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Pyrromethene–BF_2 Complexes as Laser Dyes:1.

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ABSTRACT

Condensations between 3-X-2,4-dimethylpyrroles (X = H, CH_3, C_2H_5, and $CO_2C_2H_5$) and acyl chlorides gave derivatives of 3,5,3',5'-tetramethylpyrromethene (isolated as their hydrochloride salts): 6-methyl, 6-ethyl, 4,4',6-trimethyl, 4,4'-diethyl-6-methyl, and 4,4'-dicarboethoxy-6-ethyl derivatives for conversion on treatment with boron trifluoride to 1,3,5,7-tetramethylpyrromethene–BF_2 complex (TMP–BF_2) and its 8-methyl (PMP–BF_2), 8-ethyl, 2,6,8-trimethyl (HMP–BF_2),2,6-diethyl-8-methyl (PMDEP–BF_2), and 2,6-dicarboethoxy-8-ethyl derivatives. Chlorosulfonation converted 1,3,5,7,8-pentamethylpyrromethene–BF_2 complex to its 2,6-disulfonic acid isolated as the lithium, sodium (PMPDS–BF_2), potassium, rubidium, cesium, ammonium, and tetramethylammonium disulfonate salts and the methyl disulfonate ester. Sodium 1,3,5,7-tetramethyl-8-ethylpyrromethene-2,6-disulfonate–BF_2 complex was obtained from the 8-ethyl derivative of TMP–BF_2. Nitration and bromination converted PMP–BF_2 to its 2,6-dinitro- (PMDNP–BF_2) and 2,6-dibromo- derivatives. The time required for loss of fluorescence by irradiation from a sunlamp showed the following order for P–BF_2 compounds (10^{-3} to 10^{-4} M) in ethanol: PMPDS–BF_2, 7 weeks; PMP–BF_2, 5 days; PMDNP–BF_2, 72 h; HMP–BF_2, 70 h; and PMDEP–BF_2, 65 h. Under similar irradiation PMPDS–BF_2 in water lost fluorescence after 55 h. The dibromo derivative was inactive, but each of the other pyrromethene–BF_2 complexes under flashlamp excitation showed broadband laser activity in the region λ 530–580 nm. In methanol PMPDS–BF_2 was six times more resistant to degradation by flashlamp pulses than was observed for Rhodamine-6G (R-6G). An improvement (up to 66%) in the laser power efficiency of PMPDS–BF_2 (10^{-4} M in methanol) in the presence of caffeine (a filter for light <300 nm) was dependent on flashlamp pulse width (2.0 to 7.0 μsec).

INTRODUCTION

In 1984, less than two decades after its discovery, a review described the dye laser as one of the most useful and practical of tunable coherent sources; it became serviceable over the spectral region 300 to 1300 nm by the frequency agility of over 600 laser dyes, including cyanine, xanthene (e.g., rhodamine and fluoroscein), triarylmethane, acridine, azine, chlorophyll, polybenzenoid, coumarin, quinolone, oxazole, pyrazoline, and furan derivatives. Rhodamine dyes, for example, R-6G, gave laser activity over the spectral range 530–710 nm and were cited as the most important and most efficient group of all laser materials [1]. Laser dye activity was presumed to reflect a causal relationship with various ancillary properties, including photostability, solubility and other interactions with solvent, fluorescence quantum yield, molar extinction

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of absorption, and minimal overlap of fluorescence with onset of absorption spectral regions (S–S) and triplet–triplet (T–T) [1,2]. Bathochromic and hyperchromic shifts were introduced by the substitution of auxochromic and antiauxochromic groups, but this benefit was often offset by the ability of certain groups, for example, nitro, cyano, and heavy atoms, to quench laser activity [1–3]. Since the known dyes were each deficient in one or more properties the search for new stuctures to offer superior performance standards was undertaken.

A recognition that the family of *syn*-bimanes **A** offered examples fulfilling many of the auxiliary conditions led to our discovery of their laser activity at 500–530 nm. Four bimanes **A1–4** were as efficient (80–100%) as coumarin 30 (coumarin 515) (laser activity in the same range) and showed improvements in photostability and solvent effects, and diminished overlap between fluorescence and absorption spectral regions (S–S and T–T) [3]. More recently the properties of certain pyrromethene–BF_2 complexes **10** and **11** also afforded candidates for laser dyes. We discovered laser activity at 533 nm from 1,3,5,7-tetramethylpyrromethene–BF_2 complex (TMP–BF_2) **10a** in methanol in 1988 [4]. Superior activity was rapidly discovered in 1,3,5,7,8-pentamethylpyrromethene–BF_2 complex (PMP–BF_2) and its 2,6-dimethyl (HMP–BF_2), 2,6-diethyl (PMDEP–BF_2), and 2,6-disulfonic acid (isolated as the disodium salt PMPDS–BF_2) derivatives [5,6]. Modest laser activity in the 2,6-dinitro derivative (PMDNP–BF_2) was exceptional [6] insofar as similar activity was not known for other dyes containing a nitro substituent. We report here on the synthesis of pyrromethene–BF_2 complexes and further discovery and development of them as laser dyes.

BACKGROUND INFORMATION

A generally efficient condensation between an α-acylpyrrole and a pyrrole unsubstituted at an α-position was developed as a classical synthesis of the pyrromethene precursors to porphyrins [7]. More recently the condensation reaction accommodated investigations on the pyrromethene chromophore and fluorophore in tailored derivatives that included P–BF_2 compounds [4, 5, 8, 9]. When expressed in a simplified version $[R_2N(CR{=}CR)_n CR{=}NR_2]^+$ the cationic chromophore of a cyanine dye [1] included the pyrromethene cation (n = 4); however, the role of the latter has been limited to P–BF_2 compounds for laser activity [4–6], fluorescent probes for medical and biological research [10], and photodynamic therapy for cancer [11].

