Photoinduced pitch changes in chiral nematic liquid crystals formed by doping with chiral diarylethene

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Chiral binaphthyl derivatives having two photochromic diarylethene units were synthesized in an attempt to use them as dopants for photoresponsive liquid crystals. These compounds showed thermally irreversible photochromic reactions. The circular dichroism (CD) spectra and the optical rotation values of the derivatives reversibly changed in methanol upon alternate irradiation with ultraviolet and visible light. Large photostimulated pitch changes of chiral nematic K-15 liquid crystals were observed on addition of the derivatives as dopants. The relation between the optical rotation and the twisting power force was discussed.

Introduction

Various types of photochromic compounds such as azobenzenes, spiropyrans, furylfulgides and diarylethenes have been so far reported.[1–5] These photochromic compounds have potential for applications to optical memories and photo-optical switches. Among the compounds diarylethene derivatives are the most promising photochromic compounds for the applications because of their fatigue-resistant and thermally irreversible properties.[6,7] The photochromic diarylethenes can be used as dopants for photoresponsive liquid crystals.

Photochromic dopants can induce optical rotation and refractive index changes as well as reflection band shifts in liquid crystals along with the photochromic reactions.[8–14] In previous papers,[15–17] we have reported that upon photoirradiation doped chiral cyclohexanes having two photochromic diarylethene units can switch the nematic liquid crystals from apparently nematic to chiral nematic (induced cholesteric) phases. The cyclohexane derivatives were an efficient trigger for the pitch change. In the present work, we have prepared chiral 3,3′-binaphthyl derivatives having two diarylethene units. We adopted the derivatives as dopants, which induce a photoinduced pitch change in the chiral nematic phase.

Results and discussion

Synthesis of dopants 1–4

Binaphthyl derivative **1** was prepared as shown in Scheme 1. (R)-(+)-1,1′-Binaphthyl-2,2′-diamine (1 equiv.) was reacted with the aldehyde derivative of the diarylethene (2 equiv.)[18] to produce compound **1**.

Binaphthyl derivative **2** was synthesized as shown in Scheme 2. Starting material **6** was prepared from (R)-(+)-1,1′-bi-2-naphthol.[19] Compound **6** was reacted with a hydroborated thiophene[20] to give compound **7**. The coupling reaction of compound **7** with compound **8** gave the diarylethene **2**.
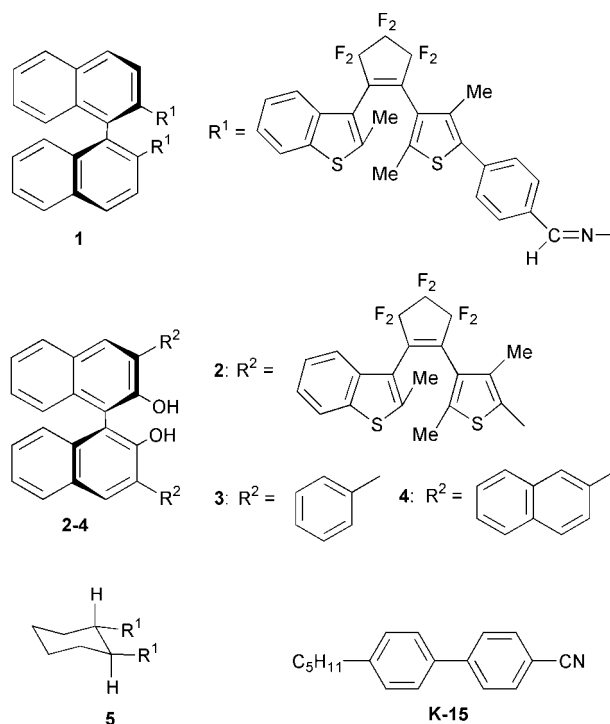
Binaphthyl derivatives **3**, **4** were also synthesized as reference compounds as shown in Scheme 3. The synthetic route was similar to compound **2**. Conc. hydrochloric acid was used in the deprotection process. The purity of the chiral binaphthyl derivatives was confirmed to be >99% by HPLC measurement using a chiral column (Chiralcel OD, eluent: hexane–propanol = 95 : 5).

Photochromic reactions of compounds 1 and 2

Fig. 1 shows the absorption spectral change of **1** in methanol. The binaphthyl having two open-form diarylethenes (**1O-O**), where **O** means the open-ring form isomer, showed absorption maxima at 318 nm (ε: 5.0×10^4 M^{-1} cm^{-1}) and 298 nm (ε: 5.1×10^4 M^{-1} cm^{-1}). Upon irradiation with UV light

Scheme 1

Scheme 2

Scheme 3

Fig. 1 Absorption spectra of three isomers of **1** in methanol ($c = 1.07 \times 10^{-5}$ M); solid line **1O-O**; dotted line **1C-O**; dashed line **1C-C**.

