finished. The planar grinding stage was carried out with a Texmet 1000 sand paper (Buehler) using a diamond polishing compound of 6  $\mu\text{m}$  as an abrasive in mineral oil as a lubricant. The final polishing stage was carried out with a G-Tuch Microcloth (Buehler), using a cloth disk Mastertex (Buehler) with diamond of 1  $\mu\text{m}$  in mineral oil as an abrasive type. The samples were pumped transversally at 532 nm with 10-ns FWHM pulses of up to 5.5 mJ from a frequency-doubled Q-switched Nd:YAG Laser (Monocrom OPL-10) at a repetition rate of up to 10 Hz. The resonator was a 2-cm long plane–plane consisting of a 99% reflectivity back aluminium mirror and the end face of the sample acting as front mirror and output coupler (reflectivity of about 4%). Details of the experimental system can be found elsewhere [13]. In order to the solid-state dye lasers become competitive with their liquid counterparts, a most important parameter is their photostability, that is, the number of pump pulses in a given position which produce a certain drop in the laser output (usually the number of pump pulses which reduce the laser output by 50%). Thus, it is necessary to characterize the active media in the actual working conditions, that is, in an oscillator rather than using small signal gain experiments.

Narrow-line-width laser emission and tuning ranges of dye solutions were obtained by placing the samples in a home-made Shoshan-type oscillator [27], consisting of full-reflecting

**Table 1**  
Photophysical<sup>a</sup> and lasing<sup>b</sup> properties of the dye PMS in different solvents

Dye	Solvent	$\lambda_{\text{abs}}$ (nm)	$\epsilon_{\text{max}}$ ( $f$ ) ( $\times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )	$\lambda_{\text{fl}}$ (nm)	$\Phi$	$\tau$ (ns)	$k_{\text{fl}}$ ( $10^8 \text{ s}^{-1}$ )	$k_{\text{nr}}$ ( $10^8 \text{ s}^{-1}$ )	$\lambda_{\text{las}}$ (nm)	Eff (%)
PMS	F <sub>3</sub> -ethanol <sup>c</sup>	563	8.8 (0.63)	582	0.88	5.88	1.49	0.20	602	17
	Methanol	566	10.0 (0.65)	584	0.82	5.36	1.53	0.33	602	13
	Ethanol	568	10.2 (0.66)	586	0.81	5.27	1.53	0.36	603	9
	Acetone	566	9.9 (0.67)	584	0.81	5.37	1.51	0.35	606	12
	Ethyl acetate	567	10.1 (0.66)	585	0.80	5.25	1.52	0.38	604	17
	Cyclohexane	574	11.6 (0.68)	590	0.72	5.02	1.43	0.55	610	7
PM567	F <sub>3</sub> -ethanol <sup>c</sup>	516	7.1 (0.47)	535	0.97	6.94	1.39	0.04		
	Methanol	516	7.9 (0.49)	532	0.91	6.10	1.49	0.15		
	Ethanol	518	8.1 (0.49)	532	0.84	6.09	1.38	0.26		
	Acetone	516	8.0 (0.50)	532	0.85	5.92	1.43	0.25		
	Ethyl acetate	516	8.0 (0.49)	532	0.80	5.78	1.38	0.35		
	Cyclohexane	522	9.3 (0.55)	537	0.70	5.60	1.25	0.53		

The corresponding data of the dye PM567 are also included for comparison [26].

<sup>a</sup> Wavelengths of maximum absorption ( $\lambda_{\text{abs}}$ ) and fluorescence emission ( $\lambda_{\text{fl}}$ ), molar absorption coefficient ( $\epsilon_{\text{max}}$ ), oscillator strength ( $f$ ), fluorescence quantum yield ( $\Phi$ ), lifetime ( $\tau$ ), radiative rate constant ( $k_{\text{fl}}$ ) and non-radiative deactivation rate constant ( $k_{\text{nr}}$ ). Dye concentration:  $2 \times 10^{-6}$  M.

<sup>b</sup>  $\lambda_{\text{las}}$ : peak of the laser emission; Eff: energy conversion efficiency. Dye concentration:  $3 \times 10^{-4}$  M. Nd:YAG pump energy: 5.5 mJ/pulse.

<sup>c</sup> 2,2,2-Trifluoroethanol.

aluminium back and tuning mirrors and a 2400-lines  $\text{mm}^{-1}$  holographic grating in grazing incidence, with outcoupling via the grating zero order. Wavelength tuning was accomplished by rotation of the tuning mirror. Tuning mirror and grating (both from Optometrics) were 5-cm wide and the angle of incidence on the grating was  $88.5^\circ$ . Laser line width was measured with a Fabry-Perot etalon (IC Optical Systems) with a free spectral range of 15.9 GHz.

