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Nobuhiro Anzai[a]; Hiroko Kurihara[a]; Masato Sone[a]; Hidemitsu Furukawa[a]; Toshiyuki Watanabe[a]; Kazuyuki Horie[a]; Sandeep Kumar[b]
[a] Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology, 4-24-16 Naka-cho, Koganei-shi, Tokyo 184-8588, Japan [b] Raman Research Institute, C. V. Raman Ave., Bangalore 560 080, India

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Light-induced formation of curved needle texture by circularly polarized light irradiation on a discotic liquid crystal containing a racemic chromium complex

NOBUHIRO ANZAI*†, HIROKO KURIHARA†, MASATO SONE†, HIDEMITSU FURUKAWA†,
TOSHIYUKI WATANABE†, KAZUYUKI HORIE† and SANDEEP KUMAR‡

†Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology,
4-24-16 Naka-cho, Koganei-shi, Tokyo 184-8588, Japan
‡Raman Research Institute, C. V. Raman Ave., Bangalore 560 080, India

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We have found that the discotic nematic liquid crystal, hexakis(4-nonylphenylethynyl)benzene (HNEB), doped with the racemic chromium complex $Cr(Ocacac)_3$, shows a novel straight-needle texture with hexagonal columnar alignments, changing to a curved-needle texture under irradiation of circularly polarized light (CPL). This novel phenomenon is specific to the mixture of HNEB and $Cr(Ocacac)_3$. The formation of curved needles means that chiroselective photoinversion of racemic $Cr(Ocacac)_3$ by CPL irradiation induces a needle direction change in a discotic liquid crystal. The change in chirality of $Cr(Ocacac)_3$ in HNEB induced by CPL irradiation, and the resulting nano-segregation of its enantiomers during cooling from the isotropic to mesophase of HNEB, are considered to influence changes in the alignment of columns and/or small domains of column aggregates in the discotic liquid crystal.

1. Introduction

Liquid crystals (LCs) have optical anisotropy and fluidity, and their orientation directions can be controlled by external electric or magnetic fields. Light-induced control of LCs was first reported by Hass *et al.* in 1969 [1] and Sackmann in 1971 [2]. Studies in this field have become active since the 1980s, and the light-control of LCs with photochromic molecules has been studied in order to apply it to an optical switch or an optical memory system [3–9].

Photochemical reaction processes are different from thermochemical reactions, in that in photochemical reactions a molecule absorbs a photon and forms an excited state which then undergoes a chemical reaction. If one of a pair of chiral enantiomers (right-handed or left-handed) has a different absorption coefficient for circularly polarized light (CPL) from the other chiral enantiomer (left-handed or right-handed), this selective excitation under CPL can be applied to photo-enantiomerization, photo-asymmetric synthesis and photo-asymmetric destruction. Attempts at asymmetric isomerizaition of racemic compounds under CPL irradiation were first reported in the 1930s [10–12]. Chiral material sources are not necessary for these reactions, but the optical purity of the reaction products are usually low, because the anisotropy factor, *g*, which is the difference in absorption coefficients of enantiomers for CPL, is small. However, the photo-enantiomerization reactions could be applied to an optical switch or an optical memory system by using a medium such as liquid crystals, because the change in chirality is amplified in LCs to their macroscopic texture change. For example, a nematic (N) LC containing chiral molecules has a particular orientational characteristic, being twisted along a normal axis, resulting in a cholesteric liquid crystal.

Light-induced changes in cholesteric pitches in LCs on introducing chirality into photochromic molecules have been studied since the 1990s [13–27]. Photoinversion reactions of chiral molecules inducing a change in chirality or helicity are a known photo-isomerization reaction; the irradiation of right-circular polarized light (*r*-CPL) changes an enantiomer molecule with structure *d* to the other enantiomer *l*. The light control of a liquid crystalline phase using a chiral compound has recently become an exciting topic.

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*Corresponding author. Present address: Asahi Kasei corporation, 2-1 Samejima, Fuji-shi, Shizuoka 416-8501, Japan; Email: anzai.nb@om.asahi-kasei.co.jp

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Feringa *et al.* [20] first reported the light-control of a liquid crystalline phase from N to cholesteric (Ch) by the irradiation of ultraviolet (UV)-CPL on a helical molecule such as 12-(9′H-thioxanthene-9′-ylidene)-12H-benzo[a]xanthene in the LC. Burnham and Schuster [17] reported reversible control of a liquid crystalline phase from N to Ch by irradiation of UV-CPL on a racemic bicyclic ketone. The values of the anisotropy factor, g, for these compounds, however, are not sufficiently high, and their absorption bands lie in the UV. When a NLC is doped with a low concentration of a chiral dopant, the cholesteric pitch, P, is inversely proportional to its concentration, C, and its helical twisting power, β_m; $P=1/(\beta_m C)$. When the concentration of the chiral dopant is controlled by CPL irradiation on a racemic dopant, C is expressed as $C=C_0\gamma$, where C_0 is the concentration of the racemic dopant and γ is an enantiomer excess. In the photostationary state, P is expressed as $P=2/(C_0 \beta_m)$ [26]. In order to induce the phase transition of a LC containing a racemic compound from N to Ch by CPL irradiation, the dopant must have sufficiently large values of g and β_m. The anisotropy factor g is related to the efficiency of inducing enantiomer excess from a racemic compound by CPL irradiation, and β_m is twisting power of the chiral dopant making the liquid crystal helical.

