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Light-induced control of textures and cholesteric pitch in liquid crystals containing chromium complexes, by means of circular and linear polarized light

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A nematic liquid crystal doped with a chiral dopant has a cholesteric texture with a regular pitch. The pitch is changed by variation of concentration of the dopant. We observed the appearance of a fingerprint texture on irradiation of a homeotropic mixed liquid crystal doped with a racemic chromium complex, $Cr(Buacac)_3$, and an auxiliary chiral dopant, with right-circular polarized light (*r*-CPL); the fingerprint texture disappeared on irradiation with left-circular polarized light (*l*-CPL). We also measured a helical twisting power, β_m, of the chromium complex from the cholesteric pitch of the mixed liquid crystal doped with optically resolved Λ-$(Cr(Buacac)_3$; and clarified the relationship between the change in the cholesteric pitch and the quantum yield of the photoinversion reaction.

1. Introduction

Liquid crystals provide a unique material for sensing small changes in environments, such as temperature and dopant molecules. In recent years, the control by light of liquid crystals containing photochromic molecules has been studied, for application of optical switch or optical memory systems [1–15]. Liquid crystalline alignment reflects dopant conformation. When photochromic molecules are used for the control, irradiation at two wavelengths is needed to change the alignment of a liquid crystalline phase. A nematic liquid crystal containing chiral molecules has a particular characteristic of its orientation direction, being twisted along a normal axis, resulting in a cholesteric liquid crystal. Photoinversion reactions of chiral molecules inducing a change in chirality or helicity are a form of photoisomerization reaction; the irradiation of right-circular polarized light (*r*-CPL) changes an enantiomer molecule with structure *d* to the *l* enantiomer [16–26]. Thus, the use of a chiral molecule which undergoes helicity conversion or an inversion reaction enables us to change the alignment of a liquid crystalline phase by irradiation at one wavelength.

The control by light of a liquid crystalline phase using a chiral compound has become a topic of great interest [16–18]. Feringa *et al.* [16] first reported the control by light of a liquid crystalline phase by irradiation at 313 nm CPL of a helical molecule in a liquid crystal. Burnham and Schuster [17] reported the reversible control of a liquid crystalline phase by irradiation of a racemic bicyclic ketone with UV-CPL. In order to induce the phase transition of a liquid crystal from a racemic compound with CPL irradiation, the dopant must have sufficiently large values of anisotropy factor *g* and twisting power β_m. The anisotropy factor *g* is related to the efficiency of inducing enantiomer excess from a racemic compound by photoirradiation with CPL; β_m is the helical twisting power of a chiral dopant on the liquid crystal. The maximum observed values of *g* are 6.4×10^{-3} *et al.* [16] and 1.4×10^{-2} [17]. The maximum values of enantiomer excess are 0.32% and 0.7%, respectively. Although the values of enantiomer excess are low, their molecules could trigger phase transitions. If a racemic molecule undergoing photoinversion has a large value of *g*, we can expect easier control of a liquid crystalline phase.

Our previous sudies [19] showed a light-induced change in cholesteric pitch of a liquid crystal, 4-pentyl-4′-biphenylcarbonitrile (5CB), by photoracemization of a chiral pyrenyl sulfoxide (PYSO). However, the chiroselective induction of a cholesteric texture by CPL from a nematic liquid crystal containing racemic pyrenyl

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sulfoxide was not realized. The measured values of *g* and β_m would be smaller than those reported in [16] and [17], which may be the reason for the absence of a phase transition from a liquid crystal with racemic PYSO by CPL irradiation. Chromium tris(acetylacetonate), $Cr(acac)_3$, is known to have a large *g* value (7.8×10^{-2}) [20] and to be stable against inversion in helicity due to temperature and chemical action. The chemical structure of $Cr(acac)_3$ is shown in figure 1; it has enantiomers, the Λ and Δ forms. Irradiation with *r*-CPL enables Λ to change into Δ, the irradiation with *l*-CPL changes Δ to Λ. It is supposed that when the Λ(Δ) form is excited by light, the Λ(Δ)Cr–O bond is cleaved, and recombined or changed to the Δ(Λ)Cr–O bond; the enantiomer excess can be provided by CPL irradiation on a racemic mixture due to the large *g* value.

We tried to use $Cr(acac)_3$ as a dopant in a nematic liquid crystal for CPL-induced texture control; however $Cr(acac)_3$ was almost insoluble in any nematic liquid crystal at room temperature. We believe that the molecular structure of the ligand is the key to the solubility of a chromium complex in a liquid crystal; ligands containing side chain alkyl group would make the complex more soluble in a liquid crystal. Our preliminary results [26] demonstrated the chiro-selective induction of a fingerprint texture by visible CPL irradiation of a homeotropic liquid crystal containing racemic chromium tris(3-butyl-2,4-pentanedionate), $Cr(Buacac)_3$, and an auxiliary chiral dopant. In the present study, we prepared 15 kinds of chromium complex with several types of ligand of various chemical structures; we then studied their solubility in nematic liquid crystals at room temperature, their capability of chiro-selective photoinversion by CPL in solution, and the chiro-selective reversible observation of fingerprint texture in a liquid crystal doped with the complexes.

