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Highly Anisotropic Molecular Materials for LCD

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Two kinds of novel molecular materials with high optical anisotropy were synthesized and evaluated. Liquid crystalline phenylacetylene derivatives, which have mesogen of a 1,4-Bis(phenylethynyl)benzene, not only showed high Δn but also were stable for heating or light. Triphenodioxazine derivatives were highly dichroic in guest-host liquid crystal mixtures, where they also showed vivid color due to a sharp peak in absorption spectra. Hence, these molecules possibly improve visual performance of some reflection type liquid crystal displays (LCDs).

Keywords: anisotropy; birefringence; dichroic dye; phenylacetylene; triphenodioxazine

INTRODUCTION

Novel materials with high anisotropy are needed particularly for reflection type liquid crystal displays (LCDs). Varieties of anisotropic materials (e.g. liquid crystals, dichroic dyes, polarizers, etc.) have been applied to LCDs. Anisotropy of these materials is essential for the fundamental optics of the devices, thus affecting basic optical performance of the devices such as brightness or contrast; novel materials with high anisotropy should improve the performance. Generally, such optical improvement is greatly preferable to reflection type LCDs because

of their limited light for use.

In principle, anisotropic molecules show birefringence(Δn) and/or dichroism, depending on whether they absorb light or not. Both are important to reflection type LCDs. Liquid crystalline compounds with high Δn ^[1] are needed for some modes using light scattering (e.g. PDLC, PNLC, etc.), where they should exhibit high brightness because of strong scattering originated from high Δn . Dichroic dyes^[2] are also needed for some new guest-host modes, where large dichroism is preferable for excellent contrast of the displays.

For these purposes, we have been doing research on the following 4 items of highly anisotropic molecular materials: (1) novel liquid crystalline compounds with high Δn , (2) novel dichroic dyes, (3) oriented solid thin molecular films with high Δn or high dichroism, and (4) a novel computed simulation of molecular assembly for design of anisotropic molecules. In this paper, we report the following two kinds of novel molecules regarding (1) and (2).

Liquid Crystalline Phenylacetylene Derivatives

Novel liquid crystalline phenylacetylene derivatives were synthesized by coupling brominated intermediates to ethynyl intermediates with a palladium catalyst $\text{PdCl}_2(\text{PPh}_3)_2$ and CuI , as reported previously.^[4]

Values of Δn were extrapolated from those of the mixtures which are 10 percent (w/w) solution of each compound in MJ931381 or E7(Merck Japan Co.Ltd.): Δn of the mixtures was measured with a Abbe refractometer at 20°C. Phase sequences with transition temperatures were measured by a polarized microscope with a hot plate. Stability for light or heat was estimated from change in purity of the compounds by light exposure or by heating: dekaline solution (0.02%, w/w) of the compounds were irradiated by the light (Xe lamp, 332W/m², 2h) in a glass cell or heated(150°C, 2h). Purity of the compounds was measured by a high performance liquid chromatography (HPLC), which was performed

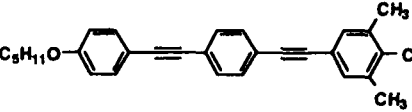
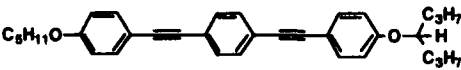
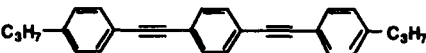
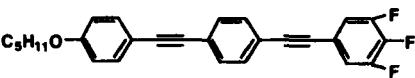
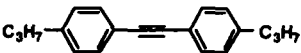
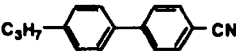
with an ODS column by eluent of acetonitrile. Residual rates (X or Y) were calculated by dividing purity after the exposure or after the heating by that before the treatment for each compound: X is for light and Y is for heat.

The compounds showed high Δn up to 0.47, as typical cases are shown in Table 1. A linear π -electron conjugation accounts for the high anisotropy. It has been known that the length of π -electron conjugation along the principal axis are responsible for high Δn .^[3] Anisotropy in molecular polarizability calculated by molecular orbitals correlates well with values of Δn measured for phenylacetylene derivatives.^[4] The compounds reported here have a long π -electron conjugation along the extremely linear axis, because their phenyl rings are coupled with acetylenes.