Chromium tris(acetylacetonate), $Cr(acac)_3$, is known to have a large g value (7.8×10^{-2}) and be stable against inversion in helicity caused by temperature and/other chemicals [28–31]. The $Cr(acac)_3$ has enantiomers, Λ and Δ forms. Irradiation with *l*-CPL enables Λ to change into Δ, and irradiation of *r*-CPL enables Δ to change into Λ. It is supposed that when the Λ (Δ) form is excited by light, Λ (Δ)Cr–O bonds would be cleaved, and recombined or changed to Δ(Λ)Cr–O bonds; and an enantiomer excess can be provided by CPL irradiation of a racemic mixture. $Cr(acac)_3$ has very low solubility in any NLC at room temperature. However, moleculer design of the ligand is a key to dissolving chromium complexes in a LC; ligands containing side chain alkyl groups increase the solubility of a complex in liquid crystals. Our previous studies [26, 27] demonstrated the chiro-optical induction of cholesteric fingerprint texture by visible CPL irradiation from a nematic mixed liquid crystal, 4′-ethoxybenzylidene-4-*n*-alkylanilines containing racemic chromium tris(3-butyl-2,4-pentanedionate), $Cr(Buacac)_3$, and an auxiliary chiral dopant. The chiro-optical control of LC texture by CPL, in the presence of a racemic chiromium complex, has been realized so far by adding a small amount of chiral binaphthol to racemic $Cr(Buacac)_3$, probably owing to rather low solubility of the chromium complex in the NLC.

The basic structure of liquid crystals is typically classified into rod-like and disc-like shapes. The discotic nematic phase of disc-like molecules has been investigated less than that of rod-like molecules [32–35]. Discotic NLCs have a similar characteristic to rod-like NLCs with regard to the formation of helical structure under the influence of a chiral dopant [36]. Hexakis(4-nonylphenylethynyl)benzene, HNEB, is a unique substance which form a discotic nematic phase at moderate temperatures ranging from 68 to 83°C [33], and is known to form blue phases on doping with chiral cellobiose [33]. Even when around 20 wt% of chiral cellobiose is dissolved in HNEB, the LC phase can be maintained. Therefore, HNEB may be a superior substance for the formation of LC phases at moderate temperatures, in the presence of large amounts of chiral dopant. The chromium complex, chromium tris(3-octyl-2,4-pentanedionate), $Cr(Ocacac)_3$, has a chemical structure well matched with HNEB, so that the orientation of liquid crystalline HNEB would not be disturbed; it is easily dissolved in discotic HNEB.

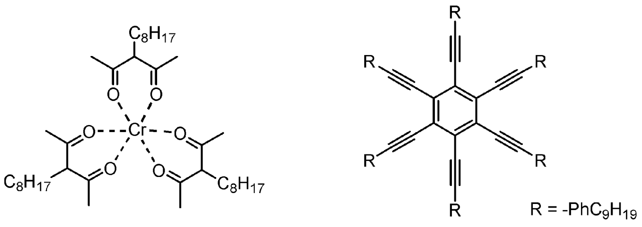
The present paper is the first report on the formation of a straight-needle texture in a discotic liquid crystal doped with racemic $Cr(Ocacac)_3$ and its change to curved-needle texture by CPL irradiation. The possibility of nanoscopic segregation of right-handed and left-handed species during cooling from isotropic to mesophase is also suggested, even for the racemic sample before CPL irradiation.

2. Experimental

2.1. *Materials*

2.1.1. Liquid crystal. The discotic liquid crystal, HNEB, was prepared by palladium-catalysed coupling of 4-nonylphenylacetylene with hexabromobenzene. Details are given elsewhere [34]. It shows a nematic phase from 68 to 83°C. The chemical structure is shown in figure 1.

2.1.2. Preparation of the ligand. The 3-octyl-2, 4-pentanedionate, Ocacac, was synthesized from



$Cr(Ocacac)_3$ HNEB

Figure 1. Chemical structures of the chromium complex, $Cr(Ocacac)_3$, and HNEB.

acetylacetone and octyl iodide. A solution of 25.0 g (0.104 mol) octyl iodide, 15.6 g (0.156 mol) acetylacetone, and 21.6 g (0.156 mol) potassium carbonate in 100 ml of acetone was heated under reflux at 80°C for 20 h. After reflux, the mixture was poured into 100 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; 11.1g of Ocacac was obtained, yield 50.1%. ^{1}H NMR($CDCl_3$); δ 0.89 (t, 3H, CH_3–) 1.25(m, 12H, CH_3–C_6H_{12}–) 1.83(q, 2H, C_7H_{15}–CH_2–) 2.18(s, 6H, CH_3–CO–) 3.61(t, 1H, Oc–$CH(COCH_3)_2$).

2.1.3. Preparation of the complex.

2.1.3. Preparation of the complex. The chemical/ structure of chromium tris(3-octyl-2, 4-pentanedionate), Cr(Ocacac)$_3$, is shown in figure 1. A solution of 5.03 g (23.7 mmol) Ocacac, 1.59 g (5.95 mmol) chromium trichloride and 1.50 g (25.0 mmol) urea in a mixture of 20 ml water and 20 ml ethanol was heated under reflux at 110°C for 24 h. The mixture was then poured into 100 ml of water, and extracted with dichloromethane. The dichloromethane solution was dried over anhydrous sodium sulphate, and evaporated. The product was purified by column chromatography on silica gel (Wako Gel C-200, eluent hexane/ dichloromethane=9/1) and recrystallized from hexane at −20°C; yield 22%. As the resulting chromium complex was paramagnetic, its ^{1}H NMR spectrum could not be measured.

