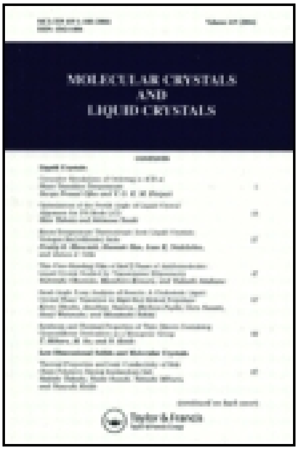

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Highly Dichroic Triphenodioxazine Dyes for Guest Host Liquid Crystalline Mixtures

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Novel triphenodioxazines have been synthesized and evaluated. The dyes were not only highly dichroic in guest-host liquid crystal mixtures but also vivid because of a sharp peak in absorption spectra. Mesogenic substituents to the 2,9- position of the chromophore improve the order parameter in the mixture. Moreover, the mixtures also showed significant polarized photoluminescence. These results would reveal a few advantages of the novel dyes for some possible applications.

Keywords: dichroic dye; triphenodioxazine; polarized photoluminescence; guest-host

INTRODUCTION

Dichroic dyes were extensively studied during the 70s and the 80s in order to apply them to guest-host liquid crystal displays (GHLCDs), which was first reported by Helmeier.[1] The most of them are azo dyes or anthraquinone dyes.[2] They have linear chromophores with their electronic transition moments parallel to their long axis. Then, they are embedded along a nematic director in an uniform orientation of LC mixture, thereby showing significant linear dichroism. Then, another chromophores were also investigated for that purpose, [2] but most of them have not used in LCDs.

Recently novel dichroic dyes are needed for some possible new applications. Vivid dyes should be useful for multilayered GHLCDs, [3,4] which have attracted much attention because of their good color performance with a possible excellent brightness in reflection modes. Vivid dyes have sharp absorption spectra, which would result in effective control of each primary color in the multilayered devices. Fluorescent dichroic dyes are also needed for polarized photoluminescence (PL) and electroluminescence, which have recently attracted much attention.[5-7] Those new demands often require new chromophores.

Triphenodioxazine dyes have had a long history since the discovery of the chromophore by Fisher in 1879.[8] They have been applied to pigments and various kinds of dyestuffs.[9] An important advantage of the dye is strong absorption due to a large molar absorption coefficient, which is about 5 times to that of anthraquinone dyes. However, they have not investigated as dichroic dyes with a few exceptions, where some dyes appeared in a few patent applications.[10]

In this paper, we report novel triphenodioxazine derivatives for GH mixtures. We found in the previous report that some triphenodioxazines having benzoate groups are highly dichroic and vivid in LC mixtures.[11] Here, we have modified their 2,9-substituents to improve the dichroism, which has been investigated by the polarized absorption and emission (EM) of the GH mixtures.

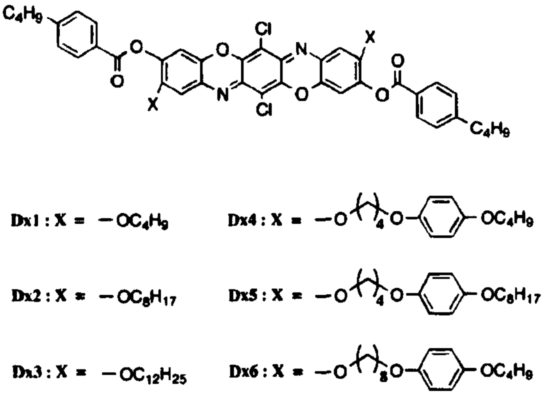

FIGURE 1 Structure of novel triphenodioxazines

EXPERIMENTAL

Novel Triphenodioxazine derivatives from **Dx-1** to **Dx-6** (Fig.1) were synthesized from dianilide compounds according to the method reported.[11] The dianilide compounds were synthesized by coupling chroranil with aniline derivatives corresponding to the final dye structure. The crude products were purified by chromatography on silica-gel using chloroform as eluent. Structure of the products was confirmed by MS and ^{1}H-NMR spectra.

GH mixtures containing the dyes were prepared by mixing them with a liquid crystal mixture (ZLI1132 , E7 or E9, Merck Japan Co.Ltd.) at about 80°C; after that, each mixture was injected into a cell. The dye concentration was 0.03%(w/w) for **Dx1** and was 0.1%(w/w) for the other dyes (**Dx2~Dx6**). The cell used consisted of two quartz glass plates, each having a rubbed polyimide layer to obtain parallel alignment. The cell gap was about 20μm.