### 3. Results and discussion

#### 3.1. Synthesis

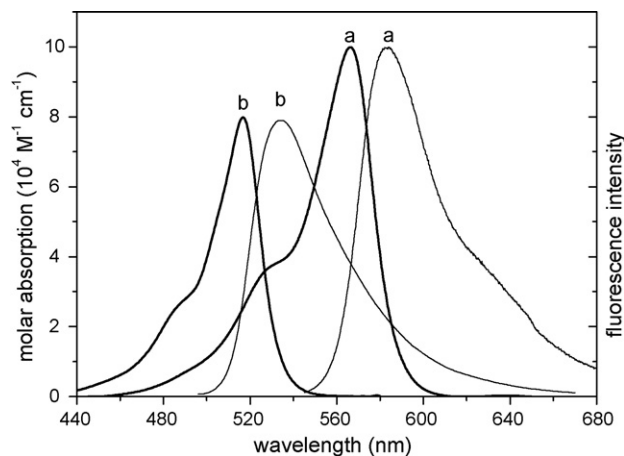
Three methods have been reported for the synthesis of 3-styryl-BDP dyes: (1) the most used has been the condensation of *p*-dimethylaminobenzaldehyde with 8-aryl-3,5-dimethyl-BDP dyes, taking advantage of the acidity of the methyl group attached to the position 3 of the chromophore core [5d,12c,12e,15b,17,19,20,22]; (2) condensation of benzaldehydes [15a] or 2-formylpyrroles [21,28] with 2-styrylpyrroles, and subsequent formation of the corresponding symmetric or asymmetric BDP dyes with boron trifluoride diethyl etherate; (3) Heck reaction between a 3,5-dichloro-BDP dye and styrene, in the presence of Pd(II) [29].

In our case, the synthesis of the target dye PMS was tried first by reaction of the commercial dye PM567 with benzaldehyde, under the conditions used for the synthesis of 8-aryl-3-styryl dyes [5d,17], but the yield of PMS was very low (<3%), in principle as a result of the presence in the BDP core of an 8-methyl group, instead of an 8-aryl group. Looking for improved yields, we tried the condensation of (*E*)-3-ethyl-4-methyl-2-styrylpyrrole (**3**) with 2-acetyl-4-ethyl-3,5-dimethylpyrrole (**4**) (Scheme 1), and the subsequent in situ reaction of the formed dipyrromethene with boron trifluoride diethyl etherate, following conditions formerly used for the synthesis of non-symmetric BDP dyes [30]. The reaction gave rise to PMS with much higher yield (31%). The method can be easily applied to the synthesis of other analogs of PMS substituted in the styryl group. The starting pyrrole **3** was synthesized from pyrrole **1** in two steps (see Appendix A), following conditions described for similar  $\alpha$ -H pyrroles [31,32].

#### 3.2. Photophysical properties in liquid solutions

The photophysical characteristics of PMS were studied in apolar (cyclohexane), polar non-protic (acetone and ethyl acetate) and polar protic (2,2,2-trifluoroethanol, ethanol, and methanol) sol-

vents in 1-cm path length cuvettes (Table 1). Although for practical applications, the use of aqueous solvents is always an advantage, this new dye, following the behaviour previously observed for other BODIPY derivatives, is nearly insoluble in water. The corresponding data of the reference dye PM567, recorded under identical experimental conditions, are also included for comparison [33]. The shapes of the absorption and fluorescence bands are similar in all the selected solvents and are also similar to the corresponding bands of PM567, but absorption and fluorescence bands of PMS present drastic bathochromic shifts, around 50 nm, with respect to those of PM567 (Fig. 2). The spectral shifts to lower energies are a consequence of the extension of the delocalized electronic  $\pi$ -system to the styryl group. Indeed, the quantum mechanical calculations of PMS at the DFT-B3LYP level by means of the GAUSSIAN03 software [34] revealed that the styryl group participates in the electronic distribution of the chromophoric  $\pi$ -system of the diazaindacene moiety in the HOMO and LUMO molecular orbitals of PMS (Fig. 3). This increase in the localization of the electronic not only implies a spectral shift to lower energies but also an augmentation in the  $S_0$ - $S_1$  transition probability. This is reflected in the fact that the values of the molar absorption coefficient and oscillator strength ( $\epsilon_{\text{max}}$  and  $f$ , respectively, Table 1) of PMS are among the highest ones obtained up to now for BDP dyes [33,35]. The fluorescence rate constant,  $k_{\text{fl}}$ , of PMS is also higher than the corresponding



**Fig. 2.** Absorption (bold curves) and corrected and height-normalized fluorescence (thin curves) spectra of  $2 \times 10^{-6}$  M solutions of the dyes PMS (a) and PM567 (b) in methanol, in 1-cm optical path length cuvettes.

