

## Highly Dichroic and Luminescent Triphenodioxazine Dyes

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We report herein a triphenodioxazine dye, which is highly dichroic and luminescent in liquid crystal (LC). The dye shows remarkable polarization dependence resulting from its high orientational order up to 0.88: the dichroic ratios from its absorption and that from the emission reach 22.1 and 67.7, respectively. Such high order has never been reported for luminescent dyes in LC, thus showing appreciable potential advantage for some applications.

Dichroic dyes have been studied in many years.<sup>1,2</sup> They orient in LC, thus showing large polarization dependence, called dichroism, in their light absorption and/or luminescence. Since the discovery of their electrooptic effects in LC,<sup>3</sup> enormous efforts have been devoted to the synthesis of novel dichroic dyes to apply them to LC display applications during the 70s.<sup>1</sup> Recently, their polarized luminescence also has attracted much attention with respect to possible applications such as fluorescent LC displays,<sup>4</sup> fluorescent polarizers,<sup>5</sup> light-emitting diodes,<sup>6</sup> and liquid crystal lasers.<sup>7</sup>

Hence, highly dichroic luminescent guest dye molecules have been needed in these emerging fields. Most conventional dichroic dyes are azo or anthraquinone derivatives and they usually do not have strong luminescence. Various other luminescent chromophores have been investigated, including naphthalimides,<sup>8,9</sup> dilactones,<sup>10</sup> thiadiazoles,<sup>11</sup> benzanthrones,<sup>12</sup> benzothiophenes,<sup>13</sup> fluorophenazines,<sup>14</sup> acenequinones,<sup>15</sup> and conjugated oligomers.<sup>16</sup> However, their dichroic ratios usually do not reach 10 and never exceed 15, thereby limiting device performance in polarization degree. A linearly  $\pi$ -conjugated thiadiazole shows a high dichroic ratio up to 12.8.<sup>11</sup>

We found previously that some triphenodioxazines are dichroic and luminescent in LC.<sup>17</sup> Although triphenodioxazines have a long history as commercial dyestuffs and pigments since their discovery by Fischer in 1879,<sup>18</sup> little has been known about their dichroic derivatives with a few exceptions.<sup>19</sup> In this report, we have improved their dichroism and luminescence further by removing the lateral chlorine atoms from the chromophore having four mesogenic substituents.

Triphenodioxazines **1** and **2** were synthesized from corresponding aniline derivatives, quinone derivatives, and acid chlorides via two-step cyclization as their schemes are shown in Figure 1.<sup>17,20,21</sup> The crude anilide intermediates from the first step were used for the second step without further purification. The structure of these intermediates was confirmed by the corresponding mass signals as their main peaks in their TOF-MS spectra.

LC mixtures containing the dyes (0.2%, w/w) were injected into cells. The cells were purchased from EHC Co., Ltd. and

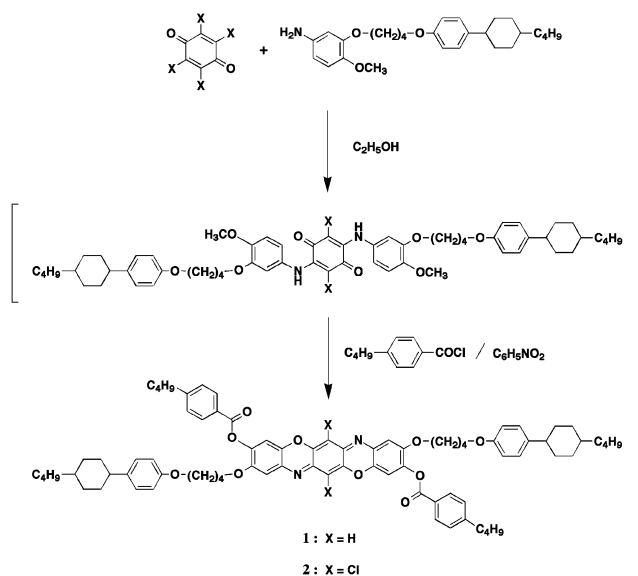


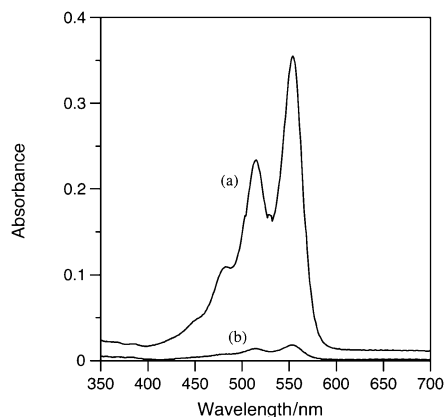
Figure 1. Synthetic scheme for dye **1** and dye **2**.

