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# Laser Active Cyanopyrromethene–$BF_2$ Complexes

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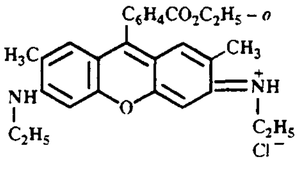
## ABSTRACT

*Treatment with a mixture of formic and hydrobromic acids converted ethyl 3,4-diethyl-5-methyl-pyrrole-2-carboxylate* **7a** *to 3,3′,4,4′-tetraethyl-5,5′-dimethylpyrromethene hydrobromide* **8a** *presumably via the condensation of α-unsubstituted and α-formylpyrrole intermediates* **7c** *and* **7e** *formed in situ. The corresponding 6-cyanohexaalkylpyrromethane* **9a** *was obtained by the addition of hydrogen cyanide to the pyrromethene* **8a** *and was oxidized with bromine to an unstable pyrromethene* **10a**, *an intermediate converted to 1,2,6,7-tetraethyl-3,5-dimethyl-8-cyanopyrromethene–$BF_2$ complex* **3**, *(PM–TEDC), $\lambda_{las}$ (plastic) 613–639 nm, in a reaction with boron trifluoride etherate. Ethyl 3,4,5-trimethylpyrrole-2-carboxylate* **7b** *was similarly converted to 1,2,3,5,6,7-hexamethyl-8-cyanopyrromethene–$BF_2$ complex* **4**, *(PM–HMC), $\lambda_{las}$ (plastic) 615–639 nm. Immediately after formation by a condensation between propionyl chloride and 2,4-dimethyl-3-cyanopyrrole* **16**, *unstable 3,3′,5,5′-tetramethyl-6-ethyl-4,4′-dicyanopyrromethene hydrochloride* **17** *was treated with boron trifluoride etherate to give 1,3,5,7-tetramethyl -2,6-dicyano-8-ethylpyrromethene–$BF_2$ complex* **18**, *$\lambda_{las}$ (ethanol) 540–565 nm.*

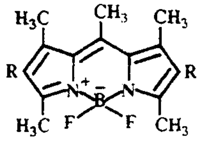
## *INTRODUCTION*

Over 40 recently discovered pyrromethene–$BF_2$ complexes (P–$BF_2$) were solids and ranged from yellow to deep blue in color. In solution, these dyes offered strong absorption ($\lambda_{max}$ 490–580 nm, log $\epsilon$ > 4.8), intense fluorescence ($\lambda_f$ 520–590 nm, $\Phi$ > 0.8), and laser activity ($\lambda_{las}$ 540–670 nm) [1,2]. A very low to vanishing extinction coefficient $\epsilon_T$ for triplet–triplet absorption over the fluorescence spectral region presumably enhanced significantly the lasing performance [3].

Truly superior power efficiency in the laser activity of certain P–$BF_2$ dyes superseded the championship performance held for 25 years by Rhodamine–6G (R–6G). Under synchronous pumping, the dye 1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene–$BF_2$ complex (PMDEP–$BF_2$) [4a] gave twice the power output efficiency obtained from R–6G and showed superior photostability [5]. In a continuous wave (CW) operation, photostable disodium 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate–$BF_2$ complex (PMPDS–$BF_2$) [4b] gave 45% power efficiency and PMDEP–$BF_2$ gave 37%, whereas R–6G delivered a power output at 32% [6].



R–6G



PMDEP–$BF_2$ R = $CH_2CH_3$
PMPDS–$BF_2$ R = $SO_3^-$ $Na^+$

Dye-doped solid-state laser materials are an attractive source of tunable laser radiation. They carry advantages over nonlinear techniques (e.g., Raman scattering and optical parametric oscilla-

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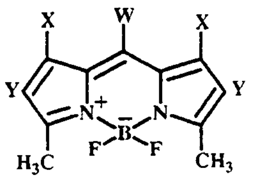
tion), such as virtually thresholdless operation, relative insensitivity to fluctuations in the pump laser intensity, and continuous tunability over the gain region; also, their excitation sources need not be coherent. Even so, solid-state dye lasers had remained impractical because of such problems as poor photostability and low quantum yield of the rhodamine and coumarin dyes.

