Photomodulation of a Chiral Nematic Liquid Crystal by the Use of a Photoresponsive Ruthenium(III) Complex

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We have attempted to control the helical pitch of a chiral nematic liquid crystal by the use of a photoresponsive chiral metal complex. For this purpose, a novel Ru(III) complex [Ru(acac)$_2$(L)] was synthesized, where acac and L denote acetylacetonato and 1,3-bis-{4-[6-(4-phenylazo-phenoxy)-hexyloxy]-phenyl}-propane-1,3 -dionato, respectively. The complex underwent cis−trans photoisomerization in methanol when under UV ($\lambda_{max} = 360$ nm) or visible ($\lambda_{max} = 450$ nm) light illumination, respectively. When the complex was doped into a room-temperature nematic liquid crystal (ZLI-1132), it induced a chiral nematic phase. Under illumination with UV or visible light, the helical pitch of the chiral nematic phase could be changed reversibly by up to 50%. Corresponding to this change, the helical twisting power (HTP) of the complex varied between 34.0 and 22.0 μm^{-1}, or between −43.9 and −26.6 μm^{-1} at 35.0 °C, where the positive and negative signs corresponded to the Λ- and Δ-enantiomers, respectively. This has been the first attempt at combining the ΔΛ chirality of an octahedral metal complex with the cis−trans isomerization of an azobenzene group in the development of a photoresponsive dopant.

Introduction

The development of optical memories and photochemically driven switches is a topic attracting extensive interest in the field of materials chemistry.[1] One of the promising possibilities that are being investigated is the ability to control molecular alignment in a liquid crystal by light illumination.[2−7] A liquid crystalline molecule itself, or a molecule in the liquid crystalline state, although still mobile, has an orientational ordering that depends on external conditions and stimuli and can switch among various alignments that are induced by changes in external conditions. Moreover, each nanoscopic molecular structure can be amplified to a macroscopic molecular orientation according to the molecular design approach that is used. In particular, chiral nematic (N*) phases, which are characterized by having superstructures with a helical arrangement, are able to undergo large structural transformations under light illumination.[2−6] Since the N* phase exhibits a number of distinctive properties, such as selective reflection and induced circular electronic and vibrational dichroisms, these light-induced transformations can be used to fabricate optical memory and other nanotechnological devices.

As is well-known, a N* phase is induced when a small amount of a chiral compound is dissolved in a nematic phase. The functional ability of such a doped molecule can be represented in terms of helical twisting power (HTP), as defined below,

$$\beta_M = \left(\frac{\partial p^{-1}}{\partial x}\right)_{x\to 0} \tag{1}$$

where p is pitch length (μm) and x is the molar ratio of the dopant. An efficient dopant for establishing a light responsive N* phase should exhibit high helical twisting power whose magnitude changes drastically under illumination with light. It should also undergo a reasonable structural transformation to accompany the drastic change in helical twisting power from the viewpoint of molecular design, such as the

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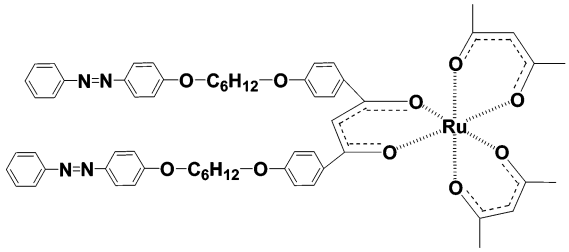

Figure 1. Molecular structure of [Ru(acac)$_2$(azo)].

theoretical relationship between host and dopant molecules. In terms of the availability of photoreactive dopants that have been identified so far, axially chiral organic materials have been developed by attaching photochromic groups to suitable molecules. These attempts have been restricted to limited groups of compounds such as binaphthyl derivatives with azobenzene[2] or diarylethene[3] moieties. Moreover, potential mechanisms for photoresponsive effects are difficult to predict since these organic molecules are too flexible to be able to determine their probable configurations. It is more desirable to synthesize a molecule with a rigid core as a dopant in order to make it possible to predict photoresponsive effects on the basis of possible molecular mechanisms.