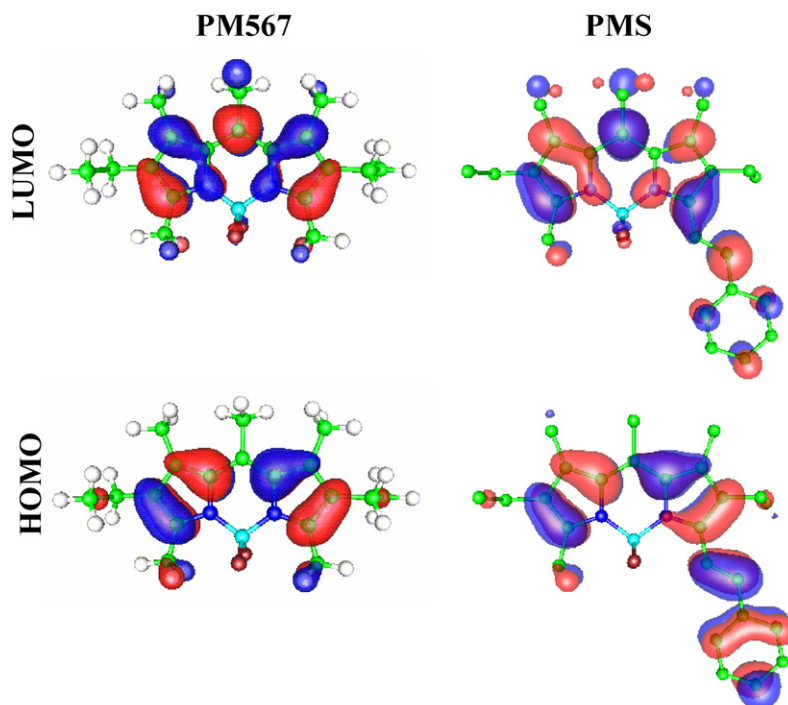


Fig. 3. Contour maps for the electronic distribution in the HOMO and LUMO states of PM567 and PMS obtained by the DFT-B3LYP method.

value of PM567 (Table 1). However, PMS shows somewhat lower fluorescence quantum yield and lifetime than PM567 in the same solvent due to an augmentation in the non-radiative deactivation probability,  $k_{nr}$  (Table 1). Taking into account the low probability of intersystem crossing in BDP dyes, the non-radiative deactivation mechanism from the excited states of PMS would be related to internal conversion processes [13e] ascribed to the flexibility/rigidity of the molecular structure, such as possible rotation and/or vibrational movements of the phenyl or styryl group. Another possible non-radiative deactivation mechanism would be (*E*)/(*Z*) photoisomerization of the (*E*)-double bond connecting phenyl and BDP groups, a well-known process in 1,2-diarylethylenes producing (*E*)/(*Z*) isomeric mixtures that depend on the particular compound [36]. However, in principle this process can be discarded in the case of PMS, because when an air-equilibrated 5-mM solution in ethyl acetate was irradiated (1-cm quartz cell) for 48 h with 525-nm light (150-W quartz-halogen lamp, 525-nm Schott filter), only traces of colorless degradation products were detected by TLC or HPLC analysis of the irradiated mixture, and the  $^1\text{H}$  NMR spectrum of the product exclusively showed signals of the (*E*) isomer.

The evolution of the photophysical properties of PMS with the solvent is similar to that observed for PM567, i.e. absorption and fluorescence bands are shifted towards higher energies, and the fluorescence quantum yield and lifetimes increase, when changing from apolar to polar protic solvents [13b]. These dependences are related to the influence of the solvent on the electrostatic stabilization of the chromophore dipole with the dielectric constant of the solvent, which decreases the non-radiative deactivation processes of the dye in polar protic solvents [33].

Other authors [15,17] have reported the photophysical properties of different BODIPY dyes bearing a styryl group at position 3 but also with an 8-phenyl group and functional groups (amines, ethers,) at *para* position of both phenyl groups. In all cases the presence of the styryl group shifts the absorption and fluorescence bands to lower energies, in agreement with the present results. In some