2.2. *Instrumentation*

Liquid crystalline textures were observed with an Olympus BH-2 polarizing optical microscope with a Linkam LK-600PM temperature controller. The observation of liquid crystalline textures was carried out mainly during cooling of the samples from the isotropic state. All UV-visible spectra were measured with a Jasco Uvidec 660 UV/Vis spectrophotometer. NMR spectra were measured with a Jeol JNM-GX400 FTNMR spectrometer. CD spectra were recorded with a Jasco J-500A spectropolarometer. High performance liquid chromatography (HPLC) was carried out with a Jasco Uvidec 100-IV UV detector equipped with a Chiralcel OD® column (Daisel) and Jasco 807-IT integrator. In UV absorption and fluorescence measurements and photoracemization, all solvents were of spectrosol or luminasol grade (Wako).

2.3. *Photoinversion in soluton*

A 2.0 ml solution of 5.0×10^{-3} M Cr(Ocacac)$_3$ in benzene was irradiated with 632.8 nm light from a He-Ne laser modified through a Baninet–Soleil compensator (*r*-CPL). The change in optical activity was traced by CD spectra. Irradiation was continued until the CD spectra peak was constant, Light intensity was measured at 633 nm using an Advantest TQ8210 optical power meter. UV spectra before and after photoinversion were measured for the same samples.

2.4. *Photoinversion and control of textures in liquid crystalline samples*

In order to observe the change in a liquid crystalline phase after the photoinversion reaction, a cell was prepared with glass plates and polyethylene film spacer (12 µm or 100 µm). The inside of the lower glass plate was usually coated with a polyvinyl alcohol (PVA) film and rubbed with a nylon cloth, while the inside of the upper glass plate was not surface-treated. The solution of HNEB and Cr(Ocacac)$_3$ in dichloromethane was poured onto the glass plate with a spacer film at 80°C. After the dichloromethane was vaporized, the sample was covered with the upper glass plate, and sealed at the edges with an epoxy adhesive. The liquid crystalline textures were observed by polarizing optical microscopy (POM) under crossed polarizers before and after irradiation by *r*-CPL. The cell was irradiated at 632.8 nm with 14 mW cm^{-2} He-Ne *r*-CPL or *l*-CPL, laser-modified through a Babinet-Soleil compensator.

2.5. *X-ray diffraction measurements*

Wide-angle X-ray diffraction (XRD) patterns of the liquid crystalline samples before and after CPL irradiation were measured with a RV200 (Rigaku) X-ray diffractometer. Sample temperature was controlled with a Mettler FP80HT temperature controller. Measurement data were calibrated with the (1 1 1) reflection from a Si powder standard.

3. Results

3.1. *Chiroselective photoinversion by CPL of Cr(Ocacac)$_3$ in solution*

The CD and UV spectra of racemic Cr(Ocacac)$_3$ in benzene before and during *r*-CPL irradiation at 632.8 nm for 74 h are shown in figure 2. 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-Cr(Ocacac)$_3$ to Λ-Cr(Ocacac)$_3$. The corresponding UV spectra did not change with CPL irradiation.

The enantiomeric excess for the photostationary state, γ_{pss}, and hence the anisotropy factor, *g*, in the case of CPL irradiation on a racemic sample were