The CD spectrum of two open-form diarylethenes (**1O-O**) showed maxima at 363 nm ($\Delta\varepsilon$: -8.9 M^{-1} cm^{-1}) and 317 nm ($\Delta\varepsilon$: $+43.0$ M^{-1} cm^{-1}). The spectrum was an exciton type spectrum, which has zero value at 340 nm. Upon irradiation with UV light, a mixture of **1C-O** and **1C-C** was obtained. The two isomers were isolated by HPLC and the CD spectra were measured. **1C-O** showed an induced type CD spectrum at 588 nm ($\Delta\varepsilon$: -3.1 M^{-1} cm^{-1}) and 298 nm ($\Delta\varepsilon$: $+25.4$ M^{-1} cm^{-1}). **1C-C** showed a spectrum at 579 nm ($\Delta\varepsilon$: -8.6 M^{-1} cm^{-1}), 360 nm ($\Delta\varepsilon$: $+2.1$ M^{-1} cm^{-1}) and 292 nm ($\Delta\varepsilon$: $+24.3$ M^{-1} cm^{-1}). The $\Delta\varepsilon$ value of **1C-C** around 363 nm and 317 nm was much smaller than the

(254 nm), the two open-ring isomers transformed into closed-ring isomers independently, producing a mixture of **1C-O** and **1C-C**, where **C** and **O** mean the closed and open-ring form isomers, respectively. Two isomers **1C-O** and **1C-C** were isolated by HPLC (column: Wakosil 5C18; eluent: methanol) and their electronic absorption and CD spectra were measured. **1C-O** showed absorption maxima at 546 nm (ε: 1.4×10^4 M^{-1} cm^{-1}), 388 nm (ε: 1.1×10^4 M^{-1} cm^{-1}) and 298 nm (ε: 5.7×10^4 M^{-1} cm^{-1}). **1C-C**, which has two closed-ring form isomers, also showed a maximum at 546 nm (ε: 2.5×10^4 M^{-1} cm^{-1}). The molar absorption coefficient of **1C-C** at 546 nm was slightly less than twice of that of **1C-O**. In the photostationary state under irradiation with 254 nm light, the main product was **1C-O** (48%) and the rest was **1C-C** (26%) and **1O-O** (26%). Upon irradiation with light of wavelength longer than 420 nm, both **1C-C** and **1C-O** returned to **1O-O**.

Fig. 2 shows the CD spectrum of **1** in methanol. The binaphthyl chromophore is inherently optically active due to the orientation of the two naphthyl groups. It gives a plus (or minus) typical Cotton effect shape, which has a molecular ellipticity of zero at the absorption maximum (exciton coupling CD). The diarylethene units are inherently achiral. They give an induced type CD spectrum in the chiral environment. The induced CD spectral intensity is proportional to the absorption coefficient and the maximum position is the same as that of the absorption maximum.
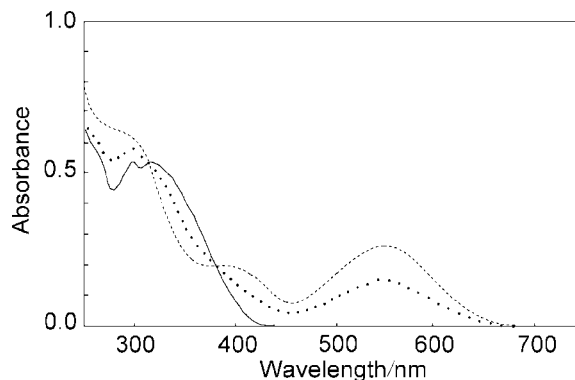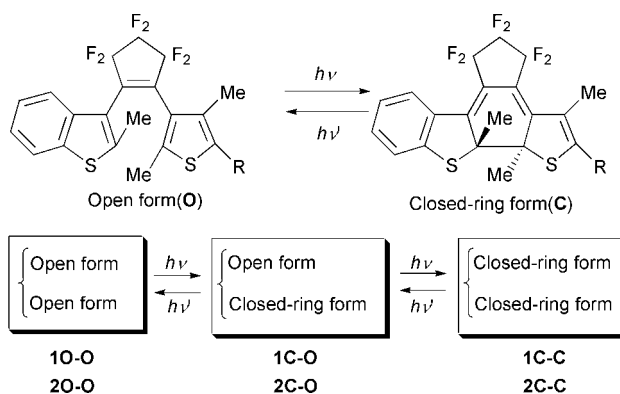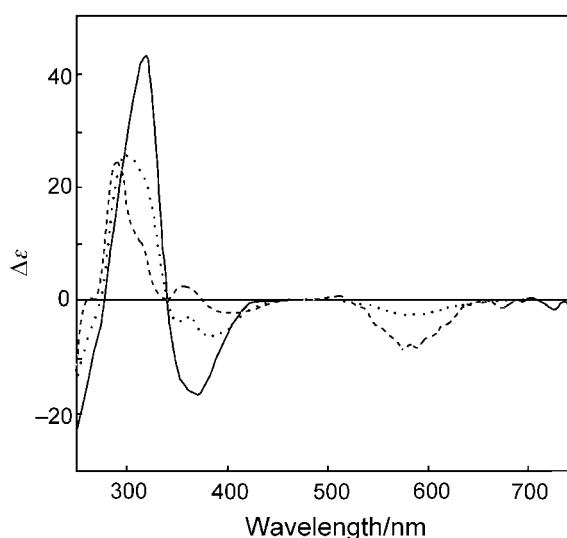