consisted of two quartz glass plates about 20  $\mu\text{m}$  apart, each having a rubbed polyimide layer to obtain a parallel uniaxial alignment of LC. Two host mixtures (**E7** and **E9**) consisting of some cyanobiphenyl derivatives were purchased from Merck Japan Co., Ltd.<sup>22,23</sup> Another mixture ASET-010 (**AS**) consisting of 4-cyano-3-fluorophenyl 4-alkylbenzoate derivatives was supplied by the laboratory of Merck Japan Co., Ltd.<sup>24</sup>

Polarized absorption spectra of the cells were recorded at 23  $^{\circ}\text{C}$  on a Cary 5E spectrophotometer equipped with a highly efficient Gran-Thomson polarizer on the optical path before the sample. The spectra were obtained at normal incidence with polarization parallel and perpendicular to the rubbing direction (nematic director), respectively. The reference spectra taken with the cells of the corresponding host without dye for each polarization were subtracted from each sample spectrum during data processing.

Emission (EM) spectra of the cells were recorded at 23  $^{\circ}\text{C}$  on a Jobin Yvon-Spex Fluorolog3 spectrofluorometer equipped with two polarizers, one for the EM beam and the other for the excitation (EX) beam at 520 nm. The EM at an oblique angle (22.5 degrees from normal to the cell surface) was recorded with the EX at normal incidence: the two polarizing directions are aligned. The EM spectra were obtained with the aligned direction parallel and perpendicular to the rubbing direction, respectively.

The dyes are oriented in host LC, thereby showing significant dichroic ratio  $D_A$  of at least 9.9. Figure 2 shows



**Figure 2.** Polarized absorption spectra of the AS mixture containing dye **1**: (a) with the light polarization parallel to the rubbing direction; and (b) with that perpendicular to the direction.

**Table 1.** Dichroism of the LC mixtures

Dye	Host	Absorption			Emission		
		$\lambda_{\max}/\text{nm}$	$D_A$	$S$	$\lambda_{\max}/\text{nm}$	Stokes shift/nm	$D_F$
<b>1</b>	<b>E7</b>	558	13.3	0.80	578	20	38
<b>1</b>	<b>E9</b>	559	15.3	0.83	578	19	43.1
<b>1</b>	<b>AS</b>	554	22.1	0.88	570	16	67.7
<b>2</b>	<b>E7</b>	566	9.9	0.75	587	21	24.9
<b>2</b>	<b>E9</b>	567	10.4	0.76	588	21	27.1
<b>2</b>	<b>AS</b>	562	14.7	0.82	578	16	50.6

typical absorption spectra and the following values are summarized in Table 1. Dichroic ratios  $D_A$  are defined for a peak ( $\lambda_{\max}$ ) in polarized spectra as

$$D_A = A_{//}/A_{\perp} \quad (1)$$

where  $A_{//}$  and  $A_{\perp}$  are the absorbance with the light polarization parallel and perpendicular to the nematic director, respectively. Order parameters  $S$  are determined from each  $D_A$  values by the following formula:<sup>1</sup>

$$S = (D_A - 1)/(D_A + 2) \quad (2)$$

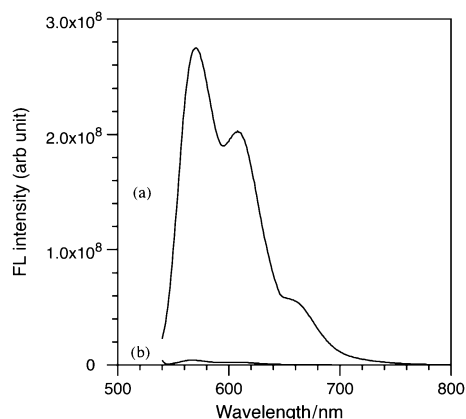
The mixtures also exhibit large polarization in EM: typical EM spectra are shown in Figure 3 and the following values are summarized in Table 1. The dichroic ratio  $D_F$  is also defined for a peak in polarized EM spectra as

$$D_F = F_{//}/F_{\perp} \quad (3)$$

where  $F_{//}$  and  $F_{\perp}$  are the PL intensity at a peak with the polarization (both EM and EX) parallel and perpendicular to the director, respectively. Both the high  $S$  and the polarized excitation accounts for the high  $D_F$  values from 24.9 up to 67.7. If transition moments do not fluctuate during the fluorescence lifetime, the  $D_F$  values should become approximately  $D_A^2$  according to the following formula for polarized excitation,<sup>8</sup> thereby showing appreciable depolarization by thermal fluctuation:

$$S = (D_F^{1/2} - 1)/(D_F^{1/2} + 2) \quad (4)$$

Dye **1** shows higher orientation in each mixture than that of dye **2**: the  $D_A$  and  $D_F$  values from dye **1** are significantly larger



