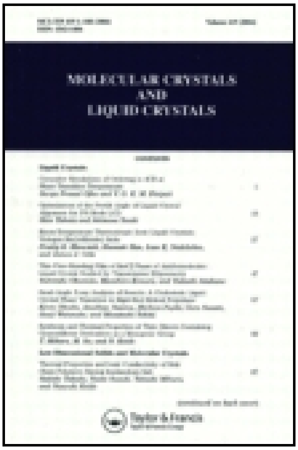

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Rewinding of Helical Systems by Use of the Cr(III) Complex as a Photoresponsive Chiral Dopant

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Vibrational circular dichroism (VCD) spectroscopy has been applied for monitoring in situ the photoinduced rewind of supramolecular helices in a liquid crystal. The monitored system was a room-temperature liquid crystal, ZLI-1132, doped with a novel chiral Cr(III) complex. Under the illumination of UV light (365 nm), the photoracemization of the Cr(III) complex led to the rewind of helices in the chiral nematic phase. In response to this, the VCD spectrum of the system exhibited the transient change, confirming the elongation of helical pitch length. The possibility of using the VCD spectrum as a memory of photoresponsive events is discussed.

Keywords: chiral dopant; Cr(III) complexes; VCD

1. INTRODUCTION

In the field of information technology, the exploitation of optical memory using a photoresponsive molecular system is a fascinating challenge [1,2]. The photosensitive characteristics of metal complexes may provide a unique possibility for this purpose when the property is linked with the ΔΛ-isomerism of octahedral configuration [3].

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Recently we have applied the ΔΛ-isomerism of octahedral metal complexes as a new source for the induction of a helical liquid-crystalline phase [4–8]. As a result, a chiral bis(chelated) complex, $[Ru(acac)_2L]$ (acac = acetylacetonate; L = an elongated ligand), has been found to efficiently induce a chiral nematic phase when it is doped in a room-temperature nematic material [4–6].

As an extension of this approach, the present article reports the use of a photoresponsive Cr(III) complex as a chiral dopant. A chiral Cr(III) complex is characterized by the stable structure in the dark as well as the coordination lability under the illumination of light [3]. The complex was doped into the nematic host material, ZLI-1132, which was chosen because of its transparency in the wavelength region of 300–400 nm. The liquid-crystalline sample may lead to the photoresponsive rewind of the helical structure because of the racemization of the doped complex. The vibrational circular dichroism (VCD) method has been initially applied for the real-time monitoring of the structural change of the present system. VCD spectroscopy measures the differential absorption of left *versus* right circularly polarized IR radiation [9–11]. The method has been recently employed to follow the amount of a chiral species in a solution [12–14]. When the method is applied to the present system, the VCD spectrum exhibits a transient change corresponding to the elongation of pitch length of an induced helix. The results suggest that the method may present a novel means of memorizing photoresponsive events in liquid-crystalline systems.

2. EXPERIMENTAL

A complex, $[Cr(acac)_2(2C12)]$ (acac = acetylacetonate; 2C12 = 4,4′-didodecyloxyated dibenzoylmethanate) (Fig. 1), was synthesized by reacting a solid mixture of equimolar amounts of $[Cr(acac)_3]$ and a ligand (2C12H) at 160°C for 12 h [5]. The crude product was eluted on a silica-gel column with 7:1 (v/v) benzene–acetonitrile. Three separated bands were obtained successively, corresponding to $n = 3$, 2, and 1 for $[Cr(acac)_{3\text{-}n}(2C12)_n]$ as identified by the mass spectrometric analyses. The last band containing $[Cr(acac)_2(2C12)]$ was collected and evaporated. The residue was eluted with methanol on an high performance liquid chromatography (HPLC) column packed with Δ-$[Ru(phen)_3]^{2+}$/synthetic hectorite (Ceramosphere RU-1, Shiseido Co. Ltd., Japan). The Λ- and Δ-enantiomers were obtained as a baseline separation. ZLI-1132 was purchased from Merck. It was a mixture of 4-cyano-(4′-trans-n-alkylcyclohexyl)-benzene and 4-cyano-(4′-trans-n-pentylcyclohexyl)-biphenyl. The melting point was 74.8°C.