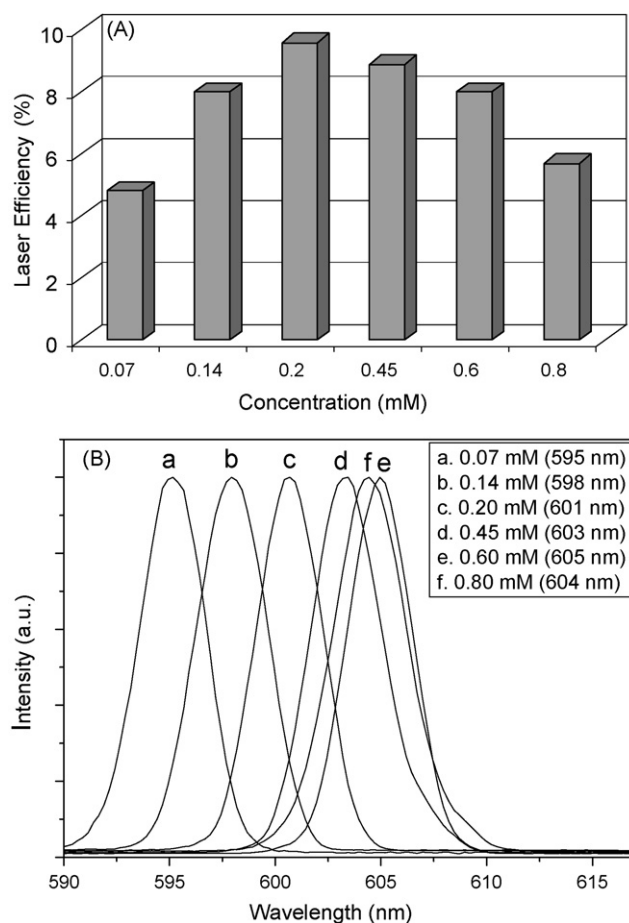
cases with high-electron donor–acceptor substituents, the absorption band is placed beyond 600 nm and the fluorescence band is furthermore red-shifted at around 650 nm due to the emission from excited charge transfer states, but with important decreases in the fluorescence quantum yield. However, high-fluorescence quantum yields (0.7–0.9) are obtained in the cases when the emission comes from the locally excited states, with lifetime values in the range 3.5–5 ns. These values are, in general, in concordance with our present results.

### 3.3. Laser action in liquid phase

The dependence of the laser action of the new dye with the concentration was analyzed in ethanol, increasing the dye concentration from  $7 \times 10^{-5}$  to  $8 \times 10^{-4}$  M, corresponding to optical densities (OD), for 1-cm path length, of ca. 1 and 40, respectively, whereas the other experimental parameters were kept constant. The lasing efficiencies and the laser emission spectra as a function of the dye concentration are reported in Fig. 4. As expected, the lasing efficiency increases fastly with the dye concentration until a maximum value for the solution with OD of ca. 10. From this point on, further increases in dye concentration result in a significant decrease of the lasing efficiency. In addition, the peak wavelength of the laser emission shifts to lower energies as the dye concentration increases. This behaviour has been previously observed in PM567, and was related to the effect of reabsorption/reemission phenomena on the emission intensity [13b].

In our experimental setup, an optical density of dye samples about 10 determines that the incoming pump radiation penetrates the sample (i.e. is absorbed) a depth similar to that to the thickness of the pump spot in the lateral surface of the sample onto which the pumping radiation is focused (about 0.3 mm). This gives rise to an emitted beam having with near circular cross-section.

The actual influence of the solvent in the laser action was also analyzed in  $3 \times 10^{-4}$  M samples, but it was found that this dependence is not evident (Table 1): the polar protic solvent



**Fig. 4.** Efficiency (A) and spectra (B) of the laser emission of the dye PMS as a function of the dye concentration in ethanol registered in the non-tunable plane–plane cavity.

2,2,2-trifluoroethanol and the polar non-protic solvent ethyl acetate induce the same lasing efficiency, while this efficiency in the polar protic solvent ethanol is similar to that in the apolar solvent cyclohexane. To gain more insight into the non-radiative deactivation mechanism, the laser action of PMS was analyzed in the high-viscosity solvent poly(ethylene glycol) dimethyl ether. The lasing efficiency in this medium (12%) is similar to the efficiencies registered in methanol and acetone. Thus, it could be concluded that the rotation of the phenyl group in the chromophore of PMS is neither the unique nor the most important internal conversion process related with the dissipation of the excitation energy. In addition, the low performance of the new dye has not been related to the excited  $S_1$ – $S_n$  absorption process since, as previous studies revealed, the excited-state absorption cross-sections for the pyrromethene derivatives are negligible [37].

The complete laser characterization of PMS requires an assessment of its tuning capability, since this is one of the most important features of dye lasers. When an ethanol solution of PMS was placed in a grazing-incidence grating cavity in Shoshan configuration, tunable laser emission with line width of the order of  $0.15\text{ cm}^{-1}$  was obtained, with a tuning range of 25 nm from 592 to 616 nm.

### 3.4. Laser action in solid polymeric matrices

In order to analyze the possibilities of the new dye as a laser material, its laser action in the form of solid solutions in polymeric materials was also studied. The composition of the matrix was decided in the light of the information obtained from both

**Table 2**

Laser parameters<sup>a</sup> for the PMS dye dissolved in PMMA, in the cross-linked copolymer MMA–EGDMA 3:2, and in the fluorinated linear copolymers MMA–TFMA 9:1 and 5:5 (v/v proportions)

Material	$\lambda_{\text{max}}$ (nm)	$\Delta\lambda$ (nm)	Eff (%)	$I_{50,000}$ (%) <sup>b</sup>	$I_n$ (%) <sup>c</sup>
PMMA	602	5	10	10	0 (8,000)
COP(MMA–EGDMA 3:2)	606	5	6	25	10 (11,000)
COP(MMA–TFMA 9:1)	609	4	18		30 (100,000)
COP(MMA–TFMA 5:5)	605	4	16		20 (60,000)

Dye concentration  $3 \times 10^{-4}$  M. Nd:YAG pump energy: 5.5 mJ/pulse.

