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Reversible Control of the Pitch of Cholesteric Liquid Crystals by Photochromism of Chiral Fulgide Derivatives

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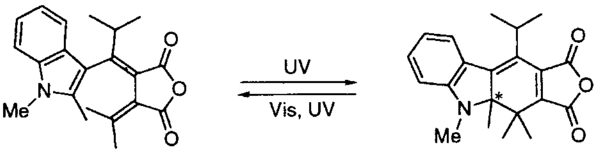
When an enantiomer of resolved indolylfulgide (**1**) or either of the (*R*)-binaphthol-condensed indolylfulgides (**2**, **3**) was mixed with a nematic liquid crystal (5CB), the cholesteric phase was induced. Their cholesteric pitches were reversibly changed by photoirradiation. Whereas the twisting ability of the cholesteric pitch (β_M) was larger for the colorless form than for the colored form in the case of **1**, it was larger for the colored form than for the colorless form in the cases of **2** and **3**. In addition, β_M of **1** is generally smaller than that of **2** and **3**. These phenomena were explained in terms of the helical conformation of the hexatriene moiety of fulgides and the chirality of the binaphthol moiety.

The cholesteric sense of a fulgide-doped liquid crystal was changed between plus and minus reversibly by the predoping of the chiral formaldehyde acetal of 1,1′-bi-2-naphthol ((*S*)-**4**).

Photochromism, a reversible structural change of a compound associated with a certain change in the absorption spectra, has been attracting a number of researchers, because the structural change may induce changes in the chemical as well as physical properties,[1,2] including the properties of the molecule, itself, and of the interaction with other chemical species.

Fulgides have been known as representatives of thermally irreversible photochromic compounds.[3] The photochromic structural change is depicted in Chart 1 for an indolylfulgide **1**. Because the photochemically induced change of the structure is fairly large, fulgides have been used, like azobenzenes[4] and other photochromic compounds,[5] as dopants which can change the bulk properties of liquid crystals by amplifying the interaction of photochromic molecules and liquid-crystalline molecules.[6,7]

Fulgides have an intrinsic chiral nature in the hexatriene moiety that undergoes cyclization upon photoirradiation to yield a cyclohexadiene derivative. The helical chirality of the hexatriene is translated to a stereogenic quaternary carbon atom on the cyclohexadiene moiety stereospecifically because the photochemical hexatriene–cyclohexadiene transformation obeys the Woodward–Hoffmann rules.[3b] We have reported that indolylfulgide **1** was able to be resolved into enantiomers in which the helicity of the photocyclizing hexatriene moiety was enantiomeric, and underwent photochromism while maintaining the optical purity (Scheme 1).[8]



1E
Yellow

1C
Blue

Chart 1.

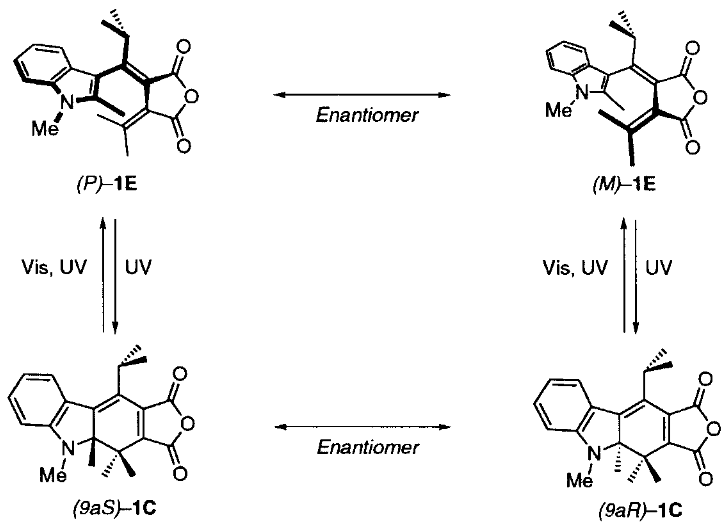
Another way to obtain an optically active photochromic compound is to introduce a chiral auxiliary to the photochromic system. We have reported that modified indolylfulgides with (*R*)-binaphthol (**2**, **3**) showed diastereoselective photochromism ascribed to the highly biased diastereomer ratio of the E-forms with regard to the helicity of their hexatriene moiety (Scheme 2).[9]

