

# Thermo and Photoresponsive Behavior of Liquid-Crystalline Helical Structures with the Aid of Dual Molecular Motions

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Light- and temperature-driven multistable chiral materials composed of a binaphthyl moiety as a twisting part and an azobenzene moiety as a photoresponsive part in a single component were investigated. It has been found that the materials show reversible change in a dihedral angle of the twisting part at various temperatures. In contrast, no change in the twisting angle of the materials during trans–cis photoisomerization was observed. Furthermore, the chiral compounds were dissolved in nematic (N) liquid crystals (LCs) to produce a chiral N phase with a helical structure. The mixture exhibited a dual molecular response to temperature and light. Helical pitch length of the chiral N LC decreased with increasing temperature because of a molecular twisting motion of the binaphthyl moiety, resulting in a stabilization of the LC helical structure. On the other hand, length of the helical pitch increased upon photoirradiation, and the resulting LC mixture was found to show photoswitching between chiral N and N phases upon trans–cis isomerization of the azobenzene moiety. The photoinduced deformation of the LC helical structure was derived from a bent shape of cis isomer of the azobenzene moiety in the chiral dopant. This dynamic modulation of the self-organizing helical structure was based on dual and selective molecular motions of the guest materials induced by external stimuli.

## Introduction

Bistable systems based on molecular machines have attracted much attention because they can change their motion in response to a variety of external stimuli such as electric field, temperature, pH, ionic strength, and light.<sup>1</sup> Photoresponsive molecular machines have received a great deal of attention in the past decade: their high sensitivity and fast response are of great interest for molecular-level devices such as light-driven switches, memories, and logic gates.<sup>1b,g,i</sup> The molecular response should be reversible, and two different states could be interchanged effectively by incident light. Photochromic reactions are one of the most promising strategies of bistable systems and enable an elegant control of a molecular structure. Azobenzene is a typical photochromic compound, which changes its molecular shape upon photoirradiation: it possesses a rod-like shape in a trans form while a cis isomer exhibits a bent shape.<sup>2</sup> The differences in the molecular shapes give rise to significant

change in viscosity,<sup>3</sup> polarity,<sup>4</sup> and refractive index<sup>5</sup> of azobenzene moieties due to trans–cis photoisomerization. Aida et al. reported scissor-like molecular machines containing azobenzene moieties, which exhibited reversible manipulation of a guest molecule with the aid of coordination between zinc porphyrin and nitrogenous compounds.<sup>6</sup> Furthermore, the azobenzene moiety shows a large change in molecular length upon photoirradiation: the distance between 4- and 4'-carbons decreases from 9.0 Å (trans form) to 5.5 Å (cis form). Several groups have demonstrated light-driven molecular machines, especially rotaxanes, by means of change in molecular length of azobenzene moieties upon trans–cis photoisomerization.<sup>7</sup>

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(1) For reviews, see: (a) Balzani, V.; Credi, A.; Venturi, M. *Molecular Devices and Machines*; Wiley-VCH: Weinheim, Germany, 2004. (b) Feringa, B. L., Ed. *Molecular Switches*; Wiley-VCH: Weinheim, Germany, 2001. (c) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3349. (d) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789. (e) Collin, J.-P.; Sauvage, J.-P. *Chem. Lett.* **2005**, *34*, 742. (f) Kottas, G. S.; Clarke, L. I.; Horinek, D.; Michl, J. *Chem. Rev.* **2005**, *105*, 1281. (g) Feringa, B. L. *J. Org. Chem.* **2007**, *72*, 6635. (h) Ballardini, R.; Ceroni, P.; Credi, A.; Gandolfi, M. T.; Maestri, M.; Semararo, M.; Venturi, M.; Balzani, V. *Adv. Funct. Mater.* **2007**, *17*, 740. (i) Angelos, S.; Johansson, E.; Stoddart, J. F.; Zink, J. I. *Adv. Funct. Mater.* **2007**, *17*, 2261. (j) Credi, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 5472.

