Photophysical and Lasing Properties of New Analogs of the Boron−Dipyrromethene Laser Dye PM567 in Liquid Solution

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We report on the photophysical properties and laser action of five newly synthesized dipyrromethene$\cdot$BF$_2$ complexes that are analogues of the laser dye PM567 dissolved in apolar, polar nonprotic, and polar protic solvents, paying attention to the effect of the dye concentration. All of these dyes have a common chromophore core and differ in the length of 8-(ω-acetoxy)polymethylene substituent. When pumped transversely at 534 nm, laser efficiencies up to 59% were obtained, which were found to be nearly independent of the nature of the solvent and the length of the polymethylene chain. Good correlations between the photophysical properties in diluted solutions and the lasing characteristics in moderately concentrated solutions have been observed. The presence of the 8-substituent does not modify significantly the photophysics of the chromophore, if the polymethylene chain has five or more methylene groups. Theoretical calculations were performed to rationalize this behavior.

I. Introduction

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 in both 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-line-width operation and tunability, and the large gain bandwidth of these molecules makes possible the generation of ultrashort pulses.

Triplet−triplet absorption over the laser spectral region turns out to be one of the most important causes limiting the laser performance of organic dyes. As a result of the continuous effort to produce improved dyes for laser applications, a new class of laser dyes with reduced triplet−triplet absorption was synthesized by Boyer and co-workers during the late 1980s and early 1990s,[2−5] and some of them are now commercially available. These new dyes are dipyrromethene$\cdot$BF$_2$ complexes, with emission covering the spectral region from the green−yellow to the red.

Like rhodamine dyes, these new compounds exhibit, in general, high quantum fluorescence yields, and the triplet extinction coefficients over the laser action spectral region of some of these dyes are only one-fifth of their rhodamine counterparts.[6] They are highly polar laser dyes with zwitterionic structure exhibiting good solubility in many solvents, including alcohols and methyl methacrylate (MMA). Many dyes of the dipyrromethene−BF$_2$ family are highly efficient laser dyes, with low intersystem crossing and low excited-state absorption coefficients.[2−4,7] In particular, some of these complexes outperform in flashlamp-pumped, laser-pumped, and continuous-wave operation the most widely employed laser dye, rhodamine 6G, considered as the benchmark in efficiency and photostability.[4,7−9] However, these dipyrromethene dyes are vulnerable to photochemical reactions with oxygen, which makes them relatively unstable in air-saturated solutions.[10] In addition, in the now commercially available dipyrromethene dyes, the laser properties are strongly dependent on the solvent used.[10−12]

The photophysical and lasing properties of some of the dipyrromethene dyes in liquid solution have shown strong dependence on their molecular structure.[12] For this reason, continuous efforts on both chemical synthesis and laser-action research are made to develop new and more valuable, efficient, and photostable laser dyes with the common chromophore of the dipyrromethene$\cdot$BF$_2$ complexes but with different substituents at certain positions.[13,14] Our group, in particular, has synthesized a new family of dipyrromethene$\cdot$BF$_2$ complexes[13] in which all dyes have a common chromophore core, the molecular structure of the pyrromethene known as PM567, differing in the substituent at position 8, an acetoxypolymethylene linear chain with 1, 3, 5, 10, or 15 methylenes, named as

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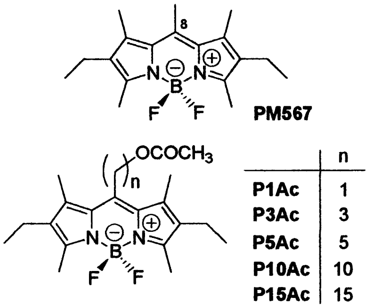

Figure 1. Molecular structure of the dipyrromethene·BF_2 complexes herein studied.

P1Ac, P3Ac, P5Ac, P10Ac, and P15Ac, respectively, of which the molecular structures are shown in Figure 1. These compounds can be considered model structures of analogues in which the same chromophore is covalently bound, through a polymethylene spacer of the same length at its 8-position, to an unsaturated polymerizable ester group (oxyacryloyl, oxymethacryloyl, etc.) or to its corresponding copolymer with methyl acrylate, methyl mathacrylate, etc., compounds of interest for our group and a topic of current research. Details of their synthesis will be reported elsewhere.[15]

In this paper, we have proceeded to properly characterize the laser action, as well as the fluorescence quantum yields and lifetimes, of these new 8-substituted dipyrromethene−BF_2 dyes in solution in a variety of solvents roughly classified as hydrogen-bond donor (or protic) (HBD) solvents, dipolar non-HBD (or aprotic) solvents, and apolar non-HBD solvents, paying attention to the effect of the dye concentration. Some of the lasing results here presented have been concisely reported in a precedent letter.[13] To obtain a deeper insight into the lasing characteristics of these fluorophores, we also report on the results of the systematic study of the photostability of some of these dyes under laser irradiation conditions in liquid solutions.

II. Experimental Section and Methods

The synthesis of the new dipyrromethene·BF_2 complexes has been reported in ref 15. 1,3,5,7,8-Pentamethyl-2,6-diethylpyrromethene−difluoroborate (PM567, laser grade from Exciton) was used as received. The purity of the dye was found to be >99%, as determined by spectroscopic and chromatographic methods. All solvents (Merck, Aldrich, or Sigma) were spectroscopic grade and were used without further purification.