The advent of P–BF$_2$ dyes, together with a development of new plastics, is now making solid-state dye lasers practical. Dye lasing absolute efficiencies [7] exceeding 80% and longevities [8] of 100,000 pulses for a fixed area at moderate (0.2 J/cm$^2$) fluence levels have been reported. Specifically, P–BF$_2$ dyes dispersed in an acrylic copolymer were found to be excellent solid-state lasers with the special feature of tunability characteristic of a laser dye. In this technological breakthrough, PMDEP–BF$_2$ in a polymer matrix (five parts methyl methacrylate and one part hydroxypropyl acrylate) gave a slope efficiency of 77% [7]. R–6G under similar treatment gave an unsatisfactory performance and was not measured; sulforhodamine–B gave a 37% efficiency. Similar tests showed other P–BF$_2$ dyes to rival and/or to surpass PMDEP–BF$_2$ in efficiency [9].

P–BF$_2$ dyes have also been successful as fluorescent probes in medicinal chemical research [10] and as photodynamic therapeutic agents for cancer [11].

In a continuing search for fluorescent and lasing dyes, the substituent effect of the cyano group on lasing activity in P–BF$_2$ molecules was selected for further examination. Laser activity 540–600 nm for P–BF$_2$ dyes was red-shifted above 600 nm by a substituent effect of an 8-cyano group; however, the syntheses of diethyl 1,3,5,7-tetramethyl-8-cyanopyrromethene-2,6-dicarboxylate–BF$_2$ complex **1** $\lambda_{las}$ 617 nm and 1,3,5,7-tetramethyl-2,6-diethyl-8-cyanopyrromethene–BF$_2$ complex **2** $\lambda_{las}$ 670 nm were impractical due to very low yields [2]. To meet a need for strongly fluorescent and lasing P–BF$_2$ dyes $\lambda_f > 600$ nm, the search for improved syntheses of cyanopyrromethene–BF$_2$ complexes was undertaken.



| Cpd | W | X | Y |
|---|---|---|---|
| 1 | CN | $CH_3$ | $CO_2C_2H_5$ |
| 2 | CN | $CH_3$ | $C_2H_5$ |
| 3 | CN | $C_2H_5$ | $C_2H_5$ |
| 4 | CN | $CH_3$ | $CH_3$ |
| 18 | $C_2H_5$ | $CH_3$ | CN |
| 19 | H | $CH_3$ | $CH_3$ |
| 20 | $CH_3$ | $CH_3$ | H |

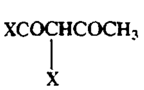
## *RESULTS AND DISCUSSION*

### *Synthesis*

According to a method reported by Wang and Chang [12], 3-ethylhexan-2,4-dione **5a** in a Knorr condensation with either diethyl aminomalonate **6a** or ethyl aminoacetoacetate **6b** gave ethyl 3-4-diethyl-5-methylpyrrole-2-carboxylate **7a**. When treated with a mixture of formic and hydrobromic acids at 90–100°C, the ester **7a** gave 3,3′,4,4′-tetraethyl-5,5′-dimethylpyrromethene hydrobromide **8a** via the presumed intermediacy of 2-methyl-3,4-diethylpyrrole **7c** and its condensation with the $\alpha$-formyl derivative **7e** formed in situ. On treatment with potassium cyanide in ethanol at 80°, the pyrromethene salt **8a** gave 3,3′,4,4′-tetraethyl-5,5′-dimethyl-6-cyanopyrromethane **9a**. An unstable and unisolated pyrromethene **10a** was obtained by oxidation and was immediately treated with boron trifluoride etherate to give 1,2,6,7-tetraethyl-3,5-dimethyl-8-cyanopyrromethene–BF$_2$ complex **3**, (PM–TEDC). In a related sequence of reactions, 3-methylpentan-1,3-dione **5b** was converted via intermediates **7b**, **7d**, **7f**, **8b**, **9b**, and **10b** to 1,2,3,5,6,7-hexamethyl-8-cyanopyrromethene–BF$_2$ complex **4** (PM–HMC).

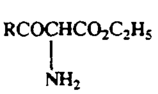
Commercially available ethyl 3,5-dimethylpyrrole-2-carboxylate **11** was converted in seven steps to 1,3,5,7-tetramethyl-8-ethyl-2,6-dicyanopyrromethene–BF$_2$ complex **18**. According to a procedure developed by Chu and Chu [13], the pyrrole **11** was converted to its 4-formyl derivative **12**. The aldehyde oxime **13** [14] was dehydrated to the corresponding 4-cyanopyrrole **14**. Saponification of the ester **14** followed by decarboxylation of the intermediate acid **15** gave 2,4-dimethyl-3-cyanopyrrole **16** [14]. A condensation with propionyl chloride converted the pyrrole **16** to unstable 3,3′,5,5′-tetramethyl-6-ethyl-4,4′-dicyanopyrromethene hydrochloride **17**. Immediate treatment with boron trifluoride etherate converted the unisolated intermediate **17** to 1,3,5,7-tetramethyl-2,6-dicyano-8-ethylpyrromethene–BF$_2$ complex **18**.

