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EFFICIENT LASER ACTION FROM 1,3,5,7,8-PENTAMETHYLPYRROMETHENE-BF_2 COMPLEX

by

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We observed efficient laser action under flashlamp excitation at 546 nm from 1,3,5,7,8-pentamethylpyrromethene-BF_2 complex (PMP-BF_2), dissolved in ethanol. This new laser dye lased about 300% more efficiently than Coumarin 545. The fluorescence, absorption (S-S), and triplet-triplet absorption spectra of PMP-BF_2 were also recorded. To achieve greater water solubility the disodium 2,6-disulfonate derivative (PMPDS-BF_2) was prepared. PMPDS-BF_2 lases about 3/4 as efficiently as PMP-BF_2 when dissolved in water and showed some photoinstability; however, in methanol it was highly resistant to photodegradation.

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EFFICIENT LASER ACTION FROM 1,3,5,7,8-PENTAMETHYLPYRROMETHENE-BF_2 COMPLEX AND ITS DISODIUM 2,6,-DISULFONATE DERIVATIVE

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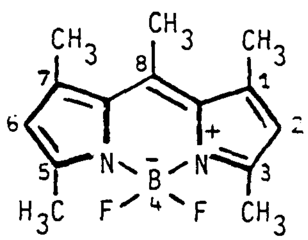
We observed efficient laser action under flashlamp excitation at 546 nm from 1,3,5,7,8-pentamethylpyrromethene-BF_2 complex (PMP-BF_2), dissolved in ethanol. This new laser dye lased about 300% more efficiently than coumarin 545. The fluorescence, absorption (S-S) and triplet-triplet absorption spectra of PMP-BF_2 were also recorded. To achieve greater water solubility the disodium 2,6-disulfonate derivative (PMPDS-BF_2) was prepared. PMPDS-BF_2 lases about 3/4 as efficiently as PMP-BF_2 when dissolved in water and showed some photo-instability; however, in methanol it was highly resistant to photodegradation.

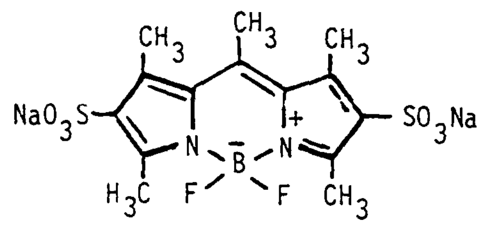
1. INTRODUCTION

Recently we reported that flashlamp excitation of 1,3,5,7-tetramethylpyrromethene-BF_2 complex (TMP-BF_2) ($2x10^{-4}$ M) in methanol brought about lasing emission (broad band BB) at 533 nm with about 10% greater efficiency than was obtained from coumarin 540A in ethanol (BB at 539 nm) [1]. Significantly, TMP-BF_2 had only a small amount of triplet-triplet (T-T) absorption over its fluorescence (laser action) spectral region. We speculated that even greater efficiency in laser action would be observed from pyrromethene complexes that show (1) extinction coefficients and quantum fluorescence yields greater than those for TMP-BF_2 [ϵ_{505} (C_2H_5OH) = 83,200 and Q_F = 0.80][2], (2) a further decrease in the overlap of T-T absorption and fluorescence spectral regions, and (3) an increased photostability. This led to the preparation of pentamethylpyrromethene-BF_2 complex (4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-s-indacene) (PMP-BF_2). Some of its laser and other spectroscopic properties were obtained.



Petamethylpyrromethene-BF_2 Complex

PMP-BF_2



Disodium Pentamethylpyrromethene-2,6-disulfonate-BF_2 Complex

PMPDS-BF_2

2. EXPERIMENTAL

2.1 The dye laser

We used the same small dye laser which had a dye cell 50 mm long and 2.5 mm diameter [3]. Again, the dye laser was used in the static mode (the dye solution not circulating). The absence of an accumulation of detectable amounts of decomposition products in the stagnant solution was evidence for a high order of the laser dye photostability. To record laser output energies, we used a Scientech model 365 power/energy meter.

2.2 The spectroscopic equipment

We used the same spectroscopic equipment to measure the fluorescence spectrum of PMP-BF_2 as in [3]. Also, the same spectroscopic equipment was used as in [3] to record the T-T absorption (triplet optical density OD_T)

spectra, employing the 496.5 nm line from an ion argon cw laser. The conventional singlet-singlet (S-S) absorption spectrum [ε_{492} (CH_3OH) = 85,200] was recorded with Cary 17 and Varian SuperScan 3 UV/visible spectrophotometers.