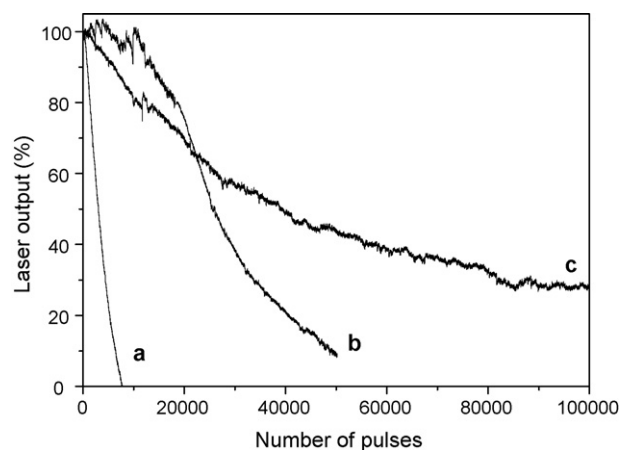
<sup>a</sup>  $\lambda_{\text{max}}$ : peak of the laser emission;  $\Delta\lambda$ : FWHM of the laser emission; Eff: energy conversion efficiency.

<sup>b</sup> Intensity of the dye laser output after 50,000 pump pulses, referred to the initial intensity  $I_0$ , at 2 Hz repetition rate:  $I_n$  (%) =  $(I_n/I_0) \times 100$ .

<sup>c</sup> Intensity of the dye laser output after the number of pump pulses indicated between parenthesis at 10 Hz repetition rate.

the photophysical and the laser action studies carried out in liquid phase [11,13]. In these studies, improvements in the lasing properties of PMS were observed when the solvent was ethyl acetate or 2,2,2-trifluoroethanol. For this reason, polymeric formulations with different plasticity (degree of cross-linking) were prepared using MMA as a basic monomer because it mimics the ethyl acetate solvent. The styryl group of PMS does not participate in the polymerization process, as evidenced by the absorbance spectrum of the polymeric samples.

The lasing results obtained with PMS, incorporated at a concentration of  $3 \times 10^{-4}$  M into the homopolymer PMMA, are summarized in Table 2. The lasing efficiency registered in the solid sample is similar to that obtained in liquid phase, taking into account that the finishing of the surfaces of the solid sample relevant to the laser operation was not laser-grade, which surely impairs efficiency. The lasing stability of PMS in PMMA was studied by following the evolution of the laser emission with the number of pump pulses in the same position of the sample. At 10 Hz repetition rate, the photostability of PMS was quite low, since the laser emission drops to zero after just 8000 pump pulses. Taking into account that some important applications of the solid-state dye lasers could not require high-pumping frequency [1,4,9], the photostability was analyzed at a lower frequency (2 Hz). The intensities of the laser output after  $n$  pump pulses,  $I_n$ , referred to the initial intensity,  $I_0$ , i.e.  $I_n$  (%) =  $(I_n/I_0) \times 100$ , at this low repetition rate, are also listed in Table 2. For the sake of clarity, in Fig. 5 the evolution of the laser output of PMS with the number of pulses is shown



**Fig. 5.** Normalized laser output as a function of the number of pump pulses for the dye PMS incorporated into: (a) PMMA, pumping at 10 Hz; (b) PMMA, pumping at 2 Hz; (c) MMA–TFMA 9:1 (v/v), pumping at 10 Hz. Dye concentration  $3 \times 10^{-4}$  M. Pump wavelength and energy: 532 nm and 5.5 mJ/pulse, respectively.

graphically for different matrices based on MMA. The lasing lifetime increases significantly when the pump repetition rate decreases, with the laser emission dropping by 90% after 50,000 pulses under the same pumping conditions, because of a drastic reduction in the photodegradation rate. This result is in good agreement with previous studies about the effect of the loaded heat on the stability of solid polymeric dye lasers, evidencing that the accumulation of heat into the material increases significantly when pumping at repetition rates higher than 1 or 2 Hz [38]. It has to be remarked that when the medium is moved (for example, by rotating it) the stability significantly increases. But we characterized the intrinsic photostability of the dye, that means to determine the lifetime or number of pump pulses in a fixed position which result in the laser output dropping by a given percent with respect to the initial emission, following the standard procedure used in the literature in order to compare the performance of different dyes in solid state.