In the lasing experiments, the dye solutions were contained in a 1-cm optical path quartz cell carefully sealed to avoid solvent evaporation during the experiments. The cell samples were mounted on translation stages, which allowed precise vertical and horizontal alignment. The dye solutions were transversely pumped at 534 nm with 5.5 mJ, 7 ns fwhm pulses from a frequency-doubled Q-switched Nd:KGW laser (Monocrom STR-2+) at a repetition rate of 1 Hz. The exciting pulses were directed toward the dye cell with a combinaton of one spherical ($f = 50$ cm) and two cylindrical quartz lenses. Of these cylindrical lenses, the first one, with $f = -15$ cm, widened the spherical cross-section of the pump beam to illuminate the complete 1-cm transverse length of the dye cell; then, the second cylindrical lens, with $f = 15$ cm and perpendicularly arranged with respect to the first one, focused the pump pulses onto the input surface of the dye cell to form a line of ca. 0.3×10 mm^2 so that the pump fluence was 180 mJ/cm^2. The oscillator cavity consisted of a 90% reflectivity flat aluminum mirror and the end face of the dye cell as the output coupler with a cavity length of 2 cm. The cavity was not optimized and did not have tuning elements to select the wavelength.

The dye and pump laser pulses were characterized with the following instruments: GenTec ED-100A and ED-200 pyroelectric energy meters, ITL TF1850 fast rise time photodiode, Tektronix 2430 digital-storage oscilloscope, CM110 monochromator (CVI Laser Corporation), and EMI 9783B photomultiplier. The dye and pump laser signals were sampled with boxcars (Stanford Research model 250). All of the integrated signals were digitized and processed using a PC computer via a Computerboard DASH-8 interface.[16] The estimated error of the energy measurements was 10%.

The photostability of each dye was evaluated by irradiating under lasing conditions 8 μL of a solution in methyl isobutyrate. The solutions were contained in a cylindrical Pyrex tube (1-cm height, 1-mm internal diameter) carefully sealed to avoid solvent evaporation during the experiments. Monitoring of sample photolysis was carried out by recording the laser-induced fluorescence emission, excited transversally to the capillary with the same pump pulses from the Nd:YAG laser used for producing dye laser emission, as a function of the number of pump pulses at 10 Hz repetition rate. The fluorescence emission was monitored perpendicular to the exciting beam, collected by an optical fiber, and imaged onto the input slit of a MacPherson-2035 monochromator and detected by a photomultiplier (EMI 9816-QB). The fluorescence signal was recorded by feeding the signal to the boxcar to be integrated before being digitized and processed by a computer. Each experience was repeated at least three times. The experimental error in the photostability measurements was estimated to be on the order of 7%.

Absorption and fluorescence (after excitation at 490 or 510 nm, depending on the dye) spectra were recorded on a Cary 4E spectrophotometer and on a Shimadzu RF-5000 spectrofluorimeter, respectively. Fluorescence quantum yields (ϕ) were determined using PM567 in methanol ($\Phi = 0.91^{8}$) as a reference. Radiative decay curves were recorded by the time-correlated single photon counting technique (Edinburgh Instruments model ηF900). The emission was monitored at about 540 nm after excitation at 490 or 510 nm by means of a hydrogen flash lamp with 1.5 ns fwhm pulses and a 40 kHz repetition rate. The photophysical properties in diluted dye solutions (2×10^{-6} M) were studied in 1-cm optical path length quartz cuvettes. The fluorescence decay curves were analyzed as a one-exponential decay ($\chi^2 < 1.2$), and the fluorescence decay time (τ) was obtained from the slope.

The fluorescence spectra and decay curves of more concentrated solutions (up to 10^{-3} M) were recorded in 0.1, 0.01, and 0.001 cm optical path quartz cuvettes using the front-face configuration, orientating the cuvettes 35° and 55° with respect to the excitation and the emission-detection beams, respectively, to minimize the reabsorption and reemission effects.[17] Samples in the 0.001 cm cuvette have to be carefully prepared to avoid the evaporation of the solvent. In this cuvette, the absolute fluorescence intensity for different samples prepared from the same dye solution was not reproducible, affecting the determination of the fluorescence quantum yield. All of the fluorescence quantum yield data presented in this work are average values of three independent measurements. On the contrary, reproducible fluorescence lifetime values were obtained with the 0.001 cm cuvette because in this case the time evolution of the fluorescence intensity was recorded. Monoexponential fluorescence decay curves ($\chi^2 < 1.3$) were also observed in the 0.001 cm cuvette.