Fig. 2 CD spectra of three isomers of **1** in methanol; solid line **1O-O**; dotted line **1C-O**; dashed line **1C-C**.
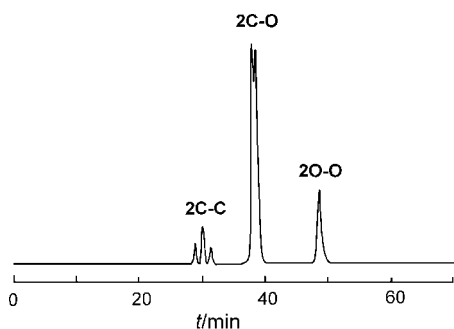
Fig. 3 An HPLC chromatogram of **2** after irradiation with 254 nm light in *n*-hexane monitored at 313 nm. Eluent hexane–ethyl acetate = 94 : 6; flow rate 2.0 ml min^{-1}.
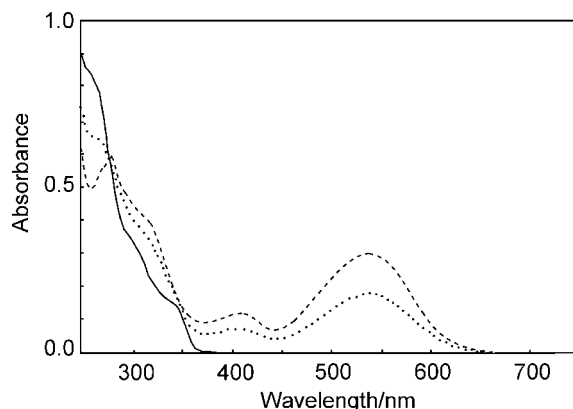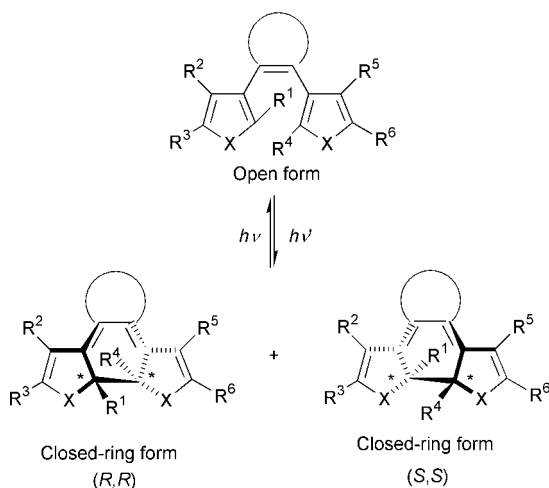

Fig. 4 Absorption spectra of three isomers of **2** in *n*-hexane ($c = 1.52 \times 10^{-5}$ M); solid line **2O-O**; dotted line **2C-O**; dashed line **2C-C**.
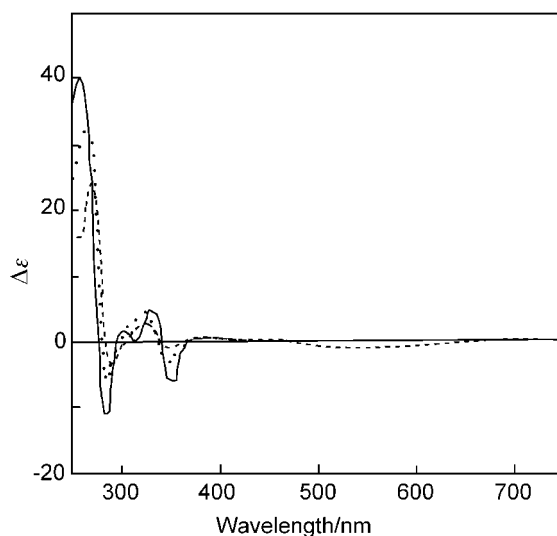

Fig. 5 CD spectra of three isomers of **2** in *n*-hexane; solid line **2O-O**; dotted line **2C-O**; dashed line **2C-C**.

values for **1O-O**. The optical rotation also changed dramatically on alternate irradiation with 254 nm and >420 nm light. The optical rotation value of **1O-O** ($[\alpha]_{650}^{25} = -237°$ ($c = 5$, CH$_3$CN)) decreased to $-735°$ upon irradiation with 254 nm light. This difference is due to the change in the ratio of the three isomers.