We have recently developed a new type of chiral dopant by making use of the $\Delta\Lambda$ chirality of octahedral coordination. As a result, metal complexes of the type [Ru(acac)$_2$L] (where acac = acetylacetonate and L = 1,3-diketonate or 2,2′-bipyridyl derivative containing phenylene groups) are shown to have large helical twisting powers.[8−10] The observed large helical twisting powers have been theoretically investigated, leading to a mechanism whereby two helically coordinated acac ligands induce the twisting of host molecules, while rodlike ligands (L) determine the orientation of the dopant in the host medium. These mechanisms have been verified by the observation that the sense of the induced helix can be determined by whether a rodlike ligand is elongated parallel with or perpendicular to the C_2 axis of a complex.[10] Therefore, by applying our theory, it could be possible to invert the sense of the induced helical superstructure photochemically.

In the present study, the above principle has been extended to a photoresponsive system. A novel dopant was developed for this purpose by coupling the Δ,Λ-isomerism of octahedral metal complexes with the photochromic functions of azobenzene moieties (Figure 1). This is the first metal complex dopant that exhibits both high helical twisting power and photochromic behavior. Under illumination with light, cis−trans isomerization takes place in the attached azobenzene groups, resulting in a change in molecular shape from linear to bent structures. According to the present molecular model, we can logically predict how the orientating ability of a rodlike ligand will be affected by such a change in the molecular shape. This may open the possibility to systematic control of helical pitch on the basis of molecular design.

Experimental Section

Synthesis of Azobenzene Ligand.[9,10] An azobenzene ligand (denoted by (azo)H) was synthesized according to Scheme 1, as shown below. The reaction to attach the azobenzene group was carried out by refluxing 4-hydroxyazobenzene (4.06 g, 20.5 mmol), KOH (1.26 g, 22.5 mmol), and 1,6-dibromohexane (25 g, 102 mmol) in ethanol (150 mL) for 6 h. After the reaction mixture was evaporated to dryness, the residue was extracted using *n*-hexane. The crude product was obtained as an orange powder (compound a) in 42% yield by recrystallizing from *n*-hexane. An alkyloxylation reaction was carried out by refluxing methyl-4-hydroxybenzoate (0.564 g, 3.70 mmol), K_2CO_3 (0.596 g, 4.31 mmol), compound a (1.81 g, 4.1 mmol), and KI (0.137 g, 0.825 mmol) in 2-butanone (150 mL) for 24 h. Another alkyloxylation was undertaken by refluxing 4-hydroxyacetophenone (0.587 g, 4.13 mmol), K_2CO_3 (0.588 g, 4.25 mmol) and compound a (1.80 g, 3.84 mmol) and KI (0.137 g, 0.825 mmol) in acetone (150 mL) for 24 h. Those products were both recrystallized from chloroform as orange powders (compounds b and c, respectively) (compound b: 54% yield; compound c: 44% yield). A coupling reaction was carried out by refluxing 1.7 mmol quantities of these materials and NaH (5 equiv) in DME (200 mL) under N_2. After reaction for 24 h, the mixture was carefully neutralized with dilute HCl while cooling. The product was extracted from CH_2Cl_2, whereby the solution was evaporated to give an orange product in 28% yield (denoted as (azo)H). No NMR spectrum was recorded because the solubility of the final compound was too low for ordinary solvents (CDCl3, CD3OD, (CD3)2CO, DMSO and so on). FAB-MS: Calcd for $C_{51}H_{52}N_4O_6$ $[M]^+$: $m/z = 817$; found: 817.