The unsubstituted pyrromethene **B1** was unstable above −30°C and gave a yellow solution (λ_{max} 400 nm) in *n*-pentane moistened with methanol at −60°C [12]. Extensive alkylation brought about a bathochromic shift from 400 nm (log ϵ 4.35) for 3,5-dimethylpyrromethene **B2** in pentane [12] to 447 nm (log ϵ 4.53) for 3,5,3′,5′-tetramethyl-4,4′-diethylpyrromethene **B3** in ethanol [13]. Further bathochromic and hyperchromic shifts to 488 nm (log ϵ 5.00) and 528 nm (log ϵ 4.71) revealed related cationic pyrromethene chromophores for the hydrobromide and BF_2–complex derivatives **C** and **D** of the pyrromethene **B3** [10, 14, 15]. The band near 440 nm was shown to be polarized parallel to the long axis of the chromophore, whereas shorter wavelength bands were shown to be perpendicular to the long axis [16].

The nearly identical fluorescence quantum yields Φ 2.6 × 10^{-4} and 4.3 × 10^{-4} in ethanol, were descriptive of comparable fluorophores for 3,5,3′,5′-tetramethyl-4,4′-diethylpyrromethene **B3** and its hydrobromide **C** [17]. To account for these low quantum yields fluorescence quenching in a pyrromethene was variously correlated with proton tunneling [9], proton exchange between nitrogen atoms in the **Z** syn conformation, and photoisomerization at the exocyclic double bond [18, 19]; however, a deactivation of a pyrromethene S_1 state via exciplex formation, a process well known for polyamines [20], was not incompatible with the available information.

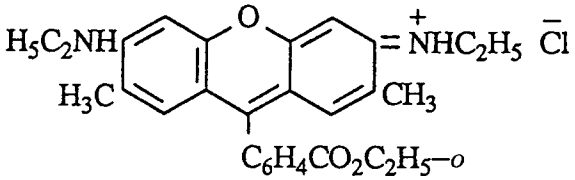
Chelation of boron difluoride by a pyrromethene bidentate anion was achieved by a treatment of a pyrromethene with boron trifluoride. Characterization of various pyrromethene–BF_2 (P–BF_2) derivatives included large extinction coefficients log $\epsilon \sim 5$ (comparable to the extinction coefficient shown for unchelated pyrromethene cations) and fluorescence quantum yields Φ 0.33 to 0.81 [14, 17]. A similar value Φ 0.31 was obtained for the corresponding $B(C_2H_5)_2$ complex **E** [17]. This thousandfold enhancement in fluorescence that was brought about by boron chelation with the pyrromethene bidentate ligand was reminiscent of a similar fluorescence enhancement that was recently attributed to the chelation of zinc dichloride by the diamino moieties in the nonfluorescent 9,10-bis(((2-(dimethylamino)ethyl)methylamino)methyl)anthracene **F**; fluorescence quenching in the tetramine **F** was attributed to exciplex formation [21].

Strong fluorescence in a bidentate BF_2 complex with nitrogen and/or oxygen atoms as ligand termini was afforded by P–BF_2 derivatives **10** and **11** (Scheme 1) and by the recently patented dicarbonyl chelates **G** (laser activity range 455–635 nm) [22]. Although fluorescence was noted for BF_2 complexes **H** [23] and **J** [24] from 1-amino-7-imino-1,3,5-cycloheptatrienes and 8-amino- and 8-hydroxyquinoline these complexes were not examined for laser activity. BF_2 complexes with less unsaturation, for example, the hexahydropyrromethene–BF_2 complex **K** with λ_{max} (C_2H_5OH) 320 nm (log ϵ 4.4) [25], were not examined for fluorescence (<400 nm) and laser activity. The hypsochromic shift ~120 nm relating P–BF_2 derivatives (λmax ~440 nm) and the

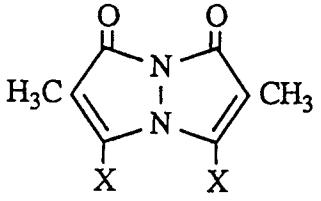
partially reduced structure **K** was typical of other cyanine dyes [1]. The structure assignment for PMP–BF_2 **10b** was supported by an X-ray crystallographic analysis [26].

Chelation of aluminum dichloride by a pyrromethene bidentate ligand gave an unstable orange solid; light absorption and emission data were not reported [25]. A different type of pyrromethene (P)–metal (M) chelate (P_2M) afforded by tetracoordinate zinc, nickel, and copper showed weak fluorescence above 500 nm ($\Phi \sim 10^{-3}$) [16, 18]. Pyrazoboles (dimeric 1-borylpyrazole chelates of dialkylboron (BR_2)) and the BF_2 complexes of 1,2,3,4-tetrahydro-1,10-phenanthroline were not fluorescent [27, 28].

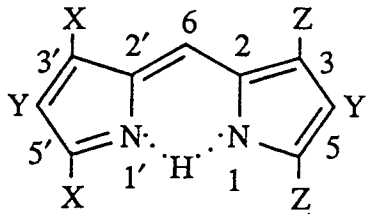
Laser activity was reported for a "boratriazinium" salt **L** and a "boradiazinium" salt **M**; however, preparations and structure characterizations for these molecules have not appeared in the literature [29].



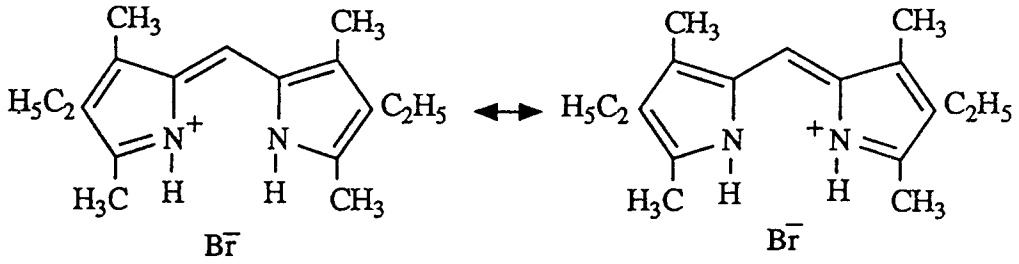
R - 6G•HCl



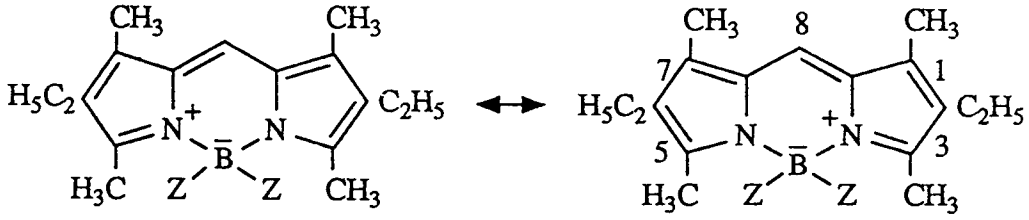
A1 X = $CH_2O_2CCH_3$
A2 X = $CH_2P(O)(OCH_3)_2$
A3 XX = $CH_2C(CO_2C_2H_5)_2CH_2$
A4 XX = $CH_2C(CO_2CH_3)_2CH_2$