Just as for **1**, compound **2** also changed the absorption and CD spectra upon irradiation with ultraviolet ($\lambda = 313$ nm) and visible light ($\lambda > 480$ nm). To assign the spectral change the photoirradiated sample was passed through an HPLC silica gel column (Wakosil 5SIL; eluent: hexane–ethyl acetate = 94 : 6) and the chromatogram in the photostationary state was measured as shown in Fig. 3.

The two peaks of **2C-O** are explained as follows. The **2C-O** isomer has two diastereomeric isomers, $(R,R),R_a$ and $(S,S),R_a$ isomers.[21,22] The $(R,R),R_a$ and $(S,S),R_a$ means the chiral (R_a)-naphthyl derivatives have two closed-ring isomers (R,R) and (S,S), respectively. The **2C-C** showed three diastereomeric isomers: the mixture of $(R,R),(S,S),R_a$ and $(S,S),(R,R),R_a$ isomers, the $(R,R),(R,R),R_a$ isomer and the $(S,S),(S,S),R_a$ isomer. The enantiomer ratio of the closed-ring forms was almost unity, which means that enantioselection did not take place in the photocyclization process. Although similar resolution of the closed-ring isomers is expected for compound **1**, we failed to detect them.

Fig. 4 shows the absorption spectral change of **2** in methanol. The binaphthyl having two open-form diarylethenes (**2O-O**) showed an absorption maximum (shoulder) at 298 nm (ε: 2.3×10^4 M^{-1} cm^{-1}). **2C-O** showed maxima at 537 nm (ε: 1.2×10^4 M^{-1} cm^{-1}), 412 nm (ε: 4.6×10^3 M^{-1} cm^{-1}) and 266 nm (ε: 4.4×10^4 M^{-1} cm^{-1}). **2C-C**, which has two closed-ring forms, showed maxima at 538 nm (ε: 2.0×10^4 M^{-1} cm^{-1}), 411 nm (ε: 7.6×10^3 M^{-1} cm^{-1}) and 280 nm (ε: 3.6×10^4 M^{-1} cm^{-1}). In the photostationary state under

irradiation with 313 nm light, the main product was **2C-O** (72%) and the rest was **2C-C** (10%) and **2O-O** (17%).

The CD spectrum and the optical rotation of compound **2** were also changed on alternate irradiation with ultraviolet ($\lambda = 313$ nm) and visible light ($\lambda > 480$ nm). Fig. 5 shows the CD spectra of **2** in methanol. **2O-O** showed maxima at 347 nm ($\Delta\varepsilon$: -6.0 M^{-1} cm^{-1}), 327 nm ($\Delta\varepsilon$: $+5.0$ M^{-1} cm^{-1}), 300 nm ($\Delta\varepsilon$: $+1.2$ M^{-1} cm^{-1}), 283 nm ($\Delta\varepsilon$: -10.7 M^{-1} cm^{-1}) and 258 nm ($\Delta\varepsilon$: $+41.0$ M^{-1} cm^{-1}). Upon irradiation with 313 nm light, a mixture of **2C-O** and **2C-C** was obtained. **2C-O** showed maxima at 346 nm ($\Delta\varepsilon$: -3.8 M^{-1} cm^{-1}), 317 nm ($\Delta\varepsilon$: $+4.9$ M^{-1} cm^{-1}), 288 nm ($\Delta\varepsilon$: -5.9 M^{-1} cm^{-1}) and 263 nm ($\Delta\varepsilon$: $+32.4$ M^{-1} cm^{-1}). **2C-C** showed maxima at 550 nm ($\Delta\varepsilon$: -1.8 M^{-1} cm^{-1}) and 347 nm ($\Delta\varepsilon$: -1.2 M^{-1} cm^{-1}), 325 nm ($\Delta\varepsilon$: $+2.9$ M^{-1} cm^{-1}), 292 nm ($\Delta\varepsilon$: -3.8 M^{-1} cm^{-1}) and 257 nm ($\Delta\varepsilon$: $+22.6$ M^{-1} cm^{-1}). The CD spectra of **2C-O** and **2C-C** in the visible region were much smaller than those of **1C-O** and **1C-C**.