The chiro-optical control by CPL of a liquid crystalline texture containing a racemic chromium complex has been realized by adding a small amount of chiral binaphthol to racemic $Cr(Buacac)_3$. The CD measurements for three kinds of racemic chromium complexes under CPL irradiation gave the values of quantum yield *Φ* for the photoinversion reaction. The observed change in cholesteric pitch after linear polarized light (LPL) irradiation for a liquid crystal doped with an optically-resolved Λ-$Cr(Buacac)_3$ agreed well with the predicted change based on the value of *Φ*, and indicated the helical twisting power β_m for this system.

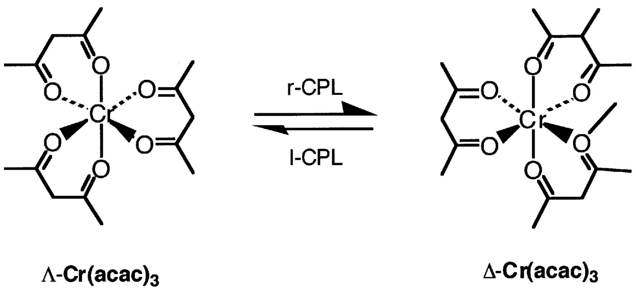


Figure 1. Enantiomeric structure of $Cr(acac)_3$.

2. Experimental

2.1. *Materials*

2.1.1. *Liquid crystals*

We used several liquid crystals, including a mixture of 4′-ethoxybenzylidene-4-*n*-alkylaniline **1** and 4′-pentyl-4-biphenylcarbonitrile **2**, which show a nematic phase at room temperature. The nematic liquid crystals **1** and **2** were supplied by Tokyo Kasei, and their chemical structures are shown in figure 2.

2.1.2. *Preparation of ligands*

Various kinds of 3-alkyl-2,4-pentanedionates with propyl, butyl, pentyl, octyl, and 2-methylbutyl groups (Pracac, Buacac, Peacac, Ocacac, (+)-MeBuacac) were synthesized from acetylacetone and the corresponding alkyl iodides [27]. For example, a solution of 15.4 ml (0.135 mol) butyl iodide, 23.0 ml (0.223 mol) acetylacetone, and 31.4 g (0.227 mol) potassium carbonate in 100 ml of acetone was heated at reflux (80°C) for 10 h. The mixture was then poured into 200 ml of water, and extracted with diethyl ether. The diethyl ether solution was dried over anhydrous sodium sulphate, and evaporated. The product was purified by vacuum distillation. Buacac:

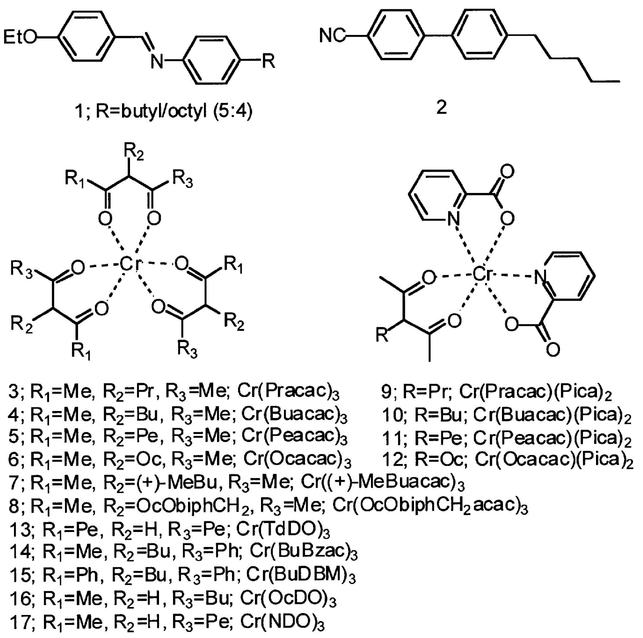


Figure 2. Chemical structures of nematic liquid crystals and chromium complexes.

^{1}H NMR ($CDCl_3$); δ 0.90 (t, 3H, CH_3–) 1.21 (m, 2H, CH_3–CH_2–) 1.34 (m, 2H, C_2H_5–CH_2–) 1.84 (q, 2H, C_3H_7–CH_2–) 2.18 (s, 6H, CH_3–CO–) 3.62 (t, 1H, Bu–$CH(COCH_3)_2$).

Alkyl β-diketones were synthesized by the reaction of a ketone with an ester [27]. For example, 6,8-tridecanedione (TdDO) was synthesized from methyl hexanoate and 2-heptanone. A solution of 25.0 ml (0.171 mol) methyl hexanoate, 25.0 ml (0.180 mol) 2-heptanone, and 9.60 g (0.178 mol) sodium methoxide was stirred at 90°C for 2.5 h. The mixture was then poured into 200 ml of water, and extracted with dichloromethane. The dichloromethane solution was dried over anhydrous sodium sulphate, and evaporated. The product was purified by vacuum distillation; 4.19 g (12% yield) of TdDO was obtained. ^{1}H NMR ($CDCl_3$); δ 0.89 (t, 6H, CH_3–) 1.31 (m, 8H, CH_3–C_2H_4–) 1.58 (m, 4H, C_3H_7–CH_2–) 2.18 (s, 2H, $CH_2(CO)_2$–) 2.42 (t, 2H, C_4H_9–CH_2–).