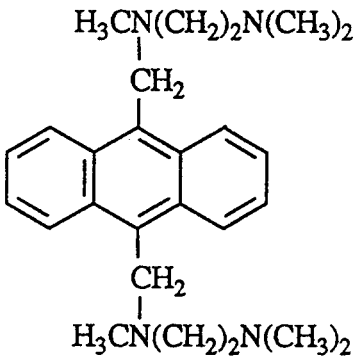
B1 X = Y = Z = H
B2 X = Y = H, Z = CH_3
B3 X = Z = CH_3, Y = C_2H_5



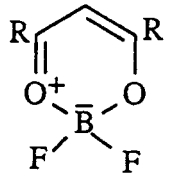
C



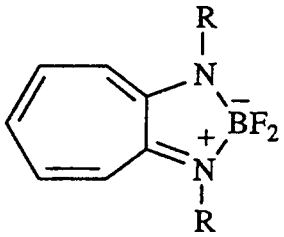
D Z = F
E Z = C_2H_5



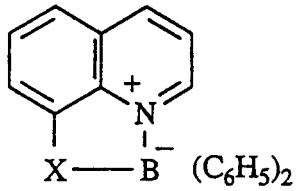
F



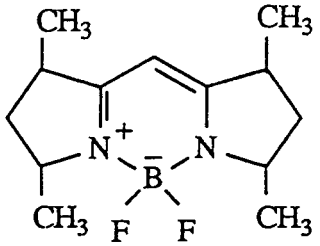
G R = $(CH{=}CH)_nAr$



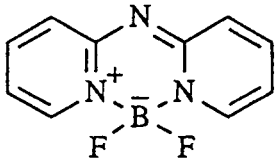
H



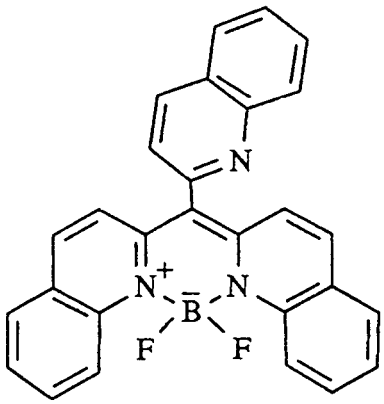
J X = NR, O



K



L

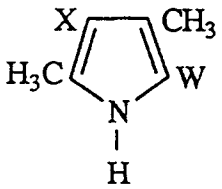


M

RESULTS AND DISCUSSION

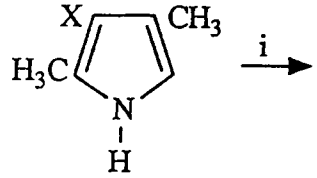
Synthesis

A general pathway shown in Scheme 1 was followed for the conversion of pyrroles **1–4** to P–BF_2 **10b–f**. Kryptopyrrole **3** was commercially available; the pyrroles **1**, **2**, and **4** were obtained by adapting reported procedures for the hydrolysis and decarboxylation of diethyl 3,5-dimethylpyrrole-2,4-dicarboxylate **5** [30, 31] and ethyl 3,4,5-trimethylpyrrole-2-carboxylate **6** [32, 33] and the thermolysis of *tert*-butyl 3,5-dimethyl-4-carboethoxypyrrole-2-carboxylate **7** [34]. In reactions with appropriate acyl chlorides pyrroles **1–4** afforded the unstable intermediate pyrromethene derivatives **9b–f**. These intermediates were isolated as hydrochloride salts and immediately converted, sometimes without purification, to their P–BF_2 derivatives **10b–f**. As C-substitution increased the pyrromethene hydrochlorides became more stable and more amenable to isolation and characterization. According to a previously reported procedure 2-formyl-3,5-dimethylpyrrole **8** and 2,4-dimethylpyrrole **1** gave unisolated 3,5,3′,5′-tetramethylpyrromethene **9a** [14].