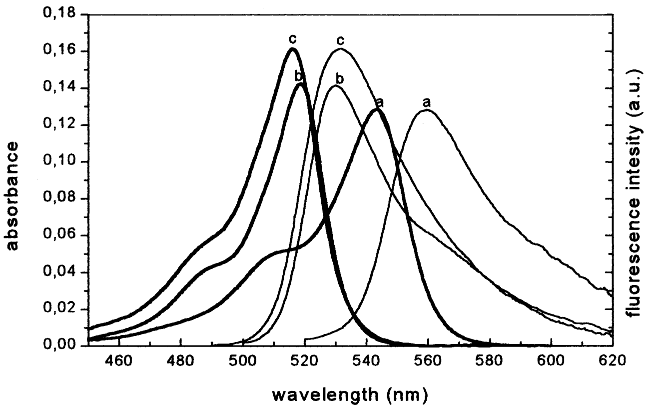

Figure 2. Absorption (bold curves) and corrected and normalized fluorescence (fine curves) spectra of diluted solutions (2×10^{-6} M) of (a) P1Ac, (b) P15Ac, and (c) PM567 in methanol (1-cm optical pathway cuvette).

Theoretical calculations were performed by the MOPAC 97 (Fujitsu) and the Gaussian 98w softwares. Semiempirical AM1 method (implanted in the MOPAC software) was used for the geometry optimization of the dyes instead of the semiempirical PM3 method because the former method parametrized the boron atom better than the PM3 method. Electronic spectroscopy parameters were calculated by the semiempirical ZINDO method and the ab initio time-dependent (TD) B3LYP method using the 6-31G basis-set functions (both methods are implanted in the Gaussian software).

III. Results and Discussion

The dyes were dissolved in polar protic (2,2,2-trifluoroethanol, ethanol, methanol), polar nonprotic (acetone, ethyl acetate), and apolar (cyclohexane) solvents, and their photophysical properties and laser action as a function of the dye concentration were determined.

The photophysical properties of the novel P*n*Ac ($n = 1$, 3, 5, 10, and 15) dyes were obtained by recording the absorption and fluorescence spectra and the fluorescence decay curves. Figure 2 shows representative spectra for the dyes with the shortest (P1Ac) and the longest (P15Ac) 8-polymethylene chain. Generally speaking, the shape and intensity of the absorption and fluorescence bands are similar to those of the commercial dye PM567,[11] indicating that the presence of the 8-acetoxymethyl group does not extensively modified the electronic π-system of the chromophore. Table 1 summarizes the photophysical data of diluted solutions of all of the studied dyes in several solvents.

The dye P1Ac presents the most drastic changes in the photophysical properties with respect to the commercial PM567 dye: both absorption (λ_{ab}) and fluorescence (λ_{fl}) bands are bathochromically shifted around 1000 cm^{-1}, the fluorescence quantum yield (ϕ) is lower, and the lifetime (τ) is higher indicating a diminution in the radiative deactivation rate constant ($k_{fl} = \phi/\tau$) and an augmentation in the nonradiative deactivation process [$k_{nr} = (1 - \phi)/\tau$]. The diminution in the spectroscopic transition probability between the S_0-S_1 electronic states is also deduced from the absorption data, because the oscillator strength (*f*) of P1Ac is smaller than that of PM567 in all of the studied solvents. The photophysics of the other P*n*Ac ($n = 3$, 5, 10, and 15) dyes progressively mimic that PM567 dye as the length of the 8-polymethylene chain increases. The exception is the position of the fluorescence band, which exhibits, for some of the dyes in certain solvents, a small hypochromic shift, up to 240 cm^{-1}, with respect to the position of the emission band of PM567 (Table 1).

TABLE 1: Photophysical Properties of Diluted Solutions (2×10^{-6} M in 1-cm Pathway Cuvettes) of the Dyes P*n*Ac in Different Solvents, Absorption and Fluorescence Wavelengths (λ_{ab} and λ_{fl}), Oscillator Strength (*f* calculated as in Ref 21), Fluorescence Quantum Yield (Φ), and Lifetime (τ)[a]

dye	solvent	λ_{ab} (±0.1 nm)	λ_{fl} (±0.1 nm)	*f*	Φ (±0.05)	τ (±0.05 ns)
P1Ac	F$_3$-ethanol[b]	545.6	562.5	0.371	0.74	7.85
	methanol	543.2	559.0	0.409	0.68	6.65
	ethanol	544.4	560.0	0.374	0.66	6.56
	acetone	542.4	557.5	0.385	0.69	6.86
	ethyl acetate	542.9	558.0	0.372	0.68	6.64
	cyclohexane	547.6	561.0	0.424	0.56	6.27
P3Ac	F$_3$-ethanol[b]	519.9	531.5	0.396	0.91	7.05
	methanol	520.0	532.0	0.414	0.81	6.06
	ethanol	521.2	533.0	0.418	0.77	5.93
	acetone	519.5	531.0	0.397	0.80	5.98
	ethyl acetate	520.1	531.0	0.420	0.75	5.88
	cyclohexane	524.9	533.5	0.433	0.58	5.54
P5Ac	F$_3$-ethanol[b]	518.0	529.0	0.410	0.95	7.21
	methanol	519.1	530.5	0.460	0.85	6.19
	ethanol	520.4	531.5	0.455	0.78	5.98
	acetone	518.6	530.5	0.470	0.76	6.02
	ethyl acetate	519.3	530.5	0.464	0.76	5.95
	cyclohexane	524.0	533.5	0.452	0.57	5.71
P10Ac	F$_3$-ethanol[b]	517.1	528.5	0.412	0.97	7.11
	methanol	518.6	530.5	0.418	0.86	6.39
	ethanol	520.0	531.0	0.423	0.80	5.99
	acetone	518.2	529.5	0.422	0.80	5.98
	ethyl acetate	519.0	530.0	0.420	0.78	5.92
	cyclohexane	523.1	533.0	0.437	0.61	5.68
P15Ac	F$_3$-ethanol[b]	517.0	528.5	0.438	0.95	7.07
	methanol	518.7	530.0	0.455	0.83	6.29
	ethanol	519.9	531.0	0.437	0.79	6.08
	acetone	518.1	529.5	0.485	0.76	6.03
	ethyl acetate	518.9	529.5	0.475	0.75	5.91
	cyclohexane	523.2	532.0	0.435	0.63	5.72
PM567	F$_3$-ethanol[b]	515.7	535.0	0.470	0.97	6.94
	methanol	516.2	531.5	0.489	0.91	6.10
	ethanol	517.7	532.5	0.490	0.84	6.09
	acetone	516.0	532.0	0.492	0.85	5.92
	ethyl acetate	516.4	531.5	0.556	0.80	5.78
	cyclohexane	522.5	537.0	0.498	0.70	5.60