The optical rotation values ($[\alpha]_{669}^{25}$ ($c = 5$, ethyl acetate)) of **2O-O** and the photostationary state sample by irradiation with 254 nm light in methanol were 0° and $-28°$, respectively. The optical rotation can be detected with light of wavelengths longer than the absorption band. Therefore, the property change is useful for non-destructive readout.[15] The optical rotation change of compound **2** was also much smaller than the change observed for compound **1**. The photoinduced specific rotation change of **1** ($\Delta[\alpha]_{650}^{25} = -498°$) was comparable to that
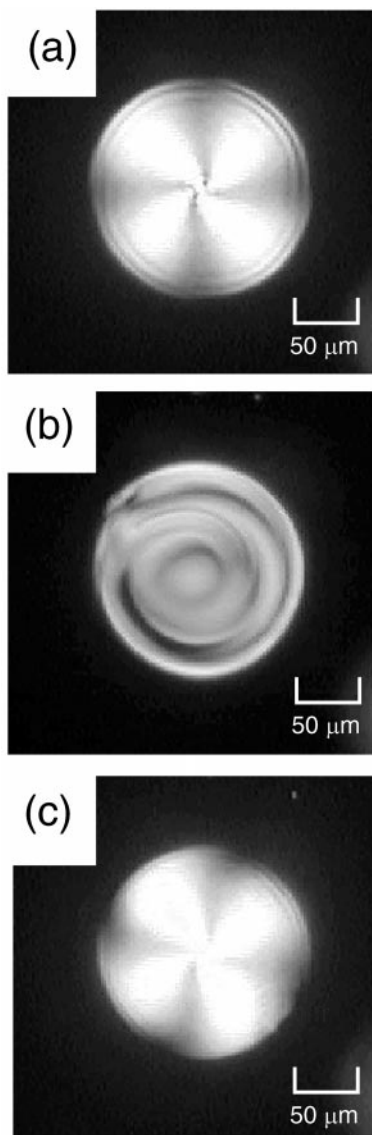

Open form

$h\nu \Updownarrow h\nu$

Closed-ring form (R,R)   +   Closed-ring form (S,S)

Fig. 6 A single droplet of K-15 containing **2** (1 wt%) suspended in glycerol viewed at 100 × magnification between crossed polarizers at 26 °C; (a) before irradiation with 254 nm light; (b) after irradiation with 254 nm light; (c) after irradiation with >420 nm light.

of a chiral bis(diarylethenyl)cyclohexane derivative ($\Delta[\alpha]_{669}^{25} = -490°$).[16]

Photoswitching of the dopants in nematic liquid crystal

Compounds **1** and **2** were doped into the nematic liquid crystal, K-15 and the phase change of the liquid crystals was followed upon alternate irradiation with ultraviolet ($\lambda = 313$ nm) and visible light ($\lambda > 480$ nm) at 26 °C. Compound **2** was an effective trigger for the switching between nematic and cholesteric phases. Fig. 6(a) shows a droplet of K-15 containing 1.0 wt% **2O-O** viewed microscopically in glycerol between crossed polarizers.[23,24] The phase is typical nematic. When the nematic liquid crystal was irradiated with 254 nm light for 1 min, the spiral texture (cholesteric phase) appeared (Fig. 6(b)). Irradiation of the sample with visible light (>420 nm) for 3 min regenerated the schlieren texture (Fig. 6(c)). The switching cycle was performed more than 10 times without deterioration of the liquid crystalline phase.

Bisimine-modified diarylethenes have been used as dopants for photoresponsive liquid crystals.[11] The addition of small amounts of bisimine-modified diarylethenes formed a chiral nematic phase. Upon irradiation with UV light, the pattern changed to an apparently nematic phase. The present

Table 1 Pitch values and helical twisting powers of K-15 liquid crystals containing compounds **1**, **2** (2.0 wt%), **3**, **4**, (R)-(+)-1,1'-bi-2-naphthol (3.0 wt%) and **5** (2.0 wt%) at 26 °C as determined by the droplet method

Compound	Pitch/μm	$\beta_m/\mu m^{-1}$ [b]
1 (Open form)	28.5	+9.1
1 (Photostationary state sample)[a]	24.4	+10.6
2 (Open form)	>100	—
2 (Photostationary state sample)[a]	24.1	+9.4
3	6.4	−8.9
4	2.9	+24
(R)-(+)-1,1'-Bi-2-naphthol	21.4	−1.7
5 (Open form)	23.7	−9.5
5 (Photostationary state sample)[a]	7.9	−28.6

[a]The sample was irradiated with 254 nm light. [b]A positive sign refers to a right-handed helix and *vice versa*.

binaphthyl derivative, on the other hand, switched phase from apparently nematic to chiral nematic upon UV irradiation. The same tendency was observed for the chiral cyclohexane **5** having two diarylethene units.[17] Doping with the chiral derivatives having two diarylethene units (open–open isomer) formed a chiral nematic phase with a very large pitch. Upon UV irradiation, the photogenerated closed-ring form tightened the pitch and the chiral nematic phase became more obvious. The complementary properties of the two systems may be useful to control the liquid crystalline phase.

Compound **1** was not an effective trigger for switching between nematic and chiral nematic phases. The pitch changes were determined by the droplet method in nematic liquid crystal K-15 and listed in Table 1 along with the values for the cyclohexane derivatives. Although compound **1** showed a large specific rotation change by UV/visible light irradiation, the liquid crystalline pitch change was very small.

The twisting power force and the helical sense of the open- and the closed-ring forms of **1** and **2** were also shown in Table 1.

The twisting power force β_M is calculated as follows[10] [eqn (1)]:

$$\beta_M = 1/Cp \tag{1}$$

where C and p represent the concentration of dopant (mol of dopant/mol of solution) and pitch, respectively. The twisting power force of the closed-ring isomer was at least 10 times larger than that of **2O-O**.