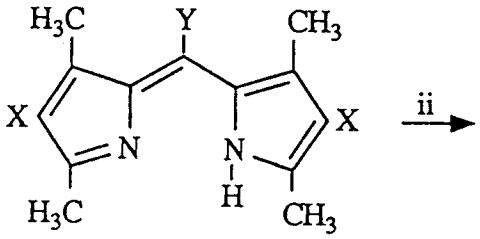


5 W = X = $CO_2C_2H_5$
6 W = $CO_2C_2H_5$, X = CH_3
7 W = $CO_2C(CH_3)_3$, X = $CO_2C_2H_5$
8 W = CHO, X = H

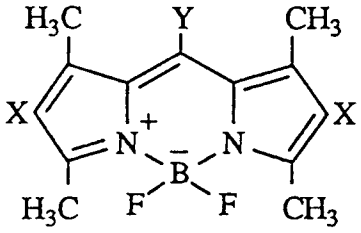
In a typical chelation the hydrochloride salt of 3,5,3′,5′-tetramethylpyrromethene **9a** gave TMP–BF_2 **10a** by treatment with boron trifluoride in the presence of triethylamine [14], or diisopropylethylamine (preferred) [16]. A similar conversion of the pyrrole derivative **4** afforded diethyl 1,3,5,7-tetramethyl-8-ethylpyrromethene-2,6-dicarboxylate-BF_2 complex **10f** [25]. To extend the method to the preparation of PMP–BF_2 **10b**, the precursor 3,5,3′,5′,6-pentamethylpyrromethene **9b** was obtained directly from the treatment of 2,4-dimethylpyrrole **1** with acetyl chloride. A similar preparation afforded the 8-ethyl- derivative **10c** from the precursor 3,5,3′,5′-tetramethyl-6-ethylpyrromethene **9c**, which was in turn obtained from 2,4-dimethylpyrrole **1** and propionyl chloride. Complete C-substitution in a pyrromethene and its BF_2–complex was rarely encountered. In addition to the complex **10f** other examples were found in chelations affording 1,2,3,5,6,7,8-heptamethyl- and 1,3,5,7,8-pentamethyl-2,6-diethyl-pyrromethene–BF_2 complexes (HMP–BF_2 and PMDEP–BF_2) **10d, 10e.**



1–4



9a–f



10a–f

i = YCOCl; ii = $BF_3{\cdot}O(C_2H_5)_2$, R_3N

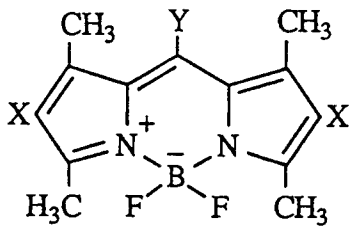
1 X = H; **2** X = CH_3; **3** X = C_2H_5; **4** X = $CO_2C_2H_5$

a X = Y = H; **b** X = H, Y = CH_3; **c** X = H, Y = C_2H_5;

d X = Y = CH_3; **e** X = C_2H_5, Y = CH_3;
f X = $CO_2C_2H_5$, Y = C_2H_5

11k, m $\xleftarrow{iv}$ **10b** $\xrightarrow{iii}$ **11a–j**

iii = $ClSO_3H$, base; iv = HNO_3 (**k**); Br_2 (**m**)



11 a–m, Y = CH_3; 11n

a–e X = SO_3M, M = H (**a**), Li (**b**), Na (**c**), K (**d**), Rb (**e**), Cs (**f**);

g X = SO_3 NH_4; **h** X = SO_3 $N(CH_3)_4$; **j** X = SO_3CH_3; **k** X = NO_2; **m** X = Br; **n** X = SO_3Na, Y = C_2H_5

SCHEME 1

Electrophilic sulfonation in the 2- and 6- positions was reported for the complex **10a** [15]. A similar substitution was initially useful in the preparation of the disodium (PMPDS–BF_2) and dimethyl 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate–BF_2 complexes **11c** and **11j**. Straightforward modifications led to the formation of other dimetal (Li, K, Rb, and Cs) salts **11b** and **11d–f** and the diammonium and the bistetramethylammonium 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate–BF_2 complexes **11g** and **11h**. Other examples of complete C-substitution were discovered in electrophilic nitration and bromination to give the 2,6-dinitro (PMDNP–BF_2) and 2,6-dibromo derivatives **11k** and **11m**. These substitution reactions were considered to be supportive of quasiaromaticity for the pyrromethene–BF_2 complexes (cf., **D**). This property is characteristic of various metal chelates [35, 36] and is further supported by proton nmr signals ∂ 6.00 to 7.62 for unsubstituted ring positions in P–BF_2 derivatives [13].

Laser Activity

Laser activity for P–BF_2 complexes (Table 1) gave RE from 0 to 100. Presumably a heavy atom effect brought about inactivity (RE 0) for 2,6-dibromo-1,3,5,7,8-pentamethylpyrromethane–BF_2 complex **11m**. Each of the P–BF_2 complexes **10a–f** and **11a–n** showed high molecular extinction coefficients (log ϵ_s 4 to 5) and high fluorescence quantum yields Φ 0.3 to 1.0) (Table 1). Minimal T–T absorption in or near the fluorescence spectral region was determined for TMP–BF_2 **10a** [4], PMP–BF_2 **10b** [5] and PMPDS–BF_2 **11c** (Figure 1). A value ϵ_T (567) = 1.5 × 10^3 L/mole cm for PMDEP–BF_2 **10e** was exceptionally low in comparison with ϵ_T (570) = 7.9 × 10^3 L/mol cm and ϵ_T (580) = 6.6 × 10^3 L/mole cm for rhodamine dyes 560 and 575 [6]. To avoid self-quenching through aggregation a dye concentration of about 10^{-4} M was generally sought. A hypsochromic shift in fluorescence from 534 to 509 nm for PMPDS–BF_2 **11c** in water was brought about by dilution from 10^{-3} to 10^{-8} M and attributed to diminished aggregation as dilution increased [37]. Although methanol (preferred), ethanol, or water were solvents of choice for laser activity from many P–BF_2, other satisfactory solvents in certain instances included acetonitrile, chloroform, dimethylsulfoxide, *N,N*-dimethylformamide, dichloromethane, dioxane, ethyl acetate, ethylene glycol, and hexafluoroisopropanol. Since the use of water minimized problems of storage and disposal or recovery of large amounts of organic solvents, water soluble dyes were sought. Aqueous solutions also offered thermooptic properties of water that often improved laser activity [2].

Just as a reaction between a P–BF_2 complex and methanolic potassium hydroxide was attributed to the initial nucleophilic attack at the 8-position that led to destruction of the chromophore [25], a similar reaction was assumed to account in part for the loss of fluorescence from PMP–BF_2 **10b** in ethanol solution after exposure to sunlamp irradiation for 5 days. In contrast, the loss of fluorescence from the complex **10b** in dichloromethane required a similar exposure to irradiation for 21 days. A greater photolability was demonstrated in the loss of fluorescence from other P–BF_2 derivatives (10^{-4} M in ethanol): PMDNP–BF_2 **10k** after 72 h, HMP–BF_2 **10d** after 70 h, and PMDEP–BF_2 **10e** after 65 h; and from PMPDS–BF_2 **11c** (10^{-4} M in water) after 55 h. In methanol PMPDS–BF_2 **11c** was markedly more stable; the loss of fluorescence in a similar experiment required 7 weeks. When photostability was determined by the number of flashlamp pulses required to lower laser power efficiency by 50% the complex **11c** in methanol or ethanol was discovered to be much more photostable than other known laser dyes (including other P–BF_2 derivatives) for the spectral region 530–560 nm [38, 39]. In one laboratory, when methanol solutions were examined the complex **11c** was six times more photostable than the dye R-6G (9000 pulses vs. 1500 pulses) [40].