[a] The correspondent data of the dye PM567[12] are also included for comparison. [b] 2,2,2-Trifluoroethanol.

These experimental results suggest that the effect of the ω-acetoxy group on the photophysics of the PM567 chromophore is not due to a direct intramolecular through-space interaction between the ester group and the π-electrons of the aromatic rings favored by the length and the flexibility of the 8-polymethylene chain but rather to the electron-withdrawing effect of the ω-acetoxy group through the linking chain. This would cause the above-mentioned modifications in the photophysics of the chromophore, and as the polymethylene chain becomes longer, this effect becomes weaker.

These arguments are supported by theoretical calculations. The optimized geometry for the P*n*Ac dyes using the semiempirical AM1 method leads to a nearly linear stair-like distribution of the methylene groups of the linking chain. Such a disposition avoids any direct through-space interaction. On the other hand, spectroscopic absorption parameters of the P*n*Ac dye are theoretically calculated by the semiempirical ZINDO method and by the time-dependent procedure of the ab initio B3LYP method using the 6-31G TD basis-set functions implanted in the Gaussian 98 software.

TABLE 2: Calculated Absorption Parameters of the P*n*Ac Dyes Using the Semiempirical ZINDO and the ab Initio B3LYP/6-31G TD Methods[a]

	ZINDO		B3LYP/6-31G TD	
dye	λ_{ab} (nm)	f	λ_{ab} (nm)	f
P1Ac	498.0	0.915	436.3	0.515
P3Ac	491.5	0.896	420.1	0.539
P5Ac	490.0	0.895	418.7	0.540
P10Ac	488.8	0.893	417.5	0.539
P15Ac	487.9	0.898	417.3	0.538
PM567	490.5	0.889	419.1	0.541

[a] Data from PM567 are included for comparison.

Table 2 lists the calculated absorption parameters for the dyes in the gas phase. The absorption wavelengths calculated by the ZINDO method are close to the experimental values, but this method cannot adequately reproduce the effect of the linking chain length on the maximum absorption wavelength. This is not the case for the more precise ab initio B3LYP/6-31G TD method, in which a good correlation between calculated and experimental data is observed for the evolution of the absorption wavelength with the linking chain of the P*n*Ac dyes; that is, the absorption band of P1Ac and P15Ac derivatives are bathochromically shifted with respect to and close to, respectively, the absorption band of PM567. However, this method subestimates the absorption wavelength for all of the dyes. Preliminary theoretical absorption parameters obtained by a more precise ab initio method (CIS method using the more complete 6-31+G* basis-set functions) for the unsubstituted dipyrromethene·BF_2 tricyclic core suggest that the subestimation in the absorption wavelength in the B3LYP/6-31G TD method is due to the contribution of the electronic (HOMO-1) state in the spectroscopic transition. Because of the large number of atoms involved in the molecular structures of the dyes, the more precise CIS/6-31+G* method was not usefully applied for these derivatives. In any case, the theoretical calculations support the effect of the linking polymethylene chain length in the photophysical properties of the P*n*Ac dyes.

The effects of the solvent on the photophysics of these dyes are nearly independent of the 8-chain length, and they are similar to those observed for the PM567 dye (Table 1). These effects for the PM567 dye were previously discussed elsewhere[11] on the basis of the polarity/polarizability or H-bond donor/acceptor ability or both of a multitude of solvents. From the data listed in Table 1, it can be concluded that the presence of the acetoxy group does not extensively modify the photophysical properties of the PM567 chromophore for chains longer than five methylene groups. The incorporation to the chain of a polymerizable ester end group, such as an acrylate or methacrylate, can provide the way to convalently link the PM567 chromophore to a polymer chain without drastic modifications in the photophysics of the dye. These are essential aspects in the development of active media for a solid-state tunable dye laser.[18,19]

In a previous work,[13] the laser action of these compounds in different solvents at a common optical density of 18 for 1-cm optical path length was investigated and compared with that of the commercial dye PM567. Laser emissions that were nearly solvent-independent with emission maxima within the range 561−584 nm and efficiencies over 40% in most cases were obtained. All new dyes lased more efficiently than PM567 in ethanol, acetone, ethyl acetate, and cyclohexane, with the dye P10Ac being also more efficient than PM567 in all of the solvents studied. Under continuous ultraviolet irradiation, the dyes P3Ac, P15Ac, P5Ac, and P10Ac, in this order, demostrated improved photostability compared with PM567.