We here report that optically active fulgide derivatives (**1**, **2**, and **3**) work as a chiral dopant to induce a cholesteric phase from the nematic liquid crystal, and that the cholesteric pitch values are controlled by photoirradiation.[10]

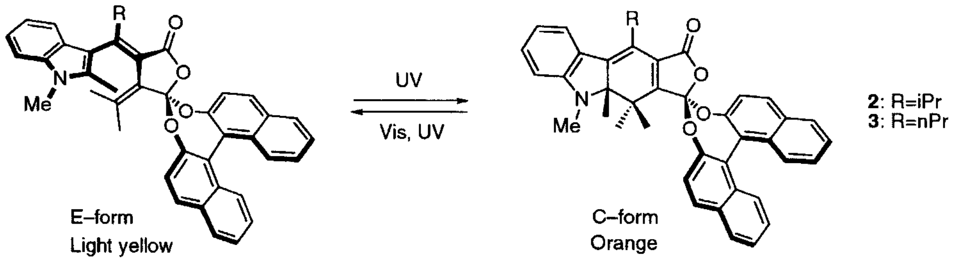
Results and Discussion

Chiral Photochromic Compounds as Chiral Dopants. The addition of small amounts of a chiral non-racemic organic compound to nematic liquid crystals can derive cholesteric liquid crystals. When this kind of chiral dopant is photochromic, and the structural change upon photoirradiation is large, the chiral interaction between the chiral photochromic dopant molecules and the non-chiral liquid crystalline molecules is changed by photoirradiation reversibly. This may be observable as a change in the cholesteric pitch. Since cholesteric liquid crystals show a selective reflection of light, and the wavelength of the reflected light is proportional to the pitch, the observable color of the cholesteric liquid crystal is controlled by photoirradiation.

Induction of Cholesteric Phase from Nematic Phase. 1. Resolved Indolylfulgide. The addition of (*P*)-**1E**[11] to 4-cyano-4′-pentylbiphenyl (5CB), a representative of a nematic liquid crystal (Chart 2), generated the cholesteric



Scheme 1. Photochromism of indolylfulgide 1.



Scheme 2. Photochromism of (*R*)-binaphthol-condensed indolylfulgides **2** and **3**.

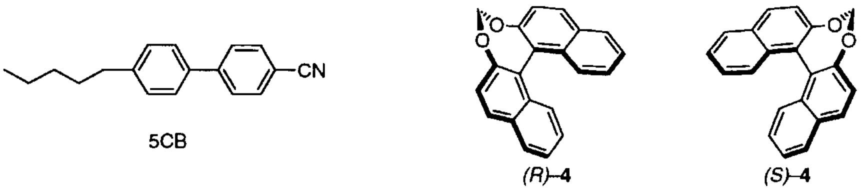


Chart 2.

phase. The pitch was determined by measuring the intervals of Cano's lines appearing on the surfaces of wedge-type liquid crystalline cells (Fig. 1). For example, the addition of 4.97×10^{-3} $\mathrm{mol_D/mol_{LC}}$ ($\mathrm{mol_D}$ represents moles of dopant, and $\mathrm{mol_{LC}}$ represents moles of 5CB) (2.03×10^{-3} mol dm^{-3}) of (*P*)-**1E** to 5CB at 30 °C generated the cholesteric phase, whose pitch was 6.23 μm. After the irradiation of 405-nm light until the photochromic dopant reached the photostationary state, the pitch became 11.22 μm.

The efficiency of the chiral dopant is evaluated by β_M,[12] which represents the degree of twisting of the stacking nematic-phase planes. By measuring the pitch values with three different concentrations of the dopant, the absolute value of β_M was determined.

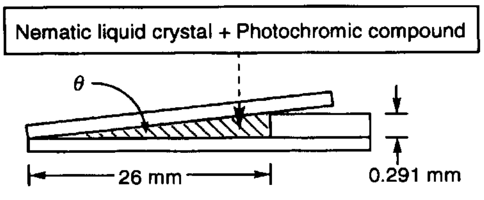


Fig. 1. Schematic side-view of Cano's wedge-type glass cell.