The compounds are also very stable. The X and Y are still at least 92% after the light irradiation or the heating. Particularly, the photostability should be remarkable. Most of them show comparable X to a well-known tolane derivative(**2PA-1**) and a common cyanobiphenyl compound(**3CB**), although these molecules absorb more energy from the light than the tolane. Figure 1 shows that absorbance of **3PA-1** is significantly larger than that of the tolane in the region which is larger than 270nm. The compounds were exposed to the light in this region, because the cells have strong absorption below 270nm. Hence, the intrinsic photoreactivity should be significantly low.

Such low photoreactivity is interesting because generally compounds with high Δn have appreciable photoreactivity, which is still a serious problem for practical applications.

TABLE I Δn and stability of phenylacetylene derivatives

No	Molecules / Phase sequence	Δn	Residual rate'	
			for light X (%)	for heat Y (%)
3PA-1	 K 149 N 169 I	0.47	100	97
3PA-2	 K 143 (Sx 110) I	0.36	100	98
3PA-3	 K 170 Sx 178 N 245 I	0.38 *	100	92
3PA-4	 K 129 (Sx 101) SA 168 N 179 I	0.42	100	97
2PA-1	 K 73 I	0.23 *	99	100
3CB	 K 66(N 23) I	-	100	99

+; X : residual rate for the light exposure(Xe lamp,332W/m²,2h),

Y : residual rate for the heating (150°C, 2h)

*: extrapolated from values of the mixture with E7 at 20°C, the others are extrapolated from those of the mixture with MJ931381 at 20°C.

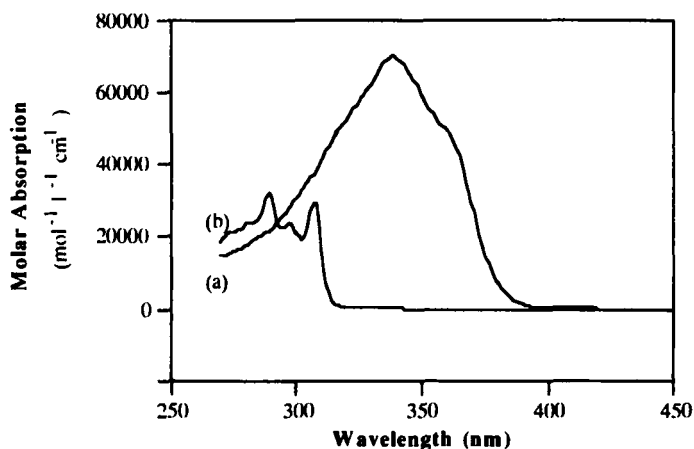


FIGURE 1 Normalized absorption spectra of phenylacetylenes in dimethylformamide solution : (a) 3PA-1 and (b) 2PA-1 .

3. Triphenodioxazine Dyes

Novel Triphenodioxazine derivatives were synthesized from a dianilide compound by intermolecular cyclization, accompanied with esterification of an acid chloride catalyst, as shown in Figure.2. The dianilide compound was synthesized by coupling chloranil with aniline derivatives. The crude products were purified by chromatography on silica-gel using chloroform as eluent. Structure of the products was confirmed by MS and $^1\text{H-NMR}$ spectra.

Guest-host mixtures containing $\sim 0.1\%$ (w/w) of the dyes were prepared by mixing them with a liquid crystal mixture (ZLI1132 or E9, Merck Japan Co. Ltd.); after that, each mixture was injected into cells. The cell used consists of two quartz glass plates, each having a rubbed polyimide layer to obtain parallel alignment. The cell gap was about $20\mu\text{m}$. The optical order parameter S of the dyes in the mixture was determined from absorption spectra with plane-polarized light at 23°C by

the formula^[2]:

$S = (N-1)/(N+2)$, where N is a dichroic ratio from the polarized absorption spectrum obtained.