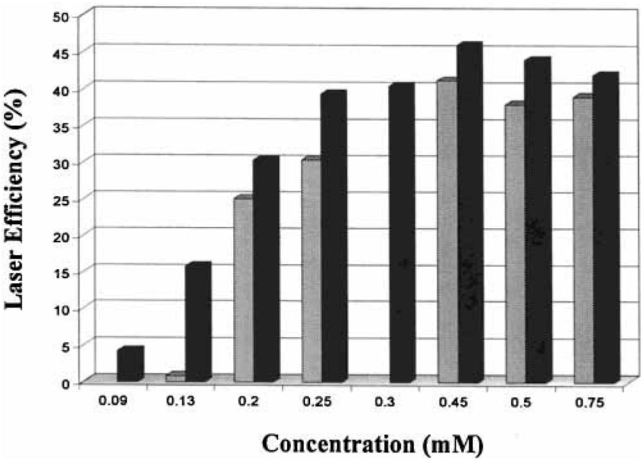

Figure 3. Lasing efficiency of the dye P1Ac as a function of the dye concentration in 2,2,2-trifluoroethanol (black bars) and cyclohexane (grey bars).

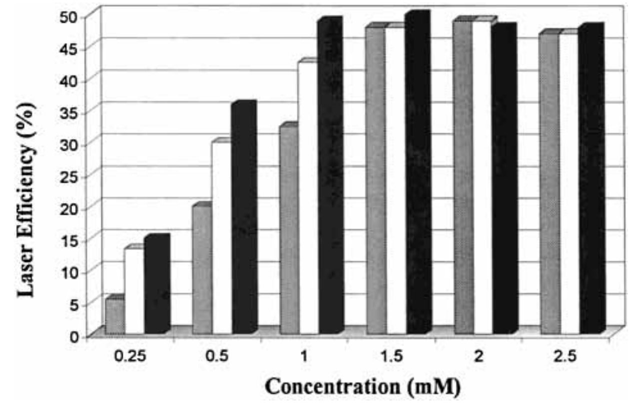

Figure 4. Lasing efficiency of the dye P5Ac as a function of the dye concentration in 2,2,2-trifluoroethanol (black bars), ethanol (white bars), and cyclohexane (grey bars).

To explain the near independence of the laser efficiency of the novel dyes on the solvent properties, the dependence of the laser action on the concentration was analyzed in 2,2,2-trifluoroethanol, ethanol, ethyl acetate, and cyclohexane. The experiments were performed increasing the dye concentration, whereas the other experimental parameters were kept constant. In this way, the dye concentration was varied to reach solutions with maximum optical density (for 1-cm path length) in the range 2.5−30. There is an exception, corresponding to the solutions in cyclohexane, in which the low solubility of the dyes prevents attaining concentrated solutions.

The lasing efficiencies of dyes P1Ac, P5Ac, P10Ac, and P15Ac in different solvents as a function of dye concentration are reported in Figures 3−6, respectively. The dye P3Ac, which had demostrated to be the most stable of all, including PM567,[13] was studied in four solvents, and the results obtained for both the energy conversion efficiency and the peak wavelength of the laser emission are reported in Table 3. As it was expected, for all of the analyzed solutions the lasing efficiency of the dyes increased significantly with the dye concentration following a complex behavior: First, the lasing efficiency increases rapidly with the dye concentration until a maximum value from solutions with optical density of ca. 12. From this point on, further increases in the dye concentration result in a slight decrease of the lasing efficiency or, depending on both the solvent nature and the length of the polymethylene chain, this laser parameter reaches a plateau. In addition, as can also be seen in Table 3, the peak wavelength of the laser emission of

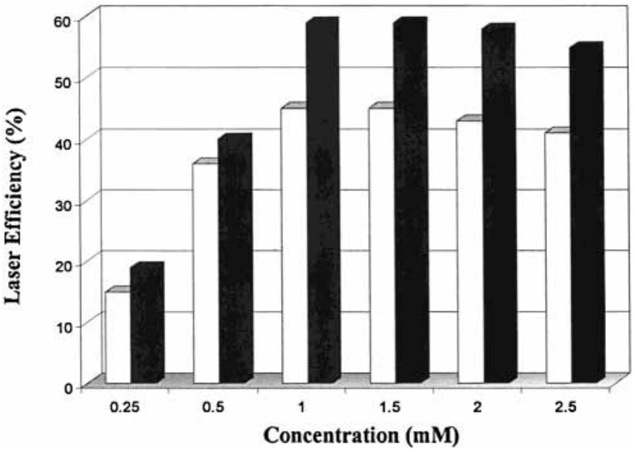

Figure 5. Lasing efficiency of the dye P10Ac as a function of the dye concentration in 2,2,2-trifluoroethanol (black bars) and ethanol (white bars).