The sign of β_M, which is the same as the cholesteric sense (helicity of pitch),[11] was determined as follows. The cholesteric sense of 5CB-(*R*)-**4** (formaldehyde acetal of (*R*)-1,1′-bi-2-naphthol: Chart 2) is known to be minus.[14] If the pitch becomes large when a photochromic dopant is added to a mixture of 5CB-(*R*)-**4**, the cholesteric sense of the 5CB-dopant is plus. If the pitch becomes small, the cholesteric sense of the 5CB-dopant is minus. The pitch as the function of the dopant concentration and β_M values at 30 °C in 5CB are listed in Table 1.

As shown in Table 1, the induced cholesteric phases by (*M*)-**1E**[11] and its photostationary state of 405-nm light irradiation are mirror images of those induced by (*P*)-**1E** and its photostationary state.

The change in the distances of Cano's lines (and hence the cholesteric pitch) for **1** was repeatable. The iterative change of the cholesteric pitch values upon the photoirradiation of visible and UV light is shown in Fig. 2.

2. (*R*)-1,1′-Bi-2-naphthol-condensed Indolylfulgide.

Table 1. Cholesteric Pitch Values and β_M Values of **1**—**4** in 5CB at 30 °C

	Concentration[a]	Pitch/μm			β_M/μm^{-1}			β_M'/μm^{-1} mol^{-1} dm^3		
	10^{-3}mol$_D$ mol$_{LC}^{-1}$ (10^{-2} mol dm^{-3})	E	C	Pss[b]	E	C	Pss[b,c]	E	C	Pss[b,c]
(*P*)-**1**	4.97 (2.03)	6.23		11.22	+31.9		+17.2	+7.8		+4.2
	5.86 (2.39)	5.50		9.84						
	9.85 (4.02)	3.16		5.96						
(*M*)-**1**	4.68 (1.91)	6.37		11.16	−32.7		−18.6	−7.9		−4.5
	5.63 (2.30)	5.40		9.43						
	7.46 (3.05)	4.16		7.34						
2	1.91 (0.78)	22.76	3.02	3.53	−23.0	−175.0	−142.3	−5.6	−43.0	−34.6
	2.35 (0.96)	18.81	2.49	3.09						
	2.73 (1.12)	15.76	2.05	2.57						
3	2.12 (0.87)	17.14	2.62	3.58	−28.0	−175.3	−136.0	−6.9	−42.7	−33.5
	2.82 (1.15)	12.23	2.01	2.59						
	2.99 (1.22)	12.20	1.94	2.43						
(*R*)-**4**[d]	1.52 (0.62)		7.07			−91.8			−22.5	
	3.46 (1.41)		3.24							
	6.40 (2.61)		1.69							

a) mol$_D$ represents moles of dopant, and mol$_{LC}$ represents moles of 5CB. b) Photostationary state of UV irradiation. **1**: 405 nm, **2** and **3**: 366 nm. c) Twisting power values at pss were calculated on the assumption that the mixture of E and C-forms was a single chemical species. d) Values are those just in 5CB.

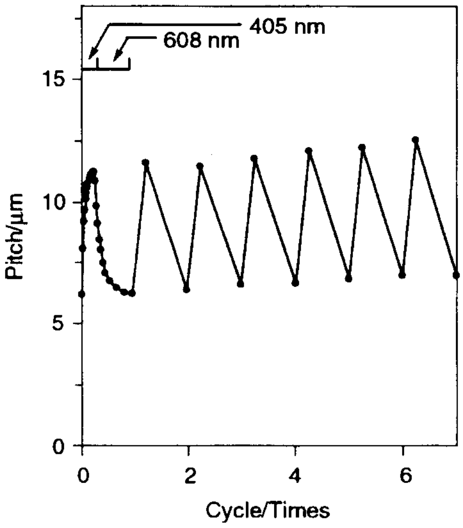


Fig. 2. Reversible change of pitch of the cholesteric phase of 5CB induced by (*P*)-**1** by photoirradiation. *c*/mol$_D$ mol$_{LC}^{-1}$: 4.97×10^{-3}. Starting with (*P*)-**1E** at 30 °C. Irradiation time: 405 nm; 10 min, 608 nm; 30 min.

(*R*)-Binaphthol-condensed indolylfulgides (**2**, **3**) also generated the cholesteric phases when added to 5CB, and the pitch lengths changed upon photoirradiation. The data obtained for **2** and **3** are also listed in Table 1.