Phenyl β-diketones were synthesized by the same method.

2.1.3. *Preparation of complexes*

We prepared several types of chromium complexes, chromium tris(β-diketone) **3**–**17**, having Λ or Δ type of enantiomer. Their chemical structures are shown in figure 2.

The chromium complexes **3**–**8** and **13**–**17** were prepared by heating under reflux chromium trichloride and urea with a ligand at 110°C for 24 h in a water/methanol solution. After reflux, the mixture was poured into water, and extracted with dichloromethane. The dichloromethane solution was dried over anhydrous sodium sulphate, and evaporated. The product was purified by recrystallization from a small amount of hexane at −20°C. The resulting chromium complexes were paramagnetic, thus ^{1}H NMR spectra could not be measured.

The chromium complexes **9**–**12** were synthesized from Cr(alkyl-acac)$_3$ with 2-pyridinecarboxylic acid (2 molar equiv) by heating at reflux for 16 h in ethanol. After evaporation, the products were purified by column chromatography on silica gel (Wako Gel C-200, eluent hexane : dichloromethane = 9 : 1) and recrystallization. The yield of **10** was 42%. The resulting chromium complexes were paramagnetic, thus ^{1}H NMR spectra could not be measured.

2.2. *Instrumentation*

Liquid crystalline textures were observed with an Olympus BH-2 polarizing optical microscope (POM). All UV-visible spectra were measured with a JASCO UVIDEC 660 UV/VIS spectrophotometer. NMR spectra were measured with a JEOL JNM-GX400 FT-NMR spectrometer. CD spectra were recorded with a JASCO J-500A spectropolarometer. In UV absorption and fluorescence measurements and photoracemization, all solvents were of spectrosol or luminasol grade (Wako).

2.3. *Photoinversion in solution*

A solution of 2.0 ml of 5.0×10^{-3} M chromium complex **3**, **4**, or **5** in benzene was irradiated with 632.8 nm light from a He-Ne laser modified through a Babinet–Soleil compensator (*r*-CPL). The changes in optical activity were traced with CD spectra. Irradiation was continued until the CD spectrum peak did not change. Light intensity was measured at 633 nm using an Advantest TQ8210 optical powermeter. UV spectra before and after photoinversion were measured for the same samples.

2.4. *Photoinversion in a liquid crystal*

In order to observe the change in a liquid crystalline texture after a photoinversion reaction, a cell was prepared with glass plates surface-treated with dimethyloctadecyl-3-trimethoxysilylpropylammonium chloride (Shin-etsu silicon) and a polyethylene film spacer (thickness 12 μm). Liquid crystal textures were observed by POM before and after irradiation with *r*-CPL and after successive irradiation with *l*-CPL. The cell was irradiated at 632.8 nm with an 8.5 mW cm^{-2} He-Ne *r*-CPL or *l*-CPL laser. The orientation of the liquid crystal in the cell was vertical to the glass plates; thus in the case of a cholesteric phase, a fingerprint texture was observed.

2.5. *Optical resolution of the chromium complex*

The racemic complex **4** was separated into Λ and Δ forms using a chiral HPLC column (Chiralcel OD®; Daisel), eluent hexane : 2-propanol = 1 : 250, flow rate 0.5 ml min^{-1}, monitored at 550 nm.

2.6. *Photoracemization in a liquid crystal*

In order to observe the change in liquid crystalline texture after the photoinversion reaction of enantiomeric **4**, a cell was prepared with glass plates surface-treated with dimethyloctadecyl-3-trimethoxysilylpropylammonium chloride (Shin-etsu silicon) and a polyethylene film spacer (thickness 12 μm). The change in the pitch of the fingerprint texture was observed by POM during LPL irradiation at 632.8 nm with a 12.3 mW cm^{-2} He-Ne laser.

3. Results and discussion

3.1. *Solubility of chromium complexes in a liquid crystal*

The complexes **3**–**17** had good solubility in common organic solvents such as dichloromethane and methanol. However, in liquid crystal solution, the complexes caused partial phase separation when the concentration became high (greater than 10 wt % in the case of **4**–**7**). We tried to dissolve the complexes in several liquid crystals such as the benzylideneanil type **1**, cyanobiphenyl type **2** etc. Although a nematic liquid crystalline phase was not stable for **2** doped with the chromium complexes, a nematic liquid crystalline phase was maintained for **1** doped with the complexes. The complexes **3**–**8** and **13**–**17** dissolved well in **1**, but, **9**–**12** were insoluble in all liquid crystals. The solubility seems to depend on the structure of the ligands; flexible alkyl chains improve solubility, but the bulky substituents in BuBzac and 3-octyloxybiphenylmethylacetylacetonate ($OcObiphCH_2acac$) complexes lower the solubility. Picolinato (Pica) complexes **9**–**12** also reduced solubility in a liquid crystal, probably due to strong self-interactions.