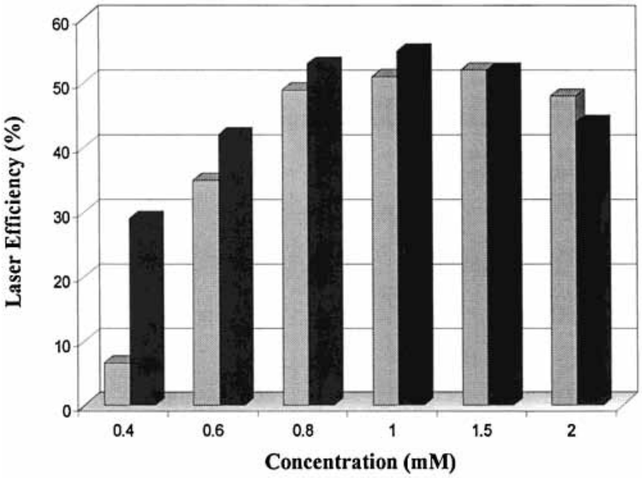

Figure 6. Lasing efficiency of the dye P15Ac as a function of the dye concentration in 2,2,2-trifluoroethanol (blak bars) and cyclohexane (grey bars).

TABLE 3: Laser Parameters[a] for the Dipyrromethene·BF$_2$ Dye P3Ac as a Function of the Dye Concentration in Different Solvents[b]

	F$_3$-ethanol[c]		ethanol		ethyl acetate		cyclohexane	
P3Ac (10^{-3} M)	eff (%)	λ_{max} (nm)	eff (%)	λ_{max} (nm)	eff (%)	λ_{max} (nm)	eff (%)	λ_{max} (nm)
0.15	11	547	9	548				
0.35	30	549	27	551	25	549	10	550
0.50	47	558	39	560	38	551	12	555
0.90	49	564	44	565	42	560	24	560
1.50	40	566	49	567	48	564	36	568
2.00	39	568	36	570	46	566		

[a] eff (energy conversion efficiency) and λ_{max} (peak wavelength of the laser emission). [b] Nd:KGW laser (second harmonic) pump energy = 5.5 mJ/pulse. [c] F$_3$-ethanol = 2,2,2-trifluoroethanol.

P3Ac shifts to lower energies as the dye concentration increases. This behavior is common with that of the other studied dyes, with independence on the nature of the solvent. This trend has been previously observed in the commercial dye PM567[11] and was related to the effect of reabsorption/reemission phenomena on the emission intensity, because the possiblity of exciting molecules by absorption of a photon previously emitted by another molecule in the medium depends on the overlapping between absorption and fluorescence spectra, which is affected by the dye concentration.[17]

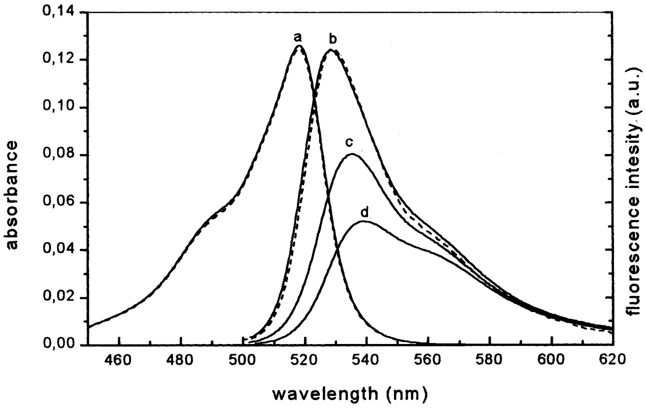

Figure 7. Absorption (a) and corrected fluorescence (b) spectra of diluted (2×10^{-6} M in 1-cm cuvette, dashed curves) and concentrated (2×10^{-3} M in 0.001-cm cuvette, solid curves) solutions of P5Ac in 2,2,2-trifluoroethanol. The fluorescence spectrum of the concentrated solution in (c) 0.01-cm and (d) 0.1-cm cuvettes are also included.

The actual effect of the solvent in the lasing efficiency can only be detected in moderately concentrated samples (optical density < 10) and follows the same dependence as that exhibited by PM567: the polar−protic nature of the solvent (2,2,2-trifluoroethanol and ethanol) improves the lasing efficiency of the dyes with respect to the values registered in polar nonprotic and apolar solvents (ethyl acetate and cyclohexane). Consequently, and in good agreement with the behavior of the dye PM567, very polar protic solvents such as 2,2,2-trifluoroethanol are recommended as the best liquid media for laser operation of these new dyes. In addition, for all of the selected solvents and in moderatly concentrated solutions, the lasing efficiency increases with the length of the polymethylene chain. However, the powerful influence of both the solvent and the 8-chain on laser action of the solute, because of its overall solvation ability, is progressively reduced as the concentration of the dye increases. Further increases of the dye concentration reduce significantly the dependence of the laser action on the nature of the 8-substitutent, resulting in a more irregular behavior.