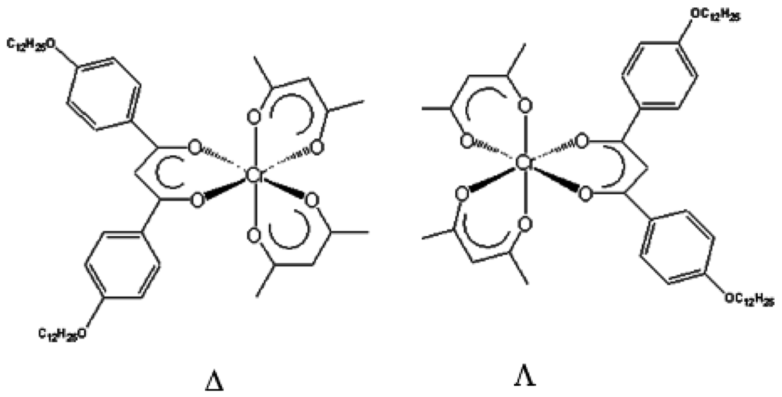

FIGURE 1 Δ- and Λ-enantiomers of $[Cr(acac)_2(2C12)]$.

When the Cr(III) complex was doped with 0.4 mol%, the melting point lowered to 73.1°C.

The VCD spectra were recorded at a 4-cm^{-1} resolution using a circular spectrometer (Bomem/Bio Tools). The measurements were repeated after 90° rotation around the light axis to confirm that no linear dichroic artifact was included. For the measurements, a sample was injected into a cell ($6.2\,cm^2 \times 10\,\mu m$) with CaF_2 windows. The pitch length (p) of an induced helix was measured by the Cano wedge method. The sense of the induced helix was determined from the sign of the circular dichroism (CD) spectrum below 300 nm, where the host molecules exhibited induced circular dichroism due to their helical arrangement [15–16].

3. RESULTS AND DISCUSSION

Figure 1 shows the CD spectra of a hexane solution of Δ-$[Cr(acac)_2(2C12)]$ when the solution was irradiated by UV light at 365 nm at the intensity of 3.94×10^{-8} Einstein s^{-1}. The intensity of the negative peak at 340 nm decreased exponentially because of the photoracemization of the complex. The quantum yield (Q.Y.) of racemization was determined to be 4.1×10^{-3}, which was compared with the Q.Y. of $[Cr(acac)_3]$ (5.2×10^{-3}) in the same solvent. The Q.Y. of $[Cr(acac)_3]$ was previously reported to be 5.5×10^{-3} in chlorobenzene [3b].

When the Δ-enantiomer was dissolved in ZLI-1132 to 0.1 ~ 0.5 mol%, the formation of the chiral nematic phase was ascertained by the appearance of a fingerprint texture in microscopic observation (not shown). By measuring the pitch length of an induced helix (p)

with the Cano method, the helical twisting power (β) was calculated according to the following equation [17].

$$\beta = \frac{1}{C_p} \tag{1}$$

in which C denotes the molar fraction of a dopant. The absolute value of β was 48.0 μm^{-1} at 30°C. From the circular dichroism spectrum of the sample, the large negative peaks were observed below 300 nm, indicating that the sense of the induced helix was *left-handed* (Fig. 2) [15]. Thus the sign of β was determined to be negative or $\beta = -48.0\ \mu m^{-1}$ for Δ-[Cr(acac)$_2$(2C12)]. The right-handed helix was also induced when Λ-[Cr(acac)$_2$(2C12)] was doped into the same host material (Fig. 2). The results were in accord with the previous results on [Ru(acac)$_2$(2C12)] as a photostable dopant [5]. Practically, a chiral nematic phase is characterized by the selective reflection of light when the pitch length of an induced helix (p) is in the visible region. In other words, at $\lambda_c = n\ p$ with n = average refractive index, the circularly