DSC measurement of the K-15 samples doped with mixture **1** and **2** (2 wt%) from 0 °C to 50 °C (1 °C min⁻¹) revealed an endothermic peak at 25.2 °C, which is due to the phase change from a crystal to a chiral nematic phase. The samples also showed endothermic peaks at 33.3 °C (for **1**) and 33.8 °C (for **2**), which are assigned to the phase changes from the chiral nematic phase to an isotropic liquid phase. The K-15 without dopants showed a nematic phase from 25.5 °C to 36.7 °C. As the additive concentration was increased, the transition temperature from a chiral nematic phase to an isotropic liquid phase was shifted to lower temperatures.

In order to elucidate the detailed mechanism of the pitch change between **2O-O** and the closed-ring isomer, compound **3** and **4** were doped into K-15. When the liquid crystal was doped with 3 wt% of **3**, which has two phenyl moieties at the 3 and 3′ positions, the pitch sense was a left-handed helix (Table 1). When 3 wt% of **4**, which has two naphthyl moieties at the 3 and 3′ positions, was added to the liquid crystal, the pitch sense was a right-handed helix. The bulkiness of the substituents at the 3 and 3′ positions of binaphthol controlled the sense in the chiral nematic phase. The twisting power force and the pitch sense of **3**, **4**, **2O-O** and the photostationary state of **2** are summarized in Fig. 7. The centerline represents a nematic phase. If the compound is far from the line, the helix of the chiral nematic
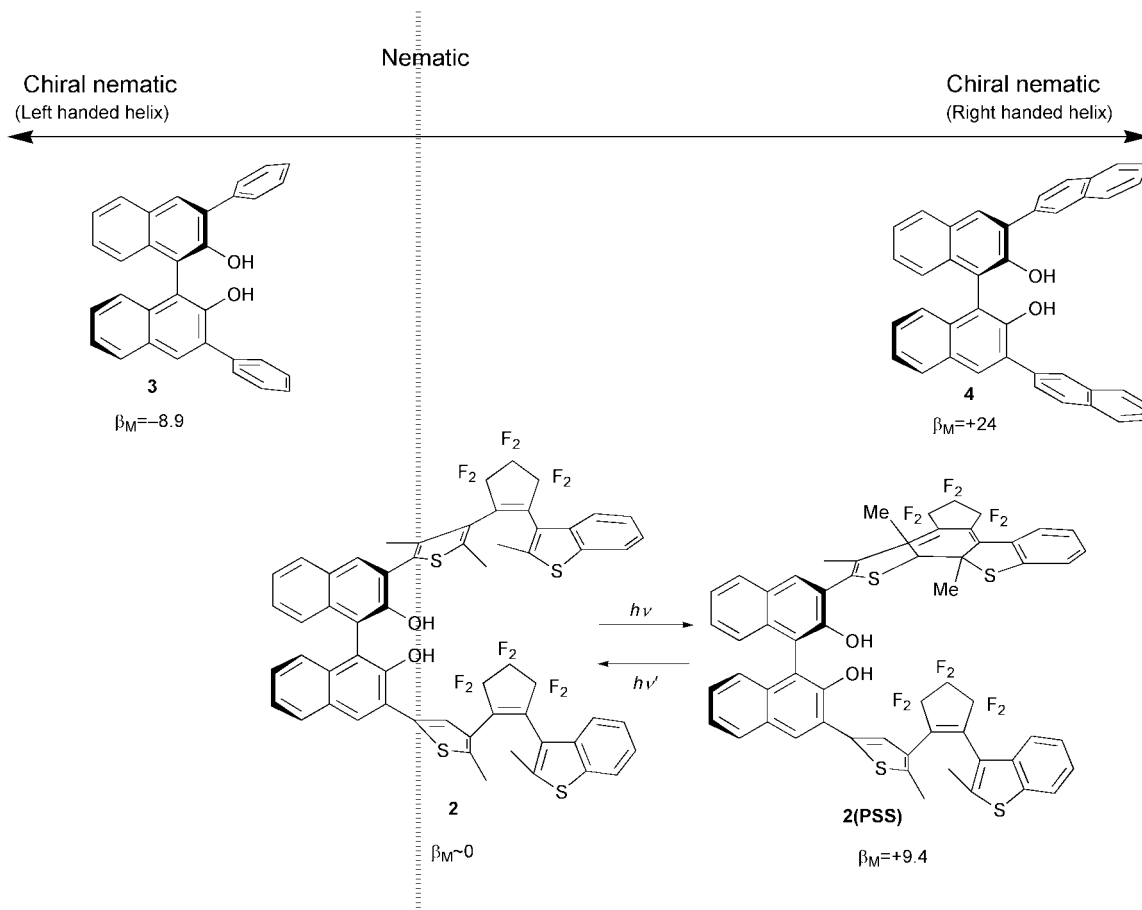
Nematic

Chiral nematic
(Left handed helix)

Chiral nematic
(Right handed helix)

3

$\beta_M = -8.9$

4

$\beta_M = +24$

$h\nu$

$h\nu'$

2

$\beta_M \sim 0$

2(PSS)

$\beta_M = +9.4$

Fig. 7 Helical sense and helical twisting powers between 3,3′-bis-substituted chiral binaphthyl derivatives.

phase is strong, in other words, the twisting power force becomes large. The compounds are aligned in their order of the twisting power force. Diarylethene **2O-O** did not effectively affect the phase, therefore the phase was apparently nematic. The closed-ring isomer induced a left handed helix. The extended aryl moiety in **2** switched the phase between the nematic and chiral nematic ones.