To rationalize the observed results, we proceeded to characterize the photophysics of these P*n*Ac dyes in solutions with higher concentration. The shape of the absorption spectrum of P*n*Ac derivatives is independent of the dye concentration up to a maximum concentration of 2×10^{-3} M, as shown in Figure 7 for the case of P5Ac in 2,2,2-trifluoroethanol. Consequently, dipyrromethene·BF$_2$ dyes do not aggregate in the concentration range studied and in the solvents used in this study, clearly improving the lasing ability of these dyes with respect to rhodamine dyes. Indeed, the rhodamine aggregates are efficient quenchers of the fluorescence emission from monomers, leading to a diminution in the fluorescence quantum yield at these high dye concentrations.[20]

The fluorescence lifetimes of P*n*Ac dyes in a highly concentrated (10^{-3} M) dye solution (Table 4) are similar to those in a diluted solution (Table 1). This means that any additional (bimolecular) deactivation process from the S$_1$ excited state does not significantly take place in concentrated dye solutions. However, moderate changes in the fluorescence quantum yield values obtained in concentrated solutions (Table 4) with respect to those in more diluted solutions (Table 1) are observed (note that, as is mentioned in the Experimental Section and Methods, the estimated experimental error in the ϕ value recorded in the 0.001 cm cuvette is very high due to the difficulty in recording the absolute fluorescence intensity and these values must be considered as approximated). As observed in diluted solutions,

TABLE 4: Fluorescence Quantum Yield (ϕ) and Lifetime (τ) of Concentrated P*n*Ac Solutions (10^{-3} M) in 0.001-cm Pathway Cells[a]

	ϕ ($\pm$0.10)						τ ($\pm$0.05 ns)					
solvent	P1Ac[b]	P3Ac	P5Ac	P10Ac	P15Ac	PM567	P1Ac[b]	P3Ac	P5Ac	P10Ac	P15Ac	PM567
F_3-ethanol[c]	0.64	0.81	0.83	0.82	0.85	0.88	7.70	7.05	7.29	7.32	7.08	6.80
methanol	0.61	0.77	0.90	0.88	0.84	0.91	6.44	6.10	6.26	6.33	6.31	5.78
ethanol	0.60	0.78	0.84	0.80	0.70	0.83	6.58	6.09	6.27	6.35	6.11	5.88
acetone	0.54	0.89	0.87	0.89	0.75	0.87	7.04	6.14	6.18	6.39	6.17	6.01
ethyl acetate	0.60	0.85	0.90	0.92	0.75	0.83	6.90	5.96	6.21	6.11	6.12	5.99
cyclohexane	0.58	0.63	0.55	0.58	0.54	0.69	6.41	5.61	5.76	5.94	5.82	5.64

[a] Other photophysical parameters such as λ_{ab}, λ_{fl}, and f are not included in this table because they have the same values as those in diluted solutions (Table 1). Values of PM567 are also listed for comparison. [b] Dye concentration = 0.45×10^{-3} M in a 0.01-cm cuvette. [c] 2,2,2-Trifuoroethanol.

the P1Ac dye has the lowest fluorescence quantum yield, and for a common dye, the lowest ϕ value is reached in the apolar cyclohexane solvent.

The evolution of the ϕ value of the dye P15Ac with the solvent in the concentrated solutions is similar to that observed in the more diluted solutions. However, the ϕ values of concentrated P*n*Ac (with $n = 1$, 3, 5, and 10) solutions become independent of the solvent in polar-aprotic and protic media, supporting the poor solvent dependence of the laser efficiency in highly concentrated P*n*Ac solutions. Although we do not totally discard that the different ϕ values observed in concentrated and diluted solutions for P*n*Ac dyes could be partially influenced by the experimental error (keeping in mind the difficulty to record the absolute fluorescence intensity in the 0.001 cm cuvette), we can take into account other arguments to explain the nearly independence of the ϕ value of P1Ac, P3Ac, P5Ac, and P10Ac with the solvent in polar media: (1) An extra bimolecular deactivation process from the S_1 excited state in concentrated solution can be discarded because the τ value is independent of the dye concentration (in those samples where the reabsorption/reemission effects are minimized, that is, using a 0.001 cm cuvette). (2) A static quenching due to the aggregation of the dye in concentrated solutions is rejected because the molar absorption coefficient at any wavelength of all of the P*n*Ac dyes is concentration-independent. (3) An energy transfer from a S_1 excited molecule to the S_0 ground state of a second molecule would not affect the ϕ and τ values.[21] Moreover, the corresponding rate constant, calculated from the absorption and fluorescence spectral overlapping by means of the Förster equation,[22] is estimated to be in the magnitude order of 10^5 M^{-1} s^{-1} for P*n*Ac dyes. Thus, for the concentration range used in this work (up to 2×10^{-3} M), this phenomenon should not be competitive with the unimolecular deactivation processes. (4) The reabsorption/reemission effects in concentrated (10^{-3} M) solutions using the 0.001 cm cuvette are drastically reduced. Indeed, the fluorescence wavelength and lifetime using this cuvette are close to the corresponding values observed in diluted solution. Moreover, the diminution in the ϕ value by an increase in the reabsorption/reemission phenomena (i.e., increasing the pathway of the cuvette in the order 0.001, 0.01, and 0.1 cm, Figure 7) is observed to be similar in all studied systems, and this effect is nearly independent of the length of the substituent and of the solvent.