Synthesis and Optical Resolution of Metal Complex.[11−13] [Ru(acac)$_2$(azo)] was synthesized by refluxing [Ru(acac)$_2$(CH$_3$CN)$_2$](PF$_6$) and (azo)H in toluene for 24 h.[11] The solution was evaporated to dryness and the residue was eluted on a silica gel column (50 cm × 3 cm (i.d.)) with benzene/acetonitrile. The fraction corresponding to the metal complex was further purified on an HPLC column (25 cm × 0.4 cm (i.d.); Capcel Pack, Shiseido Ind. Co., Japan) by eluting with chloroform/methanol. ^{1}H NMR (270 MHz, CDCl$_3$): δ (ppm) 12.61 (s, 4H), 7.82 (m, 8H), 7.37 (m, 6H), 6.39 (m, 4H), 6.14 (m, 4H), 4.05 (m, 4H), 1.41−1.91 (m, 16H), −2.84 (s, 6H), −5.01 (s, 6H), −27.67 (s, 2H), −38.24 (s, 1H). FAB-MS: Calcd for $C_{61}H_{65}N_4O_{10}Ru$ $[M]^+$: $m/z = 1115$; found: 1115.

The complex was optically resolved into pure enantiomers by means of clay column chromatography.[12] The column was packed with an ion-exchange adduct of Δ-[Ru(phen)$_3$]$^{2+}$ and synthetic hectrorite (RU-1, Shiseido Ind. Co., Japan). These columns have been proven to be useful for the resolution of a wide range of neutral metal complexes. When the product was eluted with chloroform/methanol, two major peaks were observed. The CD spectra of the collected fractions were compared with those of Δ,Λ-[Ru(acac)$_3$].[13] From the sign of the intense band at 280 nm, which is assigned to one of the exciton splitting bands of the local $\pi-\pi^*$ transition, the first and second peaks in the chromatogram were assigned to the Λ- and Δ-enantiomers, respectively.

Other Material. ZLI-1132 was purchased from Merck. This compound is stated to be a mixture of 4-(4-alkylcyclohexyl)-

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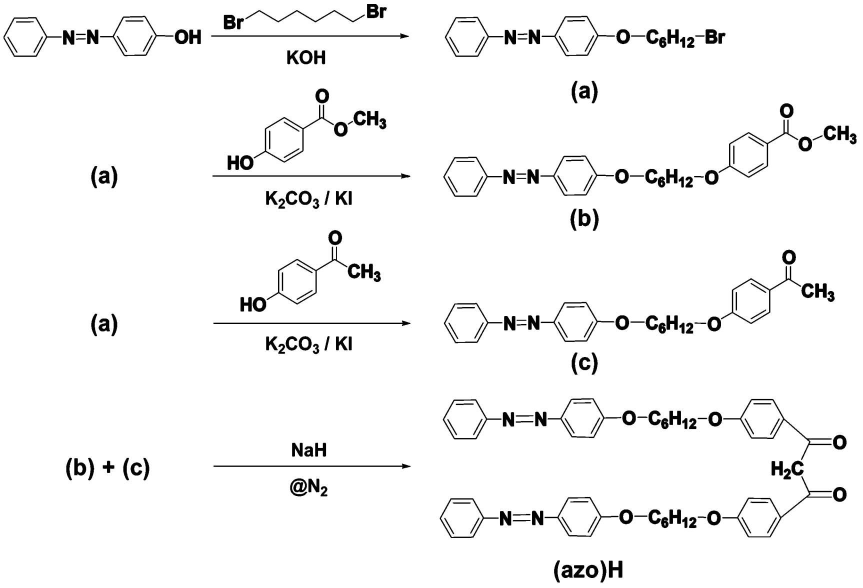
Scheme 1. Synthetic Routes of (azo)H



benzonitrile and 4-(4-alkylcyclohexyl)-4′-cyanobiphenyl derivatives. The material has $T_{NI} = 72.3$ °C and an average molecular weight of 263.2.

Determination of Helical Pitch and Helicity. Pitch measurements were performed on a chiral nematic sample at ambient temperature by the Cano wedge method.[14] Experiments were performed for doped samples using a wedge cell with a tangency of 0.027 (EHC, Japan). Several spots of Grandjean-Cano steps were measured and averaged. The helicity of the cholesteric phase was determined from the sign of their induced CD spectra,[9,10,15] as will be described in the results section. The CD spectra were measured with a spectral polarimeter J-520 (JASCO, Japan).