Order parameters S_A of dyes in the mixture were determined from two polarized absorption spectra of each cell by the formula:[2]

$$S_A = (D_A - 1)/(D_A + 2) \quad , \qquad (1)$$

where D_A is a dichroic ratio from the two spectra obtained. The two polarized UV-visible absorption spectra of each cell were recorded on a Cary 5E spectrophotometer equipped with a highly efficient Gran-Thomson polarizer before the sample at 23°C. The spectra were obtained at normal incidence in transmission mode with polarization parallel and perpendicular to the nematic director, respectively. The reference spectra, taken with cells with just the host LC in the same manner on the same two polarization respectively, were subtracted from the each sample spectra during data processing.

Another order parameters S_F were also determined from two EM spectra of each cell by the following formula:[7]

$$S_F = (D_F^{1/2} - 1)/(D_F^{1/2} + 2) \quad , \qquad (2)$$

$$D_F = F_0 / F_{90} \quad , \qquad (3)$$

where F_0 is PL intensity at a peak with both excitation (EX) and EM polarized parallel to the director and F_{90} is that perpendicular to the director.

The EM spectra of the cells were recorded on a Jobin Yvon-Spex Fluorolog3 spectrofluorometer by the EX at 520nm equipped with a polarizer both on the EX and the EM beam. The EX was done at normal incidence with polarization of the light parallel or perpendicular to the nematic director. The EM spectra with the same two polarizations were respectively obtained with an emitted light of an oblique angle (22.5 degrees from normal to the cell surface), which is also perpendicular to the nematic director. The EX spectra were also recorded with the same measurement apparatus by the EM of 585nm or of 630nm.

RESULTS AND DISCUSSION

Mesogenic 2,9-substituents (X) contribute to increase in S_A. The dyes are highly dichroic in the GH mixture, as shown in Fig.2 and in Table 1: the obtained S_A are from 0.66 to 0.76. Then, the dyes with large mesogenic groups (**Dx4**~**Dx6**) shows appreciably larger S_A than those with simple alkoxy groups (**Dx1**~**Dx3**): the increase in S_A by the 2,9-mesogens are about 0.05. The values of S_A in E9 or in ZLI-1132 are also slightly higher than those in E7; higher S_A of those hosts would account for the small differences.

These mixtures also display vivid red due to a sharp peak in absorption spectra, which was reported for a few similar derivatives previously.[11] In addition, the shape in the spectra is not influenced by the X or the hosts; two kinds of half width (W_1 and W_2) are defined in Fig.2 and those values are listed in Table 1, then the values showing no significant change by the X or the host. Because a clear subpeak due to a vibrational level appears in the spectra, the values of W_1 are larger than those of W_2. Nevertheless, the total half width ($W=W_1+W_2$) is smaller than that of known anthraquinones, which is about 100nm. Particularly, the small W_2 of triphenodioxazine should provide pure red by a combination with yellow stuffs.

The GH mixtures also exhibit polarized PL: typical polarized EX and EM spectra are shown in Fig.3 and the values of spectral parameters are summarized in Table 2.

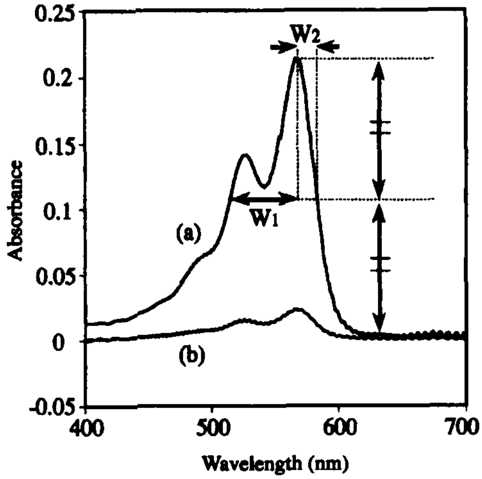

FIGURE 2 Polarized absorption spectra of **Dx6** in E9:
(a) with the incident light polarized parallel to the nematic director,
(b) with the incident light polarized perpendicular to the nematic director

TABLE 1 Values of parameters from absorption spectra of dyes in GH mixtures.