Figure 3a shows Cano's lines of 5CB-**3C**. Upon visible-light irradiation to change **3C** to **3E**, the distances of Cano's lines became wide (Fig. 3b). The irradiation of UV-light to give the photostationary state of **3** again narrowed the distances of Cano's lines (Fig. 3c).

The change in the distances of Cano's lines (and hence the cholesteric pitch) for **3** was again repeatable. The iterative change of the cholesteric pitch values upon the photoirradiation of visible and UV light is shown in Fig. 4.

Rational Explanation of the Difference of β_M between Indolylfulgide and Binaphthol-Condensed Indolylfulgide. As shown in Table 1, the absolute value of β_M of the E-form is larger than that of the C-form for (*P*)-**1**, whereas those for the C-forms are considerably larger than those for the E-forms for **2** and **3**. In addition, the signs of β_M for (*P*)-**1** and the 405-nm photostationary state are plus, whereas those for **2** and **3**, the dominant helicity of the central helical moiety of them is *P*, are minus.

1. The Difference of the Absolute Values of β_M. There are two dominant conformations for (*P*)-**1E**. One is (*P*)-**1E***α*, which has the *s-cis* conformation with regard to the single bond between the indole and the methylene carbon atom, and therefore can undergo cyclization upon photoirradiation. The other is (*M*)-**1E***β*, which has *s-trans* for the single bond, and cannot undergo photocyclization (Scheme 3). Judging from the calculated results for a furylfulgide **5** (Chart 3),[16] the thermal interconversion between (*P*)-**1E***α* and (*M*)-**1E***β* is considered to be feasible at room temperature, and the heat-of-formation values of (*P*)-**1E***α* and (*M*)-**1E***β* are thought to be close. Therefore, the twisting power of (*P*)-**1E***α* is compensated by (*M*)-**1E***β* to result in a small β_M value for (*P*)-**1E**.

For (9a*S*)-**1C**, β_M is yet smaller than (*P*)-**1E**. Because of the planar shape of (9a*S*)-**1C**, the chirality generated by the stereogenic center does not work well for twisting of the nematic phase planes.

2. The Difference of the Signs of β_M. Although the helicity of the central helical moiety of the E-forms of **2** and **3**