Our previous studies had revealed that the photophysical and photochemical properties of each particular laser dye in a solid polymeric medium require a proper adjustment of the polymer matrix structure in order to obtain optical, thermal, and mechanodynamical properties of the matrix that optimize the laser action [13]. In this regard, the rigidity of the matrix is of almost importance [11,13]. Consequently, we have explored the lasing properties of PMS incorporated into a three-dimensional cross-linked copolymer generated by copolymerization of MMA with the double functionalized monomer EGDMA in a 3:2 (v/v) proportion. The lasing results (Table 2) show that whereas the laser emission wavelength is not significantly affected by cross-linking, the lasing efficiency decreases and the photostability increases with respect to those reached with PMS dissolved in the homopolymer PMMA. This result could be related to the influence of the polymer-free volume on the laser action. It seems that, in general, this factor controls the photodegradation processes of dyes since, for a certain cross-linking degree, the free volume available within the polymeric matrix will be completely occupied by the dye, avoiding the formation of dimers and higher aggregates, with their deleterious effect on laser operation [39].

Photophysical and lasing properties of PMS in solution indicated that a very polar protic solvent such as 2,2,2-trifluoroethanol could be the best liquid media for laser operation, since the highest values of the fluorescence quantum yields and lasing efficiencies are observed in this solvent. To mimic this solvent, and in order to improve the laser action of PMS, we have selected the monomer TFMA for the preparation of linear copolymers with different proportions of MMA. The lasing properties of PMS incorporated into two copoly(MMA–TFMA) matrices with 9:1 and 5:5 (v/v) proportions are also reported in Table 2. The presence of a fluorinated monomer improves significantly the lasing efficiency and stability of the dye. As in liquid phase, the presence of fluorine leads to values of conversion efficiency much higher than in PMMA. In addition, PMS exhibits also higher photostabilities in these fluorinated matrices. In the COP(MMA–TFMA) 9:1 matrix, the laser output remains at 30% of the initial laser emission after 100,000 pulses pumping at 10 Hz at the same position of the sample (Fig. 5).

The lasing properties, especially the photostability, of PMS depend on the fluorine content of the matrix, since the increase of the volumetric proportion of TFMA from 10 to 50% leads to a decrease of the lasing lifetime. Although no single cause is expected to fully explain the working mechanism, it seems that high fluorine content plays an important role in the photodegradation processes of PMS, probably as a consequence of the higher oxygen permeability in fluorinated materials [40], and the longer lifetime of singlet molecular oxygen in these media [38]. This reactive oxygen species has been proposed in many cases as the main responsible of some laser dye degradations [41].

## 4. Conclusions

A new BDP dye with a 3-styryl substituent, PMS, has been synthesized with acceptable yield by a method that allows the synthesis of other related dyes with similar conjugated structures. PMS shows higher molar absorption coefficient and oscillator strength than the commercial PM567 dye with similar fluorescence quantum, if recorded in the same solvent, but the absorption and emission maxima of PMS appear shifted ca. 50 nm, with regard to the corresponding maxima of PM567, as a consequence of the extent of the conjugated system. The electrostatic stabilization of the chromophoric positive charge by the dielectric constant of solvents such as 2,2,2-trifluoroethanol, led to a lasing efficiency as high as ca. 18% in both liquid solution and solid-fluorinated matrices.

Laser excitation with 532-nm light of solid solutions of the dye PMS in fluorinated polymeric media, based on MMA with TFMA 9:1 (v/v), gives rise to high photostable laser emission since the system remains at 30% of the initial laser output after 100,000 pump pulses at 10 Hz repetition rate in the same position of the sample. To our knowledge, this is the first time that efficient laser emission is described for a 3-styryl-BDP dye.

The results presented in this work indicate that appropriate structural modifications in the BDP molecules can yield red-emitting fluorophores that lase efficiently and with remarkable photostability when properly incorporated into polymeric matrices, enhancing the feasibility of solid-state organic photonic devices based on BDP dyes.

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## Appendix A

### A.1. General methods

Melting points were measured on a Perkin-Elmer Differential Scanning Calorimeter (DSC 6). Analytical TLC was performed on silica gel-precoated aluminium foils (Merck 60F254, 0.25 mm). Flash column chromatography was carried out on silica gel (Merck, 230–400 mesh). Yields are referred to isolated pure compounds.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were taken on a Varian INOVA-300 spectrometer. Chemical shifts are reported in ppm using as an internal reference the peak of the trace of undeuterated solvent or the carbon signal of the deuterated solvent:  $\delta$  7.26 and 77.0 in  $\text{CDCl}_3$ . The following abbreviations are used to describe signals: s (singlet), d (doublet), t (triplet), q (quartet), and m (complex multiplet). IR spectra ( $\text{in cm}^{-1}$ ) were recorded on a Perkin-Elmer 681 spectrophotometer. Low-resolution mass spectra were recorded by electron impact (70 eV) in a Hewlett-Packard 5973 spectrometer in the direct injection mode. High-resolution mass spectra were determined by electron impact (70 eV) in an AutoSpec Micromass (Waters) apparatus in the direct injection mode (peak matching) with perfluorokerosene as an exact mass standard. UV–vis absorption spectra were registered in a Perkin-Elmer Lambda-16 spectrophotometer.