**Figure 3.** Polarized emission spectra of the AS mixture containing dye **1**: (a) with the excitation and emission polarized parallel to the rubbing direction; and (b) with that polarized perpendicular to the direction.

than those of dye **2**. In particular, the mixture AS leads to extreme orientation: the  $D_A$  value reaches 22.1 ( $S = 0.88$ ), which is at the highest rarely shown for a few nonfluorescent anthraquinone dyes in a patent application.<sup>25</sup>

The  $D_A$  and  $D_F$  dependence on the hosts accounts for the orientation of the molecules surrounding dyes. Each dye shows higher  $D_A$  and  $D_F$  values in order of nematic–isotropic transition temperature ( $T_{NI}$ ) of the hosts;  $T_{NI}$  values are 168 (AS), 84 (E9), and 60 °C (E7). The host orientation at room temperature generally depends on  $T_{NI}$ , thus leading to the higher guest orientation.

The linearity of 6,13-hydrogenated chromophore exactly contributes the orientation in LC. It has been known that the orientation of guest dyes depends on their linearity in molecular shape with respect to the steric hindrance with hosts; the geometric ratio  $L/D$  ( $L$ : length,  $D$ : diameter) of guest molecules correlates well with their  $S$  values in LC.<sup>26</sup> Substituting 6,13-chlorines with hydrogens increases  $L/D$  because of their large difference in atom size; van der Waals radii of Cl and H are 0.18 and 0.11 nm, respectively.<sup>27</sup>

Moreover, dye **1** also shows stronger EM than dye **2**, thus illustrating that the fluorescence intensity is also significantly improved by the 6,13-hydrogenation. The polarized spectra also enable us to compare the yields from **1** and **2** approximately because their spectrum shape does not vary significantly. The intensity  $F_{//}$  normalized by the  $A_{//}$  at the excitation wavelength ( $A_{//520}$ ) was calculated, thereby showing that the  $F_{//}/A_{//520}$  values from dye **1** are 1.7, 1.6, and 1.5 times to that from dye **2**, for E7, E9, and AS, respectively. The improvement in  $D_F$  of dye **1** should slightly overestimate these values because of the decrease both in the depolarization and in the lambertian emission. Then the normalized EM intensity from the chloroform solution of **1** is also 2.4 times to that of **2** without polarization, thereby confirming the yield improvement exactly. These nonpolarized absorption and emission spectra were measured in the same manner without the polarizers, respectively.

The slope in  $A_{//}$  spectra is always sharp on the bathochromic side of top peak, thereby showing rather small self-absorption for EM in spite of the small Stokes shift down to 16 nm. The  $A_{//}$  decreases almost 80% from absorption peak at the EM peak

(570 nm) and becomes negligible around the shoulder peak (605 nm) as shown in Figure 2.

We think the remarkable orientation of dye **1** with the improved fluorescence intensity provides appreciable advantage in possible applications, and anticipate much attention for this kind of dye from researchers in related fields.