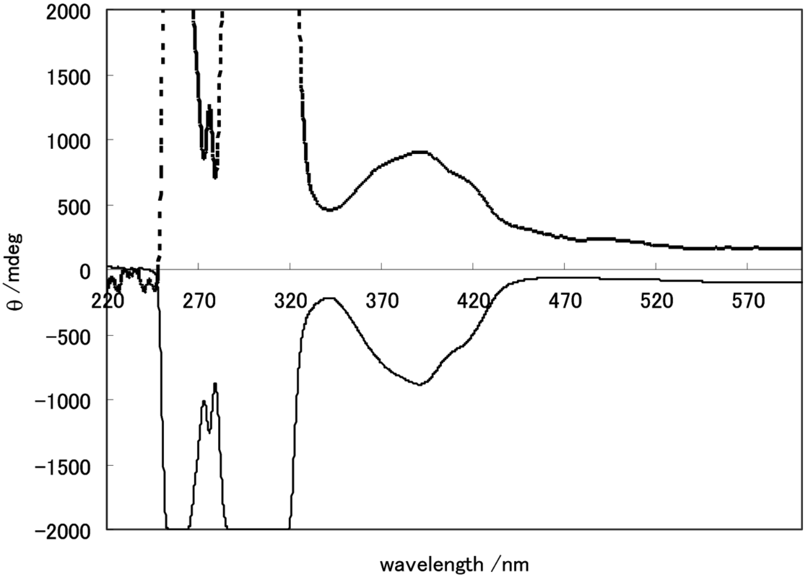

FIGURE 2 Circular dichroism (CD) spectra of the ZLI-1132 samples when Δ- or Λ-[Cr(acac)$_2$(2C12)] was doped to ca. 0.1 mol%. Solid and dotted curves show the results when the Δ- and Λ-Cr(III) complexes were doped, respectively. The liquid-crystalline samples were placed between two quartz plates. The optical length of the samples was unkown.

polarized light reflects from or passes through the sample when it has the same or opposite sense of the induced helix, respectively.

Figure 3 shows the VCD (upper) and absorption (lower) spectra on the chiral nematic sample doped by 0.548 mol% of Δ-[Cr(acac)$_2$(2C12)]. The helical pitch length of the sample was determined to be $p = 3.80\,\mu\text{m}$, indicating that the wavelength at selective reflection ($\lambda_c = n\,p$) was 5.3 µm. Here the value of n was assumed to be 1.4 from those of other room-temperature nematic materials (or 1.5 for MBBA) [18]. λ_c was shorter than the shortest wavelength of the horizontal axis of the spectrum (5.55 µm or 1800 cm^{-1} on the wavenumber scale).

The strong VCD signal ($\Delta\varepsilon = 0.1$–0.01) in Fig. 3 was ascribed to the supramolecular helical arrangement of host molecules [19]. For $\lambda/\lambda_c > 1$, the induced VCD obeyed the following relation for the case of the *left-handed* system [19];

$$\Delta\varepsilon = \frac{\Delta_n(\varepsilon_a - \varepsilon_b)p}{2\lambda}, \tag{2}$$

where $\Delta\varepsilon$, Δn, and $\varepsilon_a - \varepsilon_b$ are a circular dichorism, the anisotropy of refractive index of a medium, and a linear dichroism, respectively. The peaks at 1610, 1500, 1460, and 1180 cm^{-1} were all positive in the VCD spectrum. Assuming that Δn is positive throughout the spectrum, the results indicated $(\varepsilon_a - \varepsilon_b) > 0$ or the electronic transition moments of these peaks oriented in the direction of the director of a chiral nematic phase.

This chiral nematic sample was irradiated by the UV light (365 nm; 3.94×10^{-8} Einstein s^{-1}). After 6 h, the irradiated sample still showed a fingerprint texture, implying that the helix did not rewind

