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Laser action from 2,6,8-position trisubstituted 1,3,5,7-tetramethylpyrromethene-BF<sub>2</sub> complexes: part 1

Theodore G. Pavlopoulos, Joseph H. Boyer, Mayur Shah, Kannappan Thangaraj, and Mou-Ling Soong

Theodore Pavlopoulos is with U.S. Naval Ocean Systems Center, Marine Sciences & Technology Department, San Diego, California 92152; the other authors are with University of New Orleans, Chemistry Department, New Orleans, Louisiana 70148.

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Of the four new pyrromethene derivatives studied, 1,3,5,7,8-pentamethyl-2,6-diethylypyrromethene-BF<sub>2</sub> complex lased ~3 times more efficiently than rhodamine 560 under flashlamp excitation.

For obtaining efficient laser action under flashlamp excitation, the coumarin (blue to yellow/green) and xanthene (yellow to red spectral region) laser dyes are presently the most widely used. Among the xanthene laser dyes, the benchmark of laser dyes in efficiently and photostability is rhodamine 6G. This dye has been known since 1967<sup>1</sup> and was found by trial and error.

Recently, laser action under flashlamp excitation was reported from 1,3,5,7-tetramethylpyrromethene-BF<sub>2</sub> complex 1 (TMP-BF<sub>2</sub>) and 1,3,5,7,8-pentamethylpyrromethene-BF<sub>2</sub> complex 2 (PMP-BF<sub>2</sub>). TMP-BF<sub>2</sub> lased broadband (BB) somewhat more efficiently than coumarin 545A at 533 nm,<sup>2</sup> and PMP-BF<sub>2</sub> lased BB ~3 times more efficiently than coumarin 545 at 546 nm. To change the spectral and, therefore, the laser action properties of a pyrromethene-BF<sub>2</sub> complex (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene), we performed substitutions in the 2-, 6-, and 8-positions of the pyrromethene-BF<sub>2</sub> molecule while maintaining the four methyl groups in the 1-, 3-, 5-, and 7-positions.

For testing, the same small dye laser was used as in Ref. 4. Its highest input energy was 10 J from an EG&G FX139C-2 flashlamp, producing a pulse ~600 ns long at the halfwidth and having an ~200-ns rise time. The laser output energy was measured with a Scientech model 365 power/energy meter. The spectroscopic equipment used to measure the triplet extinction coefficients \( \epsilon_T \) of the new laser dyes was the same as in Ref. 5. McClure's method was used.<sup>6</sup> The fluorescence spectra and quantum fluorescence yields \( Q_F \) were measured with a Perkin-Elmer Corp. LS-5B luminescence spectrometer. The visible/UV absorption spectra of the dyes were recorded with a Cary 17 spectrophotometer.

The synthesis of the four substituted pyrromethene-BF<sub>2</sub> complexes 3-6 will be reported elsewhere. Rhodamine 575 was purchased from Exciton and rhodamine 110 (rhodamine 560) from Eastman Kodak Co. Methanol (99.5% spectroscopic grade) was obtained from Aldrich Chemical Co., ethyl alcohol (190 proof punctionis) from Quantum Chemical Corp., USI Division, and 2-methyltetrahydrofuran from Lancaster Synthesis, Ltd.

### Table I. Quantum Fluorescence Yield \( Q_F \), Fluorescence Intensity Maximum \( \lambda_{max} \), Absorption \((S-S)\) Intensity Maximum \( \lambda_{as} \) \((S-S)\) Absorption (Extinction) Coefficient \( \epsilon_\lambda \) and Laser Action Wavelength \( \lambda_{la} \) of the Pyrromethene Complexes 3-6

