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Coumarin and Thiocoumarin Dyes for Guest–Host Type Liquid Crystal Displays

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To realize bright and pure colors in Guest–Host type Liquid Crystal Displays (GH-LCDs), the solubilities and/or absorption coefficients of dichroic dyes which are dissolved in liquid crystals are the most important properties. We have found that a mixture of coumarin and anthraquinone dyes was very useful because it had a large absorption coefficient and little fluorescence. On the other hand, substitution of a sulfur atom for an oxygen atom of the coumarin dye contributes to increase its solubility to liquid crystals, particularly at low temperatures.

Reflective Liquid Crystal Displays (LCDs) are the most suitable for portable information systems because of their remarkably low power consumption. Various display-modes for reflective LCDs are proposed in order to realize fully useful brightness and contrast. Among these variations, the Guest–Host modes (GH-modes), wherein dichroic dyes are dissolved in liquid crystals, have relatively wide viewing angles and high reflectance, and are expected to be one of the most promising display modes in future.[1—4] In particular, three-Layered GH-LCDs with subtractive color mixing of yellow, magenta and cyan are expected to allow the development of "full-color" reflective displays.[5—7]

To realize bright and pure colors in the GH-LCDs, a high solubility (>1 wt%) in liquid crystals and/or a large absorption coefficient are essential for dyes to be used. This study focuses on dichroic coumarin dyes because dyes of this kind have large absorption coefficients. Substitution of a sulfur atom for an oxygen atom of a coumarin dye was studied to increase the solubility.

Experimental

PPP-CI Chemical Quantum Calculation Method. We have used the Pariser–Parr–Pople Configuration Interaction (PPP-CI) quantum chemical calculation method[8] in our theoretical investigation of anthraquinone and coumarin dyes. We determined I_p parameters of several hetero-atoms:[9] 22 eV (SPh), 24 (NHPh), 19 (C=O).

Configuration interaction is also very important to predict the maximum absorption wavelength. We performed configuration interaction calculations on the condition that the maximum number of iterations, N_{CI}, is 25. By this calculation, the first excitation energy is almost saturated in our compounds.

Method of Measuring Solubility. The solubilities of the dyes in liquid crystals were measured spectroscopically. A saturated solution was obtained by adding an excess amount of a dye to the liquid crystal host, thoroughly shaking and leaving the mixture for a month at 24 and -5 °C, and then passing it through a 0.2 μm filter. A measured quantity of the solution was dissolved in a standard volume of cyclohexane and its absorbance was measured and compared with the absorbance of a standard solution of the dye.

NMR and MS Spectra. ^{1}H- and ^{13}C-NMR spectra were measured with a JEOL JNM-LA400WB or JEOL GSX-270W spectrometer. Mass spectra were recorded with a JEOL SX-102A spectrometer.

Materials. 1) Dyes:

Anthraquinone Dye 1. Anthraquinone dye **1** was synthesized from 1,5-dichloroanthraquinone through substitution with 4-*t*-butylbenzenethiol and benzenethiol. The starting materials 1,5-dichloroanthraquinone and $NaCO_3$ were first dissolved in DMF. The mixture was then heated to 80 °C; to this a mixture of 4-*t*-butylbenzenethiol and benzenethiol was added. The reaction mixture was stirred at 80 °C for 3 h and allowed to cool to room temperature. After the precipitate was filtered off, the solution was poured into water. The second precipitate was filtered and washed with DMF and water, and purified by dry column chromatography on SiO_2 (toluene) to give a yellow crystalline powder. ^{1}H NMR (270 MHz, solvent $CDCl_3$; standard TMS) $\delta_H = 1.38$ (9H, s, *t*-Bu), 7.03—8.20 (15H, m, aromatic); ^{13}C NMR (270 MHz, solvent $CDCl_3$; standard TMS $\delta_C = 31.1$ (q, *t*-Bu), 34.8 (s, *t*-Bu), 124.0 (d), 124.1 (d), 124.2 (d), 127.0 (d), 128.0 (s), 129.7 (d), 130.0 (d), 131.2 (d), 131.6 (s), 132.9 (d), 135.3 (s), 135.4 (s), 135.7 (d), 136.0 (d), 146.0, (s, C(AQ)–SPh), 146.5 (s, C(AQ)–SPh), 153.1 (s, C-*t*-Bu), 183.1 (s, C=O), 183.2 (s, C=O).