Dye	S_A			λ max (nm)			W_1 (nm)			W_2 (nm)		
	E7	E9	1132	E7	E9	1132	E7	E9	1132	E7	E9	1132
Dx1	0.66	0.67	0.67	566	568	562	55	53	55	15	16	18
Dx2	0.69	0.70	0.70	567	565	563	53	52	51	14	16	16
Dx3	0.69	0.71	0.71	566	567	563	51	53	49	13	15	14
Dx4	0.73	0.76	0.75	566	567	563	51	51	51	15	14	16
Dx5	0.73	0.75	0.73	567	566	562	52	50	53	13	16	13
Dx6	0.72	0.75	0.75	567	567	563	51	53	51	15	14	14

1132: in ZLI-1132, λmax: peak wavelength

The EX maxima from 561 to 567nm arise from optical absorption of the guests. The shape of EX spectra is identical with that of absorption spectra. Moreover, differences in the peak wavelength (λmax) are negligible between the absorption and the EX spectrum for each of the dyes.

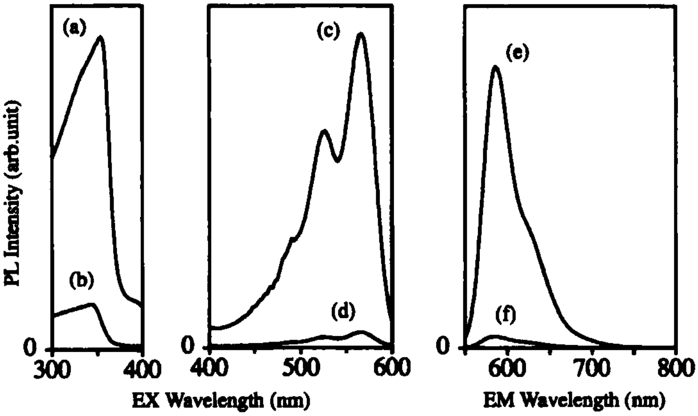

FIGURE 3 EX and EM spectra of Dx6 in E9 :
(a) EX profile, the EM (585nm) and EX both polarized parallel to the director,
(b) EX profile, the EM (585nm) and EX both polarized perpendicular to the director,
(c) EX profile, the EM (630nm) and EX both polarized parallel to the director,
(d) EX profile, the EM (630nm) and EX both polarized perpendicular to the director,
(e) EM profile, the EM and EX (520nm) both polarized parallel to the director,
(f) EM profile, the EM and EX (520nm) both polarized perpendicular to the director.

TABLE 2 Values of parameters from EX and EM spectra of dyes in GH mixtures.

		λ max (nm)				
Dye	LC	EX	EM	SS (nm)	DF	SF
Dx3	E9	567	586	19	19.1	0.53
Dx4	E9	566	586	20	25.0	0.57
Dx5	E9	566	587	21	24.6	0.57
Dx6	E7	565	584	19	19.6	0.53
Dx6	E9	566	586	20	23.5	0.56
Dx6	ZLI-1132	561	580	19	27.7	0.59

SS: Stokes Shift, λmax: peak wavelength

On the other hand, another EX maxima near 350nm originate from the host because the dyes did not show appreciable absorption in this region. Moreover, the hosts showed λmax near 350nm in their absorption spectra. Hence, an energy transfer should take place from the hosts to the dyes. However, the details of the transfer including the mechanism are not yet known.

The values of S_F are smaller than those of S_A. We think that the difference would arise from the angle between the emission transition moment and the nematic director of dye molecules in the mixtures. The moment of emission should be a little different from that of absorption transition because the values of Stokes shift (SS) obtained are about 20nm. Nevertheless, these values are relatively small with comparison with other chromophores. We have to consider whether the difference in structure between the excited and the ground state would be large enough to generate such decrease in S_F or not.

CONCLUSION

We have revealed the following results on the novel triphenodioxazine dyes:

(1) The mesogenic 2,9-subsituents can improve the order of the dye in the GH mixture.

(2) The mesogenic 2,9-subsituents do not influence the shape in absorption spectra of the dye, thereby displaying a vivid red due to the sharp spectrum.

(3) The GH mixtures exhibit bright photoluminescence with significant dichroism in polarization.

Hence, we think the vividness with the high order or the photoluminescence would be a sonsiderable advantage in some possible new applications.

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