The cyano auxochrome in the 8-position of P–BF$_2$ dyes brought about a red shift of 60 nm from $\lambda_{max}$ 528 nm (log $\epsilon$ 4.84) and $\lambda_f$ 552 nm ($\Phi$ 0.56) for 1,2,3,5,6,7-hexamethylpyrromethene–BF$_2$ complex **19** [2] to $\lambda_{max}$ 580–592 nm (log $\epsilon$ 4.66–4.86) and $\lambda_f$ 609–620 nm ($\Phi$ 0.54–0.56) for hexaalkyl-8-cyanopyrromethene–BF$_2$ complexes **2–4** [15]. In contrast, a comparison of 1,3,5,7,8-pentamethylpyrromethene–BF$_2$ complex **20** ($\lambda_{max}$ 493 nm, log $\epsilon$ 4.90 and $\lambda_f$ 519 nm, $\Phi$ 0.99) [2] with 1,3,5,7-tetramethyl-8-ethyl-2,6-dicyanopyrromethene–BF$_2$ complex **18** ($\lambda_{max}$ 496 nm, log $\epsilon$ 5.12 and $\lambda_f$ 511 nm, $\Phi$ 0.79) revealed no auxochrome effect from the 2,6-dicyano substituents. These results supported our belief in the existence of a P–BF$_2$ chromophore dipole along the short axis. The effective auxochromic 8-cyano group ran parallel to the axis, whereas the ineffective 2,6-dicyano substituents were perpendicular to the axis [18]. For a similar reason, there was no auxochrome effect on P–BF$_2$ dyes substituted in the 2,6-positions with carboethoxy, acetamido, sulfonate anion, bromo, or nitro groups [1,2].



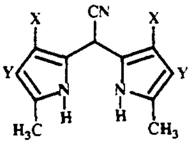
$\mathrm{XCO\underset{X}{C}HCOCH_3}$

5a $X = C_2H_5$
5b $X = CH_3$

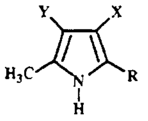


$\mathrm{RCO\underset{NH_2}{C}HCO_2C_2H_5}$

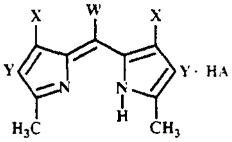
6a $R = OC_2H_5$
6b $R = CH_3$



9a $X = Y = C_2H_5$
9b $X = Y = CH_3$



| Cpd | R | X | Y |
|---|---|---|---|
| 7a | $CO_2C_2H_5$ | $C_2H_5$ | $C_2H_5$ |
| 7b | $CO_2C_2H_5$ | $CH_3$ | $CH_3$ |
| 7c | H | $C_2H_5$ | $C_2H_5$ |
| 7d | H | $CH_3$ | $CH_3$ |
| 7e | CHO | $C_2H_5$ | $C_2H_5$ |
| 7f | CHO | $CH_3$ | $CH_3$ |
| 11 | $CO_2C_2H_5$ | $CH_3$ | H |
| 12 | $CO_2C_2H_5$ | $CH_3$ | CHO |
| 13 | $CO_2C_2H_5$ | $CH_3$ | CH=NOH |
| 14 | $CO_2C_2H_5$ | $CH_3$ | CN |
| 15 | $CO_2H$ | $CH_3$ | CN |
| 16 | H | $CH_3$ | CN |



| Cpd | W | X | Y | HA |
|---|---|---|---|---|
| 8a | H | $C_2H_5$ | $C_2H_5$ | HBr |
| 8b | H | $CH_3$ | $CH_3$ | HBr |
| 10a | CN | $C_2H_5$ | $C_2H_5$ | — |
| 10b | CN | $CH_3$ | $CH_3$ | — |
| 17 | $C_2H_5$ | $CH_3$ | CN | HCl |

## *EXPERIMENTAL*

Spectral data were obtained by use of the following instruments: Varian Gemini-300, NMR, Perkin-Elmer LS-5B Luminescence Spectrometer, Perkin-Elmer 1600 FT-IR, and Perkin-Elmer Lambda 6 (UV/VIS) Spectrometer. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN, and Midwest Micro Lab, Indianapolis, In. Melting points were obtained by use of a Laboratory Devices Mel-Temp II and were uncorrected. IR data supported the assigned structures. The solvent for $^1H$ and $^{13}C$ NMR spectra was chloroform-*d*. Each recorded UV absorption was restricted to the wavelength with the strongest absorption.