Photochemical Reactions of the Homogeneous and Liquid Crystalline Phases. Photoisomerization in methanol was performed at room temperature by illuminating samples that were contained in quartz cells. The photoisomerization of [Ru(acac)$_2$(azo)] in the liquid crystalline phase was performed on a temperature-controlled stage (Mettler FP82HT hot stage with an FP90 control unit) using a glass cell with a 25 μm gap (EHC, Japan). The products were characterized by their UV/vis absorption spectra and CD spectra. Photomodulation of the helical pitch was performed and measured in wedge cells using a temperature-controlled stage. UV illumination (filtered light, $\lambda_{max} = 360$ nm, 10 mW/cm^2) was carried out using an Hg light source (Hypercure 200, Yamashita Denso). Visible illumination (filtered light, $\lambda_{max} = 450$ nm, 10 mW/cm^2) was carried out using a Xenon light source (XFL-300, Yamashita Denso). UV/vis absorption spectra were recorded on a V-560 spectrophotometer (JASCO, Japan).

Results

Photochemical Isomerization of [Ru(acac)$_2$(azo)]. Figures 2A and 2B show the UV/vis absorption and CD spectra, respectively, when a methanol solution of [Ru(acac)$_2$(azo)] was illuminated by either UV or visible light. According to Figure 2A, the $\pi-\pi^*$ transition band at about 350 nm due to the *trans*-azobenzene moiety decreased on illumination with UV light ($\lambda_{max} = 360$), while the n$-\pi^*$ transition band at about 450 nm due to the *cis*-azobenzene moiety increased concomitantly. The process was reversed on illumination with visible light ($\lambda_{max} = 450$ nm), and this cycle could be repeated several times without apparent fatigue. The results demonstrated that the azobenzene ligands of [Ru(acac)$_2$(azo)]

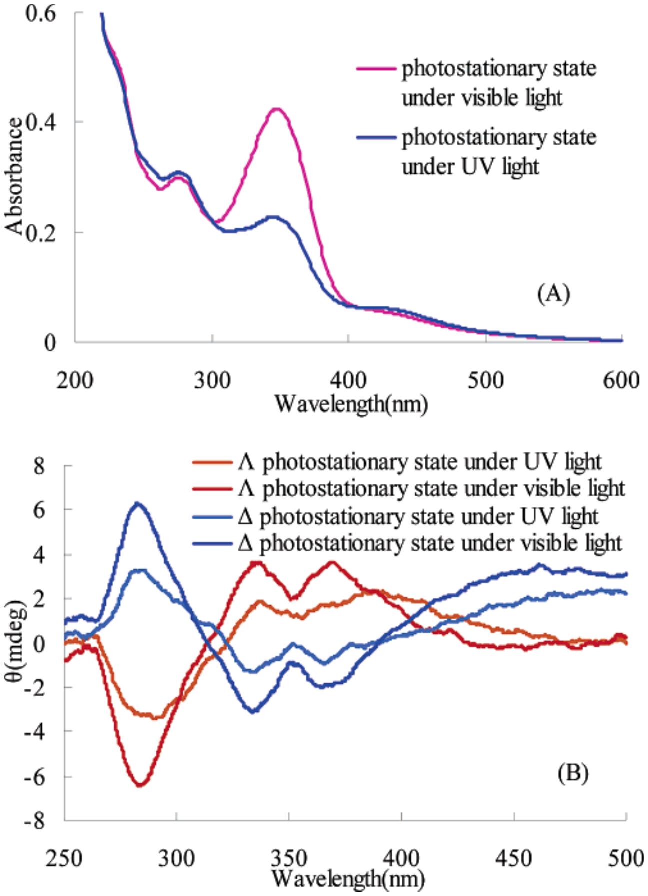


Figure 2. Changes in the UV−visible (A) and CD (B) spectra of [Ru(acac)$_2$(azo)] in methanol under illumination with UV and visible light at RT.

