

Efficient and stable dye laser action from modified dipyrromethene BF₂ complexes

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We report on the lasing action of modified dipyrromethene BF₂ complexes in air-equilibrated liquid solutions. All recent dyes share a common chromophore core and were dissolved in apolar, polar nonprotic, and polar protic solvents. When pumped transversely at 534 nm, nearly solvent-independent laser emission was obtained with efficiencies well over 40% in most cases. Highest lasing efficiency was 59%. Under continuous ultraviolet irradiation some of these dyes demonstrated improved photostability as compared with commercial dye pyromethene 567.

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From the mid-1960s dye lasers have been attractive sources of coherent tunable visible radiation because of their unique operational flexibility.¹ Dye lasers can emit both in pulsed and continuous-wave forms, can be pumped with a wide variety of excitation sources, and exhibit an inherent ability to yield high pulse energies and high average powers. Hundreds of dyes have been demonstrated to lase measurably covering the spectral range from the ultraviolet to the near infrared. The introduction of wavelength-selective elements in the laser cavity allows narrow-linewidth operation and tunability, and the large gain bandwidth of these molecules makes possible the generation of ultrashort pulses.

The laser performance of organic dyes is ultimately limited by triplet-triplet absorption over their lasing spectral region. Along the late eighties and early nineties, Boyer and co-workers synthesized a number of organic dyes belonging to a recent class of laser dyes, namely, the pyromethene BF₂ complexes,²⁻⁴ which exhibit reduced triplet-triplet absorption and high fluorescence quantum yields. Depending on the substituents on the chromophore, these dyes present laser emission over the spectral region from the green/yellow to the red, competing with the well-known rhodamine dyes.^{5,6} In particular, some of these recent dyes outperform both in efficiency and tunability the widely employed rhodamine 6G and rhodamine B laser dyes in liquid solution.⁷ On the other hand, the presence of amine aromatic groups in their structure renders these pyromethene dyes vulnerable to photochemical reactions with oxygen which makes them relatively unstable in air saturated solutions.⁸ In addition, in commercially available pyromethene dyes there is a strong dependence of the laser properties on the solvent.⁸⁻¹⁰

In this letter, we report efficient and nearly solvent-independent laser emission with improved photostability from some recently synthesized pyromethene BF₂ complexes in air-equilibrated solutions of apolar, polar nonprotic,

and polar protic solvents. All recent dyes have a common chromophore core, differing in the substituent in position 8: an acetoxypolymethylene linear chain or a *p*-acetoxymethylphenyl group (Fig. 1). The former compounds can be considered model structures where the same chromophore is covalently bound through an unsaturated (acrylate or methacrylate) group and a spacer of variable length to a polymeric chain, a subject of interest in our group and topic of current investigation. Details of their synthesis will be reported elsewhere.

Laser emission was obtained from air-equilibrated dye solutions contained in a 1 cm optical-path silica cell. In all solvents the dye concentration was chosen so that the optical density of the solution at the excitation wavelength was about 18 for a 1 cm optical path. The samples (mounted on translation stages) were transversely pumped at 534 nm with 5.5 mJ, 6 ns full width at half maximum pulses from a frequency-doubled *Q*-switched Nd:KGW laser (Monocrom STR-2+) at a repetition rate of 1 Hz. The excitation pulses were directed towards the dye cell with a combination of one spherical ($f=50$ cm) and two cylindrical lenses ($f=-15$ cm

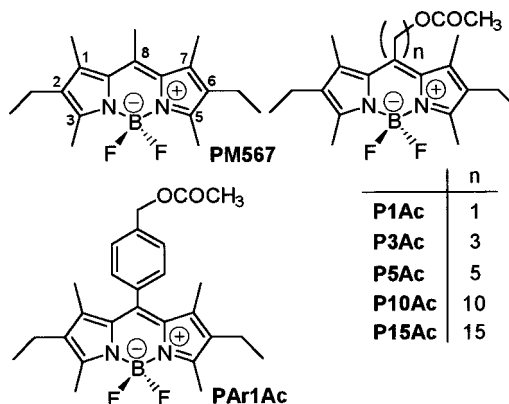


FIG. 1. Molecular structure of the dipyrromethene BF₂ complexes herein studied.