Coumarin Dye 4,6. Coumarin dyes produced by Nippon Kankoh Shikiso Kenkyusho Co., Ltd. were used in the experiment.

Thiocoumarin Dye 5. Thiocoumarin dye **5** was synthesized from coumarin dye **4** through substitution of a sulfur atom for an oxygen atom. The synthesis process is shown in Fig. 1. Coumarin dye **4** and Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide)[10,11] were dissolved in toluene. The mixture was heated to 110 °C, stirred for 15 h, and allowed to cool to room temperature. After the precipitate (a white crystalline powder) was filtered off, the solution was concentrated and separated by dry column chromatography on $SiO_2(CHCl_3)$ followed by Preparative Thin-Layer Chromatography (PTLC) on $SiO_2(CHCl_3)$ to give a red crystalline powder.

^{1}H NMR (400 MHz, solvent $CDCl_3$; standard TMS) $\delta_H = 1.27$ (6H, t, CH_3), 3.49 (4H, q, CH_2), 6.71 (1H, S, N–C–$\underline{C}$H=C–O), 6.76

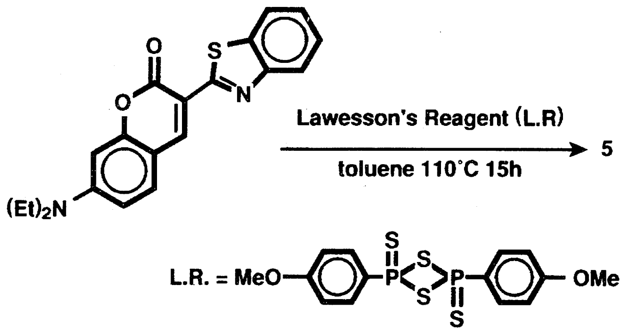


Fig. 1. Synthesis process of thiocoumarin dye **5**.

(1H, d, CH_2–N–C=C$\underline{H}$–CH), 7.38 (1H, t, S–C=CH–C$\underline{H}$), 7.49 (1H, t, N–C=CH–C$\underline{H}$), 7.56 (1H, d, N–C=CH–C$\underline{H}$), 7.96 (1H, d, S–C=C$\underline{H}$), 8.02 (1H, d, N–C=C$\underline{H}$), 8.99 (1H, S, S=C–C=C$\underline{H}$); ^{13}C NMR (400 MHz, solvent $CDCl_3$; standard TMS) $\delta_C = 12.5$ (q, CH_3), 45.3 (t, CH_2), 96.3 (d), 111.2 (s), 111.7 (d), 121.5 (d), 122.1 (d), 124.7 (d), 126.0 (d), 131.1 (d), 136.5 (s), 138.7 (d), 151.8 (s), 152.8 (s), 160.0 (s), 164.1 (s), 192.8 (s, C=S); MS ($m/z = 366$).

2) Liquid Crystals and Chiral Agent. The nematic-cholesteric phase transition liquid crystals used here were the mixtures of ZLI-2806 (liquid crystals of negative dielectric anisotropy), and S811 (chiral agent) obtained from E. Merck. The concentration of S811 was 0.86 wt%.