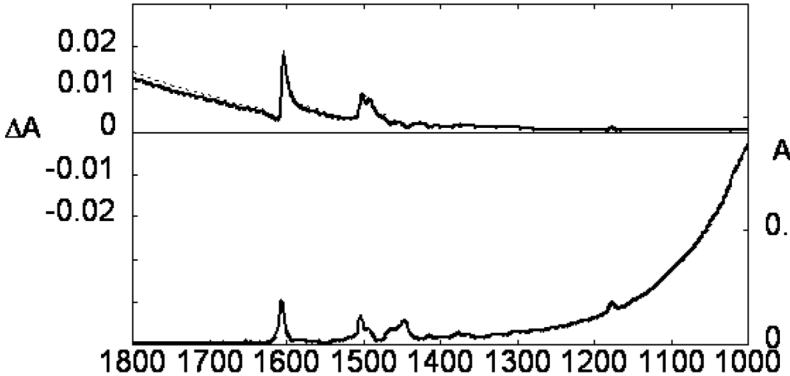

FIGURE 3 FT-VCD (upper) and FT-IR spectra (lower) of the chiral nematic sample of ZLI-1132 doped by Δ-[Cr(acac)$_2$(2C12)] (0.548 mol%).

completely under this treatment. At this stage, the helical pitch of the sample was 18.5 μm. The change was ascribed to the photoracemization of Δ-[Cr(acac)$_2$(2C12)]. Supposing that the racemic fraction of the complex gave no effect on a chiral nematic phase, the enantiomer excess (e.e.) of the complex was calculated to decrease from 100% to 25%. For further irradiation by UV light, the helical pitch of the sample continued to elongate until no chiral nematic phase was observed after 12 h.

Figure 4 shows the time course of the VCD spectrum when it was recorded every 30 min. Notably the rewinding process of the helix was visualized by following the change of the spectral shape at the observed four vibrational peaks (1610, 1500, 1460, and 1180 cm^{-1}). The peak at 1610 cm^{-1}, for example, increased its intensity for the initial 1 h. Because the more accurate expression for $\Delta\varepsilon$ in Eq. (2) contains the additional factor of $[(\lambda/\lambda_c)^2 - 1]^{-1}$ [20], the change reflected the elongation of the pitch maintaining the relation of $\lambda/\lambda_c > 1$. The peak underwent a drastic change at 1.5 h, when the spectral shape transformed from a Gaussian to a biphasic one. According to the theory, this indicated that the relation of $\lambda/\lambda_c = 1$ was fulfilled at this stage [20]. After 2 h, the peak returned to a Gaussian shape with a negative sign, indicating the relation of $\lambda/\lambda_c < 1$. In this way, the observed inversion of the VCD sign is theoretically predicted. Reflecting the further

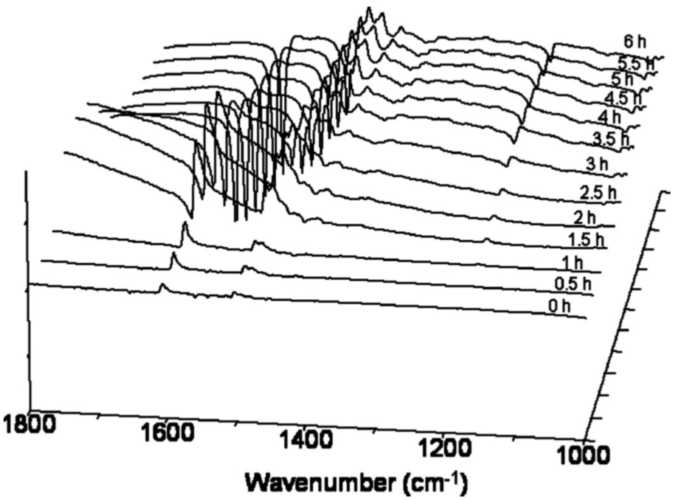

FIGURE 4 VCD spectra of a chiral nematic sample of ZLI-1132 doped with 0.538 mol% Δ-[Cr(acac)$_2$(2C12)] at various times after UV light (365 nm) irradiation.

elongation of the helical pitch, the position of a biphasic peak shifted toward the longer wavelength.