### A.2. Ethyl 4-ethyl-3-methyl-5-styrylpyrrol-2-yl-carboxylate (2)

A mixture of bencyltriphenylphosphonium bromide (4.91 g, 11.3 mmol), sodium methoxide (0.63 g, 11.8 mmol) and THF

(30 mL) was stirred under argon for 30 min at room temperature. Ethyl 4-ethyl-5-formyl-3-methylpyrrol-2-yl-carboxylate (2.17 g, 10.3 mmol) in THF (30 mL) was then added, the mixture was again stirred 2 h under the same conditions and refluxed 1 h. After cooling, the reaction mixture was filtered and the solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel (hexane–ethyl acetate 99:1 as eluent), allowing the separation of (*Z*)-**2** (eluted first) and (*E*)-**2**. Ratio (*E*)-**2**/*Z*-**2** = 1.1. Data of (*Z*)-**2**: yield 0.70 g (24%), yellowish oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.13 (t, 3H, *J* = 7.3 Hz, CH<sub>3</sub>CH<sub>2</sub>-C4), 1.25 (t, 3H, *J* = 7.3 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 2.30 (s, 3H, CH<sub>3</sub>-C3), 2.51 (q, 2H, *J* = 7.3 Hz, CH<sub>3</sub>CH<sub>2</sub>-C4), 4.18 (q, 2H, *J* = 7.3 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 6.43 (d, 1H, *J* = 12.2 Hz, CH=CHPh), 6.59 (d, 1H, *J* = 12.2 Hz, CH=CHPh), 7.40 (m, 5H, *H*-Ph), 8.60 (broad s, 1H, NH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 10.4 (CH<sub>3</sub>-C3), 14.8 (CH<sub>3</sub>CH<sub>2</sub>O), 16.2 (CH<sub>3</sub>CH<sub>2</sub>-C4), 17.6 (CH<sub>3</sub>CH<sub>2</sub>-C4), 60.0 (CH<sub>3</sub>CH<sub>2</sub>-O), 116.7 (C2), 118.3 (CH=CHPh), 126.2 (C3), 128.5, 128.6, 128.8, 129.2, 129.4 (C5, C-Ph, CH=CHPh), 138.1 (C4, C-Ph), 161.4 (C=O). MS (EI), *m/z* (%): 284 [nominal mass, M<sup>+</sup>] (70), 236 (100), 222 (35). IR (neat): ν<sub>max</sub> 3290, 1673, 1440, 1264 cm<sup>-1</sup>. Data of (*E*)-**2**: yield 0.8 g (27%), white crystals, m.p. 101–103 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.14 (t, 3H, *J* = 7.6 Hz, CH<sub>3</sub>CH<sub>2</sub>-C4), 1.39 (t, 3H, *J* = 7.1 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 2.30 (s, 3H, CH<sub>3</sub>-C3), 2.57 (q, 2H, *J* = 7.6 Hz, CH<sub>3</sub>CH<sub>2</sub>-C4), 4.34 (q, 2H, *J* = 7.1 Hz, CH<sub>3</sub>CH<sub>2</sub>O), 6.80 (d, 1H, *J* = 16.6 Hz, CH=CHPh), 7.00 (d, 1H, *J* = 16.6 Hz, CH=CHPh), 7.40 (m, 5H, *H*-Ph), 8.80 (broad s, 1H, NH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 10.7 (CH<sub>3</sub>-C3), 14.9 (CH<sub>3</sub>CH<sub>2</sub>O), 16.2 (CH<sub>3</sub>CH<sub>2</sub>-C4), 17.7 (CH<sub>3</sub>CH<sub>2</sub>-C4), 60.5 (CH<sub>3</sub>CH<sub>2</sub>O), 116.8 (C2), 119.8 (CH=CHPh), 126.6 (C3), 127.4, 127.9, 129.2, 130.6 (C5, C-Ph, CH=CHPh), 137.6 (C4, C-Ph), 163.9 (C=O). MS (EI), *m/z* (%): 284 [nominal mass, M<sup>+</sup>] (70), 236 (100), 222 (35). IR (KBr): ν<sub>max</sub> 3296, 1673, 1440, 1283 cm<sup>-1</sup>.