The above discussion reveals the difficulty in understanding this phenomenon, and at the present time, we cannot offer any nonspeculative explanation for this effect. Experimental and theoretical studies are currently in progress to gain more insights on the influence of the solvent on the photophysical behavior of these dipyrromethene·BF_2 dyes at high concentrations.

To analyze the photostability of these new dyes and to gain a better insight into their degradation mechanism, some studies were carried out under experimental conditions identical to that selected to irradiate the fluorophores when embedded in solid polymeric matrixes, which will allow comparison, in due time, of their stability in both liquid and solid phases under laser irradiation. Methyl isobutyrate was selected as the solvent because it mimics adequately the MMA monomer present in most of the solid polymeric formulations tested in our previous work. Because 8 μL was estimated to be the irradiated volume in the solid samples under the selected experimental conditions, capillary tubes into which the liquid solutions were incorporated offer the best geometry to reproduce the irradiated area in the solid samples, thus maintaining the same laser pump conditions in both cases.

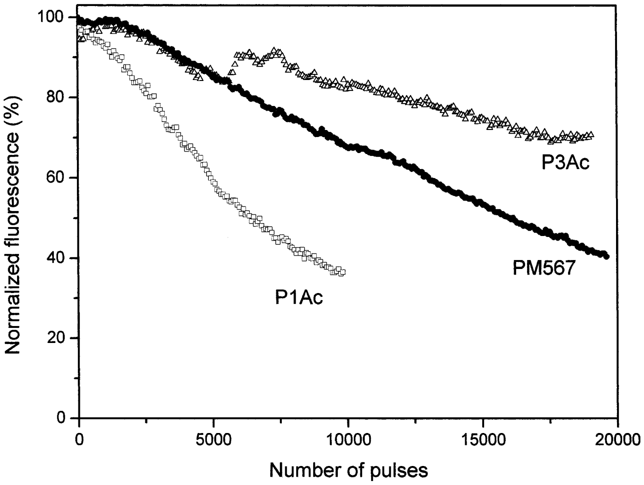

Figure 8. Normalized laser-induced fluorescence emission as a function of the number of pump pulses at 10-Hz repetition rate for the dyes P1Ac, P3Ac, and PM567 in methyl isobutyrate solution.

Although the optical quality of the capillary prevents laser emission from the dipyrromethene·BF_2 dyes tested, information about the amount of bleached molecules can be obtained by monitoring the decrease in laser-induced fluorescence intensity as a function of the number of pump laser pulses. The results obtained from the dyes P1Ac and P3Ac are plotted in Figure 8. To put these results in proper perspective, measurements were made of the degradation rate of the fluorescence emission from PM567 under the same experimental conditions. The concentrations of PM567, P1Ac, and P3Ac in methyl isobutyrate solution (1.5×10^{-3}, 0.45×10^{-3}, and 1.5×10^{-3} M, respectively) were adjusted so that the three samples had the same optical density (OD $\approx$ 18) at 534 nm.

The results indicate that P3Ac is more photostable than the reference dye PM567, while P1Ac is more easily photodegraded. This is in good agreement with results reached in our previous study on the photostability of the dipyrromethene·BF_2 dyes evaluated by continuous and simultaneous irradiation with a high-intensity ultraviolet lamp.[13] In addition, the analysis of the laser-induced fluorescence spectra before and after irradiation reveals that the photodegradation is an irreversible process leading to the generation of products in low concentration or without significant absorption at the laser irradiation wavelength because no new features appear in the spectrum registered after irradiation.

The results presented in this work indicate that appropriate chemical modifications in the pyrromethene chromophore can yield dyes with improved laser efficiency and photostability. Recently, we have completed sucessfully the incorporation of an unsaturated ester group at the end of the chain in position 8 instead of the acetate group of the structures shown in Figure 1, allowing the copolymerization of these new monomeric dipyrromethene$\cdot$BF$_2$ complexes with conventional monomers.[15] Consequently, our next step will be to incorporate these novel monomeric molecules into the main structure of polymeric matrixes, to develop even more efficient and stable solid-state dye lasers.

IV. Conclusions

The lasing efficiency of highly concentrated solutions of the new dipyrromethene$\cdot$BF$_2$ dyes herein studied becomes nearly independent of the dye concentration, the nature of the solvent, and the polymethylene chain length at position 8. Good correlations between the photophysical properties in more diluted solutions and the lasing characteristics in moderately concentrated solutions of these dyes have been observed in different solvents. The presence of the acetoxy group at the end of the chain at position 8 practically does not modify the photophysics of the chromophore, if this chain has five or more methylene groups. Consequently, the incorporation to the chromophore of a long enough chain ending with a polymerizable methacryloyloxy group would be a potential candidate for covalently linking dipyrromethene$\cdot$BF$_2$ dyes to a polymeric chain to develop solid-state dipyrromethene$\cdot$BF$_2$ active media for synthesizable dye lasers.

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