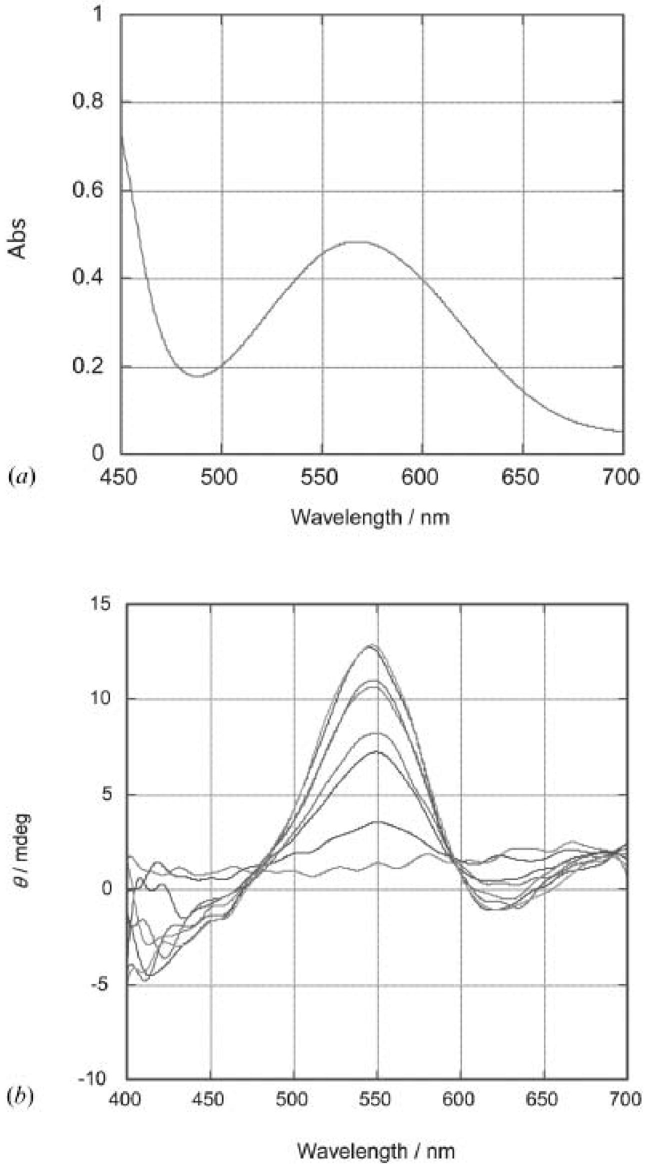


Figure 2. (*a*) UV spectrum and (*b*) changes in the CD spectra of racemic Cr(Ocacac)$_3$ in benzene (5.0×10^{-3} M) during *r*-CPL irradiation for 0, 8, 24, 30, 46, 52, 69 and 74 h (from bottom to top at 540 nm).

calculated from UV absorption and CD spectra from:

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

where $\Delta\varepsilon=\varepsilon_{l\Delta}-\varepsilon_{r\Delta}=\varepsilon_{r\Lambda}-\varepsilon_{l\Lambda}$ is the difference in molar extinction coefficients, ε_r and ε_l, of the Δ- or Λ- type dopant for *r*- and *l*-CPL, respectively; ε is the molar extinction coefficient for racemic dopant, $OD=\varepsilon Cl$ is the optical density, C is the molar concentration and l is the path length of the light.

Cr(Ocacac)$_3$ shows g values of -0.04 (maximum) at 530 nm and 0.025 at 633 nm in benzene (figure 3). When Cr(Ocacac)$_3$ was irradiated at 632.8 nm with He-Ne CPL, the enantiomer excess for the photostationary state, γ_{pss}, was 1.25%. The g values are 0.078 for Cr(acac)$_3$ and 0.05 for Cr(Buacac)$_3$. Cr(Ocacac)$_3$ shows a little smaller g value than those for other short alkyl types of Cr(alkyl-acac)$_3$, however, the value is still large compared with other organic compounds that undergo photoisomerization [37].

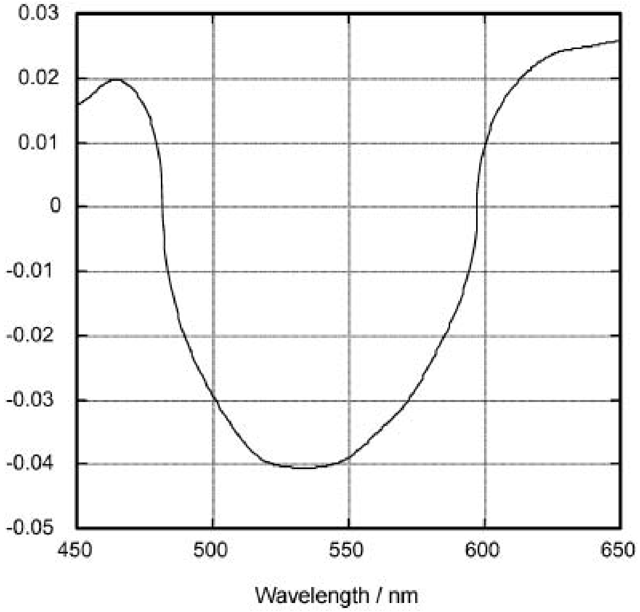


Figure 3. The anisotropy factor, g, calculated from CD and UV spectra, equation (1), for Cr(Ocacac)$_3$ in benzene.

3.2. *Light-induced texture change by CPL in a discotic liquid crystal*

The textures of the discotic nematic liquid crystal HNEB, doped with Cr(Ocacac)$_3$, were observed by POM before and after CPL irradiation. Samples without Cr(Ocacac)$_3$ were also observed as reference. Table 1 summarizes the compositions and cell preparation conditions of the samples.

Sample 1 without Cr(Ocacac)$_3$, in a surface-treated cell, changed from isotropic to nematic at 83°C and became crystal at 68°C. Only a dark picture was observed for the N phase due to cross-polarized observation of the homeotropic (face-on) orientation of the discotic N phase. However sample 2, in a cell without surface treatment, showed birefringence at 83°C just after the phase transition from isotropic to mesophase, figure 4 (*a*), but it changed to dark at 81°C during cooling, figure 4 (*b*), due to face-on orientation of the discotic HNEB molecules.

When 10 wt % of Cr(Ocacac)$_3$ was doped in HNEB in a 100 μm gap cell without surface treatment (sample 3),

Table 1. Preparation conditions of discotic liquid crystal samples of HNEB with Cr(Ocacac)$_3$.

Sample No.	Components, wt% of Cr(Ocacac)$_3$	Spacer thickness/µm	Surface treatment	
			Upper	Lower
1	HNEB only	12	none	PVA and rubbing
2	HNEB only	no spacer	none	none
3	HNEB/Cr(Ocacac)$_3$, 10	100	none	none
4	HNEB/Cr(Ocacac)$_3$, 18	12	none	PVA and rubbing
5	HNEB/Cr(Ocacac)$_3$, 10	12	none	PVA and rubbing

nematic schlieren texture was observed at 70°C before CPL irradiation, figure 4 (*c*); after *l*-CPL irradiation for 39 h an oily streak texture of white lines connecting disclinations appeared at 70°C, figure 4 (*d*), which is known to appear in chiral nematic phases [38].