Figure 5 shows the plot of the inverse of p as a function of time. Because p^{-1} was proportional to $C_{\Delta}-C_{\Lambda}$ or enantiomer excess, the plot corresponded to the photoracemization of a chiral dopant. Figure 5 also contains the results for the racemization of Δ-[Cr(acac)$_2$(2C12)] in a hexane solution under the equivalent concentration. The photoracemization rate in a chiral nematic phase was found to be 20 times slower than that in a homogeneous solution. Two different mechanisms have been postulated for the racemization of [Cr(acac)$_3$] in a homogeneous solvent: (1) one of the metal-to-ligand bonds in excited [Cr(acac)$_3$] (denoted by [Cr(acac)$_3$]* ($^4T_{2g}$)) is cleaved under the attack of solvent molecules. The inversion of the coordination structure takes place when the new metal-to-ligand is reformed. (2) [Cr(acac)$_3$]* ($^4T_{2g}$) undergoes a unimolecular conversion to its opposite enantiomer by the pseudorotation of T_{2u} symmetry. Because neither hexane nor ZLI-1132 molecules are capable of coordinating a Cr(III) ion, the

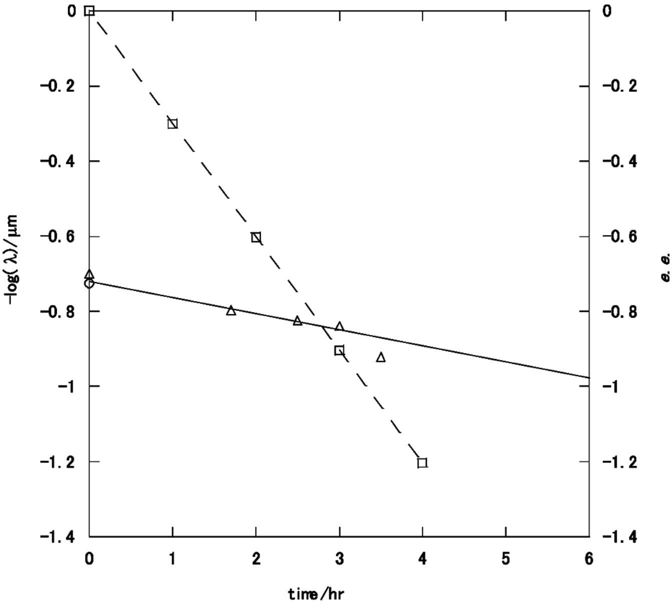

FIGURE 5 Plot of the inverse of λ_C as a function of time (solid line). The initial point was obtained by the Cano wedge method. The rest of the four points were obtained from the time-dependent VCD spectra. The dotted line is the plot of ee. *versus* time for the photoracemization of Δ-[Cr(acac)$_2$(2C12)] in a hexane solution with equivalent concentrations and the same light intensity.

unimolecular conversion (mechanism 2) seemed to be more plausible in both hexane and liquid-crystalline systems. Thus the slower rate of racemization in the latter system is ascribed to the fact that the lifetime of the excited state ($^4T_{2g}$) is shorter, due to the thermal quenching by the liquid-crystalline medium. Under mechanism 2, the high viscosity of the liquid crystal is not thought to be a main factor for the rate decrease.

Another explanation for the slower rate is that the supramolecular helical structure of a chiral nematic phase behaves as a barrier for photoracemization by stabilizing either one of the enantiomeric configuration of the complex, or an Δ-enantiomer is more stable in a *left-handed* system than in a *right-handed* system in the present case. It seems to be unrealistic, however, to assume that the chiral structure on a micrometer scale has any substantial effect on the molecular processes on a nanometer scale. In spite of this view, there have been several examples reported in which a chiral nematic system achieves the asymmetric induction of molecular processes [21].

It should be emphasized that the VCD spectroscopy has been applied to dynamic processes in a liquid-crystalline system for the first time. In the conventional method, the change of the pitch length was followed by measuring pitch length in a Cano wedge cell at appropriate time intervals [4]. The method is, however, often time consuming and encounters difficulties arising from the line defects or bubbles caused by illumination of light. In addition, the real-time monitoring of the pitch-elongation process by use of VCD has a potentiality as a novel tool in the following aspects: (1) the subtle change of a helical pitch is detected if the two peaks that are closely located in a vibrational spectrum are monitored, (2) the local structural change of a chiral phase is revealed if a microscopic VCD apparatus is available, (3) the time-resolution of a structural change is scaled down to a millisecond range, and (4) the orientational change of a host molecule is revealed because the spectral shape of a VCD peak is dependent on the orientation of the electronic transition moment with respect to a director.