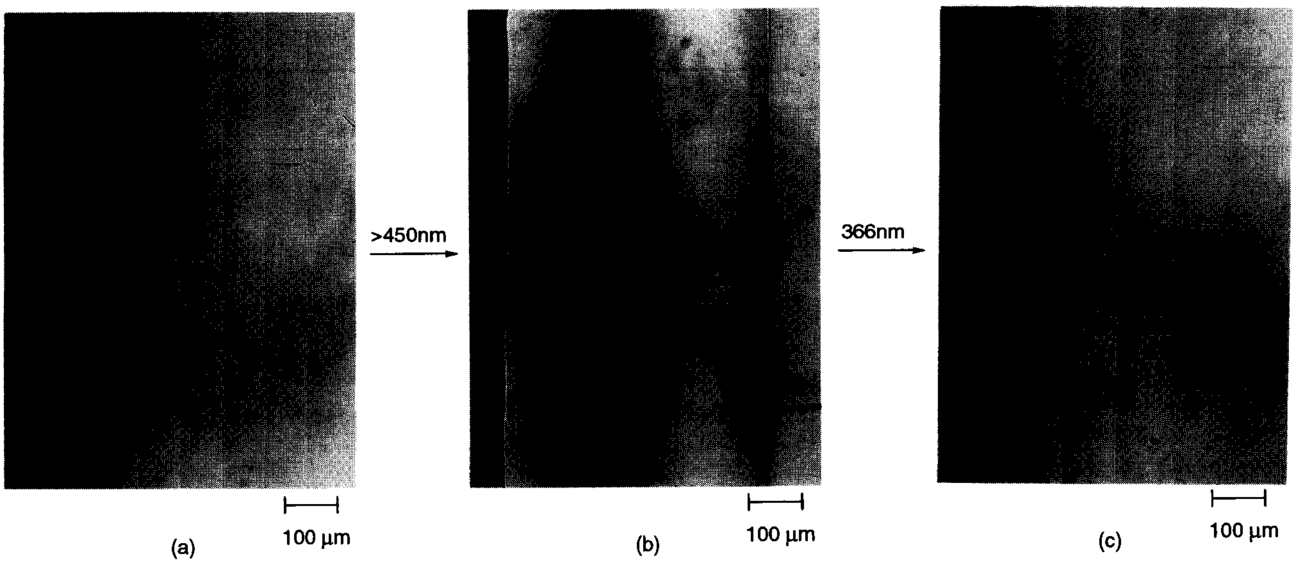


Fig. 3. Polarized optical micrographs of the Cano's lines of a 5CB–3 mixture at 30 °C: (a) the initial state (**3C**), (b) after > 450-nm light irradiation (**3E**), (c) after 366-nm light irradiation (**3E**/**3C** = ca. 15/85). $c/\text{mol}_\text{D}\ \text{mol}_\text{LC}^{-1}$: 2.99×10^{-3}.

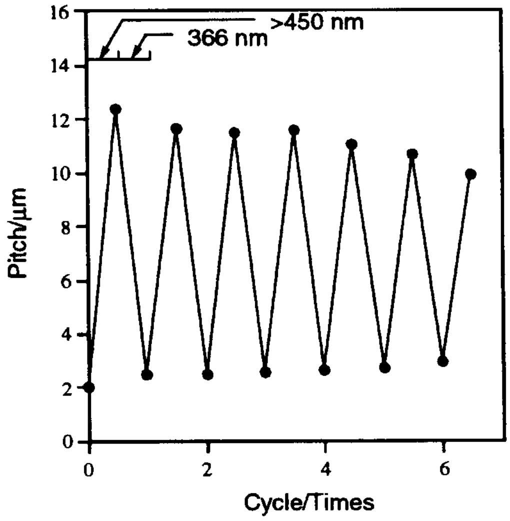


Fig. 4. Reversible change of pitch of the cholesteric phase of 5CB induced by **3** by photoirradiation. $c/\text{mol}_\text{D}\ \text{mol}_\text{LC}^{-1}$: 2.99×10^{-3}. Starting with **3C** at 30 °C. Irradiation time: > 450 nm; 5 min, 366 nm; 60 min.

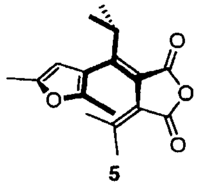


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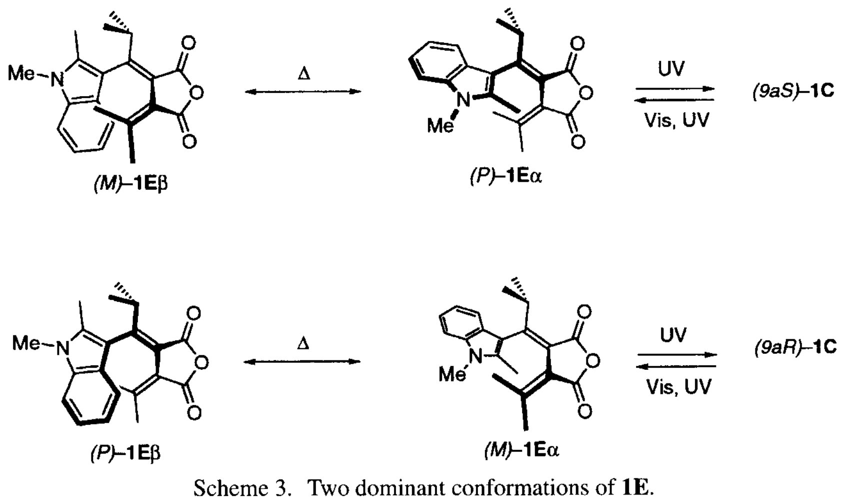
Chart 3.

is *P* and the chirality of the stereogenic center of the C-forms of them is *S*, which are the same as those for (*P*)-**1E**, the sign of the β_M of **2** and **3** is always minus, which is opposite to that of (*P*)-**1E**. Because the sign of β_M of (*R*)-**4** is minus, the sign of the β_M values for **2** and **3** should be governed by the attaching (*R*)-binaphthol moiety.