When no surface treatment of the cell was carried out, the orientations of the liquid crystals were not arranged to the same direction, and therefore schlieren texture appeared. The disclination is a characteristic defect of nematic schlieren texture and two- or four-brush-like lines appear at a disclination core because alignments of LC molecules change gradually. An oily streak texture of white lines after CPL irradiation is also considered to indicate a defect, but it is different from brush-like lines, and would be caused by drastic anisotropy change due to CPL irradiation and resulting change in enantiomer concentration in the sample. The appearance of the oily streak texture would be closely related to the chirality change of Cr(Ocacac)$_3$ dopant on CPL irradiation.

The texture of HNEB doped with 18 wt% of Cr(Ocacac)$_3$ in a surface-treated cell (sample 4) was

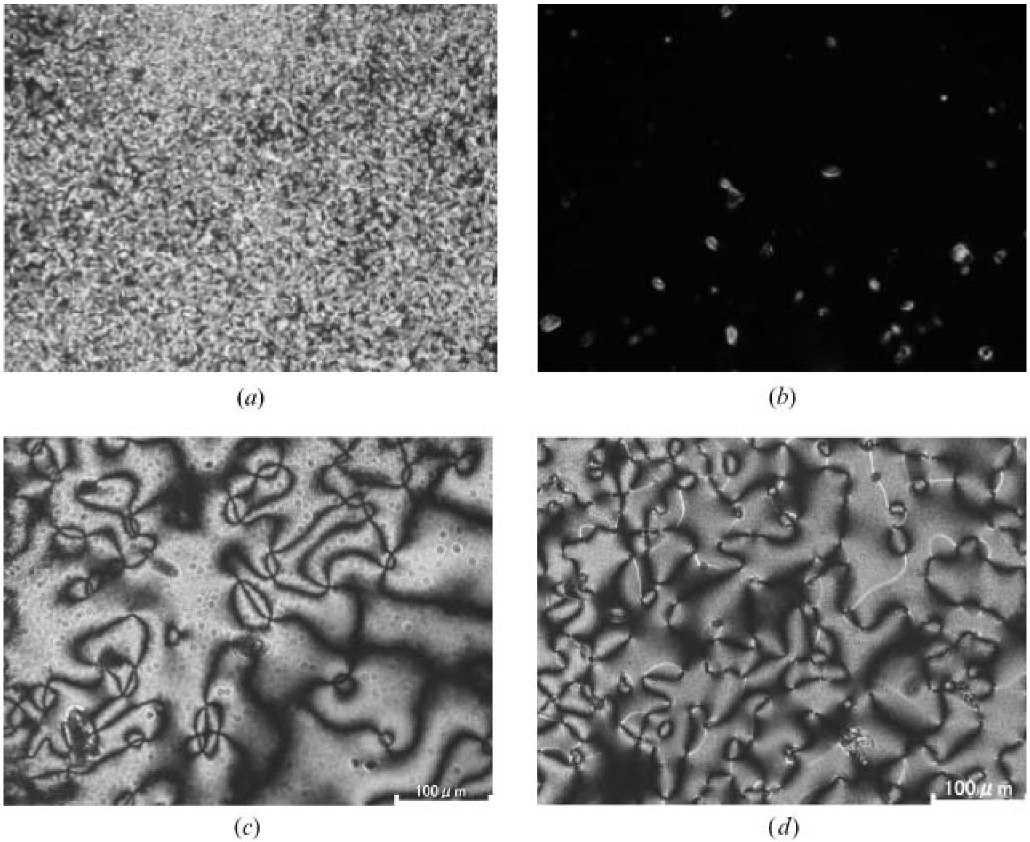


Figure 4. Textures of HNEB alone without surface treatment (sample 2) and HNEB doped with 10 wt% of racemic Cr(Ocacac)$_3$ without surface treatment (sample 3), observed by POM. (*a*) Sample 2 during cooling at 83°C, birefringence appears; (*b*) sample 2 during cooling at 81°C, the picture turns black; (*c*) sample 3 before irradiation by CPL, a schlieren texture appears cell not surface-treated, *l*=100 µm); (*d*) sample 3 after irradiation by *l*-CPL at 632.8 nm for 39 h, an oily-streak texture appears.

observed by POM before and after CPL irradiation. Before CPL irradiation of sample 4, a mono-domain texture of columnar structure was observed at 60°C, figure 5 (*a*), during slow cooling from the isotropic state (100°C). The columnar structure was ascertained by its XRD pattern (see § 3.3). Biaxial anisotropy of the mono-domain texture parallel to the cell surface was ascertained by the disappearence of the bright image with 45° rotation of the sample stage on the cross-polarized optical microscope. Since no columnar mesophase was observed for HNEB samples without Cr(Ocacac)$_3$, intermolecular interaction between the dopant Cr(Ocacac)$_3$ and HNEB molecules is thought to cause the columnar phase formation in sample 4.

