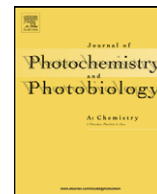




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## New laser dye based on the 3-styryl analog of the BODIPY dye PM567

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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

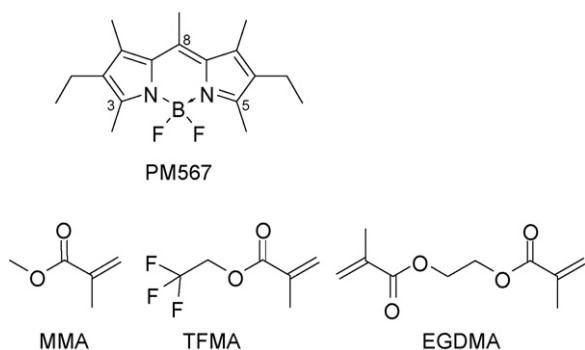
Some modern biotechnological and electronic applications require new fluorophores with predetermined properties such as high-fluorescence quantum yield, large Stokes shift and optimized absorption profile, so as to meet the demands for more sensitive analytical protocols, sensors and light-emitting devices [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.

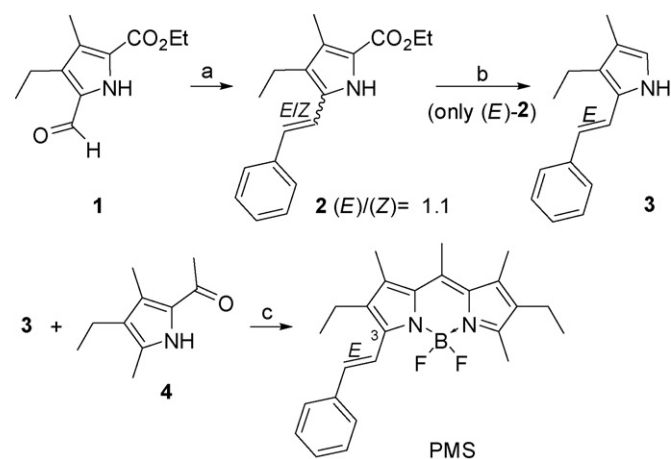
photophysical properties are strongly influenced by the solvent and the medium pH [17,18], so that these dyes have been proposed as molecular switches [15b], pH [15a], anion [19,20] and cation [5d] sensors, fluorescent labels for cholesterol and sphingolipids [21], logic circuits [12e], and, in the form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

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