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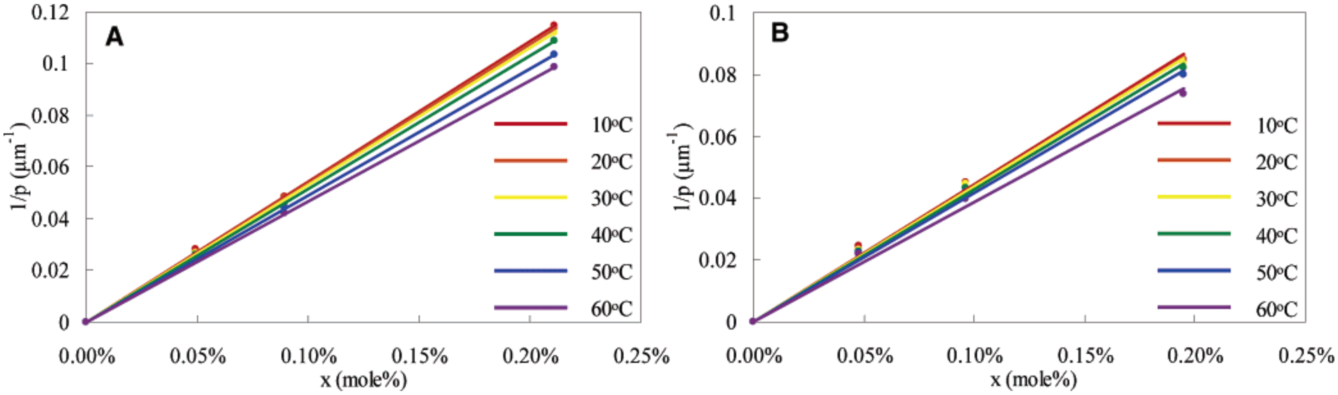
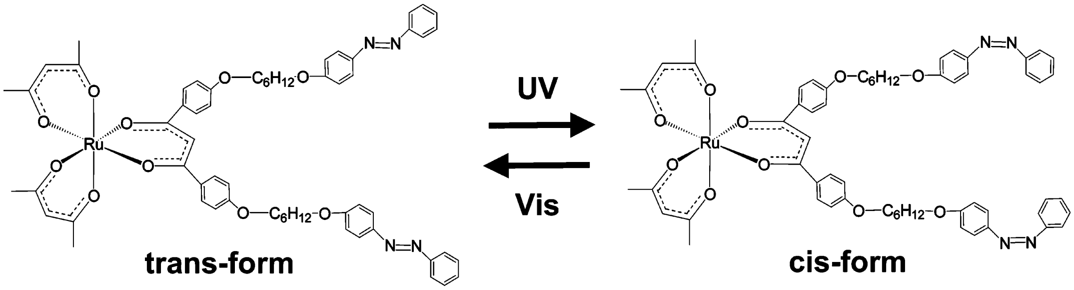


Figure 3. Plots of the inverse of pitch length (p^{-1}) versus mole fraction of dopant (x) for ZLI-1132 doped with either Δ- (left) or Λ- (right) [Ru(acac)$_2$(azo)].

Scheme 2. Photoisomerization of Λ-[Ru(acac)$_2$(azo)]



underwent photochemically reversible cis−trans isomerization (Scheme 2).

In the CD spectra of the Δ- and Λ-enantiomers of [Ru(acac)$_2$(azo)] (Figure 2B), all of the peaks at about 280, 330, and 370 nm decreased on illumination with UV light, and they recovered to their initial values when they were illuminated with visible light. This process also could be repeated several times without apparent fatigue. The results demonstrated that photochemically irreversible racemization did not occur, but photochemically reversible isomerization just occurred. According to the molecular structure of the complex (Scheme 2), the chiral center (or the coordination part) is remote from the photochromic azobenzene moieties. Thus, no changes were expected to occur in the CD spectra. Contrary to this expectation, appreciable changes did occur for both the chiral center and the azobenzene moieties.