Conclusions

We have demonstrated that a small amount of chiral binaphthyl **2** having two photochromic diarylethenes in nematic liquid crystalline K-15 can induce a stable photoswitching between the apparently nematic and chiral nematic phases. The present system can alter the wavelength of selective reflection of light by photoirradiation. The wavelength change can be potentially used for non-destructive readout of rewriteable photochromic memory media.

Experimental

General

Solvents used were spectrograde and purified by distillation before use. Absorption spectra were measured with a spectrophotometer (Shimadzu, UV-3100PC). A mercury lamp (Ushio, 500 W) and a Xenon lamp (Ushio, 1kW) were used as the light sources. Monochromic light was obtained by passing the light through a Toshiba cut-off filter (L-42 and Y-48). ^{1}H NMR spectra were recorded on a JNM EX 270 (270 MHz) spectrometer. The signals were expressed as ppm downfield from tetramethylsilane (δ value). Mass spectra were taken with a Finnigan MAT TSQ-70 mass spectrometer. Circular dichroism

was measured with a JASCO J-720WI spectrometer. Optical rotations were measured using a Union GIKEN PM-101 and are given in units of 10^{-1} deg cm^2 g^{-1}. HPLC was carried out on a Shimadzu LC-10AD liquid chromatography coupled with a Shimadzu SPD-10AV spectrophotomeric detector. Optical purity of the compounds was measured with HPLC using a chiral column (Daicel Chiralcel OD). Silica gel columns (Wakosil 5SIL and Wakosil 5C18, Wako) were used for the analysis of diastereomers. Differential scanning calorimetry (DSC) measurement was carried out with a RIGAKU TAS-200. The sample was heated from 0 °C to 50 °C (the temperature scan rate: 1 °C min^{-1}). The pitch changes were monitored using a polarization microscope (Nikon OPTIPHOT2-POL). Irradiation for the pitch measurement was carried out with a mercury lamp (254 nm, 10 W), and a halogen lamp (100 W). The cell was constructed according to the previous paper.[17]

(*R*)-1,1′-Bis(4-{3-[1-(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopent-1-en-2-yl]-2,4-dimethylthiophen-5-yl}benzylideneamino)naphthalene (1)

4-{3-[1-(2-Methyl-1-benzothiophen-3-yl)hexafluorocyclopent-1-en-2-yl]-2,4-dimethylthiophen-5-yl}benzaldehyde[16] (0.51 g) in 35 ml methanol solution and excess magnesium sulfate were added to (*R*)-(+)-1,1-binaphthyl-2,2′-diamine (0.135 g), and the solution was stirred for 24 h. The magnesium sulfate was filtered, and the solvent was removed to give **1** in quantitative yield: mp 154–155 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.86 (s, 2H), 2.16 (s, 6H), 2.38–2.45 (m, 10H), 7.09 (s, 2H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.70–7.73 (m, 2H), 7.87–7.90 (m, 4H), 8.11–8.19 (m, 2H); FAB-MS (*m/z*, %): 1320 (M$^+$, 100%). Anal. Calcd for C$_{74}$H$_{48}$F$_{12}$N$_2$S$_4$: C, 67.26; H, 3.66; N, 2.12. Found: C, 67.14; H, 3.68; N, 2.18%. **1O-O** $[\alpha]_{650}^{25} = -237°$) *c* = 5, CH$_3$CN).

(*R*)-2,2′-Bis(methoxymethoxy)-3,3′-bis(3-bromo-2,4-dimethylthiophen-5-yl)-1,1′-binaphthalene (7)

(*R*)-2,2′-Bis(methoxymethoxy)-3,3′-diiodo-1,1′-binaphthalene **6** (1.68 g),[19] tetrakis(triphenylphosphine)palladium(0) salt (0.278 g) and 1 M sodium carbonate solution (12 ml) in 80 ml THF solution were added to 3-bromo-2,4-thienylboronic acid[20] (0.51 g), and the solution was refluxed for 48 h. The saturated sodium chloride aqueous solution was added to the solution, the product was extracted with diethyl ether, and dried over anhydrous sodium sulfate. The organic layer was evaporated. The residue was purified using a column chromatography (Wakogel C300; eluent: hexane–ethyl acetate = 5 : 1) to give **7** in 82% yield: mp 155–156 °C; ^{1}H NMR (270 MHz, CDCl₃) δ 2.16 (s, 6H), 2.38–2.45 (m, 10H), 7.09 (s, 2H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.70–7.73 (m, 2H), 7.87–7.90 (m, 4H), 8.11–8.19 (m, 2H); FAB-MS (*m/z*, %): 750 (M$^+$, 66%), 752 (M$^+$ + 2, 100%), 754 (M$^+$ + 4, 66%). Anal. Calcd for C₃₆H₃₂Br₂O₄S₂: C, 57.45; H, 4.29. Found: C, 57.56; H, 4.30%.