The formation of columnar mono-domain, as in figure 5 (*a*), is a very slow process and took 30 min holding at 60°C during the cooling process, but narrower and sharp filament-like needles, figure 5 (*b*),

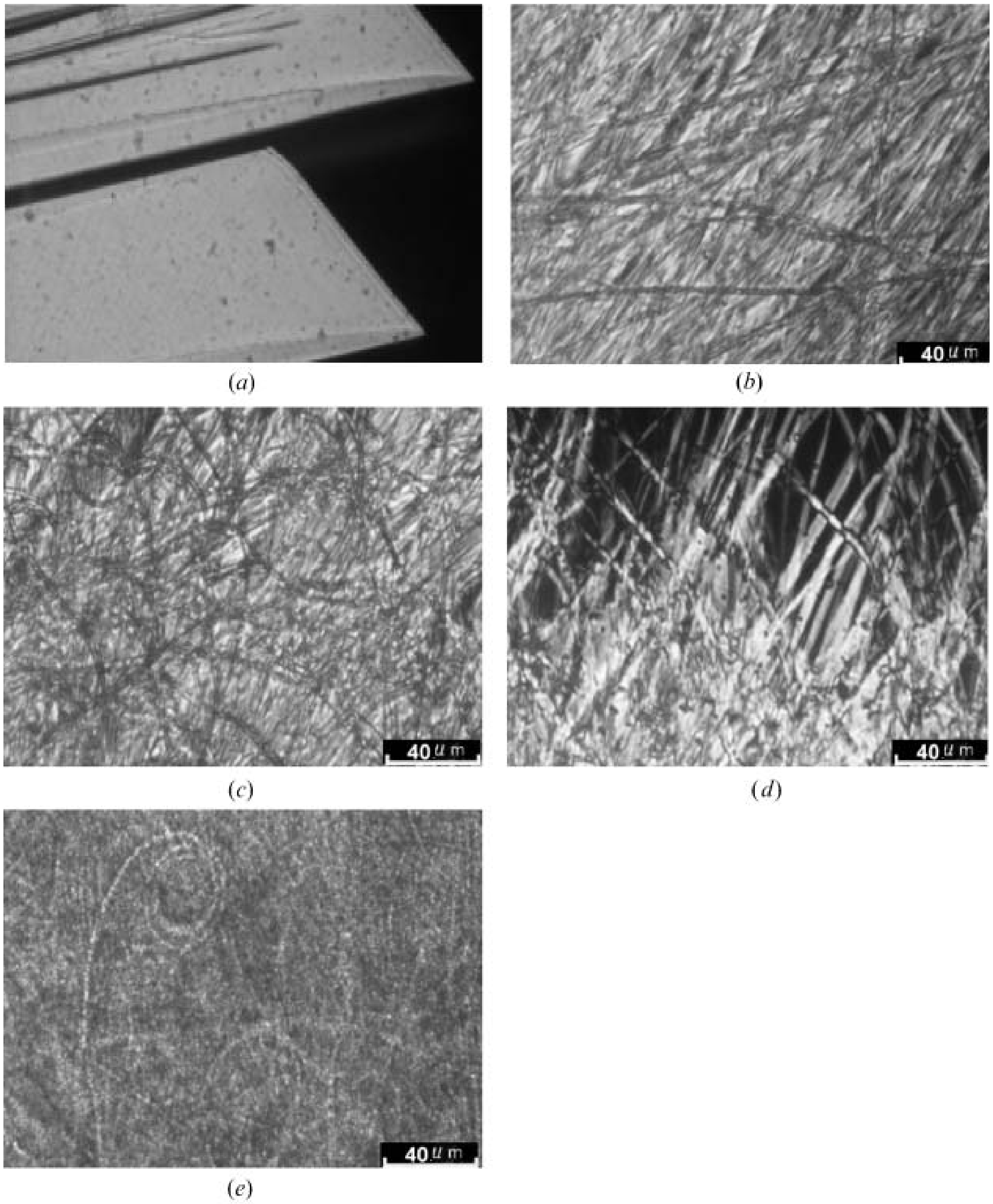


Figure 5. Textures of HNEB doped with 18 and 10 wt% of racemic Cr(Ocacac)$_3$ observed by POM. (*a*) Before irradiation by CPL for 18 wt% sample (sample 4), mono-domain of liquid crystal column is observed (PVA coated cell, *l*=12 μm); (*b*) before irradiation by CPL for 18 wt% sample (sample 4), a straight-needle texture is also observed; (*c*) after irradiation by *l*-CPL at 632.8 nm for 21 h, a curved-needle texture appears; (*d*) before irradiation by CPL for 10 wt% sample (sample 5), a straight-needle texture is observed; (*e*) after irradiation by *l*-CPL at 632.8 nm for 21 h, a curved-needle texture appears.

were observed more easily during cooling at 60°C, at less than 5°C min^{-1}, for sample 4 of HNEB doped with 18 wt% racemic Cr(Ocacac)$_3$ before CPL irradiation. The majority of needles were aligned in a straight line, with biaxial anisotropy. We consider that these needles are also composed of a columnar structure. We call the aligned texture a straight-needle texture.

After *l*-CPL irradiation for 21 h on sample 4, curved needles were observed at 56°C during cooling, after heating to 100°C, as is shown in figure 5 (*c*). Since such curved needles could not be observed before CPL irradiation, their is related to a chirality change in the racemic Cr(Ocacac)$_3$. Such direction changes of needles from straight to curved were also observed for sample 5 with 10 wt% of Cr(Ocacac)$_3$ in HNEB, figures 5 (*d*, *e*). A round filament-like texture, as well as curved needles, is observed in figures 5 (*c*, *e*). After CPL irradiation of samples 4 and 5, no mono-domain texture was observed when cooling them from the isotropic state.