3.2. *Chiroselective photoinversion in solution with CPL*

The CD and UV spectra of racemic $Cr(Pracac)_3$ **3** in benzene before and after *l*-CPL irradiation at 632.8 nm for 66 h are shown in figure 3. The increase in absolute values of optical rotation θ, with a peak at 546 nm due to d-d transition of the chromium complex, corresponds to photoinversion from Δ-**3** to Λ-**3**. The corresponding UV spectra do not change under CPL irradiation.

The enantiomeric excess for the photostationary state, γ_{pss}, and hence the anisotropic factor g for CPL irradiation on a racemic sample, are calculated from UV absorption and CD spectra from

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

where $\Delta\varepsilon$ is the difference in extinction coefficient ε of the dopant for *r*- and *l*-CPL, $OD = \varepsilon Cl$ is the optical density; C is the molar concentration, and l is the optical path length. The complexes **3**–**5** show large values of g in benzene (−0.05 (maximum) at 525 nm and 0.032 at 633 nm) (figure 4). When **3** was irradiated at 632.8 nm with He-Ne CPL, the enantiomer excess for the photostationary state, γ_{pss}, was 1.5%.

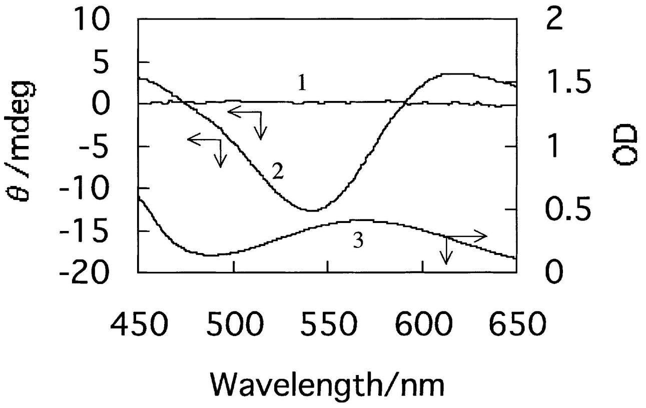


Figure 3. CD spectrum (1, 2) and UV absorption (3) of racemic **3** in benzene (5.0×10^{-3} M) before (1) and after (2) *l*-CPL irradiation for 66 h.

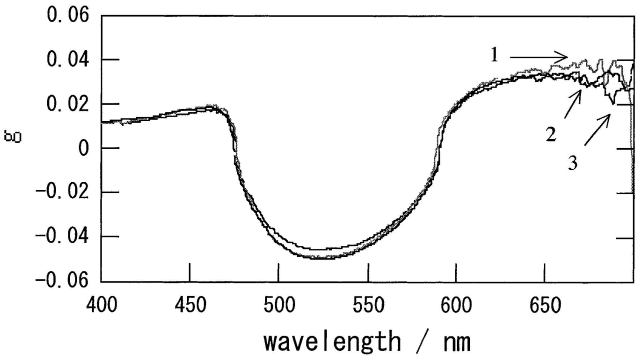


Figure 4. The anisotropy factor g, calculated from CD and UV spectra in figure 3 using equation (1). (1): $Cr(Pracac)_3$, (2): $Cr(Buacac)_3$, (3): $Cr(Peacac)_3$ in benzene.

In order to obtain the quantum yields Φ for the photoinversion reactions of **3**–**5**, we measured the course of CD spectra with time (figure 5). The quantum yield Φ is expressed as follows,

$$\ln(1 - \theta/\theta_{pss}) = -2\Phi I_0(1 - 10^{-\varepsilon Cl})t/Cl \qquad (2)$$

where θ is the optical rotation obtained from CD spectra, the subscript pss corresponds to photostationary state, I_0 is the incident light intensity, and ε is the molar extinction coefficient at the irradiation wavelength.

First order plots of the optical rotation $\theta(t)$ against time t in benzene are shown in figure 6. The quantum yield of the photoinversion reaction was calculated from the slopes of the first order plots. The quantum yield Φ was determined to be 0.0022 for **3**, 0.0024 for **4** and 0.0023 for **5**, within 10% experimental error. They are almost the same as the value for $Cr(acac)_3$ [20]. The complexes **3**–**6** showed almost the same changes in CD spectra. The complexes **8**, **13**–**17** showed no peaks in the CD spectra; absence of photoinversion was probably due to the bulky ligand structure.

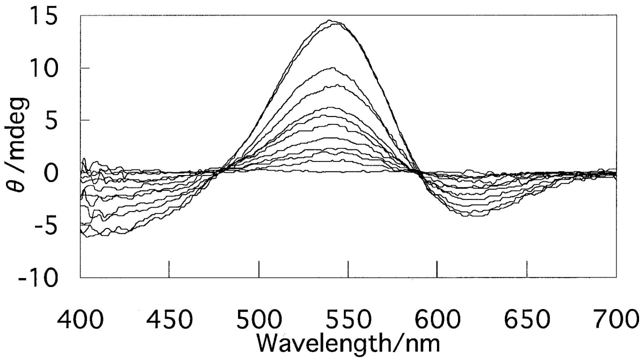


Figure 5. Changes in the CD spectra of racemic **3** in benzene (5.0×10^{-3} M) during *r*-CPL irradiation for 0, 1, 2, 3, 4, 6, 8, 10, 15, 20, 46 and 52 h (from bottom to top at 540 nm).