(*R*)-1,1′-Bis{3-[1-(2-methyl-1-benzothiophen-3-yl)hexafluorocyclopent-1-en-2-yl]-2,4-dimethylthiophen-5-yl}-bi-2-naphthol (2)

Compound **7** (0.753 g) in 15 ml of dry THF was cooled at −77 °C under nitrogen gas. A solution of 1.6 M *n*-butyllithium (1.56 ml) was added dropwise to the above solution, and then the solution was stirred for 1 h at −77 °C. A THF solution (10 ml) of 1-(2-methyl-1-benzothiophen-3-yl)heptafluorocyclo-pent-1-ene **8** (0.851 g) was added dropwise to the above solution, and the solution was stirred for 2 h at −77 °C. 30 ml of sodium thiosulfate aqueous solution was added to the solution, and the product was extracted with diethyl ether. The organic layer was dried over anhydrous sodium sulfate, and then the solvent was evaporated. Trimethysilyl iodide (0.70 g) was added to the residue in 40 ml of acetonitrile. After 24 h stirring at room temperature, the organic layer was evaporated. The residue was purified using a column chromatography (Wakogel C300; eluent: hexane–ethyl acetate = 5 : 1) to give **2** in 18% yield: mp 144–145 °C; ^{1}H NMR (270 MHz, CDCl₃) δ 2.22 (s, 6H), 2.36 (s, 6H), 2.46 (s, 6H), 7.31 (d, *J* = 4.3 Hz, 4H), 7.40–7.46 (m, 2H), 7.86 (d, *J* = 7.9 Hz, 2H), 7.91 (s, 2H); FAB-MS (*m/z*, %): 1146 (M$^+$, 100%). Anal. Calcd for C₆₀H₃₈F₁₂N₂S₄ + C₂H₅O: C, 62.94; H, 3.96. Found: C, 62.77; H, 3.96%. **2O-O** [α]$_{669}^{25}$ = 0° (*c* = 5, ethyl acetate).

(*R*)-3,3′-Diphenyl-1,1′-bi-2-naphthol (3)

The (*R*)-2,2′-bis(methoxymethoxy)-3,3′-diiodo-1,1′-binaphthalene **6** (0.63 g), tetrakis(triphenylphosphine)palladium(0) salt (0.173 g) and 1 M sodium carbonate solution (7.5 ml) in 60 ml THF solution were added to phenylboronic acid (0.61 g),[15] and the solution was refluxed for 48 h. Saturated aqueous sodium chloride solution was added to the solution, and the product was extracted with diethyl ether. The organic layer was dried over anhydrous sodium sulfate, and then the solvent was evaporated. Concentrated hydrochloric acid (10 ml) was added to the residue in 40 ml of chloroform. The solution was refluxed for 5 h and then 30 ml of water was added to the solution, and the product was extracted with diethyl ether. The organic layer was dried over anhydrous sodium sulfate, and then the solvent was removed. The residue was purified using column chromatography (Wakogel C300; eluent: hexane–ethyl acetate = 5 : 1) to give **3** in 75%: yield: mp 204–205 °C; ^{1}H NMR (270 MHz, CDCl₃) δ 5.36 (s, 2H), 7.21–7.52 (m, 12H), 7.73 (dd, *J* = 6.9, 3.0, 2H), 7.87–7.92 (d, *J* = 7.5 Hz, 2H), 8.02 (s, 2H); FAB-MS (*m/z*, %): 438 (M$^+$, 100%). Anal. Calcd for C₃₂H₂₂O₂: C, 87.65; H, 5.06. Found: C, 87.65; H, 5.04%. [α]$_{650}^{25}$ = + 35 (*c* = 5, ethyl acetate).

(*R*)-3,3′-Di(2-naphthyl)-1,1′-bi-2-naphthol (4)

The synthetic procedure was the same as that for **3** except that 2-naphthylboronic acid was used instead of phenylboronic acid. For **4**: mp 177–178 °C; ^{1}H NMR (270 MHz, CDCl₃) δ 7.28–7.54 (m, 6H), 7.86–7.98 (m, 4H), 8.14 (s, 2H), 8.21 (s, 2H); FAB-MS (*m/z*, %): 538 (M$^+$, 100%). Anal. Calcd for C₄₀H₂₆O₂: C, 89.19; H, 4.87. Found: C, 88.87; H, 4.92%. [α]$_{650}^{25}$ = −44° (*c* = 5, ethyl acetate).

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