(2) For reviews, see: (a) Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915. (b) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847. (c) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139. (d) Ikeda, T. *J. Mater. Chem.* **2003**, *13*, 2037. (3) (a) Irie, M.; Hirano, Y.; Hashimoto, S.; Hayashi, K. *Macromolecules* **1981**, *14*, 262. (b) Lee, C. T., Jr.; Smith, K. A.; Hatton, T. A. *Macromolecules* **2004**, *37*, 5397. (c) Tomatsu, I.; Hashidzume, A.; Harada, A. *J. Am. Chem. Soc.* **2006**, *128*, 2226. (4) (a) Büchel, M.; Weichart, B.; Minx, C.; Menzel, H.; Johannsmann, D. *Phys. Rev. E* **1997**, *55*, 455. (b) Ichimura, K.; Oh, S.-K.; Nakagawa, M. *Science* **2000**, *288*, 1624. (c) Khoukh, S.; Oda, R.; Labrot, Th.; Perrin, P.; Tribet, C. *Langmuir* **2007**, *23*, 94. (5) (a) Shi, Y.; Steier, W. H.; Yu, L.; Chen, M.; Dalton, L. R. *Appl. Phys. Lett.* **1991**, *58*, 1131. (b) Morino, S.; Machida, S.; Yamashita, T.; Horie, K. *J. Phys. Chem.* **1995**, *99*, 10280. (c) Bian, S.; Li, L.; Kumar, J.; Kim, D. Y.; Williams, J.; Tripathy, S. K. *Appl. Phys. Lett.* **1998**, *73*, 1817. (d) Barille, R.; Ahmadi-Kandjani, S.; Ortyl, E.; Kucharski, S.; Nunzi, J.-M. *Phys. Rev. Lett.* **2006**, *97*, 048701. (e) Okano, K.; Tsutsumi, O.; Shishido, A.; Ikeda, T. *J. Am. Chem. Soc.* **2006**, *128*, 15368. (6) (a) Muraoka, T.; Kinbara, K.; Kobayashi, Y.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 5612. (b) Muraoka, T.; Kinbara, K.; Aida, T. *Nature* **2006**, *440*, 512. (c) Muraoka, T.; Kinbara, K.; Aida, T. *Chem. Commun.* **2007**, 1441. (d) Muraoka, T.; Kinbara, K.; Wakamiya, A.; Yamaguchi, S.; Aida, T. *Chem. Eur. J.* **2007**, *13*, 1724.

Liquid crystals (LCs) have been used as active media in LC displays and spatial light modulators, and they are typical self-organizing materials with unique properties.<sup>8</sup> Cooperative motion of LC moieties is most advantageous in changing an orientation of LCs by external stimuli. For example, a small amount of chiral moieties is incorporated into nematic (N) LCs, and the resulting guest/host LC mixtures are found to exhibit a helical structure of a chiral N phase.<sup>9</sup> Chiral N LCs show unique properties arising from helical structures: selective reflection of light. The selective reflection is observed only when the helix axis is normal to a substrate. Furthermore, in general as the helical pitch is very sensitive to temperature, pressure, and impurity, the wavelength of the selective reflection is also strongly dependent on these factors. Chiral N LCs are expected as active media for reflection-type displays, particularly if the wavelength of the selective reflection is in a visible region, these materials have high potential for full-color displays with extremely low energy consumption. Furthermore, if pitch length of the chiral N phase can be altered by light, all-optical control of the selective reflection could be possible. For instance, when azobenzene-doped LC systems are irradiated to cause trans–cis photoisomerization, change in the molecular shape of the azobenzene moiety is responsible for order–order or order–disorder photoinduced modulation of LCs.<sup>2d</sup> Sackmann reported the first example of a photomodulation of chiral N LCs.<sup>10</sup> He found that the helical pitch of the LCs could be altered by trans–cis photoisomerization of azobenzene and stilbene derivatives. More recently, several groups have examined change in the helical pitch of the chiral N LCs doped with azobenzene derivatives in the visible region.<sup>11</sup> Photoirradiation of the chiral N LCs results in change in the reflection color due to the ratio of isomers of