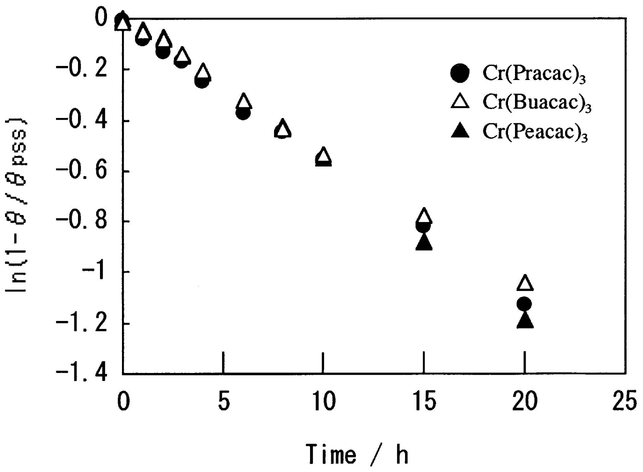


Figure 6. First order plots of $\theta(t)$ vs. time for racemic **3**–**5** in benzene (5.0×10^{-3} M).

3.3. *Chiroselective photoinversion in liquid crystal with CPL*

The room temperature homeotropic liquid crystal **1** doped with racemic **4** and (*R*)-(+)-1,1′-bi-2-naphthol (weight ratio, 1000 : 75 : 3.2) was prepared for photo-optical control experiments; liquid crystal textures were observed under a POM. Before CPL irradiation, the liquid crystal mixture was homeotropic, figure 7 (*a*); sphere-like images might be due to the existence of an inversion wall. After *r*-CPL irradiation at 632.8 nm from a He-Ne laser modified through a Babinet–Soleil compensator, the orientation was changed to a helical structure with a fingerprint texture, figure 7 (*b*). The cholesteric pitch *p* was 210 µm, and after *l*-CPL irradiation of this helical sample, the helix was suppressed and the homeotropic texture reappeared, as the enantiomeric excess of **4** approached zero, figure 7 (*c*). If the *l*-CPL irradiation was continued, the enantiomeric excess of **4** was inverted and again a helix might be expected to form; but the opposite handedness texture was not observed, because the formation of such a helix was counteracted by the inherent twisting power of the (*R*)-(+)-1,1′-bi-2-naphthol.

The present liquid crystal mixture before *r*-CPL irradiation is inherently chiral due to the presence of (*R*)-(+)-1,1′-bi-2-naphthol, and in the bulk might form a helical superstructure with a certain pitch. But in the thin sandwich cell used, treated to give homeotropic surface anchoring (i.e. favouring the director to be perpendicular to the surfaces), the helix is unwound and a homeotropic texture is achieved. Thus the chiral mixture forms a non-helical structure. When the sample was illuminated with *r*-CPL, the twisting power of the sample mixture increased and the cell surfaces could no longer prevent the liquid crystal from adopting a helical structure. This is the reason of the present changes from homeotropic to fingerprint texture and *vice versa* by CPL-induced photoinversion of chromium complex **4**. A small amount of (*R*)-(+)-1,1′-bi-2-naphthol was used as an auxiliary chiral dopant in the present case, since no visible change in the texture was observed under CPL irradiation when the dopant was racemic chromium complex **4** alone. This suggests that helical twisting power β_m for **4** with the liquid crystal **1** is still too small to induce a fingerprint texture by itself.

The results for solubility and photoinversion of chromium complexes in liquid crystals are summarized in table 1. We designed three categories of complex: (a) (**3**–**7**) those having three alkyl substituents which extend in three directions such as Cr(Buacac)$_3$; (b) (**9**–**12**) those having one alkyl substituent which extends in one direction such as Cr(Buacac)(Pica)$_2$; (c) (**8**, **13**–**17**) those having bulky substituents on both sides of β-diketone ligands such as Cr(BuDBM)$_3$. The complexes (a) have good solubility and undergo photoinversion under CPL irradiation. The complexes (b) underwent photoinversion under CPL irradiation, but have poor solubility. The