As for the E-forms of **2** and **3**, the absolute values of β_M are much smaller than those of the C-forms. As described previously, the central helical moiety of indolylfulgide has two major conformations, α and β. In **2E** and **3E**, the diastereomeric relationship between this helicity and the C_2 chirality of the binaphthyl unit generates four possible con-



Scheme 3. Two dominant conformations of **1E**.

formations, as shown in Scheme 4.[9] However, because of the steric repulsion between one of the naphthalene rings and the outer methyl group of the isopropylidene group, the populations of two of the conformers possessing *M* helicity with regard to the central helical moiety are considerably low at thermal equilibrium. Therefore, the helicity of the central helical moiety of **2E** and **3E** is *P*, which should induce a plus $\beta_{\rm M}$. On the other hand, the (*R*)-binaphthyl moiety, which is categorized to *M*-helicity, acts to give a minus $\beta_{\rm M}$. Therefore, for **2E** and **3E**, the twisting power is intramolecularly compensated to be small. For the C-forms in which the stereogenic carbon atom is a poor $\beta_{\rm M}$ generator, the value is mainly governed by the (*R*)-binaphthyl moiety, to give a minus $\beta_{\rm M}$.

Control of Cholesteric Sense. We have thus shown that the $\beta_{\rm M}$ values, and therefore the cholesteric pitch values, are controlled by the iterative photoirradiation of visible and UV light. However, the sign of the cholesteric helicity was not changed by photoirradiation. We next tried to control the cholesteric helical sense by photochromism of the dopant. To change the helical sense means that it takes the nematic phase (i.e. $\beta_{\rm M}$ is zero) while changing.[17]

The addition of 4.89×10^{-3} mol$_{\rm D}$/mol$_{\rm LC}$ (2.01×10^{-2} mol dm^{-3}) of (*S*)-**4** and 5.13×10^{-3} mol$_{\rm D}$/mol$_{\rm LC}$ (2.10×10^{-2} mol dm^{-3}) of (*9aS*)-**3C** to 5CB afforded a cholesteric phase with a pitch of −2.26 µm. The irradiation of > 450-nm light expanded the intervals of Cano's lines (i.e. enlarged the absolute value of pitch length), and again the intervals became small. The pitch became +3.63 µm when all of the photochromic dopant became the *E*-form. The irradiation of 366-nm light again expanded the intervals of Cano's lines, and then became smaller. Control of three liquid-crystalline phases (two cholesteric states with regard to the helicity, and a nematic phase) was thus achieved, and could be repeated (Fig. 5).

Conclusion. We have demonstrated that (i) chiral fulgide derivatives can induce cholesteric liquid crystalline phases when doped in a nematic liquid crystal, (ii) the cholesteric pitch values of the induced cholesteric phases could be changed reversibly by iterative irradiation with visible and UV lights, (iii) with the aid of a non-photochromic chiral dopant, the cholesteric sense of the induced cholesteric phases could be changed reversibly. This may be the basic result for research to alter the wavelength of the light of