The laser experiments on PM–HMC and PM–TEDC were performed with either a Continuum model YG-581C or Surelite-II frequency doubled Nd:YAG laser as the excitation source. The dyes were longitudinally pumped as previously described [19]. Dye tunability data were taken with a stable resonator cavity using a grating in the grazing angle of incidence configuration [20]. The input pump diameter for this configuration was 4 mm. The dichroic input concave mirror had 97% transmission at 532 nm and nearly 100% reflectivity above 570 nm and 4 m radius of curvature. The lasing materials used to determine the tuning ranges were two MIL–STD high-temperature plastics (HTP) doped independently with $1.3 \times 10^{-4}$ M PM–TEDC and PM–HMC. HTP is a thermosetting material developed by Korry Electronics and used as an optical medium in military applications [8]. The laser performance of 1,3,5,7-tetramethyl-2,6-dicyano-8-ethylpyrromethene–$BF_2$ complex **18** in ethanol was measured with a Phase-R-DL-1100 dye laser with a DL-5Y coaxial flashlamp.

The preparations of ethyl 3,4-diethyl-5-methylpyrrole-2-carboxylate **7a** [12], ethyl 3,4,5-trimethylpyrrole-2-carboxylate **7b** [21], 3,4-diethyl-2-methylpyrrole **7c** [22], 3,3′,4,4′,5,5′-hexamethylpyrromethene hydrobromide **8b** [23], ethyl 3,5-dimethyl-4-cyanopyrrole-2-carboxylate **14** [12], and 2,4-dimethyl-3-cyanopyrrole **16** [14] were carried out by the methods cited.

### *1,2,6,7-Tetraethyl-3,5-dimethyl-8-cyanopyrromethene–$BF_2$ Complex **3**, (PM–TEDC), and 1,2,3,5,6,7-Hexamethyl-8-cyanopyrromethene–$BF_2$ Complex **4**, (PM–HMC)*

A general procedure previously described [1,2] was followed. Hydrobromic acid (48%, 5 mL) was added to a solution of ethyl, 3,4-diethyl-5-methylpyrrole-2-carboxylate **7a** (5.0 g, 23.9 mmol) in formic acid (5 mL) at 90–100°C. The mixture was heated (100°C, 3 hours), cooled, filtered, and washed with water (50 mL), ether (50 mL), and methanol (50 mL). A solid residue recrystallized from a mixture of chloroform and petroleum ether (bp 60–80°C) to give the 3,3′,4,4′-tetraethyl-5,5′-dimethylpyrromethene hydrobromide **8a** as dark red prisms with a metallic sheen, 6.5 g (75%), mp 195–197°C (dec). $^1H$ NMR: $\delta$ 12.92 (bs, 2H), 6.90 (s, 1H), 2.65 (s, 6H), 2.50 (q, 4H), 2.48 (q, 4H), 1.30 (t, 6H), 1.16 (t, 6H). $^{13}C$ NMR: $\delta$ 153.71, 147.43, 129.59, 124.90, 118.11, 18.48, 18.18, 17.14, 15.04, 12.87. Anal. calcd for $C_{19}H_{29}N_2Br$: C, 62.47; H, 7.95; N, 7.67. Found: C, 62.61; H, 7.81; N, 7.66.

A mixture of the pyrromethene hydrobromide **8a** (5.25 g, 14.4 mmol) and potassium cyanide (4.64 g, 71.6 mmol) in ethanol (95%, 70 mL) was heated at 80°C with stirring for 45 minutes, cooled to 40°C, and diluted with water (80 mL) to bring about the precipitation of a brown solid. Column chromatographic separation from silica gel (200 g, 230–400 mesh, 60 Å, dichloromethane) gave 3,3′,4,4′-tetraethyl-5,5′-dimethyl-6-cyanopyrromethane **9a** as an impure solid, 2.15 g (48%), mp 172–174°C (dec). The impure cyanomethane **9a** (2.52 g, 8.1 mmol) in chloroform (25 mL) was treated dropwise with bromine (1.28 g, 8.0 mmol) in chloroform (3 mL) over a period of 5 minutes. Removal of solvent left the unstable pyrromethene hydrobromide **10a**. Without further purification, the hydrobromide **10a** (1.20 g, 3.3 mmol) in toluene (150 mL) was treated with triethylamine (1.21 g, 11.9 mmol) over a pe-