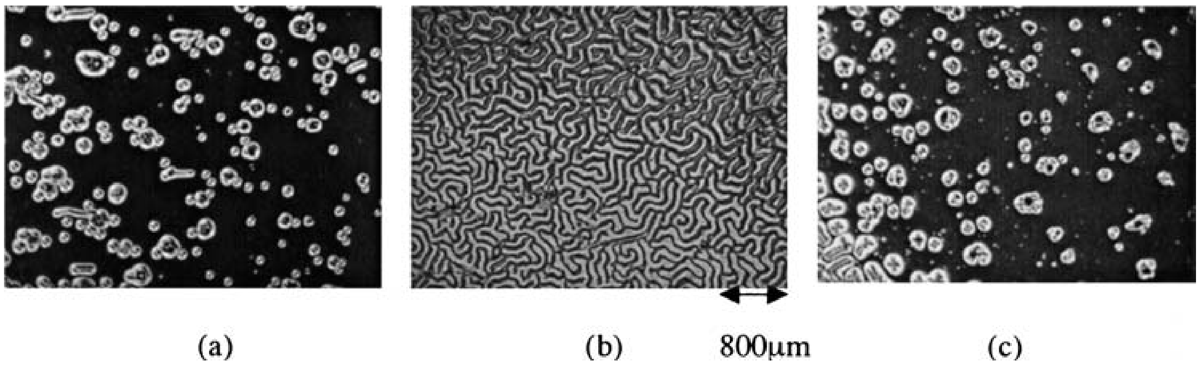


Figure 7. Textures for a mixture of racemic **4** and (*R*)-(+)-1,1′-bi-2-naphthol dissolved in 4′-ethoxybenzylidene-4-*n*-alkylaniline **1** (weight ratio, 75 : 3.2 : 1000) observed by POM. (*a*) Before irradiation of CPL; (*b*) after *r*-CPL irradiation at 632.8 nm for 16 h, showing fingerprint texture; (*c*) after *l*-CPL irradiation for 20 h onto (*b*), the texture was erased.

Table 1. Results of solubility in a liquid crystal **1** and photoinversion experiments of chromium complexes with various ligands.

Complex	Solubility in **1**[a]	Chiroselective photoinversion with CPL[b]	Fingerprint texture observation[c]
3 $\mathrm{Cr(Pracac)_3}$	○	○	—
4 $\mathrm{Cr(Buacac)_3}$	◎	○	○
5 $\mathrm{Cr(Peacac)_3}$	◎	○	—
6 $\mathrm{Cr(Ocacac)_3}$	◎	○	—
7 $\mathrm{(Cr((+)\text{-}MeBuacac)_3}$	◎	○	○
8 $\mathrm{Cr(OcObiphCH_2acac)_3}$	△	×	×
9 $\mathrm{Cr(Pracac)(Pica)_2}$	×	○	×
10 $\mathrm{Cr(Buacac)(Pica)_2}$	×	○	×
11 $\mathrm{Cr(Peacac)(Pica)_2}$	×	○	×
12 $\mathrm{Cr(Ocacac)(Pica)_2}$	×	○	×
13 $\mathrm{Cr(TdDO)_3}$	◎	×	×
14 $\mathrm{Cr(BuBzac)_3}$	○	×	×
15 $\mathrm{Cr(BuDBM)_3}$	○	×	×
16 $\mathrm{Cr(OcDO)_3}$	○	×	×
17 $\mathrm{Cr(NDO)_3}$	○	×	×

[a] ◎ soluble up to 10 wt %, ○ soluble up to *c*. 5 wt %, △ soluble up to *c*. 3 wt %, × soluble.
[b] ○ occurs, × does not occur.
[c] ○ yes, × no, — not examined.

complexes (c) have good solubility, but no photoinversion reaction was induced. Alkyl substituents in the ligands make the complexes soluble in liquid crystals, thus **3**–**7** have good solubility. The helical twisting power β_m reflects the interaction between complexes and the liquid crystal and hence depends on the chemical structure of the ligands. The fact that the complexes **8** and **13**–**17** do not undergo a photoinversion reaction suggests that complex formation with three ligands having bulky substituents on both sides of a β-diketone, or bulky mesogenic substituents in three directions, is again of little use for chiro-selective control of the liquid crystalline texture.

3.4. *Photoracemization of chiral* $Cr(Buacac)_3$ *in a liquid crystal*

When a nematic liquid crystal is doped with a low concentration of a chiral dopant, a cholesteric pitch P appears, which is inversely proportional to the concentration C and the enantiomer excess, γ,

$$P = 1/(\beta_\mathrm{m} C\gamma) \tag{3}$$

where β_m is the helical twisting power of the chiral dopant.

In order to determine the value of β_m, we obtained **Λ-4** by the optical resolution of racemic **4**. The cholesteric fingerprint texture of **Λ-4** dissolved in 4′-ethoxybenzylidene-4-*n*-alkylaniline (weight ratio, 9.1 : 1000) was observed by POM, figure 8 (*a*), and the cholesteric pitch was measured to be 150 μm. This value gives β_m to be 1.0 μm mol^{-1}. However, the measured value of the pitch is about 10 times larger than the present cell thickness (12 μm). In such a case the observed pitch depends on the cell gap due to the effect of cell surface, and the observed pitch in thin cells is generally supposed to be larger than the pitch in the bulk. Hence, a helical twisting power β_m for **4** in 4′-ethoxybenzylidene-4-*n*-alkylaniline was determined to be not less than 1.0 μm^{-1} mol^{-1}.