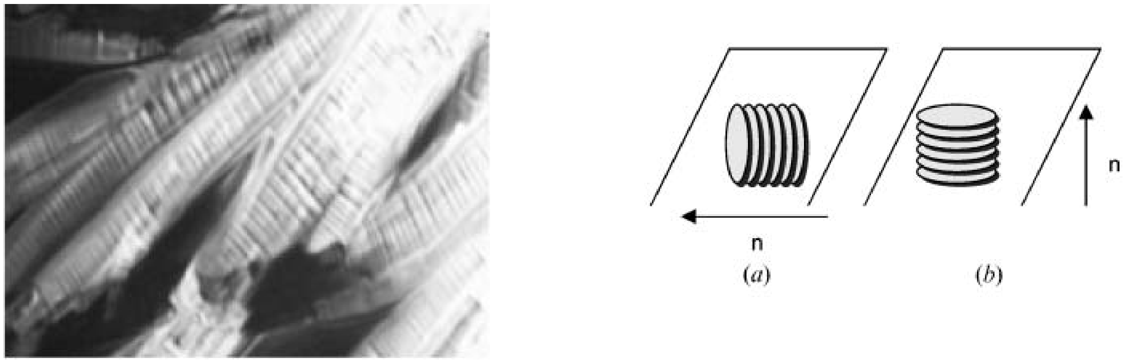
Black lines, crossing at right angles against the growth direction of straight needles, were observed (figure 6), after sliding the upper glass plate of sample 4 before irradiation to impart shear stress. The black lines would be defects of column angles against the cell axis, because the shear stress and pitches of the black lines were irregular. Aligned columns with biaxial anisotropy parallel to the surface form straight needles, and sheared parts in the column aggregates may be modified by the change of column axis, either in an along-the-surface direction to some extent or to homeotropic (face-on). In the present case, the alignment of the liquid crystal columns in needles are considered to be described as in figure 6 (*a*) rather than figure 6 (*b*).

3.3. *X-ray diffraction of the liquid crystal of HNEB with Cr(Ocacac)$_3$*

Wide-angle XRD observations on sample 4 (HNEB with 18 wt% Cr(Ocacac)$_3$), before and after CPL irradiation for 21 h, were carried out at room temperature after heating to the isotropic transition temperature (70°C) and cooling gradually. Their one-dimensional intensity patterns are shown in figure 7. Since the samples were observed to be in the mesophase at room temperature for several hours after heating to the isotropic state and cooling gradually to room temperature, the room temperature observations are considered to reflect the structure of the mesophase. The spacings, *d*, are listed in table 2.

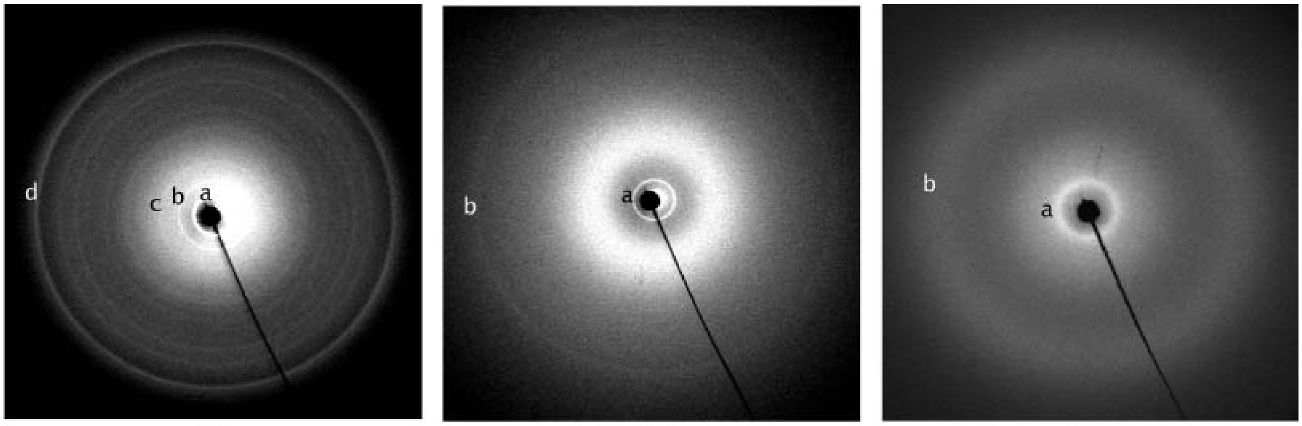
For sample 4, with 18 wt% Cr(Ocacac)$_3$ before CPL irradiation, figure 7 (*a*), the three inner peaks a, b, c, are observed in the ratio $1:1/\sqrt{3}:1/\sqrt{7}$. By identifying the first peak with the Miller index (1 0 0), the ratios conform to the expected values for a two-dimensional hexagonal lattice. The inner diffraction peak, a, at about 31.4 Å corresponds to the disc diameter d_{100}. The second inner diffraction peak, b, at about 18.6 Å and the third, c, at about 12.1 Å are identified with the Miller indices (1 1 0) and (2 1 0), respectively. The peak outermost diffuse diffraction, d, at about 3.9 Å corresponds to the stacking distance between cores of HNEB molecules. This diffuse peak suggests that the stacking of the discs within each column is correlated over short distances. Several very weak and diffuse peaks appeared at the wide Bragg angle (about 4.3 to 7.2 Å) and these correspond to the intermolecular distance between the composite molecules [39].