Determination of HTP and Helical Sense. Δ- or Λ-[Ru(acac)$_2$(azo)] was dissolved in a room-temperature nematic solvent, ZLI-1132. The induction of an N* phase was confirmed by the appearance of fingerprint textures under microscopic observation. The helical pitches were evaluated by the Cano method, in which the inverse of the pitch length (p^{-1}) was plotted against the mole fraction of the dopant (x) (Figure 3). The HTPs of these complexes were determined to be 45−50 μm^{-1} at 10−60 °C. The HTP was found to decrease slightly when the temperature increased in this temperature change.[16]

To determine the helical senses of these N* phases, we measured their CD spectra.[9,10] As shown in Figure 4, the ZLI-1132 samples showed a positive or negative CD absorption around 360 nm when doped with Λ- or Δ-Ru(III) complexes, respectively. This absorption in the CD spectrum must have been induced by the dopant since the host had no electronic absorptions around the wavelength in question. According to the theory regarding induced CD spectra in an N* phase, positive or negative absorptions correspond to right- or left-handed helical structures of the host molecules when the relevant transition moment lies along the director direction.[15] In contrast to this, the CD absorption below 320 nm was due to the conjugated part of the ZLI-1132.

Photochemical Control of the Chiral Nematic Pitch. When a solution of Δ- or Λ-[Ru(acac)$_2$(azo)] in ZLI-1132 was illuminated by UV or visible light, the UV/vis absorption and the CD spectra exhibited drastic changes in the wavelength region between 330 and 400 nm, as shown in Figure 5. The changes at 350 nm ($\pi-\pi^*$) and 450 nm ($n-\pi^*$) in the absorption spectra confirmed that the azobenzene ligands

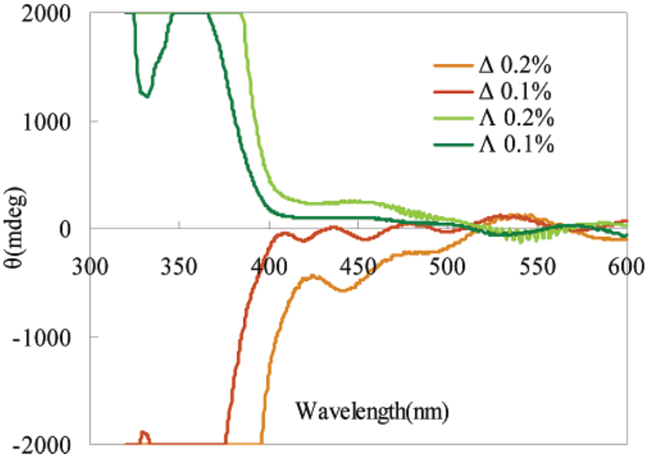


Figure 4. CD spectra of Δ- and Λ-[Ru(acac)$_2$(azo)] in ZLI-1132 at 35.0 °C.

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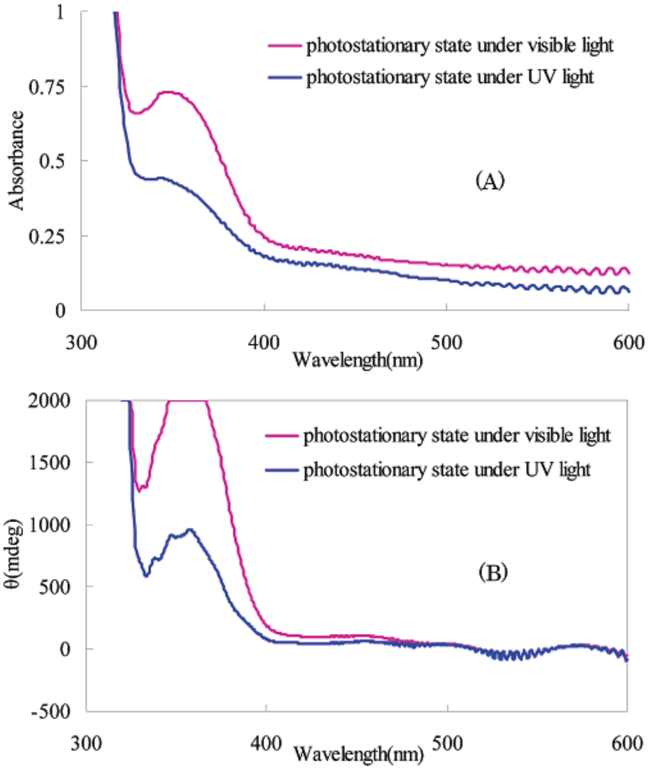