**Table 1** Laser Slope Efficiencies and Center Wavelengths for PM–TEDC and PM–HMC in Xylene and a High-Temperature Plastic (HTP)

| | *Slope Efficiency (%)* | *Center Wavelength (nm)* |
|---|---|---|
| PM–TEDC | | |
| Xylene | 48 | 630 and 658 |
| HTP | 26 | 627 |
| PM–HMC | | |
| Xylene | 31 | 631 |
| HTP | 57 | 624 |

riod of 10 minutes. Boron trifluoride etherate (3.0 g, 21.2 mmol) was added, and the mixture was heated (80°C, 1 hour), cooled to 25°C, filtered, washed with water (4 × 100 mL), dried ($MgSO_4$), and concentrated. Column chromatographic separation from silica gel (125 g, 230–400 mesh, 60 Å, toluene) gave 1,2,6,7-tetraethyl-3,5-dimethyl-8-cyanopyrromethene–$BF_2$ complex **3**, (PM–TEDC), as a golden green amorphous solid, 0.38 g (35%), mp 115–118°C (dec). $^1H$ NMR: $\delta$ 2.87 (q, 4H), 2.53 (s, 6H), 2.40 (q, 4H), 1.52 (t, 6H), 1.24 (t, 6H). $^{13}C$ NMR: $\delta$ 158.01, 134.11, 131.39, 114.77, 114.10, 102.87, 18.48, 17.10, 16.34, 15.08, 13.07. Anal. calcd for $C_{20}H_{26}N_3BF_2$: C, 67.22; H, 7.28; N, 11.76; F, 10.64. Found: C, 67.55; H, 7.45; N, 11.18; F, 10.47. UV (ethanol) $\lambda_{max}$ 592 nm, log $\epsilon$ 4.86; fluorescence (ethanol) $\lambda_{max}$ 609 nm, $\Phi$ 0.56 (excitation at 540 nm with Nile blue A perchlorate [24] as a standard).

A similar conversion of 3,3′,4,4′,5,5′-hexamethylpyrromethene hydrobromide **8b** gave 3,3′,4,4′,5,5′-hexamethyl-6-cyanopyrromethane **9b** as a golden green amorphous solid (57%), mp 202–205°C (dec). $^1H$ NMR: $\delta$ 2.34 (s, 6H), 2.27 (s, 6H), 1.92 (s, 6H). Anal. calcd for $C_{16}H_{21}N_3$: C, 75.29; H, 8.23; N, 16.47. Found: C, 75.11; H, 8.29; N, 16.40.

In an adaptation of the procedure described above, the pyrromethane **9b** gave 1,2,3,5,6,7-hexamethyl-8-cyanopyrromethene–$BF_2$ complex **4**, (PM–HMC), 32%, as a golden green solid, mp 253–255°C (dec). $^1H$ NMR: $\delta$ 2.49 (s, 6H), 2.39 (s, 6H), 1.94 (s, 6H). $^{13}C$ NMR: $\delta$ 158.04, 138.57, 132.17, 128.38, 114.97, 102.93, 13.06, 11.58, 8.98. Anal. calcd for $C_{16}H_{18}N_3BF_2$: C, 63.78; H, 5.98; N, 13.96; F, 12.63. Found: C, 63.92; H, 6.01; N, 13.74; F, 12.56. UV (ethanol) $\lambda_{max}$ 588 nm, log $\epsilon$ 4.66; fluorescence (ethanol) $\lambda_{max}$ 612 nm, $\Phi$ 0.54 (excitation at 540 nm with Nile blue A perchlorate [24] as a standard).

Successful laser performance of PM–TEDC and PM–HMC has been demonstrated both in liquids [19] and solids [8]. Table 1 summarizes the published efficiencies and center wavelength laser results in both xylene [19] and HTP [8]. In the solid state, with an input energy of 15 mJ, PM–TEDC exhibited tunable laser emission from 613 to 639 nm, while PM–HMC produced laser output between 615 and 639 nm.