A comparison of laser energy output as a function of flashlamp pump energy showed PMPDS–BF_2 **11c** in ethanol offered three times the power efficiency from coumarin 545 and was comparable in efficiency to R-6G [5]. Because of its exceptional photostability in methanol, PMPDS–BF_2 **11c** was selected for further examination. From flashlamp excitation (pulsewidth 2 μsec, risetime 0.7 μsec) with pump energy at 300 J in conjunction with an LFDL-8 laser, a 30% improvement in power efficiency for PMPDS–BF_2 **11c** over R-6G (each 10^{-4} M in methanol) was realized [41, 42]. In the presence of caffeine (a filter for light <300 nm) PMPDS–BF_2 (10^{-4} M in methanol) gave an improvement (28% to 66%) in laser efficiency that was dependent on flashlamp pulse width (2.0 to 7.0 μsec) [38, 39]. In contrast with an enhancement in laser activity from 10^{-3} M aqueous solutions of R-6G and other xanthene dyes brought about by the presence of β-cyclodextrin (10^{-2} M), the fluorescence of PNPDS–BF_2 (10^{-3} to 10^{-8} M) in water was unaffected by similar treatment [37]. An interest in the effect on laser activity by the formation of a salt between R-6G (the free base) and 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonic acid **11a** was thwarted by the failure to obtain a tractable product from their interaction. There was no improvement in laser ac-

TABLE 1 Pyrromethene–BF_2 Complexes[a]

No.	λ_{max} nm	log ϵ	λ_{Fl} nm	Φ	λ_{las} nm	RE[b] %
10a	505	4.92	516	0.80	533	30
10b	493	4.90	519	0.99	542	100
10c	495	4.99	517	1.0	546	90
10d	518	4.67	543	0.70[c]	570	75
10e	517	4.81	546	0.83[c]	570	100
10f	493[d]	4.97[d]	531	0.38[c]	556	50
11b	497	4.96	533	0.62[c]	554	65
11c	492	4.86	533	0.73[e]	560	90
11d	498	4.96	534	0.78[e]	556	100
11e	497	4.91	533	0.88[e]	553	95
11f	497	4.91	531	0.81[e]	553	95
11g	496	4.92	533	0.90[e]	557	95
11h	497	4.97	535	0.89[e]	556	95
11j	483[f]	4.82	520[f]	0.82[g]	554[f]	35
11k	493	4.62	533	[h]	[h]	[h]
11m	516[f]	4.81	546[f]	0.45[g]		
11n	498	4.90	530	0.44[c]	555	50

[a]Methanol was used as solvent except where noted otherwise.
[b]Relative Efficiency in laser power output. RE 100 assigned to PMP–BF_2 **10b**. RE 30 observed for Coumarin 545 [5].
[c]In ethanol.
[d]λ_{max} 495 nm (log ϵ 5.26) [23].
[e]In water.
[f]In a mixture (9:1) of methanol and dichloromethane.
[g]In dichloromethane.
[h]Due to photoinstability the data was not reproducible.

TABLE 2 Pyrromethene–BF_2 Complexes

No.	Yield %	mp °C	Formula	Calculated, % Found, %
10b	66	254–257 dec	$C_{14}H_{17}N_2F_2B$	C, 64.15; H, 6.53; N, 10.74 C, 64.34; H, 6.71; N, 10.84
10c	45	214–216	$C_{15}H_{19}N_2F_2B$	C, 65.24; H, 6.92; N, 10.15 C, 64.97; H, 6.88; N, 10.05
10d	34	286–287 dec	$C_{16}H_{21}N_2F_2B$	C, 66.20; H, 7.24; N, 9.65 C, 66.23; H, 7.35; N, 9.57
10e	34	207–208	$C_{18}H_{25}N_2F_2B$	C, 67.92; H, 7.86; N, 8.80 C, 67.88; H, 8.06; N, 8.79
11b	84	>280	$C_{14}H_{25}N_2O_6F_2BS_2Li \cdot 2H_2O$	C, 35.74; H, 3.19; N, 5.95 C, 36.16; H, 3.50; N, 5.97
11c	75	> 300	$C_{14}H_{15}N_2O_6F_2BS_2Na_2$	C, 36.07; H, 3.24; N, 6.01 C, 36.42; H, 3.35; N, 6.14
11d	82	>280	$C_{14}H_{15}N_2O_6F_2BS_2K_2$	C, 33.79; H, 3.01; N, 5.62 C, 33.91; H, 3.02; N, 5.62
11e	62	>280	$C_{14}H_{15}N_2O_6F_2BS_2Rb_2$	C, 28.42; H, 2.53; N, 4.73 C, 28.36; H, 2.45; N, 4.69
11f	57	>280	$C_{14}H_{15}N_2O_6F_2BS_2Cs_2$	C, 24.49; H, 2.18; N, 4.08 C, 24.58; H, 2.18; N, 4.13
11g	60	>300	$C_{14}H_{23}N_4O_6F_2BS_2$	C, 36.85; H, 5.08; N, 12.28 C, 36.91; H, 5.02; N, 12.20
11h	78	281–282 dec	$C_{22}H_{39}N_4O_6F_2BS_2 \cdot H_2O$	C, 45.05; H, 7.05; N, 9.55 C, 45.29; H, 6.73; N, 9.50
11j	40	218–222 dec	$C_{16}H_{21}N_2O_6F_2BS_2$	C, 42.67; H, 4.70; N, 6.22 C, 42.54; H, 4.76; N, 5.96
11k	71	279–281 dec	$C_{14}H_{15}N_4O_4F_2B$	C, 47.70; H, 4.26; N, 15.90 C, 48.18; H, 4.46; N, 15.94
11m	50	300–302 dec	$C_{14}H_{15}N_2Br_2F_2B$	C, 40.00; H, 3.57; N, 6.66 C, 40.13; H, 3.67; N, 6.59
11n	69	>260	$C_{15}H_{17}N_2O_6F_2BS_2Na_2$	C, 37.52; H, 3.57; N, 5.84 C, 38.20; H, 3.79; N, 5.75

tivity from an equimolar mixture of the two dyes R-6G (as the hydrochloride salt) and PMPDS–BF_2 **11c**, in methanol.