To obtain triplet extinction coefficients $\varepsilon_T(\lambda)$ from the measured $OD_T(\lambda)$ values we employed McClure's method [4-6]. Because of the limited solubility of PMP-BF_2 in ethanol, we used 2-methyltetrahydrofuran as a glassy solvent.

2.3. The laser dyes and chemicals

The synthesis of PMP-BF_2 and the disodium salt of 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonic acid-BF_2 complex (PMPDS-BF_2) will be reported elsewhere. Coumarin 545 was obtained from Exciton and rhodamine 6G from the Eastman Kodak Company. Ethanol was purchased from the U.S. Industrial Company, 2-methyltetrahydrofuran from Lancaster Synthesis, and N,N-dimethylformamide from the Aldrich Chemical Company.

3. RESULTS AND DISCUSSION

3.1 Pentamethylpyrromethene-BF_2 complex

In figure 1 we present the energy output ΔE (in mJ) of a 1.5×10^{-4} molar solution of PMP-BF_2 in ethanol as a function of flashlamp pump energy E (in J). In the same figure, we also show the energy output of a 2×10^{-4} molar solution of coumarin 545 in ethanol and a 2×10^{-4} molar solution of rhodamine 6G also dissolved in ethanol. PMP-BF_2 lases BB at 546 nm, coumarin 545 at 546 nm, and rhodamine 6G at 595 nm. From Figure 1 it is apparent that PMP-BF_2 lases about 300% more efficiently than coumarin 545 and about 20% less efficiently than rhodamine 6G. PMP-BF_2 was about as photostable as rhodamine 6G.

Figure 2 shows the fluorescence, S-S absorption and T-T absorption of PMP-BF_2. A striking feature is the exceptionally low value of the triplet extinction coefficient $\epsilon_T \sim 1x10^3$ L/mole cm over the laser action spectral region.

In a comparison evaluation with acridine orange (Q_F = 0.46) fluorescense quantum yields (Q_F) were obtained for PMP-BF_2 (0.73) PMPDS-BF_2 (0.98) and TMP-BF_2 (0.83, compare 0.80 [2]).*

3.2 Disodium Pentamethylpyrromethene-2,6-disulfonate-BF_2-Complex (PMPDS-BF_2)

PMP-BF_2 was partially soluble in ethanol/water mixtures and other aqueous solvents, but had limited solubility in water only. PMPDS-BF_2 was readily soluble in water, but showed poor photostability. It showed laser action BB at 555 nm that was about 50% as efficient as that obtained from PMP-BF_2. The salt dissolved in dimethylformamide showed greater photostability and lased BB at 577 nm with about 50% of the efficiency for PMP-BF_2. In methanol PMPDS-BF_2 ($2x10^{-4}$ M) lased at 551 nm. A comparison of the laser energy output Δ E of ethanol solutions of selected laser dyes as a function of flashlamp pump energy E, figure 1, shows PMPDS-BF_2 to be about 75% as efficient as PMP-BF_2 in ethanol. In methanol PMPDS-BF_2 was vastly superior to rhodamine 6G in photostability.

3.3 Discussion

Our experimental results on the lasing efficiency of PMP-BF_2 and PMPDS-BF_2 places these new laser dyes and TMP-BF_2 among the most impressive laser dyes known. Nevertheless, we are surprised that they did not lase with even greater efficiency. From Figure 2 it follows that PMP-BF_2 is the dye

* We are indebted to Dr. Scott Whittenburg for these Q_F determinations.

with the lowest $\varepsilon_T(\lambda_{las})$ of any laser dye known [6]. The prolonged laser action efficiency of these three dyes, TMP-BF_2, PMP-BF_2, and PMPDS-BF_2, can be attributed to a combination of their high extinction coefficients, moderately high fluorescence quantum yields, minimal S-S and T-T absorption in the fluorescence spectral region, and superior photostability in selected solvents. Photodegradation of PMP-BF_2 from flashlamp irradiation was not detected. Continuous irradiation of PMP-BF_2 (10^{-4} M) in methanol by a Westinghouse sunlamp (275 w) at a distance of about 20 cm. from the flask brought about the disappearance of fluorescence after one week. In a similar experiment in which methanol as solvent was replaced by methylene chloride fluorescence had not disappeared after one month. To obtain increased prolonged power efficiency tailor made derivatives of the pyrromethene-BF_2 complex that offer further improvement in these characteristic features are sought.