According to the method developed by Chu and Chu [13], ethyl 3,5-dimethylpyrrole-2-carboxylate **11** (obtained from the Aldrich Chemical Company) was treated with phosphorus oxychloride and N,N-dimethylformamide to give ethyl 3,5-dimethyl-4-formylpyrrole-2-carboxylate **12** (93%) as colorless needles, mp 144–146°C (Ref. [11] and [12] mp 145–145.5°C). $^1H$ NMR: $\delta$ 9.99 (s, 1H), 9.78 (bs, 1H), 4.34 (q, 2H), 2.57 (s, 3H), 2.55 (s, 3H), 1.38 (t, 3H).

The aldoxime **13**, mp 195–197°C (Ref. [14] mp 195–196°C) was obtained (85%) by treating the aldehyde in ethanol with an aqueous solution of hydroxylamine hydrochloride and sodium acetate [14] and was dehydrated by heating at 125°C in acetic anhydride [14] to give ethyl 3,5-dimethyl-4-cyanopyrrole-2-carboxylate **14** (88%) mp 169–171°C (Ref. [14] mp 170–171°C). $^1H$ NMR: $\delta$ 9.87 (bs, 1H), 4.12 (q, 2H), 2.57 (s, 3H), 2.56 (s, 3H), 1.39 (t, 3H).

By a procedure previously employed [2,14] for the degradation of a pyrrole-2-carboxylate, 3,5-dimethyl-4-cyanopyrrole-2-carboxylic acid **15** (96%) mp 245–248°C (Ref. [14] 245–250°C) was obtained from the ester **14** by hydrolysis in aqueous potassium hydroxide and was decarboxylated by heating (180°C) in ethanolamine to give 2,4-dimethyl-3-cyanopyrrole **16** (75%) mp 106–108°C (Ref. [14] mp 107°C). $^1H$ NMR: $\delta$ 8.31 (bs, 1H), 6.39 (s, 1H), 2.38 (s, 3H), 2.14 (s, 3H). $^{13}C$ NMR: $\delta$ 136.69, 121.70, 116.80, 114.53, 92.67, 12.40, 10.66.

### *3,3′,5,5′-Tetramethyl-4,4′-dicyano-6-ethylpyrromethene hydrochloride* **17** *and 1,3,5,7-Tetramethyl-8-ethyl-2,6-dicyanopyrromethene–$BF_2$ Complex* **18**

Propionyl chloride (6.11 g, 66.0 mmol) was added dropwise with stirring over a period of 30 min to a solution of 2,4-dimethyl-3-cyanopyrrole **16** (2.2 g, 18.3 mmol) in 1,2-dichloroethane (10 mL). The mixture was heated at 80°C for 4 hours, cooled to room temperature, diluted with petroleum ether (300 mL), and triturated for 12 hours to bring about the separation of the hydrochloride **17** (2.0 g, 70%), mp 220–225°C (dec).

The unstable hydrochloride was converted to the P–$BF_2$ complex without further purification. Triethylamine (4.2 g, 41.6 mmol) was added at room temperature to a suspension of the hydrochloride **17** (1.5 g, 4.7 mmol) in toluene (300 mL). The mixture was stirred for 20 minutes, and boron trifluoride etherate (8.06 g, 57.2 mmol) was added. The reaction mixture was heated at 80°C for 1 hour, cooled to room temperature, washed with water (2 × 100 mL), and dried (magnesium sulfate). Concentration and purification of the crude product by column chromatography (silica gel, 100 g, 230–400 mesh, 60 Å, toluene) yielded 1,3,5,7-tetramethyl-2,6-dicyano-8-ethylpyrromethene–$BF_2$ complex **18** as an orange crystalline solid (0.75 g, 48%), mp 295–297°C (dec). $^1$H NMR: $\delta$ 3.15 (q, 2H), 2.70 (s, 6H), 2.68 (s, 6H), 1.39 (t, 3H). $^{13}$C NMR: $\delta$ 158.37, 153.94, 146.31, 131.37, 113.66, 106.74, 22.18, 15.56, 15.15, 13.72. Anal. calcd for $C_{17}H_{17}N_4BF_2$: C, 62.58; H, 5.22; N, 17.18; F, 11.66. Found: C, 62.69; H, 5.31; N, 17.19; F, 11.61. UV (dioxane) $\lambda_{max}$ 496 nm, log $\epsilon$ 5.12; fluorescence (dioxane) $\lambda_{max}$ 511 nm, $\Phi$ 0.79 (excitation at 460 nm, with acridine orange as a standard); $\lambda_{las}$ (ethanol) 540–565 nm.

## *ACKNOWLEDGMENTS*

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