EXPERIMENTAL

Spectral data was obtained from the following instruments: Pye-Unicam SP 200 and Sargent-Welch 3-200 IR, Varian EM 360A, and IBM AF200 NMR [43], Hewlett-Packard 5985 (70 eV) (GC-MS), Cary 17 (UV), and Perkin-Elmer LS-5B Luminescence Spectrometers. A dye laser was constructed at the Naval Ocean Systems Center [44]. It operated in the non-flowing (static) mode and had no tuning capability. The dye cell (2.5 mm diameter, 50 mm long) had an eliptical cavity configuration of small eccentricity. The flashlamp EG & G model FX 139C-2, produced a pulse that had a rise time of 200 ns, half-width length of 600 ns, and input energy of 2 J at 6.32 kV, 5 J at 10.00 kV, 7.2 J at 12.00 kV, and 10 J at 14.14 kV [44, 45]. Laser energy outputs were measured with an accuracy of ±5% by a Scientech 365 power and energy meter [46]. Light absorption, luminescence, and laser activity properties are described in Table 1.

For each product the IR and EI-MS data agreed with the literature data and/or supported the assigned structure. Each recorded UV absorption was restricted to the highest wave length. ^1H NMR spectra were run in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR were recorded at 22.5 MHz with the deuterated solvent as an internal reference; the central peak of the solvent multiplet signal was assigned: ∂ 77.00 ($CDCl_3$), 39.50 ($(CD_3)_2(SO)$. Poor solubility precluded NMR analyses in many instances. Fluorescence quantum yields of the dyes were determined for methanol solutions with excitation at 450 and 460 nm by reference to acridine orange, φ 0.46 [14], in ethanol. Melting points were determined on a Thomas Hoover melting point apparatus and were uncorrected. Elemental analyses were obtained from Midwest Micro Lab, Indianapolis, Indiana and Galbraith Laboratories, Inc., Knoxville, Tenn. Solvents were removed by rotary evaporation under reduced pressure unless indicated otherwise. Column chromatography was performed on silica gel (various grades). Triplet extinction coefficients over the laser action spectral region of the dye were measured at the temperature of liquid nitrogen by equipment previously described [47] using McClure's method [48].

Solvents, reagents, and starting materials that

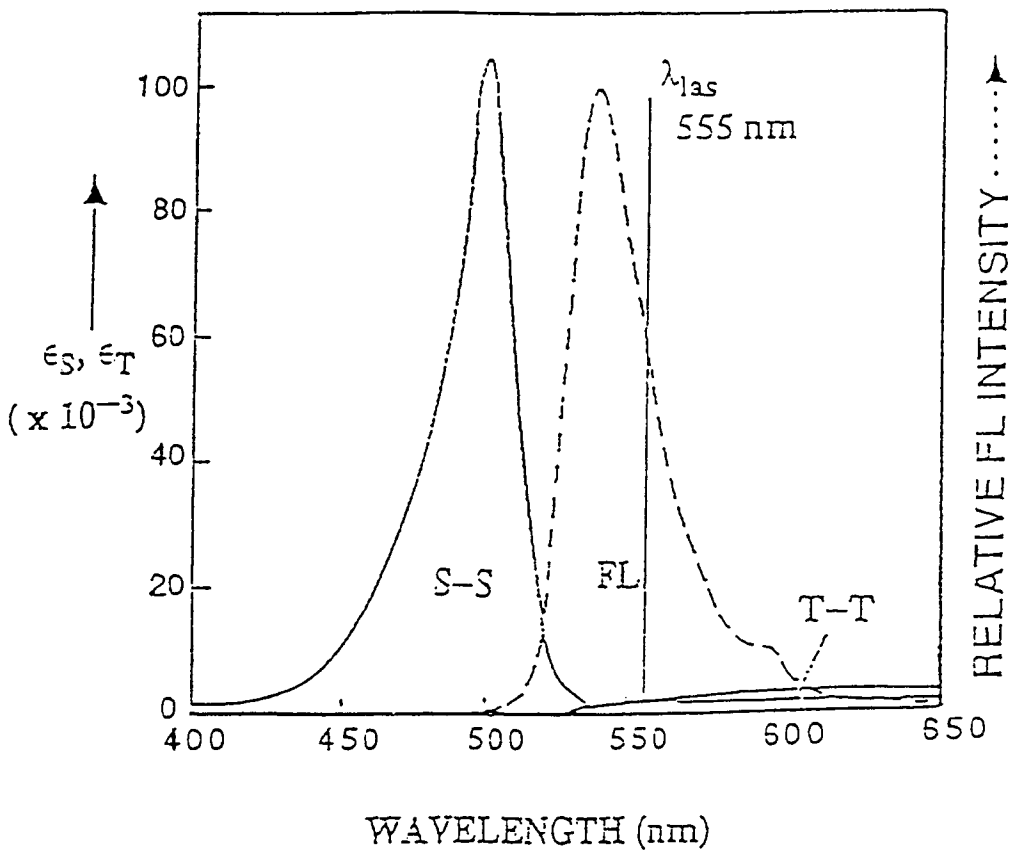


FIGURE 1 Absorption and luminescence for PMPDS–BF_2 complex **11c**. T–T absorption: 1×10^{-4} M in α-methyltetrahydrofuran at 77 °K. S–S absorption and fluorescence: 1×10^{-4} M in ethanol. Broadband laser action: 2×10^{-4} M in ethanol.