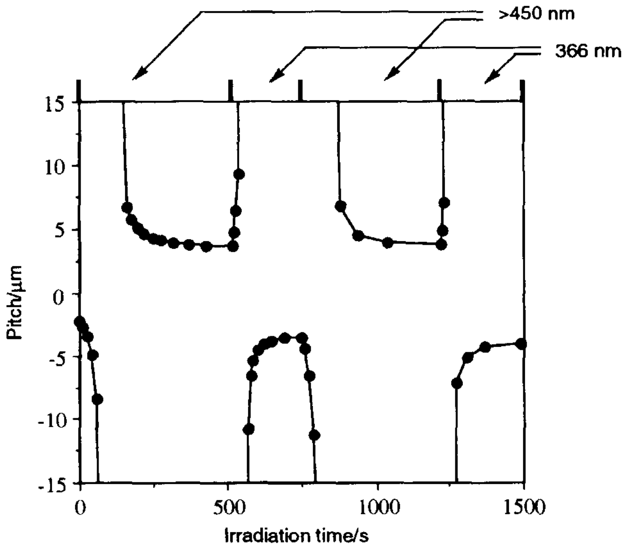
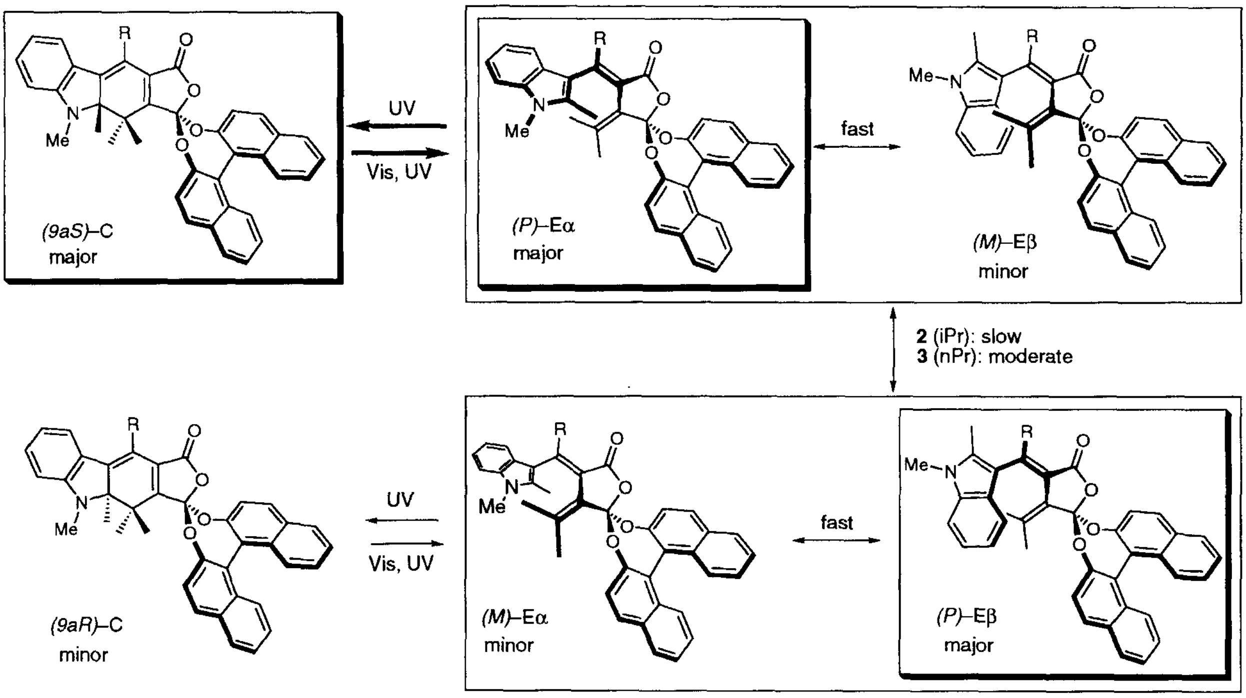


Fig. 5. Reversible change of cholesteric sense by photoirradiation. *c* of **3**/mol$_{\rm D}$ mol$_{\rm LC}^{-1}$: 4.89×10^{-3}, *c* of (*S*)-**4**/mol$_{\rm D}$ mol$_{\rm LC}^{-1}$: 5.13×10^{-3}. Starting with **3C** at 30 °C.



Scheme 4. Diastereoselective photochromism of **2** and **3**.

selective reflection of the cholesteric liquid crystal by the photochromism of the photochromic dopants, which is now under way in our laboratory.

Experimental

The syntheses of **1**,[18] **2**,[9] and **3**[9] were described previously.

Cano's lines were observed using Cano–Wedge-type cells (EHC, KCRK-03S), an Olympus BH-2 microscope, and a Mettler FP82HT hot stage attached to a Mettler FP90 central processor, at 30 °C. The determination of the cholesteric pitch values was performed by Cano's method.[19]

The relationship between the distances of Cano's lines and the cholesteric pitch (Fig. 1) is

$$p = 2R\tan\theta, \qquad (1)$$

where p represents the pitch length, R is the distance between Cano's lines, and θ is the angle defined in Fig. 1. Thus, the pitch length was calculated from the average value of the distances of Cano's lines.

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11 The nomenclature P (abbreviation of *plus*) denotes the right-handed helicity, and M (abbreviation of *minus*) denotes the left-handed helicity. They are also used for the cholesteric senses of liquid crystals.

12 The twisting power β_M is expressed as $\beta_M = (pcr)^{-1}$ where p is the pitch length measured in µm, c is the concentration expressed in molar ratio of the photochromic dopant and the liquid crystal, and r is the optical purity of the dopant.[13] In the preliminary communication,[10] we used c expressed in molarity (moles of dopant per dm^3 of the solution). In this paper, however, in addition to the molarity for c to calculate the twisting power (expressed as $\beta_M{}'$), we used the molar ratio as c (expressed as β_M) because it is convenient to compare our twisting power values with other non-photochromic dopants.[14,15]

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