The Structure of Liquid Crystal Display. The cell structure used in our study is shown in Fig. 2. This is composed of two glass plates, with an inner area of 1×1 cm, each having a transparent electrode of indium(III) tin oxide. The oxide films were coated with a polymer layer which induced a homeotropic structure, in which state the liquid crystals and dyes are aligned vertically to the glass plates. The liquid crystals used here have a negative dielectric anisotropy, and when voltage is applied to the cell, liquid crystals would align horizontally to the plates. However, the chiral agent which induces helical structure is dissolved in liquid crystals, therefore changing the structure of liquid crystals to a helical one. This helical state is called the cholesteric state. Dichroic dyes which are dissolved in liquid crystals have transition moments polarized to the direction of the molecular axis. In a homeotropic structure, dichroic dyes absorb a small quantity of light (off-state) while they absorb a large quantity of light in the helical structure (on-state). These LCDs are called nematic-cholesteric phase transition LCDs.

Measurement of Optical Properties. Absorption spectra were measured with a Shimadzu UV-260 spectrophotometer. Fluorescence spectra were measured with a Hitachi F3000 spectro fluorescence photometer.

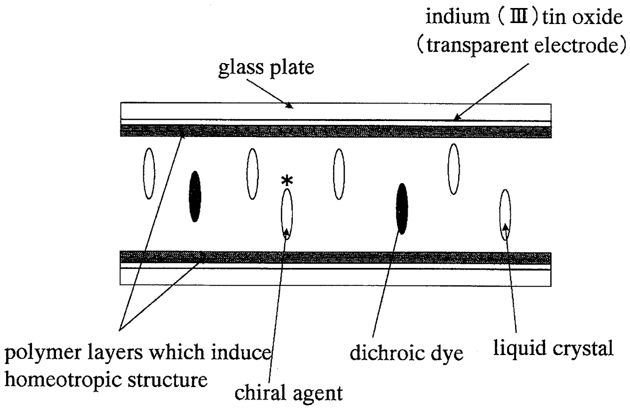


Fig. 2. The LCD structure used in this study.

1) Method of Measuring Maximum Absorption Wavelength: The maximum absorption wavelength (λ_{max}) was measured in ethyl acetate or in liquid crystals.

2) Method of Measuring Fluorescence Spectra: The anthraquinone and coumarin dyes in each ratio were dissolved in liquid crystals. Constant weights of colored liquid crystals were then measured and dissolved in ethyl acetate to obtain a 5 ml solution. The excitation energy was 450 nm. These dye solutions are very dilute (about 0.01 wt%).

Results and Discussion

Anthraquinone and Coumarin Dyes for Three-Layered GH-LCDs. Three-layered GH-LCDs with subtractive color mixing of yellow, magenta, and cyan have been attracting great attention because of their potential for realizing full-color reflective displays. Anthraquinone dyes are widely used because of their high stability.[12—17)]

We have employed the PPP-CI quantum chemical calculation method in our theoretical investigation of anthraquinone and coumarin dyes.[8,9)] This method has proved very effective for predicting dye energy levels and maximum absorption wavelengths.[7)] As a consequence, we can select dyes suitable for our purpose prior to experiments.

The PPP calculation deals only with π-electrons. Nevertheless, the results can be reliable enough because π-electrons determine most of the optical and electric properties of dyes studied in this paper. Various properties of large molecules can be calculated without exact knowledge of the coordinates of atoms in dye molecules. The calculation time is short even using a personal computer. This fact enables us to determine calculation parameters by trial and error. The PPP method is a semi-empirical one. The determination of the calculation parameters is the most important step to obtain reliable and quantitative results.

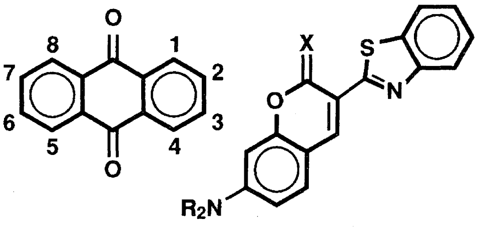
The optical properties of studied dyes are those in a liquid crystal, not those in a vacuum. However, quantum calculations, in principle, deal with molecules in a vacuum. In liquid crystals, ionic species can be stabilized by the polarization energy (P). The polarization energy is generated by reorientation of atoms or molecules and by localization of electric charges. Therefore, in liquid crystals observed ionization potential values (I_P) decrease, whereas observed electron affinity values (E_A) increase. In the calculation, this corresponds to the fact that HOMO and LUMO energy levels become substantially shallower and deeper, respectively. Excited states obtained by light absorption have polar structures and are generally stabilized by the polarization energy. Therefore, estimation of P is important in the PPP method.

In order to estimate the polarization energy (P), I_P parameters in the PPP program were modified so that these parameters for donor hetero-atoms were decreased and those for acceptor hetero-atoms were increased. In the calculation, an I_P increment corresponds to an E_A increment.

The molecular structures of these dyes are shown in Fig. 3. Table 1 lists the observed and calculated maximum absorption wavelength (λ_{obsd} and λ_{calcd}, respectively), the observed

Table 1. Observed and Calculated Properties of Anthraquinone and Coumarin dyes

No.	Dyes	λ (obsd)	λ (calcd)	HW (nm)	f
1	1,5-$(\mathrm{SPh})_2$AQ	435	433	82	0.37
2	1,4,5,8-$(\mathrm{SPh})_4$AQ	524	513	84	0.52
3	1,4-$(\mathrm{SPh})_2$-5,8-$(\mathrm{NHPh})_2$AQ	646	664	124	0.78
4	Coumarin	441	437	64	1.30



1 : 1,5-$(\mathrm{SPh})_2$ **4 : R=Et,X=O**
2 : 1,4,5,8-$(\mathrm{SPh})_4$ **5 : R=Et,X=S**
3 : 1,4-$(\mathrm{SPh})_2$-5,8-$(\mathrm{NHPh})_2$ **6 : R=n-Bu,X=O**

Fig. 3. Molecular structure of anthraquinone and coumarin dyes.

half band width of absorption spectra (HW: the width of the absorbance range when the absorbance is half of the maximum), and calculated oscillator strengths (f). The calculated maximum absorption wavelengths are almost consistent with the observed ones. This means that the PPP-CI quantum chemical method is useful to select guest dyes. The maximum absorption wavelengths which are generally thought to be desirable for three-layered GH-LCDs are shown in Table 2. The observed maximum absorption wavelengths are the ones in ethyl acetate (AcOEt). In liquid crystals, they shift to longer wavelength. Tables 1 and 2 show that these anthraquinone and coumarin dyes are suitable for this purpose, respecting the maximum absorption wavelength. Furthermore, these dyes have narrow HW, which means they can realize clear colors.

The relationship between the molar absorption coefficient (ε) and oscillator strength (f) is shown in Eq. 1.

$$f = 4.32 \times 10^{-9} \varepsilon \Delta\nu, \qquad \Delta\nu = \text{half band width}. \tag{1}$$

From Table 1, the ε value of the yellow anthraquinone dye **1** is predicted to be small, because its calculated oscillator strength ($f = 0.37$) is small. On the other hand, the coumarin dye is expected to have a large ε values ($f = 1.3$) and to act as a yellow dichroic dye. However, there are two problems with the coumarin dye **4**. One is that its strong fluorescence adversely affects the hues it exhibits. The other is that its solubility in liquid crystals is very small, especially at low temperatures.

Table 2. Suitable Maximum Absorption Wavelengths for Three-Layered GH-LCDs

Color	Wavelength (nm)
Yellow	430—460
Magenta	530—560
Cyan	630—660

For the coumarin dye **4**, two methods are considered for realizing excellent yellow colors in GH-LCDs, as shown next.

1) Quenching fluorescence.

2) Increasing solubilities to liquid crystals.

To diminish the fluorescence of coumarin dye **4**, selection of an efficient quencher is very important. We considered the best quencher to be dichroic dye quencher, a yellow dichroic dye that diminish fluorescence of coumarin dye efficiently.

The calculated HOMO and LUMO energy levels of anthraquinone dye **1** and coumarin dye **4** are shown in Fig. 4. The lower HOMO and LUMO energy levels of anthraquinone dye **1** relative to coumarin dye **4** indicate that electron transfer will occur from the coumarin dye in the excited state to the anthraquinone dye. This means that the strong fluorescence of coumarin dye is quenched.

There is one more possible fluorescence quenching mechanism. The transmittance spectra of dye **1** and **4** are shown in Fig. 5. The wider absorption tail (>500 nm) of dye **1** relative to dye **4** implies that fluorescence is quenched by energy transfer. For these two reasons, the anthraquinone dye **1** is

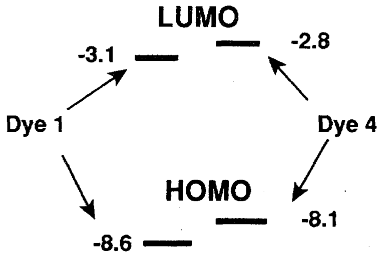


Fig. 4. Calculated energy levels (eV) of the anthraquinone dye **1** and coumarin dye **4**.

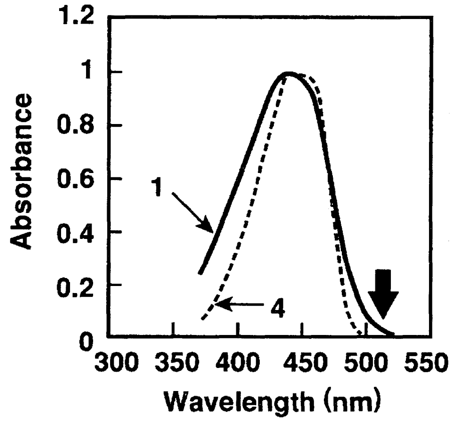


Fig. 5. Absorption spectra of the anthraquinone dye **1** and coumarin dye **4** (in AcOEt).

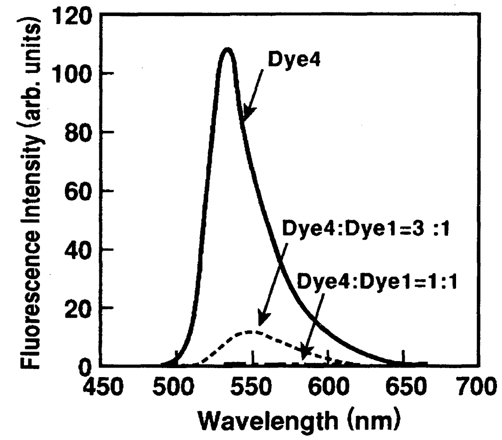


Fig. 6. Fluorescence quenching of the coumarin dye **4**.

thought to behave as an efficient quencher.

The fluorescence spectra of the anthraquinone and coumarin dye mixture in AcOEt at 24 °C are shown in Fig. 6. As the concentrations of the anthraquinone dye **1** increase to the constant concentration of coumarin dye **4**, a rapid decrease of the fluorescence intensity was observed, as predicted. The AcOEt solution of anthraquinone dye **1** only was found to have little fluorescence.

Fluorescence intensities were measured in very dilute solutions. The fluorescence quenching was therefore considered to occur by energy transfer.

We can also notice an important phenomenon in Fig. 6. By increasing the ratio of the anthraquinone dye **1** to coumarin dye **4**, the top of the fluorescence spectra shifts to a longer wavelength. This result may indicate that an excitation complex of anthraquinone and coumarin dyes has been formed, but the degree of shift is small.

The absorption spectra of the liquid crystal solution of the anthraquinone/coumarin dye mixture are shown in Fig. 7. The composition of the dye mixture used to obtain Fig. 7 is [anthraquinone dye **1** (0.46 wt%) : coumarin dye **4** (0.19 wt%) = 5 : 2]. This composition was determined in order to balance the colors of the three layers; when these dyes are mixed in this ratio, the fluorescence of coumarin dye almost vanishes. In addition, the spectrum is very sharp and can realize a clear yellow color in three-layered GH-LCDs.

The electrooptical effect of this Guest–Host liquid crystal is also shown in Fig. 7. Here, the absorption spectra were measured in a homeotropic structure liquid crystal cell whose thickness was 10 μm. The electrooptical effect was observed by applying a 60 Hz-square wave electric field with a ±10 V amplitude. The contrast is good enough to obtain clear images.

These studies show that the mixture of the yellow anthraquinone dye and yellow coumarin dye gives a good yellow spectrum, weak fluorescence, excellent electrooptical effect and high absorption capability. Thus only a small dye concentration is required.

Solubilities of Coumarin and Thiocoumarin Dyes. To increase the solubilities of coumarin dye is another method of obtaining clear colors in GH-LCDs, as shown below.

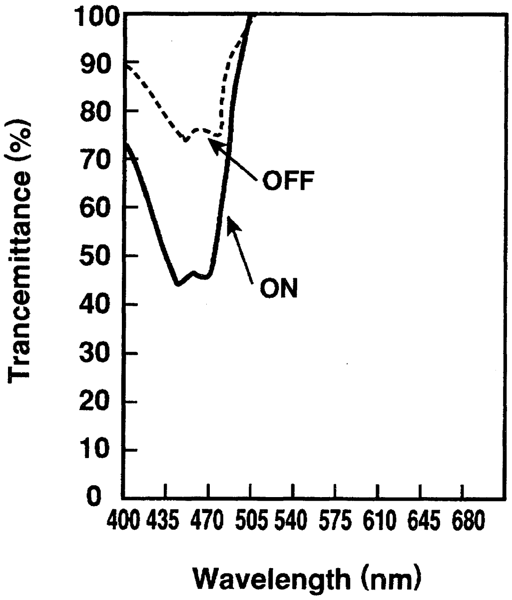


Fig. 7. Electrooptical effect of liquid crystals that contain mixture of coumarin and anthraquinone dyes.

Table 3. Solubility of Coumarin and Thiocoumarin Dyes

Dye	Solubility (wt%: 24 °C)	Solubility (wt%: −5 °C)
4	0.28	0.02
5	0.45	0.44
6	0.90	0.01

The solubility data of the dyes studied are shown in Table 3. The solubility of dye **4** at low temperatures was small. We have substituted a sulfur atom for an oxygen atom of the coumarin dye to increase the hydrophobicity of the dye molecule, and thus obtained thiocoumarin dye **5**. Dyes of this type were previously unknown (see Fig. 3).

In ^{13}C NMR, in contrast to coumarin dye **4**, the chemical shift of the thiocarbonyl carbon increased by 31 ppm to lower magnetic fields. This shift does not obey the chemical shift rules of carbonyl and thiocarbonyl carbon.[18)]

Table 3 indicates that the thiocoumarin dye **5** is 1.6 times as soluble as dye **4** at room temperature and that its solubility does not decrease even at −5 °C. On the other hand, coumarin dye **6** with butyl groups (see Fig. 3: R = *n*-Bu) was much more soluble at room temperature. However, its solubility drastically decreased at −5 °C. It has been a usual practice to introduce normal alkyl groups into dyes to increase their solubility. However, this study showed that the solubilities of such dyes have a large temperature dependence.

The present result indicates that introduction of a heteroatom such as sulfur is essential to obtain dyes which are highly soluble even at low temperatures. The absorption spectrum of thiocoumarin dye **5** is shown in Fig. 8. In contrast to the corresponding coumarin dye **4**, the maximum absorption wavelength shifts by about 45 nm to a longer wavelength. The fluorescence intensity of thiocoumarin dye **5** is found to be very small. Therefor, since the hues of GH-

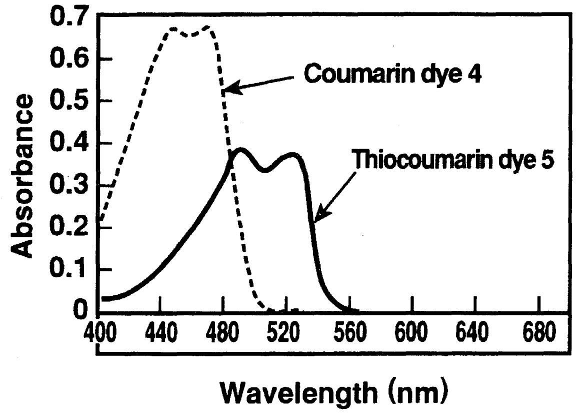


Fig. 8. Absorption spectra of thiocoumarin and coumarin dyes.

LCDs are not changed by the fluorescence, quencher is not required.

Conclusion

The mixture of coumarin and anthraquinone dyes has a large absorption coefficient and can realize a pure yellow color. However, the solubility of coumarin dye is not large enough at low temperatures. On the other hand, the thiocoumarin dye which we have prepared has a high solubility even at low temperatures. This result suggests that a soft hetero-atom substitution is a useful method to increase the solubility of a coumarin dye. We also investigated the relation between molecular structures of anthraquinone dichroic dyes and solubilities. These results are shown in other papers.[19,20]

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References

1) D. L. White and G. N. Taylor, *J. Appl. Phys.*, **45**, 4718 (1974).

2) T. Uchida, "Euro Display '81 Digest," p. 39 (1981).

3) T. Uchida, *Opt. Eng.*, **23**, 247 (1984).

4) T. Uchida, H. Seki, C. Shishido, and M. Wada, "SID '81 Digest," p. 41 (1981).

5) K. Sunohara, K. Naito, M. Tanaka, Y. Nakai, N. Kamiura, and K. Taira, "SID '96 Digest," p. 103 (1996).

6) K. Taira, H. Iwanaga, A. Hotta, Y. Nakai, T. Ohtake, and K. Sunohara, "AM-LCD '96," p. 333 (1996).

7) K. Naito, H. Iwanaga, K. Sunohara, and M. Okajima, "Euro Display '96," p. 127 (1996).

8) S. Tokita, M. Matuoka, Y. Kogo, and H. Kihara, "Molecular Design of Functional Dyes (in Japanese)," Maruzen, Tokyo (1989), p. 113.

9) K. Naito, M. Sakurai, and S. Egusa, *J. Phys. Chem. A*, **101**, 2350 (1997).

10) H. Z. Lecher et al., *J. Am. Chem. Soc.*, **78**, 5018 (1956).

11) B. S. Pedersen et al., *Bull. Soc. Chim. Belg.*, **87**, 223 (1978).

12) M. G. Pellatt, I. H. C. Roe, and J. Costant, *Mol. Cryst. Liq. Cryst.*, **59**, 299 (1980).

13) J. Cognard and T. H. Phan, *Mol. Cryst. Liq. Cryst.*, **70**, 1 (1981).

14) G. Heppke, B. Knippenberg, A. Moller, and G. Scherowsky, *Mol. Cryst. Liq. Cryst.*, **94**, 191 (1983).

15) N. Bastulk, J. Cognard, and T. H. Pann, *Mol Cryst. Liq. Cryst.*, **95**, 71 (1983).

16) F. C. Saunders, K. J. Harrison, E. P. Raynes, and D. L. Thompson, *IEEE Trans. Electron Devices*, **ED-30**, 499 (1983).

17) S. Imazeki, *Mol. Cryst. Liq. Cryst.*, **140**, 119 (1986).

18) B. S. Pedersen et al., *Bull. Soc. Chim. Belg.*, **87**, 293 (1978).

19) H. Iwanaga and K. Naito, *Jpn. J. Appl. Phys.*, **37**, L356 (1998).

20) K. Naito and H. Iwanaga, *Jpn. J. Appl. Phys.*, in press.