#### A.3. (*E*)-3-Ethyl-4-methyl-2-styrylpyrrole (3)

A mixture of (*E*)-**2** (0.5 g, 1.7 mmol) in ethanol (15 mL) and sodium hydroxide (136 mg, 3.4 mmol) in water (6 mL) in a closed pressure tube under Ar was stirred at 80 °C for 2 h. After cooling, the tube was opened and the reaction mixture was neutralized with acid acetic and extracted with dichloromethane. The subsequent workup yielded a residue that was dried by addition of acetonitrile and reduced-pressure elimination of the solvent. The product was used in the next reaction without further purification. Yield 0.23 g (64%), white crystals, m.p. 85–87 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.14 (t, 3H, *J* = 7.3 Hz, CH<sub>3</sub>CH<sub>2</sub>), 2.35 (s, 3H, CH<sub>3</sub>-C4), 2.57 (q, 2H, *J* = 7.3 Hz, CH<sub>3</sub>CH<sub>2</sub>), 6.84 (d, 1H, *J* = 16.6 Hz, CH=CHPh), 6.92 (d, 1H, *J* = 16.6 Hz, CH=CHPh), 7.50 (m, 5H, *H*-Ph), 8.10 (d, 1H, *J* = 8.1 Hz, CH-N), 8.94 (broad s, 1H, NH) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 10.8 (CH<sub>3</sub>-C4), 16.2 (CH<sub>3</sub>CH<sub>2</sub>-C3), 17.7 (CH<sub>3</sub>CH<sub>2</sub>-C3), 118.8 (CH=CHPh), 126.8 (C5), 127.8 (C3, C4), 128.5, 129.2, 131.0, 131.7 (C2, C-Ph, CH=CHPh), 137.4 (C-Ph). MS (EI), *m/z* (%): 211 [nominal mass, M<sup>+</sup>] (100), 196 (60), 179 (70). IR (KBr): ν<sub>max</sub> 3457, 1646, 1469, and 1266 cm<sup>-1</sup>.

#### A.4. (*E*)-2,6-Diethyl-4,4-difluoro-1,5,7,8-tetramethyl-3-styryl-4-bora-3a,4a-diazas-indacene (PMS)

A mixture of pyrrole **4** (160 mg, 0.97 mmol) in chloroform (10 mL) and phosphorus oxychloride (0.1 mL, 1.1 mmol) was stirred at room temperature for 30 min. Then, a solution of pyrrole **3** (205 mg, 0.97 mmol) in chloroform (10 mL) was added and the mixture was stirred again for 12 h. Triethylamine (0.675 mL, 4.85 mmol) was added and, after stirring for 30 min, boron trifluoride diethyl etherate (0.86 mL, 6.79 mmol). After 3 h, the reaction mixture was washed with water, extracted with dichloromethane and dried over MgSO<sub>4</sub>. The product was purified by column chromatography (sil-

ica gel, hexane–ethyl acetate 95:5). Yield 121 mg (31%), red crystals, m.p. 228–230 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.06 (t, 3H, *J* = 7.6 Hz, CH<sub>3</sub>CH<sub>2</sub>-C6), 1.21 (m, 3H, *J* = 9.2 Hz, CH<sub>3</sub>CH<sub>2</sub>-C2), 2.26, 2.36 (two s, each 3H, CH<sub>3</sub>-C5/CH<sub>3</sub>-C7), 2.42 (q, 2H, *J* = 7.6 Hz, CH<sub>3</sub>CH<sub>2</sub>-C6), 2.55 (s, 3H, CH<sub>3</sub>-C8), 2.64 (s, 3H, CH<sub>3</sub>-C1), 2.68 (m, 2H, *J* = 9.2 Hz, CH<sub>3</sub>CH<sub>2</sub>-C2), 7.16 (d, 1H, *J* = 16.5 Hz, CH=CHPh), 7.28 (m, 1H, *H*-Ph), 7.36 (t, 2H, *J* = 7.3 Hz, 2 × *H*-Ph), 7.58 (d, 2H, *J* = 7.8 Hz, 2 × *H*-Ph), 7.74 (t, 1H, *J* = 16.5 Hz, CH=CHPh) ppm. <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>): δ 11.9 (CH<sub>3</sub>CH<sub>2</sub>-C6), 13.1 (CH<sub>3</sub>CH<sub>2</sub>-C2), 14.5 (CH<sub>3</sub>-C7), 14.9 (CH<sub>3</sub>-C5), 15.1 (CH<sub>3</sub>CH<sub>2</sub>-C6), 16.8 (CH<sub>3</sub>-C8), 17.6 (CH<sub>3</sub>-C1), 20.7 (CH<sub>2</sub>-C2), 120.6 (C6), 120.9 (C7), 127.4 (C8), 128.6 (C1), 129.1 (C7a and C8a), 133.9 (C5), 134.7 (C2), 135.6 (C3), 137.7, 137.9 (CH=CHPh), 139.5, 139.7, 143.6, 148.3, 154.4 (C-Ph). MS (EI), *m/z* (%): 406 [nominal mass, M<sup>+</sup>] (42), 391 (28), 181 (17), 107 (30), 91 (100). IR (KBr): ν<sub>max</sub> 1151, 1441, 1200, 1045, and 991.9 cm<sup>-1</sup>. UV–vis (EtOAc), λ<sub>max</sub> (ε, M<sup>-1</sup> cm<sup>-1</sup>): 567 nm (78,000). HRMS (EI): calcd for C<sub>25</sub>H<sub>29</sub>BF<sub>2</sub>N<sub>2</sub> 406.2392, found 406.2395.

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