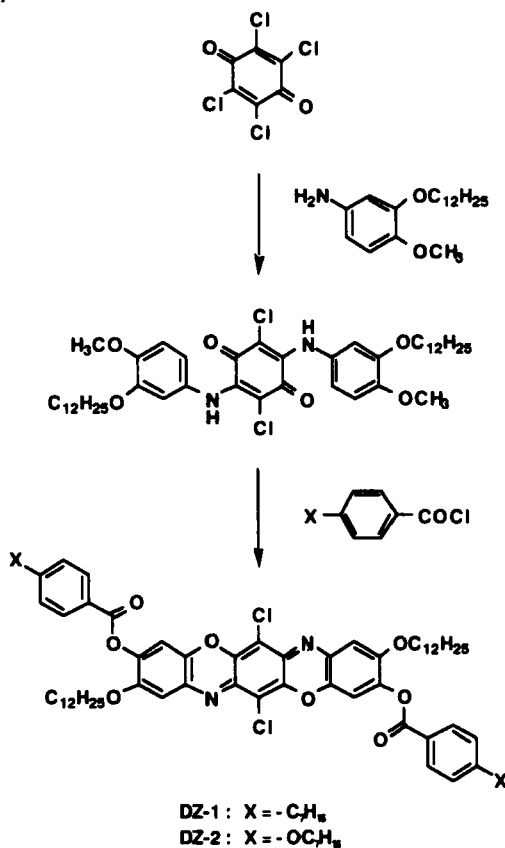


FIGURE.2 Synthesis of novel triphenodioxazines

The triphenodioxazine derivatives were highly dichroic in guest-host liquid crystal mixtures. S were comparable to those reported for azo or anthraquinone dichroic dyes, as shown in Table.2.

Moreover, they showed vivid color due to sharp peaks in absorption spectra, as shown in Figure 3. Half width(W) is significantly smaller than those of azo or anthraquinone dichroic dyes, although there are two peaks in the spectra.

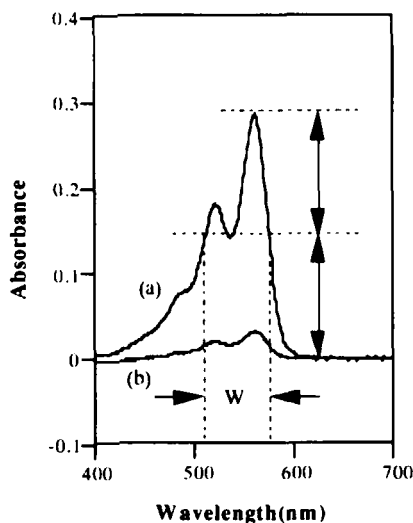


FIGURE 3 Absorption spectrum of DZ-1 in ZLI-1132

TABLE 2 Dichroism and W of guest-host mixtures

Guest dye	Host	S	W (nm)
DZ-1	E9	0.73	69
DZ-1	ZLI-1132	0.73	67
DZ-2	ZLI-1132	0.72	67
anthraquinones	-	0.6~0.8	90~100
azos	-	0.6~0.8	110~150

The vivid color should be useful for various colored guest-host LCDs including a multi-layered type^[5] where high brightness is expected. Since an each layer should control a primary color independently in the

multi-layered type, low W is preferable and would facilitate an excellent full color LCD with good brightness by a reflection mode.

Summary

We have revealed the following results on novel molecular materials:

- (1) Liquid crystalline phenyl acetylenes having the mesogen of 1,4-Bis(phenylethynyl)benzene show high Δn and remarkable photostability.
- (2) The triphenodioxazine dyes are highly dichroic in a guest-host liquid crystalline mixture and have a vivid color due to a sharp peak in the spectra.

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References

- [1] H. Takatsu, K. Takeuchi, Y. Tanaka, and M. Sasaki, *Mol. Cryst. Liq. Cryst.*, **141**, 279 (1986).
- [2] A. V. Ivashchenko, *Dichroic Dyes for Liquid Crystal Displays*, CRC Press, (1994).
- [3] Shin-Tson Wu, *Mol. Cryst. Liq. Cryst.*, **261**, 79 (1995).
- [4] C. Sekine, K. Fujisawa, Y. Fujimoto, and M. Minai, *Mol. Cryst. Liq. Cryst.*, to be published.
- [5] Y. Nakai, T. Ohtake, and A. Sugahara, et al., *SID 97 Digest*, 83 (1997).