the azobenzene moieties. When photoirradiation ceased at various exposure energies, rewritable full-color images<sup>11b,h</sup> and patterns<sup>11f,g</sup> were obtained. Feringa et al. exploited helical-shaped overcrowded alkenes as bistable compounds to be used as chiroptical materials.<sup>1g</sup> Steric hindrance between the groups attached to the alkene-based bond forces these molecules to adopt the helical structure. Upon irradiation at appropriate wavelengths, these materials undergo cis–trans photoisomerization, which simultaneously results in change in helicity of the molecules. They also successfully demonstrated that a light-driven molecular rotor acts as a chiral dopant that can induce the chiral N phase.<sup>12</sup> The molecular rotor rotates an object placed on a chiral N LC film that exceeded the size of the dopant by a factor of  $10^4$ .<sup>12e,f</sup> A surface of the LC film was found to possess a uniform relief, whose periodicity coincided with typical chiral N textures. The authors concluded the surface relief originates from the helical superstructure in the LC film, which results in the presence of the light-driven chiral molecular rotor.

Recently, we designed and synthesized a novel type of a light-driven bistable chiral material containing an azobenzene moiety as a photoresponsive part and a binaphthyl moiety as a chiral part in a single species.<sup>13</sup> 2,2'-Disubstituted binaphthyl derivatives have been used as asymmetric catalysts and chiral recognition agents because of their stable chiral configuration.<sup>14</sup> The binaphthyl moiety is observed to show change in a dihedral angle ( $\theta$ ) between two naphthalene rings without racemization. The moieties are classified into two categories: one is a *cisoid* ( $0^\circ < \theta < 90^\circ$ ) and the other is a *transoid* ( $90^\circ < \theta < 180^\circ$ ) conformation. If structural modifications are attempted, it is possible to change their dihedral angles. We found that the chiral material exhibits photoinduced change in the dihedral angle of the binaphthyl moiety by means of trans–cis isomerization of the azobenzene moiety. The cyclic linkage of the material gives a strong correlation among terminal groups of the azobenzene moiety attached to the binaphthyl moiety. We consider if materials precisely change the molecular shape of each segment in response to external stimuli; these materials can be characterized as a new type of multistable molecular systems.<sup>15</sup> Furthermore, if the materials exhibit dual molecular motions, one may control the self-organizing helical structure of the LC in a unique fashion.

## Experimental Section

**Synthesis and Characterization.** Photoresponsive chiral materials, **RBAC4** and **SBAC4**, were prepared from 4-butyl-4'-hydroxya-