<table>
<thead>
<tr>
<th>Complex</th>
<th>( Q_F )</th>
<th>( \lambda_{as} (\text{nm}) )</th>
<th>( \lambda_{opt} (\text{nm}) )</th>
<th>( \epsilon_\lambda )</th>
<th>( \lambda_{la} (\text{nm}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.70</td>
<td>544</td>
<td>518</td>
<td>4.83</td>
<td>566</td>
</tr>
<tr>
<td>4</td>
<td>0.83</td>
<td>547</td>
<td>518</td>
<td>4.86</td>
<td>567</td>
</tr>
<tr>
<td>5</td>
<td>0.35</td>
<td>530</td>
<td>493</td>
<td>5.00</td>
<td>556</td>
</tr>
<tr>
<td>6</td>
<td>0.31</td>
<td>533</td>
<td>494</td>
<td>4.62</td>
<td>559</td>
</tr>
</tbody>
</table>

rhodamine 575. HMP-BF₂ and rhodamine 575 showed comparable photostability.

1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene-BF₂, complex 4 exhibited efficient laser action in a 2 x 10⁻¹⁴ M solution in ethyl alcohol. In methyl alcohol, it lased with about 2/3 the efficiency shown in the ethyl alcohol solution.

From the experimental results shown in Fig. 1, complex 4 lased ~3 times more efficiently than rhodamine 560 and ~50% more efficiently than rhodamine 575. Compared with rhodamine 6G, it lases ~10% more efficiently. Complex 4 and rhodamine 575 showed about the same photostability.

To obtain the eₔ values, we used the 514.5-nm line from an ion-argon cw laser for excitation. Noteworthy is the exceptionally low eₔ value of complex 4 over the fluorescence (laser action) spectral region. This eₔ (567) = 1.5 x 10³ liter/mole cm was similar to that obtained for HMP-BF₂ (reported in Ref. 3) and appears to be the key factor in the remarkable laser action properties of the pyrromethene-BF₂ laser dyes. We have eₔ (570) = 7.2 x 10³ liter/mole cm for rhodamine 560 (Ref. 7) and eₔ (580) = 6.6 x 10³ liter/mole cm for rhodamine 575. It is probable that complex 4 lases with a higher efficiency than HMP-BF₂ because of its higher QF value.

1,3,5,7-tetramerthyl-2,6-diethyloxy-2,6-dinitro-pyrromethene-BF₂ complex 5. This dye lased with considerably less efficiency than dyes 3 and 4, which is not surprising considering its low QF value. Nevertheless, this new dye lases with higher efficiency than rhodamine 560 (Fig. 1). The data in this figure were obtained from a 2 x 10⁻⁴ M solution in methyl alcohol, where the dye lased ~10% more efficiently than observed from a solution in ethyl alcohol.

1,3,5,7,8-pentamethyl-2,6-dinitropyromethene-BF₂ complex 6. This compound is an oddity among laser dyes, because it exhibits laser action under flashlamp excitation—although not very efficiently. It is well known that aromatic nitrocompounds rarely show fluorescence; however, in a few cases weak fluorescence has been noted. Heretofore, nitrocompounds were not known to show laser action under flashlamp excitation. Complex 6 was routinely prepared in investigating P-BF₂ chemistry. Because it showed some fluorescence (QF = 0.31), we tested its ability to lase. Photochemically, the compound was unstable. Therefore, the values for QF and λₔ shown in Table I are not too accurate.

In summary, of the four new dyes we tested, complex 4 easily surpassed rhodamine 560 in efficiency and rivals rhodamine 6G as one of the most efficient of the laser dyes. Other 2,6,8-position trisubstituted pyrromethene-BF₂ complexes should either lase in different spectral regions or possess different laser/physical properties, e.g., efficiency, solubility (water), and photostability. Employing these new laser dyes should result in improved performance (increased average power output) in dye lasers.

Over the last few years, it has been stated that dye lasers do not have much of a future compared with the exceptional performance of the newly developed solid state devices like Ti:sapphire and diode lasers. This may be the case for small dye lasers. However, when tunability, high average power operation, and visible laser light output at low cost are required, a large flashlamp pumped dye laser operating with improved laser dyes should be difficult to beat.

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References