When the VCD spectrum is regarded as a memory signal for the photoresponsive events in liquid-crystalline systems, it is characterized by the following properties in comparison to the conventional memories: (1) the signal based on the VCD spectrum is thought to have high signal-to-noise ratio (S/N), because it changes the sign as well as the intensity, (2) The position of the peak showing a biphasic shape shifts toward the longer wavelength on continuing the light irradiation. Thus the spectral change can be thought to have the information of time memory, (3) The racemization process is an irreversible process accompanying the increase of entropy, which is contrasted with the reversible processes such as photoiosmerization. In this sense, it can be an extremely stable memory, free from deletion by any accident.

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REFERENCES

[1] Feringa, B. L., van Delden, R. A., Koumura, N., & Geetscma, E. M. (2000). *Chem. Rev.*, *100*, 1789, and references therein.

[2] Feringa, B. L. (2001). *Acc. Chem. Res.*, *34*, 504.

[3] (a) Anzai, N., Machida, S., & Horie, K. (2003). *Liquid Crystals*, *30*, 359; (b) Anzai, N., Machida, S., & Horire, K. (2001). *Chem. Lett.*, 888; (c) Cimolino, M. C., Shopley, N. J., & Linck, R. G. (1980). *Inorg. Chem.*, *19*, 3291; (d) Stevenson, K. L. (1972). *J. Am. Chem. Soc.*, *94*, 6652.

[4] Hoshino, N., Matsuoka, Y., Okamoto, K., & Yamagishi, A. (2003). *J. Am. Chem. Soc.*, *125*, 1718.

[5] Yoshida, J., Sato, H., Yamaghsi, A., & Hoshino, N. (2005). *J. Am. Chem. Soc.*, *127*, 8453.

[6] Matsuoka, Y., Sato, H., Yamagishi, A., & Hoshino, N. (2005). *Chem. Mater.*, *17*, 4910.

[7] Sato, H., Yamagishi, A., Yoshida, J., Nakano, H., & Hoshino, N. (2005). *Jpn. J. Appl. Phys.*, *44*, 4067.

[8] Kakegawa, N., Hoshino, N., Matsuoka, Y., Wakabayashi, N., Nishimura, S.-I., & Yamagishi, A. (2005). *Chem. Comm.*, 2375.

[9] Monde, K., Taniguchi, T., Miura, N., & Nishimura, S.-I. (2004). *J. Am. Chem. Soc.*, *126*, 9496.

[10] Taniguchi, T., Miura, N., Nishimura, S.-I., & Monde, K. (2004). *Mol. Nutra. Food Res.*, *48*, 246.

[11] He, Y., Cao, X., Nafie, L. A., & Freedman, T. B. (2001). *J. Am. Chem. Soc.*, *123*, 11320.

[12] Chabay, H. (1972). *Chem. Phys. Lett.*, *17*, 283.

[13] Guo, C., Shah, R. D., Dukor, R. K., Cao, X., Freedman, T. B., & Nafie, L. A. (2004). *Anal. Chem.*, *76*, 6956.

[14] Urbanovà, M., Setnička, V., & Volka, K. (2000). *Chirality*, *12*, 199.

[15] Sacmann, E. & Voss, J. (1972). *Chem. Phys. Lett.*, *14*, 528.

[16] Saeva, F. D., Sharpe, P. E., & Olin, G. R. (1973). *J. Am. Chem. Soc.*, *95*, 7656.

[17] Kuball, H. G. & Höfer, T. (2001). In: *Chirality in Liquid Crystals*, Bahr, C. & Kitzerow, H.-S. (Eds.), Springer-Verlag: New York.

[18] Saeva, F. D., Sharpe, P. E., & Olin, G. R. (1973). *J. Am. Chem. Soc.*, *95*, 7656.

[19] Dudley, R. J., Mason, S. F., & Peacock, R. D. (1972). *Chem. Comm.*, *1084*.

[20] Holzwarth, G. & Holzwarth, N. A. W. (1973). *J. Opt. Soc. Am.*, *63*, 324.

[21] Thisayukta, J., Niwano, H., Takezoe, H., & Watanabe, J. (2002). *J. Am. Chem. Soc.*, *124*, 3354.