- (7) (a) Murakami, H.; Kawabuchi, A.; Kotoo, K.; Kunitake, M.; Nakashima, N. *J. Am. Chem. Soc.* **1997**, *119*, 7605. (b) Balzani, V.; Credi, A.; Marchioni, F.; Stoddart, J. F. *Chem. Commun.* **2001**, 1860. (c) Stanier, C. A.; Alderman, S. J.; Claridge, T. D. W.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 1769. (d) Qu, D.-H.; Wang, Q.-C.; Ren, J.; Tian, H. *Org. Lett.* **2004**, *6*, 2085. (e) Murakami, H.; Kawabuchi, A.; Matsumoto, R.; Ido, T.; Nakashima, N. *J. Am. Chem. Soc.* **2005**, *125*, 15891. (f) Qu, D.-H.; Wang, Q.-C.; Ma, X.; Tian, H. *Chem. Eur. J.* **2005**, *11*, 5929. (g) Qu, D.-H.; Wang, Q.-C.; Tian, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 5296. (h) Tomatsu, I.; Hashidzume, A.; Harada, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 4605. (i) Ma, X.; Qu, D.; Ji, F.; Wang, Q.; Zhu, L.; Xu, Y.; Tian, H. *Chem. Commun.* **2007**, 1409. (j) Inoue, Y.; Kuad, P.; Okumura, Y.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2007**, *129*, 6396. (k) Sakai, T.; Murayama, H.; Nagano, S.; Takeoka, Y.; Kidowaki, M.; Ito, K.; Seki, T. *Adv. Mater.* **2007**, *19*, 2023. (l) Ma, X.; Wang, Q.; Qu, D.; Xu, Y.; Ji, F.; Tian, H. *Adv. Funct. Mater.* **2007**, *17*, 829.
- (8) (a) Demus, D.; Goodby, J.; Gray, G. W.; Spiess, H.-W.; Vill, V. *Handbook of Liquid Crystals*; Wiley-VCH: Weinheim, Germany, 1998; Vol. 1, Fundamentals. (b) Chandrasekhar, S. *Liquid Crystals*, 2nd Ed.; Cambridge University Press: New York, 1992.
- (9) Tamaoki, N. *Adv. Mater.* **2001**, *13*, 1135, and references therein.
- (10) Sackmann, E. *J. Am. Chem. Soc.* **1971**, *93*, 7088.
- (11) (a) Bobrovsky, A. Y.; Boiko, N. I.; Shibaev, V. P.; Springer, J. *Adv. Mater.* **2000**, *12*, 1180. (b) Tamaoki, N.; Song, S.; Moriyama, M.; Matsuda, H. *Adv. Mater.* **2000**, *12*, 94. (c) Lee, H.-K.; Doi, K.; Harada, H.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Phys. Chem. B* **2000**, *104*, 7023. (d) Moriyama, M.; Mizoshita, N.; Yokota, T.; Kishimoto, K.; Kato, T. *Adv. Mater.* **2003**, *15*, 1335. (e) Li, Q.; Li, L.; Kim, J.; Park, H.-S.; Williams, J. *Chem. Mater.* **2005**, *17*, 6018. (f) Yoshioka, T.; Ogata, T.; Nonaka, T.; Moritsugu, M.; Kim, S.-M.; Kurihara, S. *Adv. Mater.* **2005**, *17*, 1226. (g) Hrozhyk, U. A.; Serak, S. V.; Tabiryan, N. V.; Burnning, T. J. *Adv. Funct. Mater.* **2007**, *17*, 1735. (h) Li, Q.; Green, L.; Venkataraman, N.; Shiyantovskaya, I.; Khan, A.; Urbas, A.; Doane, J. W. *J. Am. Chem. Soc.* **2007**, *129*, 12908.

- (12) (a) Feringa, B. L.; Huck, N. P. M.; van Doren, H. A. *J. Am. Chem. Soc.* **1995**, *117*, 9929. (b) Huck, N. P. M.; Jager, W. F.; de Lange, B.; Feringa, B. L. *Science* **1996**, *273*, 1686. (c) van Delden, R. A.; van Gelder, M. B.; Huck, N. P. M.; Feringa, B. L. *Adv. Funct. Mater.* **2003**, *13*, 319. (d) Eelkema, R.; Feringa, B. L. *Chem. Asian J.* **2006**, *1*, 367. (e) Eelkema, R.; Pollard, M. M.; Vicario, J.; Katsonis, N.; Ramon, B. S.; Bastiaansen, C. W. M.; Broer, D. J.; Feringa, B. L. *Nature* **2006**, *440*, 163. (f) Eelkema, R.; Pollard, M. M.; Katsonis, N.; Vicario, J.; Broer, D. J.; Feringa, B. L. *J. Am. Chem. Soc.* **2006**, *128*, 14397.
- (13) Kawamoto, M.; Aoki, T.; Wada, T. *Chem. Commun.* **2007**, 930.
- (14) (a) Cram, D. J.; Cram, J. M. *Science* **1974**, *183*, 803. (b) Pu, L. *Chem. Rev.* **1998**, *98*, 2405. (c) Gin, M. S.; Yokozawa, T.; Prince, R. B.; Moore, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 2643. (d) Hill, D. J.; Moore, J. S. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5053.

zobenzene in two steps as shown in Supporting Information, Scheme S1. