

## Chiroptical Control of Liquid Crystalline Textures Containing Chromium Complex by Irradiation of Circular Polarized Light

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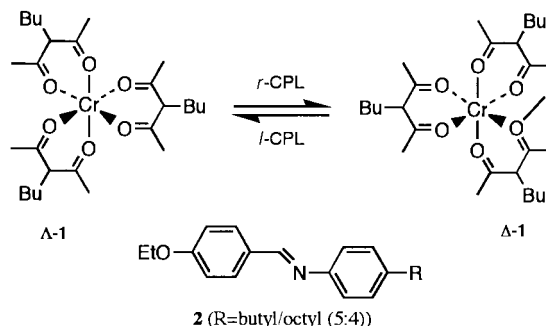
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A cholesteric texture was induced in the liquid crystal (a mixture of *N*-(4-ethoxybenzylidene)-4-*n*-alkylanilines doped with (*R*)-(+)-1,1'-bi-2-naphthol and racemic chromium tris(3-butyl-2,4-pentanedionate) (Cr(3-Buacac)<sub>3</sub>) by the irradiation of right circular polarized light (*r*-CPL) and resulting chiroselective photoinversion of Cr(3-Buacac)<sub>3</sub>. After irradiation of left circular polarized light (*l*-CPL), the cholesteric fingerprint texture was erased.

Liquid crystals are a unique medium for sensing small structural changes in the environment. Recently a light control of a liquid crystal with the photochromic molecules has been studied<sup>1-4</sup> in order to apply it to a light switch or an optical memory system. The light control with photochromic molecules necessitates irradiation at two wavelengths. However, when we use a chiral molecule which undergoes helicity conversion or inversion reaction under photoirradiation,<sup>5</sup> we can modulate two distinct states of its enantiomers with irradiation at a single wavelength by changing the handedness of the light. Feringa et al.<sup>6</sup> first reported the light control of a liquid crystal phase by the irradiation of 313 nm circular polarized light (CPL) on a helical molecule in the liquid crystal. Schuster et al.<sup>7</sup> recently showed a reversible light control of a liquid crystalline phase by irradiation of UV CPL on a racemic bicyclic ketone. Our previous study<sup>8</sup> showed a light induced change in cholesteric pitch of a liquid crystal by photoracemization of a chiral pyrenyl sulfoxide. However, chiro-selective induction of cholesteric texture from a nematic liquid crystal containing racemic pyrenyl sulfoxide by CPL irradiation was not realized. In the present letter, we present a chiroptical induction of cholesteric texture by photoinversion reaction of an octahedral chromium complex under CPL irradiation.

In order to induce a liquid crystalline phase transition by CPL, the trigger must be chiral. It must have sufficient values of helical twisting power,  $\beta_m$ , and anisotropy factor,  $g$ , large enough to yield an observable chiral phase. Chromium trisacetylacetonate has a large  $g$  value,<sup>9</sup> but, it is hardly soluble in any liquid crystals. If the solubility of a chromium complex in liquid crystals is much improved, it is expected to control its texture by irradiation of CPL. So, we prepared chromium tris(3-butyl-2,4-pentanedionate) (Cr(3-Bu-acac)<sub>3</sub>) (**1**), which has enantiomers,  $\Lambda$  and  $\Delta$ , and can be dissolved in several liquid crystals such as 4'-pentyl-4-biphenylcarbonitrile (5CB) and a mixture of *N*-(4-ethoxybenzylidene)-4-*n*-alkylanilines (**2**) at room temperature. The chemical structures of **1** and **2** are shown in Figure 1.

The chromium complex **1** was prepared by refluxing at 110 °C for 24 h the water/methanol solution of chromium trichloride and urea with 3-butyl-2,4-pentanedione, which was pre-



**Figure 1.** Chemical structures of chiral Cr(3-Buacac)<sub>3</sub> complexes,  $\Lambda$ -**1** and  $\Delta$ -**1**, and a mixed nematic liquid crystal **2**.

pared by the reaction of butyl iodide, acetylacetonate, and potassium carbonate in acetone at 80 °C for 10 h. Details are given elsewhere.<sup>10</sup> Liquid crystals (5CB and **2**) were supplied by Tokyo Kasei.

Figures 2 and 3 show the change in CD spectra of **1** in benzene during *r*-CPL irradiation and also its UV-vis absorption spectrum, respectively. The increase in optical rotation,  $\theta$ , with a peak at 546 nm due to d-d transition of the chromium complex corresponds to photoinversion from  $\Lambda$ -**1** to  $\Delta$ -**1**. Photostationary state of photoinversion was attained in about 70 h in the present experimental condition. The enantiomer excess for photostationary state,  $\gamma_{pss}$ , and hence the anisotropy factor,  $g$ , in the case of CPL irradiation on a racemic sample are calculated from UV absorption and CD spectra by using

$$g = \Delta\epsilon / \epsilon = 2\gamma_{pss} = (2\theta / 33OD)^{1/2} \quad (1)$$

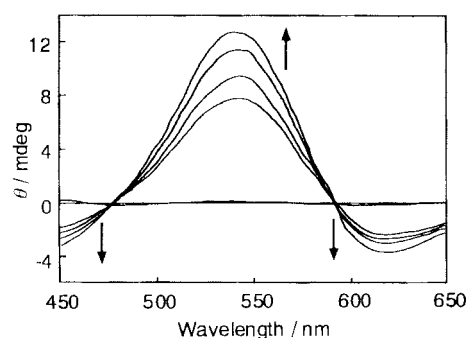
where  $\Delta\epsilon$  is the difference in extinction coefficient,  $\epsilon$ , of the dopant for *r*- and *l*-CPL,  $OD = \epsilon cl$  is the optical density,  $c$  is the molar concentration, and  $l$  is the path length of light. The present chromium complex **1** shows a large anisotropy factor,  $g$ , in benzene (0.05 (maximum) at 525 nm and -0.032 at 633 nm), compared to -0.0064 at 314 nm for the helical molecule<sup>5</sup> and 0.014 at 300 nm for the chiral bicyclic ketone.<sup>6</sup> When **1** was irradiated at 632.8 nm with a He-Ne CPL, the enantiomer excess,  $\gamma_{pss}$ , was 1.5%.

When a nematic liquid crystal is doped with a low concentration of chiral dopant, a cholesteric texture is induced, and the cholesteric pitch,  $p$ , is inversely proportional to the concentration of the chiral dopant,  $c$ , and expressed as follows,

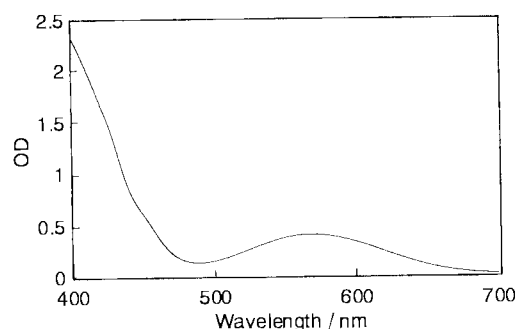
$$p = 1/(\beta_m c \gamma) \quad (2)$$

where  $\beta_m$  is the helical twisting power of the chiral dopant in the liquid crystal and  $\gamma$  is the enantiomer excess.

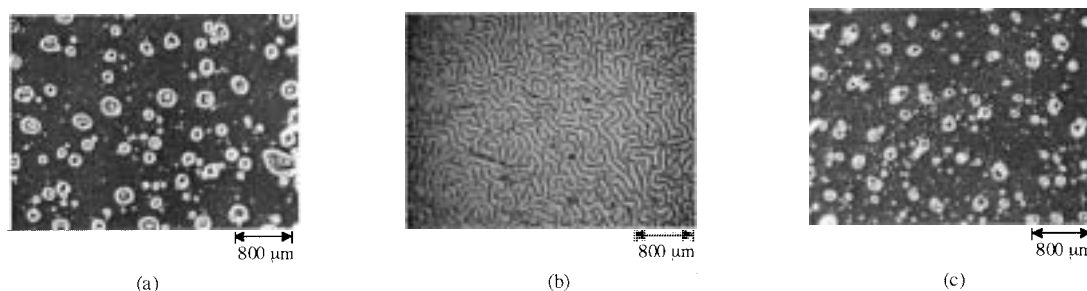
A room-temperature nematic liquid crystal **2** doped with racemic **1** ( $\Lambda = \Delta$ ) and (*R*)-(+)-1,1'-bi-2-naphthol **3** (the weight



**Figure 2.** Change in CD spectrum during *r*-CPL irradiation onto racemic **1** ( $5.0 \times 10^{-3}$  M) in benzene. Irradiation time is, 0, 15, 20, 38 and 66 h from bottom to top at 546 nm.



**Figure 3.** UV vis absorption spectrum of  $5.0 \times 10^{-3}$  M of **1** in benzene.



**Figure 4.** Textures of racemic **1** and (*R*)-(+)-1,1'-bi-2-naphthol dissolved in *N*-(4-ethoxybenzylidene)-4-*n*-alkylanilines **2** (the weight ratio, 75:3.2:1000) observed with a polarized light microscopy (cell thickness, 12  $\mu\text{m}$ ). (a) Before irradiation of CPL.; (b) After irradiation of *r*-CPL at 632.8 nm, for 20 h. A fingerprint texture was observed.; (c) After irradiation of *l*-CPL, for 20 h, to (b). The fingerprint texture was erased.

ratio, 1000:75:3.2) was prepared for photooptical control experiments. A liquid crystal texture was observed with a polarized light microscopy. Before irradiation of CPL, the phase of the liquid crystal was almost nematic (Figure 4(a)). After *r*-CPL irradiation at 632.8 nm from a He-Ne laser modified through a Babinet-Soleil compensator, the phase was changed to cholesteric with fingerprint texture (Figure 4(b)). The cholesteric pitch  $p$  was 210  $\mu\text{m}$ , and moreover, after irradiation of *l*-CPL onto this cholesteric sample, the fingerprint texture was erased (Figure 4(c)). Thus, we succeeded in inducing the phase change of a liquid crystal sample from nematic to cholesteric and vice versa by CPL irradiation photoinversion of the chromium complex **1**. A small amount of (*R*)-(+)-1,1'-bi-2-naphthol **3** was used as an auxiliary chiral dopant in the present case, since the visible change was not observed by CPL irradiation when the dopant was chromium complex **1** alone. This suggests that  $\beta_m$  for **1** is still small for inducing fingerprint texture by itself.

In order to determine the value of  $\beta_m$ , an enantiomer  $\Lambda$ -1, was separated from a racemic **1** by using an HPLC (Jasco) with a Chiralcel OD<sup>®</sup> column (Daicel). The liquid crystalline sample of **2** doped with  $\Lambda$ -1 (the weight ratio, 1000:9.1) was observed with a polarized light microscopy, and its cholesteric pitch was measured. A helical twisting power,  $\beta_m$ , for **1** in **2** was determined to be  $1.0 \mu\text{m}^{-1} \text{mol}^{-1}$ . This value is rather small compared to that for molecules such as a chiral bicyclic ketone ( $15 \mu\text{m}^{-1} \text{mol}^{-1}$ ).<sup>6</sup> Feringa et al.<sup>5</sup> did not report the  $\beta_m$  value for their system.

In conclusion, we first reported in the present letter chirooptical control of liquid crystalline texture, from nematic to cholesteric and vice versa, by irradiation of visible CPL on a

chromium complex. Chromium complexes have wide UV and visible light absorption, which enables us to carry out photoinversion reaction with the visible CPL. In the case of application to photo-optical switching of liquid crystals by CPL, however, molecules which have larger  $\beta_m$  should be preferably used.

## References

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