Figure 5. Changes in the UV−visible (A) and CD (B) spectra of Λ-[Ru-(acac)$_2$(azo)] in ZLI-1132 under illumination with UV and visible light at RT. (A; 0.2%, B; 0.1%, respectively)

of the complex underwent reversible cis−trans isomerization, even in the liquid crystalline phase (Figure 5A). On illumination with UV light, the intensities of the CD signals around 360 nm that were induced due to the dopant decreased (Figure 5B), which was thought to be an indication that the helical pitch of the N* phase was elongated by the trans-to-cis isomerization. This conclusion was based on the theoretical prediction that the intensity of the induced CD was inversely proportional to the helical pitch.[15] The induced CD in this wavelength region recovered to nearly its initial value on illumination with visible light, indicating that the helical pitch shortened again after the cis-to-trans isomerization.

The reversible change of the helical pitch was confirmed directly when a sample in a wedge cell was observed with a polarized optical microscope under illumination with UV or visible light (Figure 6). Variations in the pitch length and the HTP values corresponding to the spectral changes mentioned above were confirmed, as presented in Table 1.

The process was repeated several times with no apparent fatigue. Significantly, it took less than 2 min for the helical pitch to reach the photostationary state under UV or visible light illumination at 35.0 °C. On the other hand, it took about 20 min to stabilize when the same experiment was performed at 20.0 °C. At both temperatures, the photoisomerization of the dopant itself took place within 1 min according to the changes in the UV/vis absorption spectra. Thus, more time was required for the superstructure of the host medium to adjust itself to the new dopant conformation. The rate of change depended on the temperature, which was most probably related to the viscosity or liquidity of the host medium. When the azobenzene moieties of the dopant underwent cis−trans isomerization in liquid crystalline phase at 35.0 or 20.0 °C by photoillumination, it was confirmed that the host molecules hold the helical superstructure. No clear phase appeared under these conditions.

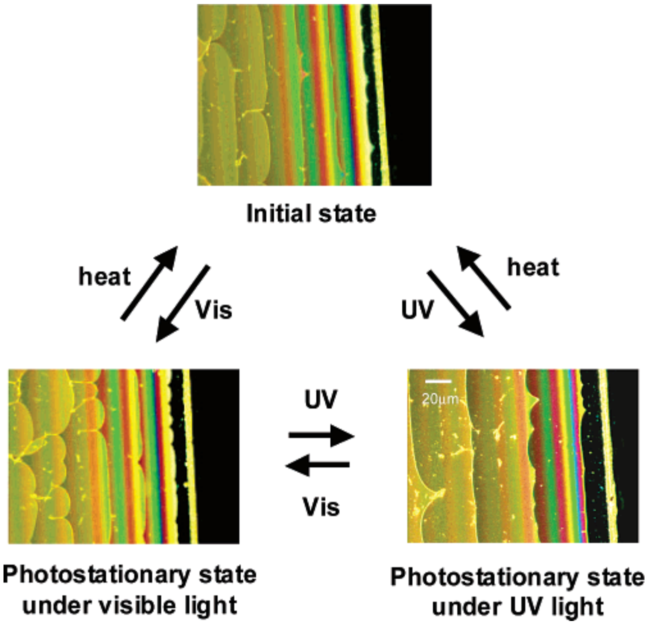

Figure 6. Changes in the optical textures of Λ-[Ru(acac)$_2$(azo)] (0.2%) in ZLI-1132 at 35.0 °C through the Cano wedge cells.