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- 1**: 1,4-benzoquinone (0.5 g) and 3-[4-[4-(4-butylcyclohexyl)phenoxy]butoxy]-4-methoxyaniline (4.3 g) were added to ethanol (50 mL) and the mixture was heated to reflux for 7 h. After cooling the mixture to room temperature, the precipitates were filtered. The precipitates on the filter were washed with water and dried, followed by the purification by silica gel column chromatography with chloroform as eluents, thereby obtaining 0.8 g of crude intermediate. The intermediate (0.1 g) and 4-butylbenzoyl chloride (1.0 g) were added to nitrobenzene (20 mL) and the mixture was heated at 140 °C for 7 h. After cooling the mixture to room temperature, the resulting precipitates were filtered and washed with methanol on the filter. The precipitates were purified 3 times by silica gel thin layer chromatography with chloroform as eluents, thereby obtaining 10 mg of the final dye **1** reddish powder. IR (KBr): 2956, 2924, 2856, 1741 (C=O), 1611, 1565, 1512, 1487, 1468, 1435, 1378, 1261, 1224, 1179, 1129, 1056, 1017, 826, 578 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.10 (d, *J* = 8 Hz, 4H), 7.30 (d, *J* = 8.5 Hz, 4H), 7.08–7.05 (overlapping, 6H), 6.97 (s, 2H), 6.73 (q, 4H), 6.48 (s, 2H), 4.06 (t, *J* = 6 Hz, 4H), 3.83 (t, *J* = 8.5 Hz, 4H), 2.69 (t, *J* = 8 Hz, 4H), 2.39 (t, *J* = 12.8 Hz, 2H), 1.86–1.78 (overlapping, 16H), 1.67–1.61 (m, 4H), 1.43–1.33 (m, 8H), 1.31–1.25 (m, 12H), 1.22 (s, 2H), 1.06–0.99 (m, 4H), 0.97–0.89 (overlapping, 12H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ 164.25, 156.76, 150.93, 149.30, 148.10, 147.64, 140.62, 139.80, 138.04, 130.17, 128.50, 127.34, 126.14, 114.01, 111.30, 110.27, 105.65, 77.32, 77.14, 77.09, 76.88, 76.63, 67.06, 43.67, 37.26, 37.08, 35.76, 34.55, 33.62, 33.17, 29.21, 25.72, 22.99, 22.34, 14.15, 13.90. High-resolution MS with laser desorption/ionization: *m/z* 1243 [M + H]<sup>+</sup>, 1265 [M + Na]<sup>+</sup>. Assignment of the <sup>1</sup>H and <sup>13</sup>C NMR signals was done on the basis of <sup>1</sup>H–<sup>1</sup>H shift-correlated 2D NMR (COSY) and <sup>13</sup>C–<sup>1</sup>H COSY.
- 2**: Chloranil (0.5 g), 3-[4-[4-(4-butylcyclohexyl)phenoxy]butoxy]-4-methoxyaniline (1.7 g), and sodium acetate (0.32 g) were added to ethanol (20 mL) and the mixture was heated to reflux for 5 h. After cooling the mixture to room temperature, the precipitates were filtered. The reactant left on the filter was washed with water and dried, thereby obtaining 1.8 g of crude intermediate. The intermediate (0.1 g) and 4-butylbenzoyl chloride (1.0 g) were added to nitrobenzene (20 mL) and the mixture was heated at 160 °C for 4 h. After cooling the mixture to room temperature, the resulting precipitates were filtered. The precipitates were purified 3 times by silica gel thin layer chromatography with chloroform as eluents, thereby obtaining 10 mg of the final dye **2** reddish powder. IR (KBr): 2956, 2920, 2851, 1744 (C=O), 1610, 1585, 1558, 1512, 1487, 1467, 1433, 1287, 1260, 1181, 1134, 1055, 1017, 911, 824, 582 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.10 (d, *J* = 8 Hz, 4H), 7.30 (d, *J* = 8.5 Hz, 4H), 7.26 (overlapping), 7.16 (s, 2H), 7.08 (d, *J* = 9 Hz, 4H), 6.74 (d, *J* = 9 Hz, 4H), 4.09 (t, *J* = 6 Hz, 4H), 3.84 (t, *J* = 6.3 Hz, 4H), 2.69 (t, *J* = 7.5 Hz, 4H), 2.39 (t, *J* = 11.8 Hz, 2H), 1.87–1.79 (m, 16H), 1.67–1.61 (m, 4H), 1.41–1.36 (m, 8H), 1.31–1.28 (m, 12H), 1.25 (s, 12H), 1.22 (br, 2H), 1.06–1.01 (m, 4H), 0.97–0.89 (overlapping, 12H). High-resolution MS with laser desorption/ionization: *m/z* 1311 [M + H]<sup>+</sup>, 1333 [M + Na]<sup>+</sup>. Assignment of the <sup>1</sup>H signals was done on the basis of those from dye **1**.
- E7**: 4-*n*-pentyl-4'-cyanobiphenyl 51%, 4-*n*-heptyl-4'-cyanobiphenyl 25%, 4-*n*-octyl-4'-cyanobiphenyl 16%, 4-*n*-pentyl-4''-cyanoterphenyl 8%.
- E9**: 4-*n*-propyloxy-4'-cyanobiphenyl 15%, 4-*n*-pentyloxy-4'-cyanobiphenyl 38%, 4-*n*-heptyloxy-4'-cyanobiphenyl 38%, 4-*n*-pentyl-4''-cyanoterphenyl 9%.
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