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TABLE I. Laser parameters^a for a number of recently synthesized dipyrromethene BF₂ complexes in different solvents. Nd:KGW laser (second harmonic) pump energy: 5.5 mJ/pulse. Data from PM567 are included for comparison.

Solvent	PM567 ^b (1 × 10 ⁻³ M)		P1Ac (0.45 × 10 ⁻³ M)		P3Ac (1.5 × 10 ⁻³ M)		P5Ac (1.5 × 10 ⁻³ M)		P10Ac (1.5 × 10 ⁻³ M)		P15Ac (0.6/2 × 10 ⁻³ M) ^c		PAr1Ac (0.8 × 10 ⁻³ M)	
	eff (%)	λ _{max} (nm)	eff (%)	λ _{max} (nm)	eff (%)	λ _{max} (nm)	eff (%)	λ _{max} (nm)	eff (%)	λ _{max} (nm)	eff (%)	λ _{max} (nm)	eff (%)	λ _{max} (nm)
F ₃ -ethanol ^d	56	563	43	577	40	566	48	563	59	563	52	561	41	552
methanol	52	563	43	584	42	565	48	565	55	565	47	562	41	556
ethanol	37	565	44	579	49	567	50	566	45	566	58	567	43	555
acetone	42	564	47	582	45	565	47	566	45	562	48	564	44	554
ethyl acetate	33	563	46	580	48	564	51	565	38	566	42	566	44	554
<i>c</i> -hexane	28	571	41	583	36 ^e	568	48	572	^f	^f	44	566	41	555

^aEff: energy conversion efficiency, λ_{max}: peak wavelength of the laser emission.

^bData from Ref. 9. There is a shift of 2 nm in the peak wavelength of the laser emission because of recalibration of the measurement instruments.

^cP15Ac concentration was 0.6 × 10⁻³ M in F₃-ethanol, methanol and ethanol, and 2 × 10⁻³ M in acetone, ethyl acetate, and *c*-hexane.

^dF₃-ethanol: 2,2,2-trifluoroethanol.

^eThe dye was not completely dissolved even after long periods of sonication.

^fPB-10-Ac dye did not properly dissolve in *c*-hexane.

and +15 cm, respectively) perpendicularly arranged. The first cylindrical lens widened the spherical cross section of the pump beam so that it illuminates the complete 1 cm length of the dye cell; then, the second cylindrical lens focused the pump pulses onto the input surface of the cell to form a line of about 0.3 × 10 mm, so that the pump fluence was about 180 mJ/cm². The oscillation cavity consisted of a 90% reflectivity flat aluminum mirror and the end face of the dye cell as output coupler, with a cavity length of 2 cm.

The dye and pump laser pulses were characterized with the following instruments: GenTec ED-100A and ED-200 energy meters, ITL TF 1850 fast risetime photodiode, Tektronix 2430 digital oscilloscope, CVI CM110 monochromator, and EMI 9783B photomultiplier. Dye and pump laser signals were sampled with boxcars (Stanford Research, Model 250). All the integrated signals were digitized and processed using a personal computer *via* a computerboard DASH-8 interface.¹¹ All the energy measurements were averaged over 16 shots.

A summary of the data obtained is shown in Table I where previous results⁹ obtained with the commercial dye pyromethene 567 (PM567) are also included for comparison. The dyes were dissolved in polar protic (trifluoroethanol, methanol, ethanol), polar nonprotic (acetone, ethyl acetate), and apolar (cyclohexane) solvents, and their lasing efficiencies and laser emission spectra were determined. It is seen in Table I that all recent dyes lase efficiently, with energy conversion efficiencies nearly solvent independent in most of them. Dyes P10Ac and P15Ac, which contain long substituents in position 8, are the only exception to this behavior and lase with an efficiency significantly higher in some of the polar alcoholic solvents. All the recent dyes lase more efficiently than the commercial PM567 dye in ethanol, acetone, ethyl acetate, and cyclohexane, with the dye P10Ac being more efficient than PM567 in all the solvents studied. The highest efficiencies were obtained with P10Ac in trifluoroethanol (59%) and P15Ac in ethanol (58%). The increase of the length of the substituent in position 8 produces a blue-shift of the laser emission peak. The highest blue shift was observed with the *p*-acetoxyethylphenyl substituent.