Table 1. Photoinduced Modulation of Pitch Length and HTP in 0.2% Solutions of Δ- and Λ-[Ru(acac)$_2$(azo)] in ZLI-1132 at 35.0 °C

	initial	Vis	UV
Λ pitch (μm)	13.5	15.1	23.3
Λ β_M (μm^{-1})	+38.0	+34.0	+22.0
Δ pitch (μm)	9.42	10.8	17.8
Δ β_M (μm^{-1})	−50.3	−43.9	−26.6

Discussion

The present work attempted to achieve the switching of HTP values or of helical pitch lengths in a chiral nematic (N*) phase by a photon mode, that is, by illumination under UV or visible light. In designing a dopant for such a purpose, a novel type of metal complex has been developed in which the ΔΛ isomerism of a tris(chelated) complex was coupled with the photoinduced cis−trans transformation of an azobenzene moiety. As far as we know, this was a first attempt at combining a chiral coordination structure and a photochemical isomerization in order to develop a photoresponsive chiral dopant.

Our strategy was based on the following mechanism: the photoinduced cis−trans isomerization of an azobenzene part attached to the rodlike ligand of a dopant affects the molecular orientation of the dopant in a host medium. In other words, the cis form that is induced by UV light illumination presents a higher steric hindrance against host molecules than the trans form because of its bent structure, and therefore turns toward the different direction with respect to the chiral center compared to the trans form. This may consequently decrease the HTP value and increase the pitch length of the medium, or change the sense of the induced helix.

Photoisomerization influenced the CD intensity on both the chiral center and the azobenzene moieties. The results were surprising since the azobenzene groups were remote from the chiral center ($>$1.6 nm). There are two possibilities that could explain these results. The first is that conformational changes in the ligands caused by the isomerization of azobenzene groups influence the geometry near the chiral center through the alkyl chains and aromatic parts. The second possibility is that a subtle change at one end of a molecule induced changes in the electronic properties at the other terminal, and the relative orientation of the azobenzene with respect to the chiral center affects the signs of the induced CD through the helical conformation. In other words, the second mechanism is an induced CD effect within a molecule. At present, it is not clear which of these possibilities is the more plausible.

In terms of the main purpose of the present work, $\Delta\Lambda$-[Ru(acac)$_2$(azo)] was successfully used to realize the photomodulation of a chiral nematic liquid crystal by reversibly changing its helical pitch. However, no inversion of the helical sense was exhibited, probably due to too little switching of the direction of the azobenzene with respect to the chiral center. The mechanism for the reformation of the superstructure[17] is thought to be as follows. First, a photoinduced trans-to-cis isomerization of the azobenzene part takes place. Second, the bent shape of the dopant causes a disturbance of the helical orientation of the neighboring host molecules. Such a disturbance propagates through the medium to lead to the elongation of the macroscopic helical length. Based on this mechanism, the rate of change of the helical pitch may significantly depend on the liquidity of the medium; in other words, it depends on the temperature of the medium.

The present attempt at combining the $\Delta\Lambda$ chirality of an octahedral metal complex with the cis−trans isomerization of an azobenzene group seems to be promising because more divergent performances can be expected by changing the kinds of metal ions or the geometry of the ligands that are used. The use of a paramagnetic metal ion, for example, may be developed in order to exhibit opto-magnetic properties.

Conclusion

A novel chiral photochromic complex was developed in order to induce photoresponsive structural changes in a chiral nematic phase. This complex itself underwent cis−trans photoisomerization, accompanied by a drastic change in its CD spectra. When the compound was doped in a room-temperature nematic material (ZLI-1132), it induced a large change of pitch length under illumination with UV or visible light, without any fatigue.

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