were obtained from the Aldrich Chemical Company, Milwaukee, WI included acetic anhydride, acetone, acetonitrile, acetyl chloride, alumina, ammonium carbonate, ammonium chloride, benzene, boron trifluoride etherate, bromine, carbon tetrachloride, celite, cesium carbonate, chloroform-d, chlorosulfonic acid, deuterium oxide, dichloromethane, *N,N*-diisopropylethylamine, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide-d_6 (DMSO-d_6), *p*-dioxane, ethanol, ethyl acetate, hexane, hexafluoroisopropanol, hydrazine hydrate, lithium carbonate, isopropanol, isopropyl ether, kryptopyrrole (2,4-dimethyl-3-ethylpyrrole **3**), magnesium sulfate, methanol, nitric acid, 2-methyltetrahydrofuran, petroleum ether, phosphoric acid, potassium bromide, potassium carbonate, potassium fluoride, propionyl chloride, rubidium carbonate, silica gel (230–400 mesh, 60 Å), sodium bicarbonate, sodium hydroxide, sodium sulfate, tetrahydrofuran (THF), tetramethylammonium carbonate, toluene, triethylamine, and trifluoroethanol. Rhodamine 6G and thin layer chromatography sheets were obtained from Eastman Kodak Co., Rochester, NY. Chlorine was obtained from Matheson Gas Products, Secaccus, NJ. Nitrogen was obtained from Air Products and Chemicals, Inc., Allentown, PA.

The following compounds were prepared according to the directions cited: ethyl 2,4-dimethylpyrrole-3-carboxylate **4** [34]; diethyl 3,5-dimethylpyrrole-2,4-dicarboxylate **5** [30, 31]; ethyl 3,4,5-trimethylpyrrole-2-carboxylate **6** [32]; *tert*-butyl 3,5-dimethyl-4-carboethoxypyrrole-2-carboxylate **7** [34]; 2-formyl-3,5-dimethylpyrrole **8** [12]; 3,5,3′,5′-tetramethylpyrromethene **9a** (modified for isolation as its hydrochloride salt) [14]; 1,3,5,7-tetramethylpyrromethene–BF_2 complex **10a** (modified procedure) [14]; and 4,4′-dicarboethoxy-6-ethyl-3,5,3′,5′-tetramethylpyrromethene **9g** (modified for isolation as the hydrochloride derivative, mp 227–232°C (dec), EI-MS (relative abundance): 373 (100, $M^+ - Cl$)) [34].

2,4-Dimethylpyrrole **1**

In an adaptation of a procedure [30], diethyl 3,5-dimethylpyrrole-2,4-dicarboxylate **5** (160.0 g, 0.66 mol) as a melt at 140°C was treated with phosphoric acid (85%, 320 mL). The mixture was heated at 180°C for 30 min and poured into aqueous sodium

hydroxide (3.5 M, 3.5 L). Codistillation gave 3 L that was extracted with isopropyl ether (3 × 500 mL). The organic phase was dried (potassium carbonate) and concentrated to give a dark brown oil that distilled, 70–80°C (10 mm), to give 2,4-dimethylpyrrole **1** as a colorless oil, 40.00 g (64%); bp 162–165°C (lit. [30] 160–165°C), ^{1}H NMR ($CDCl_3$): ∂ 2.07 (s, 3H), 2.16 (s, 3H), 5.72 (s, 1H) 6.31 (s, 1H), 7.20–7.87 (br s, 1H). Similarly, ethyl 3,4,5-trimethyl-2-carboxylate **6** was converted to 2,3,4-trimethylpyrrole **2** as a colorless solid (67%), mp 37–38°C (lit. [32] mp 36–38°C).

3,5,3′,5′,6-Pentamethylpyrromethene Hydrochloride **9b**

Acetyl chloride (35 mL, 0.49 mol) was added dropwise with stirring over a period of 15 min to a solution of 2,4-dimethylpyrrole **1** (20.0 g, 0.21 mol) in dichloromethane (150 mL). The reaction mixture was heated at 40°C for 1 h, cooled to room temperature, diluted with petroleum ether (1.5 L), and triturated for 12 h to bring about the separation of 3,5,3′,5′,6-pentamethylpyrromethene hydrochloride **9b**. It was isolated by vacuum filtration as a red-brown powder, 24.0 g (91%), mp 180–185°C (dec); EI-MS (relative abundance): 214 (51.8) $M^+ - HCl$); ^{1}H NMR ($CDCl_3$); ∂ 2.02 (s, 6H); 2.20 (s, 6H); 2.49 (s, 3H); 6.20 (s, 2H) [43]. Instability precluded elemental analysis.

Similarly, the hydrochloride salts of derivatives of 3,5,3′,5′-tetramethylpyrromethene were obtained. The pyrrole **1** and propionyl chloride gave the 6-ethyl- derivative **9c**, 81%, mp 192–195°C (dec). Anal. Calcd. for $C_{15}H_{21}N_2Cl$: C, 68.04; H, 7.99; N, 10.58. Found: C, 67.47; H, 7.80; N, 10.17. The pyrrole **2** and acetyl chloride gave the 4,4′,6-trimethyl derivative **9d**, 80%, mp 210–212°C (dec); ^{1}H NMR ($CDCl_3$): ∂ 1.90 (s, 6H), 2.00 (s, 6H), 2.45 (s, 6H), 2.75 (s, 3H) [33]. Anal. Calcd. for $C_{16}H_{23}N_2Cl$: C, 68.94; H, 8.25; N, 10.05; Cl, 12.74. Found: C, 69.41; H, 7.72; N, 10.21; Cl, 12.97. The pyrrole **3** and acetyl chloride gave the 4,4′-diethyl-6-methyl derivative **9e**, 77%, mp 185–186°C (dec); ^{1}H NMR ($CDCl_3$): ∂ 1.01 (t, 6H), 2.07 (s, 6H), 2.35 (q, 4H), 2.46 (s, 6H), 2.76 (s, 3H) [43]. Anal. Calcd. for $C_{18}H_{27}N_2Cl$: C, 70.47; H, 8.80; N, 9.13; Cl, 11.58. Found: C, 70.67; H, 9.00; N, 9.15; Cl, 11.73.