The photostability of the different dyes was evaluated by continuous and simultaneous irradiation of the samples with

a high intensity ultraviolet lamp for time intervals of up to 20 h. A standard homemade UV-accelerometer device (American Society for Testing and Materials G-53-77 and UME S3104) was employed in these measurements. The UV source consists of eight fluorescent tubes (Philips TL-40W/12) which emit over the wavelength range 280–360 nm with emission maximum at 310 nm. The lamps are arranged vertically on the circumference of a drum around which samples rotate at a distance of 3.5 cm from the lamps. Ethanolic solutions of the different dyes were irradiated in standard quartz cells, with their concentrations adjusted so that the same initial absorbance (Abs=2) was obtained. All the irradiations were conducted at 40 °C. A sample of PM567, simultaneously irradiated, was used as a reference. Monitoring of sample photolysis was carried out by recording their full ultraviolet/visible absorption spectra on a CARY 4E spectrophotometer at different times of irradiation. The shape of the absorption spectrum of the different samples did not change with irradiation time, but their peak value decreased, indicating a progressive disappearance of dye molecules as the irradiation time increased.

The time dependence of the absorbance normalized to the absorbance before irradiation for PM567 and synthesized dipyrromethene BF₂ complexes is represented in Fig. 2. It is seen that all the dyes but P1Ac and PAr1Ac are more photostable than the reference dye PM567, the photostability decreasing in the order: P3Ac > P15Ac > P5Ac > P10Ac > PM567 > P1Ac > PAr1Ac. The rate of photobleaching for the reference dye PM567 was 1.4 × 10⁻⁵ s⁻¹. The most stable dye was P3Ac with a photobleaching rate of 5.5 × 10⁻⁶ s⁻¹. After 20 h of continuous ultraviolet irradiation, the absorbance of dye P3Ac dropped by only 17%, whereas that of PM567 dropped by 41%. With P1Ac the absorbance dropped by 98% after 20 h irradiation, indicating near complete photobleaching of the dye molecules. The least photostable dye was PAr1Ac, for which an irradiation time of just 8 h brought the absorbance down to zero.

The results presented in this work indicate that appropriate chemical modifications in the pyromethene dye molecules can yield dyes with improved laser efficiency and photostability. Our next step will be to incorporate the molecules into polymeric matrices in order to develop efficient

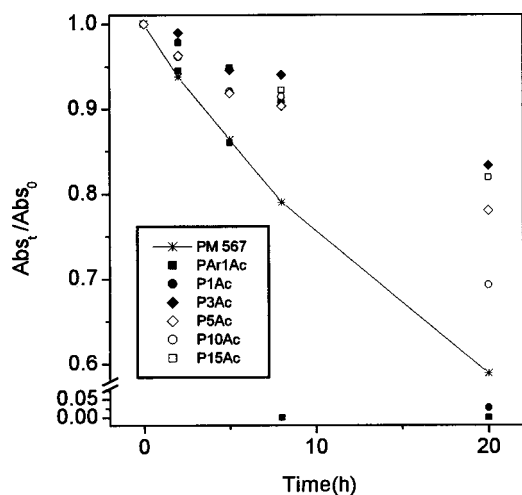


FIG. 2. Normalized absorbance as a function of the irradiation time at a temperature of 40 °C for the different compounds studied in this work dissolved in ethanol. Abs_t =absorbance at time t . Initial absorbance for all solutions=2. The line joining the points corresponding to the reference dye PM567 is just a guide for the eye.

and stable solid-state dye lasers based on these molecules. Incorporation of an unsaturated functional group in position 8 of the structures of Fig. 1, would enable the copolymerization of these dipyrromethene BF_2 complexes with conventional appropriate monomers.

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