The rates of photoinversion are expressed by equations (4)–(8) [28, 29],

$$-(\mathrm{d}C_\Delta(t)/\mathrm{d}t)Sl \times 10^{-3} = (A_\Delta(t)\Phi - A_\Lambda(t)\Phi)S \tag{4}$$

$$-(\mathrm{d}C_\Lambda(t)/\mathrm{d}t)Sl \times 10^{-3} = (A_\Lambda(t)\Phi - A_\Delta(t)\Phi)S \tag{5}$$

$$A_\Delta(t) = I_0(1 - 10^{-OD})C_\Delta(t)/C_0 \tag{6}$$

$$A_\Lambda(t) = I_0(1 - 10^{-OD})C_\Lambda(t)/C_0 \tag{7}$$

$$C_\Lambda(t) - C_\Delta(t) = C_0 \exp[-2I_0(1 - 10^{-OD})\Phi \times 10^3 t/C_0 l] \tag{8}$$

where I_0 is the number of irradiated photons per unit time and unit cross section, S is the area of irradiated cross section, $C_\Delta(t)$ and $C_\Lambda(t)$ are the concentrations of **Δ-4** and **Λ-4**, respectively, as functions of time; l is the thickness of system, $A_\Delta(t)$ and $A_\Lambda(t)$ are the numbers of photons per unit time and unit cross section absorbed by **Δ-4** and **Λ-4**, respectively, Φ is the quantum yield of the photoinversion reaction, and t is time. It is obvious that the quantum yields of the reaction for **Δ-4** and **Λ-4** are equal because of symmetry.

The optical rotation at 546 nm, $\theta(t)$, is expressed by equation (9). The quantum yield of the photoinversion

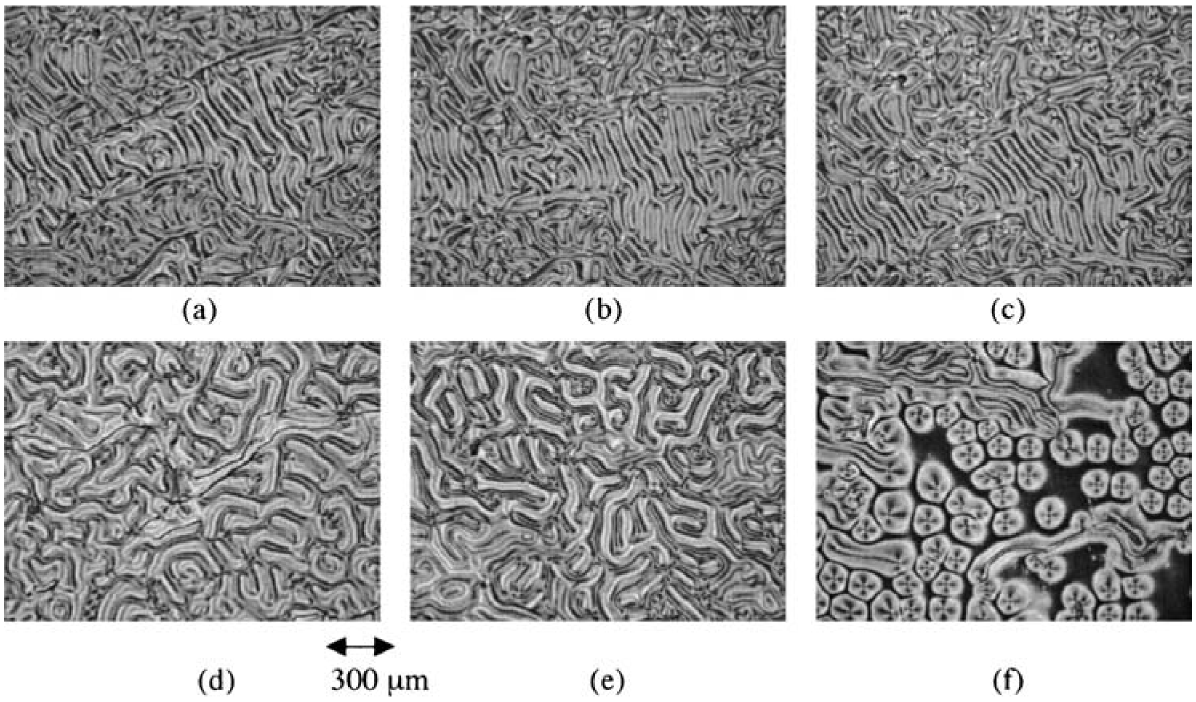


Figure 8. Changes in cholesteric pitch of **1** containing Λ-**4** (weight ratio, 1000 : 9.1) after irradiation of LPL. (*a*) Before irradiation, (*b*) after 30 min irradiation, (*c*) after 60 min, (*d*) after 180 min, (*e*) after 300 min, (*f*) after 480 min irradiation.

reaction Φ is obtained from changes in $\theta(t)$ using equation (15) [28, 29].

$$\theta(t) = 33 \times \delta OD \tag{9}$$

$$\delta\varepsilon = \varepsilon_{l\Delta} - \varepsilon_{r\Delta} = \varepsilon_{r\Lambda} - \varepsilon_{l\Lambda} \tag{10}$$

$$OD_l(t) = [\varepsilon_{l\Delta} C_\Delta(t) + \varepsilon_{l\Lambda} C_\Lambda(t)]l \tag{11}$$

$$OD_r(t) = [\varepsilon_{r\Delta} C_\Delta(t) + \varepsilon_{r\Lambda} C_\Lambda(t)]l \tag{12}$$

$$\delta OD(t) = OD_l(t) - OD_r(t) = \delta\varepsilon[C_\Delta(t) - C_\Lambda(t)]l \tag{13}$$

$$C_\Lambda(t) - C_\Delta(t) = C_0(t) - 2C_\Delta(t) = \delta OD(t)/\delta\varepsilon l = \theta(t)/33\delta\varepsilon l \tag{14}$$

$$\ln[\theta(t)/\theta_0] = -2I_0(1 - 10^{-OD})\Phi \times 10^3 t/(C_0 l) \tag{15}$$

where $\varepsilon_{l\Delta}$ and $\varepsilon_{r\Delta}$ are the molar extinction coefficients of Δ-**4** for *l*-CPL and *r*-CPL, respectively; $\varepsilon_{l\Lambda}$ and $\varepsilon_{r\Lambda}$ are the molar extinction coefficients of Λ-**4** for *l*-CPL and *r*-CPL, respectively.