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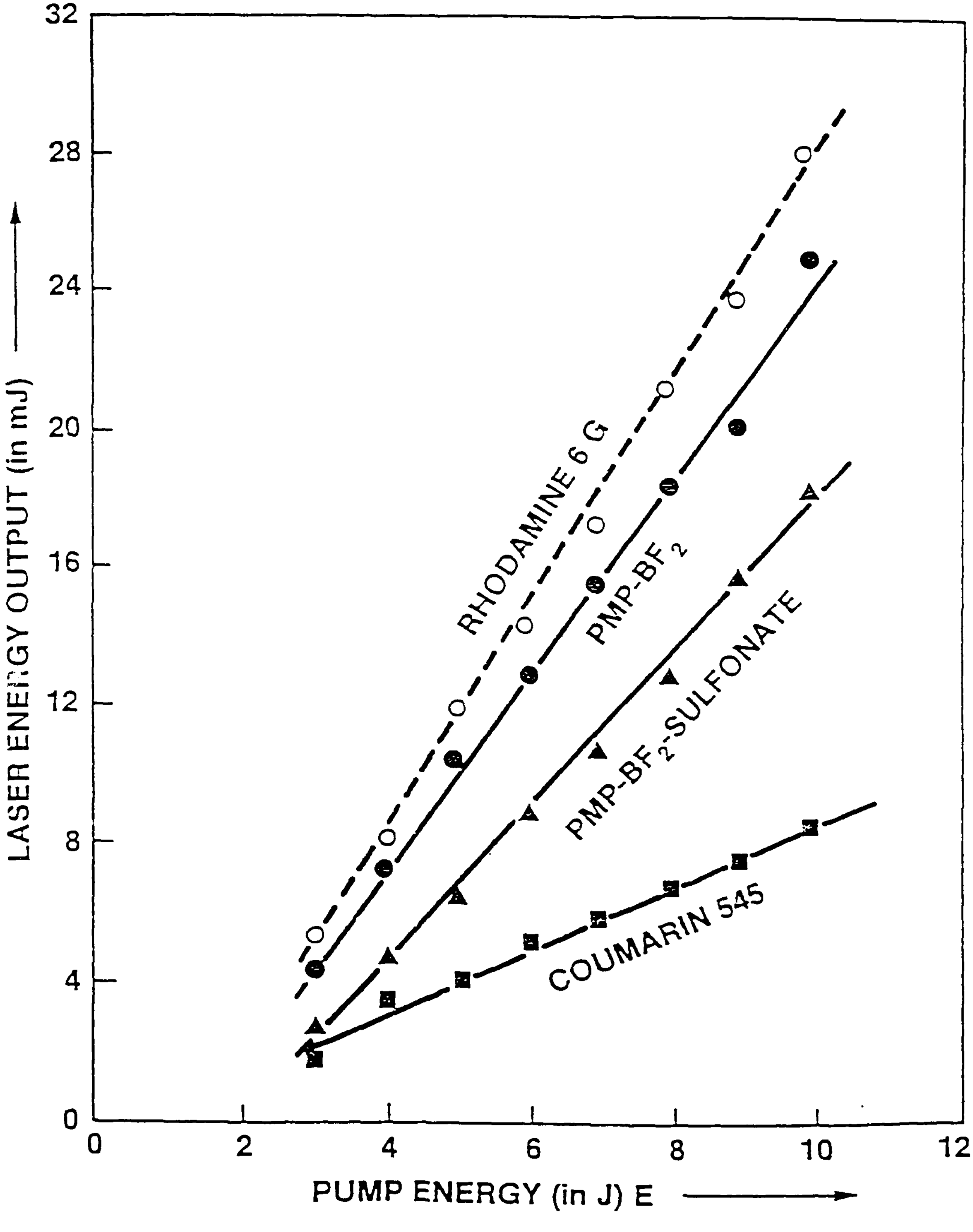
Figure 1.