1,3,5,7,8-Pentamethylpyrromethene–BF_2 Complex (PMP–BF_2) **10b**

Triethylamine (15 mL, 113 mmol) was added at room temperature to a suspension of 3,5,3′,5′,6-pentamethylpyrromethene hydrochloride **9b** (6.0 g, 24 mmol) in toluene (600 mL) and the mixture was stirred for 15 min. Boron trifluoride etherate (20 mL, 163 mmol) was added dropwise with stirring as a green fluorescence developed. The reaction mixture was heated (80°C) for 15 min, cooled to 40°C, washed with warm water (3 × 100 mL), dried (magnesium sulfate), and concentrated to give a dark brown solid. Flash chromatographic [49] separation of a solid mixture (silica gel, 250 g, 230–400 mesh, 60 Å, a mixture (80:20) of toluene and hexane), followed by concentration of the intense green-yellow fluorescent fractions, gave PMP–BF_2 **10b**. It recrystallized from ethyl acetate as an orange crystalline solid, 4.1 g (66%) (see Tables 1 and 2 for other properties). In reactions with boron trifluoride the hydrochlorides of pyrromethenes **9c–f** gave the corresponding P–BF_2 derivatives **10c–f** (Table 1). ^{1}H NMR [43]: HMP–BF_2 **10d** ($CDCl_3$): ∂ 1.91 (s, 6H), 2.29 (s, 6H), 2.46 (s, 6H), and 2.57 (s, 3H); PMDEP–BF_2 **10e** ($CDCl_3$): ∂ 1.01 (t, 6H), 2.30 (s, 6H), 2.37 (q, 4H), 2.47 (s, 6H), and 2.57 (s, 3H).

Disodium 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate–BF_2 Complex (PMPDS–BF_2) **11c**

A solution of chlorosulfonic acid (3.26 g, 28 mmol) in dichloromethane (20 mL) was added dropwise to a suspension of PMP–BF_2 **10b** (3.65 g, 14 mmol) in dichloromethane (50 mL) at −50°C. A yellow solid separated as the reaction mixture warmed slowly to room temperature. The disulfonic acid **11a** was isolated by vacuum filtration and treated with water (600 mL). The aqueous solution was neutralized with sodium bicarbonate (2.52 g, 30 mmol). The solution was concentrated to 75 mL and treated with ethanol (400 mL) to bring about the separation of the salt **11c**. It was isolated by vacuum filtration, recrystallized from aqueous ethanol (80%), and dried in air to give a yellow-orange powder, 5.0 g (75%) (Table 1). The dilithium, dipotassium, dirubidium, dicesium, diammonium, and the bistetramethylammonium salts **11b, 11d–h** (Tables 1 and 2) were prepared in straightforward reactions. A similar conversion of 1,3,5,7-tetramethyl-8-ethylpyrromethene–BF_2 complex **10c** gave disodium 1,3,5,7-tetramethyl-8-ethylpyrromethene-2,6-disulfonate–BF_2 complex **11n** (Tables 1 and 2).

Dimethyl 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate–BF_2 Complex **11j**

A solution of chlorosulfonic acid (3.6 g, 30 mmol) in dichloromethane (20 mL) was added dropwise to a cooled suspension of 1,3,5,7,8-pentamethylpyrromethene–BF_2 complex **10b** (2.0 g, 7.6 mmol) in dichloromethane (30 mL) at −50°C. A brown oil separated as the clear yellow solution warmed to room temperature. It was treated with methanol (10 mL), stirred for 0.5 h at room temperature, concentrated to a brown viscous oil, treated with methanol (40 mL), and stirred to bring about the separation of a yellow-brown solid that was isolated by vacuum filtration, treated with methanol (100 mL), and heated (60°C) for 0.5 h to complete an esteri-

fication. The solid ester **11j**, 1.4 g (40%), was isolated and purified from methanol to give an orange-yellow powder (Tables 1 and 2).

1,3,5,7,8-Pentamethyl-2,6-dinitropyrromethene–BF_2 complex (PMDNP-BF_2) **11k**

After PMP–BF_2 **10b** (3.0 g, 11.5 mmol) was added to nitric acid (50 mL, 70%) at 0°C, the orange-red mixture was stirred at 0°C for 1.5 h and poured into ice water (200 mL) to precipitate the 2,6-dinitro derivative **11k** as an orange solid, isolated by filtration and washed with water. It recrystallized from ethyl acetate as an orange powder (2.9 g) (Tables 1 and 2).

1,3,5,7,8-Pentamethyl-2,6-dibromopyrromethene–BF_2 Complex **11m**

Bromine (16.0 g, 100 mmol) in dichloromethane (50 mL) was added dropwise to PMP–BF_2 **10b** (2.0 g, 7.6 mmol) in dichloromethane (150 mL) over a period of 10 min at 25°C with stirring. An orange precipitate was separated, triturated with dichloromethane (150 mL), and dried to give the dibromo derivative **11m** as an orange crystalline solid, 1.6 g (Tables 1 and 2); ^{1}H NMR [43] ($CDCl_3$): δ 2.41 (s, 6H), 2.55 (s, 6H), and 2.60 (s, 3H).

Pyrromethene–BF_2 Complexes Photostability

A solution of 1,3,5,7,8-pentamethylpyrromethene–BF_2 complex (PMP–BF_2) **10b** (0.10 g, 0.3 mmol) in ethanol (250 mL) was irradiated by a sunlamp (GE 275W) at a distance of 30 cm. Fluorescence at 500 nm became undetectable after 5 days. In similar experiments other P–BF_2 derivatives (10^{-4} M in ethanol) also lost fluorescence: PMDNP–BF_2 **11k** after 72 h, HMP–BF_2 **10d** after 70 h, and PMDEP–BF_2 **10e** after 65 h. Disodium 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate–BF_2 complex (PMPDS–BF_2) **11c** (2.0 mg) in water (50 mL) lost its fluorescence at 492 nm after 55 h of similar irradiation; when water was replaced with methanol the duration of fluorescence was 7 weeks. In brown bottles all P–BF_2 compounds were indefinitely stable to storage at 25°C.

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