The enantiomeric excess γ is expressed as follows,

$$\gamma = [C_\Lambda(t) - C_\Delta(t)]/C_0 \tag{16}$$

and then equation (17) is derived from equations (3), (15) and (16):

$$P(t) = P_0 \exp[-2I_0(1 - 10^{-OD})\Phi \times 10^3 t/C_0 l] \tag{17}$$

where P_0 is the initial cholesteric pitch.

The value of cholesteric pitch $P(t)$ at time t can be predicted from equation (17), by using the values of I_0, C_0, and OD obtained from UV measurements; $\Phi = 0.0024$ in benzene, and $l = 12\,\mu m$ from the thickness of the spacer.

During LPL irradiation of the liquid crystal **1** doped with Λ-**4** (weight ratio, 1000 : 9.1), cholesteric pitch $P(t)$ changed from 150 to 240 µm, as shown in figure 8, owing to photoracemization of Λ-**4** and the resulting change in enantiomeric excess. After irradiation for 480 min, the fingerprint texture was erased. Changes in $P(t)$ during LPL irradiation and a predicted curve from equation (17) are shown in figure 9. The experimental results of changes in $P(t)$ are in good accord with the predicted curve, supporting the above discussion. The observed

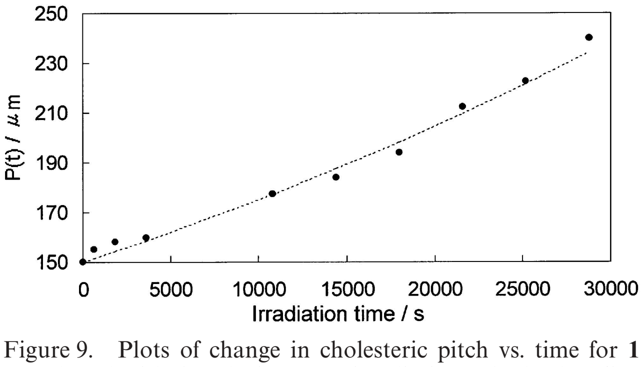
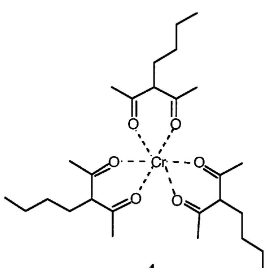
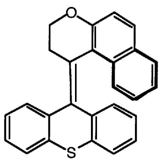


Figure 9. Plots of change in cholesteric pitch vs. time for **1** doped with Λ-**4** during LPL irradiation. The broken line is the result predicted by equation (17).

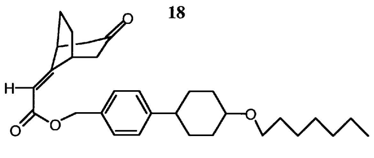
Table 2. Comparison of g and β_m for compounds reported for photoinversion reactions in liquid crystals.



4



18



19

Chiral compound	Anisotropy factor g	Helical twisting power $\beta_m/\mu m^{-1} mol^{-1}$
Cr(Buacac)$_3$, **4**	5.0×10^{-2}	>1.0
Helical alkene **18** [16]	6.4×10^{-3}	—
Bycyclic ketone **19** [17]	1.4×10^{-2}	15

pitches depend on the cell gap in the present case, but the present result suggests that the relative change in pitch as a function of concentration may be little influenced by the cell thickness.

The values of g and β_m for the present system, **4** in **1**, are compared in table 2 with results for compounds that have been reported to control homeotropic-fingerprint texture change. A sterically overcrowded helical alkene **18** is reported by Feringa *et al.* [16], and a chiral bicyclic ketone **19** is reported by Burnham and Schuster [17]. In regard to the anisotropy factor g, **4** has a higher value than other molecules, however, β_m and solubility are lower than for the others. It is recognized that the low β_m and limited solubility of Cr(Buacac)$_3$ **4** is the reason for reversible control of homeotropic-fingerprint texture only in the presence of an auxiliary chiral dopant.

4. Conclusions

We report in the present paper chiro-optical control of liquid crystalline texture, from homeotropic to fingerprint, by irradiation with vis-*r*-CPL, and from fingerprint to homeotropic by irradiation with vis-*l*-CPL or LPL. Chromium complexes have a wide visible light absorption which enabled us to carry out photoinversion reactions with visible CPL. Cr(Buacac)$_3$ has a large value of g, but β_m is rather low. It is recognized that g and β_m are influenced by the chemical structure of the ligands. The influences of ligand structure on the solubility of the resulting chromium complexes in liquid crystals, and on photoinversion reactions by CPL irradiation have been widely examined.

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