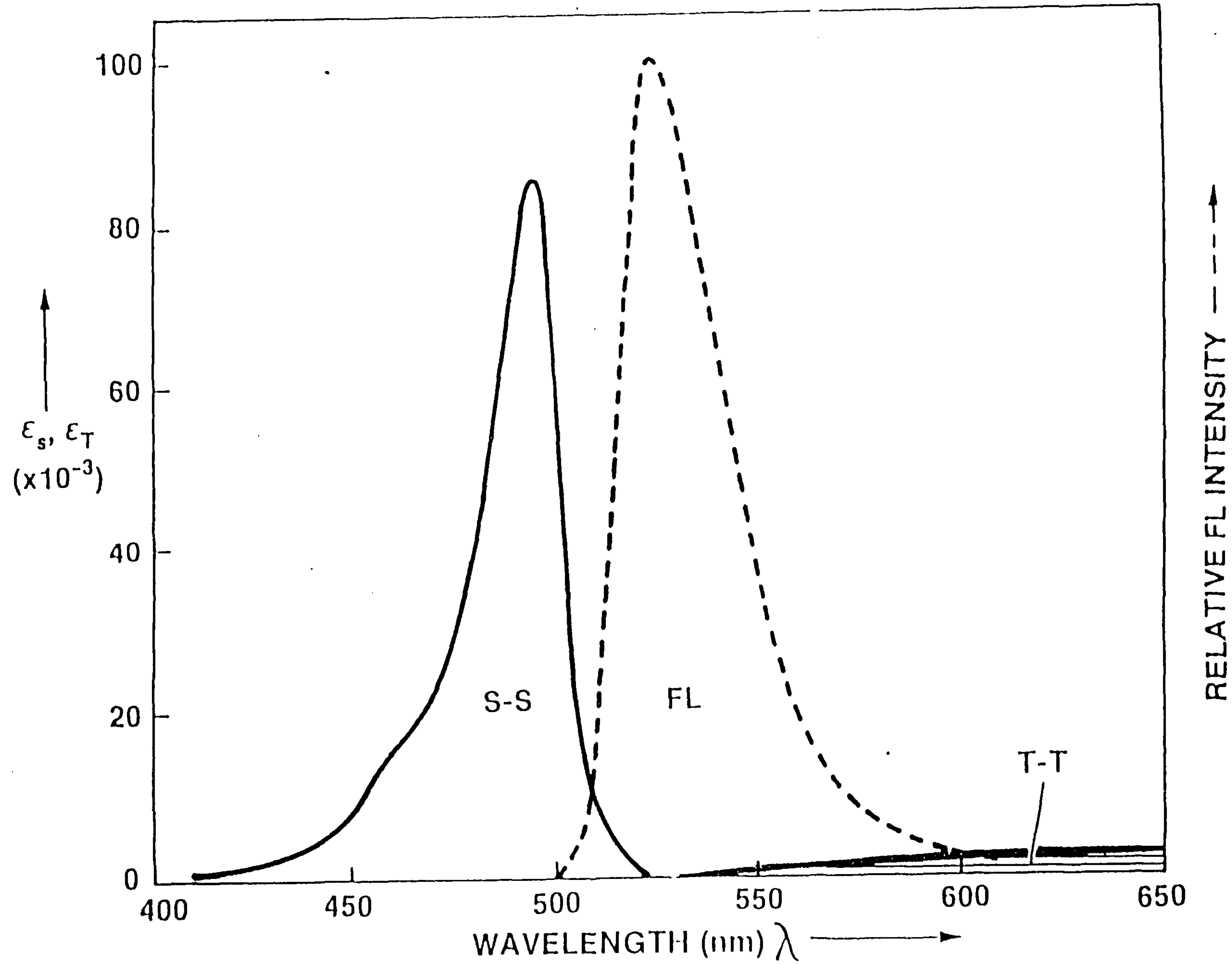
Laser energy output ΔE (in mJoule) as a function of energy E (in Joule) of a 1.5×10^{-4} molar solution of te pentamethylpyrromethene-BF_2 complex (PMP-BF_2) dissolved in ethanol, a 2×10^{-4} molar solution of Coumarin 545 dissolved in ethanol, a 2×10^{-4} molar solution of Rhodamine 6G dissolved in ethanol, and a 2×10^{-4} molar solution of pentamethylpyrromethene-BF_2 sulfonate (PMP-BF_2-sulfonate) also dissolved in ethanol.



LASER ENERGY OUTPUT (in mJ)
PUMP ENERGY (in J) E
RHODAMINE 6 G
PMP-BF 2
PMP-BF 2-SULFONATE
COUMARIN 545
32
28
24
20
16
12
8
4
0
0
2
4
6
8
10
12

Figure 2.

Absorption (S-S) and fluorescence Fl spectra of pentamethylpyrromethene-BF_2 complex (PMP-BF_2) dissolved in ethanol. The T-T absorption spectrum was recorded at 77 K, employing a $1x10^{-4}$ molar solution of 2-methyltetrahydrofuran as a glassy solvent.


εs, εT
(x10^-3)
100
80
60
40
20
0
400
450
500
550
600
650
WAVELENGTH (nm) λ
S-S
FL
T-T
RELATIVE FL INTENSITY

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