Thus, these X-ray peaks ascertain the formation of columns and their aggregation to a two-dimensional hexagonal lattice for this HNEB discotic liquid crystal with 18 wt% racemic Cr(Ocacac)$_3$. For sample 4 after CPL irradiation, figure 7 (*b*), the inner diffraction peak, a, at about 32.0 Å and an outer peak, b, at about 3.9 Å were detected; however, other peaks corresponding to Miller indices (1 1 0) and (2 1 0) could not be detected, because the sharp reflection peaks broadened. This suggests that the packing of the Cr(Ocacac)$_3$/HNEB



(*a*) (*b*)

Figure 6. Textures of HNEB doped with 18 wt% of racemic Cr(Ocacac)$_3$ (sample 4) observed by POM after sliding the upper glass plate to impart shear stress.



(*a*) (*b*) (*c*)

Figure 7. One-dimensional wide angle XRD patterns for mixtures of HNEB with 18 (sample 4) and 10 (sample 5) wt% Cr(Ocacac)$_3$. (*a*) Before CPL irradiation for sample 4; (*b*) after CPL irradiation for sample 4; (*c*) before CPL irradiation for sample 5.

Table 2. Measurements of *d*-spacing by XRD.

Sample No.	CPL irradiation	Position of reflection peaks	Spacing *d*/Å
4	None	a	31.4
		b	18.6
		c	12.1
		between c and d	7.2
		between c and d	6.0
		between c and d	4.6
		between c and d	4.3
	21 h	d	3.9
		a	32.0
		b	3.9
5	None	a	22.5
		b	4.5

mixture has been subjected to some structural change such as destruction of crystal-like packing, due to enantiomerization of Cr(Ocacac)$_3$ by CPL irradiation.

For sample 5 with 10 wt% racemic Cr(Ocacac)$_3$ before CPL irradiation, figure 7 (*c*), broad peaks are observed in the inner area, but could not be identified with Millar indices. The diffuse outer diffraction peak, b, at about 4.5 Å corresponds to the distance between core–core stacking of HNEB molecules, and this distance is wider than the corresponding distance in sample 4. The smaller amount of Cr(Ocacac)$_3$ dopant in HNEB compared with sample 4 might have caused the increase in nematic tendency in the mesophase reflected by the diffuse diffraction pattern in figure 7 (*c*), because HNEB itself shows a discotic nematic phase in the absence of Cr(Ocacac)$_3$.

4. Discussion

A possible explanation of the mechanism of straight-needle formation before CPL irradiation, and its change to curved-needle after CPL irradiation may be given as follows. The Cr(Ocacac)$_3$ molecules are considered to be situated between HNEB cores and also among aligned columns. In the case of a high concentration of Cr(Ocacac)$_3$ such as 18 wt%, the interaction between HNEB and Cr(Ocacac)$_3$ assists the column formation of the LC molecules. The aggregates of columns composed of HNEB and Cr(Ocacac)$_3$ molecules are arranged regularly to form straight-needles before CPL irradiation. The direction of the column axis may be perpendicular or parallel to the straight-needle growth direction, but a perpendicular direction would be more likely based on the appearance of black-line stripes under shear stress, as shown in figure 6. When Cr(Ocacac)$_3$ molecules are exposed to CPL, the change in the ratio of Δ- and Λ-enantiomers in the LC phase may lead to a change in direction of the HNEB columns.

The possibility of nanosegregation of the samples during cooling from the isotropic state can be pointed out, because molecular interaction of HNEB molecules with each Cr(Ocacac)$_3$ enantiomer should be different. Hence, there may exist right-handed and left-handed columns and/or small domains of right-handed and left-handed column aggregates, even in the racemic condition. The numbers of both types of aggregates are equal in the racemic condition, and therefore the columns would form straight needles. However, the enantiomeric excess of Λ-Cr(Ocacac)$_3$ molecules after CPL irradiation may change the direction of column aggregates formed during cooling. Such direction changes of

HNEB columns could be observed as a curved-needle texture by POM. This novel phenomenon of the formation of straight and curved needles appears so far only in the mixture of HNEB with $Cr(Ocacac)_3$. Indeed, a mixture of HNEB with 0.5 wt% chiral (*R*)-(+)-1,1′-bi-2-naphthol showed no needles under POM in the mesophase region during cooling. The combination of HNEB and $Cr(Ocacac)_3$, forming a discotic columnar phase in the racemic condition, would be essential to cause the needle structure.

5. Conclusions

This paper reports for the first time the chiro-optical control of discotic liquid crystalline textures by irradiation with circularly polarized light (CPL). A mixture of HNEB with racemic $Cr(Ocacac)_3$ shows a straight-needle texture during cooling from the isotropic state, as well as a mono-domain texture with biaxial anisotropy, while HNEB alone shows a discotic nematic phase during cooling. The photoinversion of racemic $Cr(Ocacac)_3$ in HNEB by CPL irradiation changes the straight-needle texture to a curved-needle texture, due to the asymmetric composition of the right-handed and left-handed species. These results suggest that the existence of chirality in $Cr(Ocacac)_3$, and nano-segregation of its enantiomers during the phase transition process, influence the alignment of HNEB columns during cooling from isotropic to mesophase. This work indicates the possibility of nano-structure control by CPL, which could be applied to optical devices.

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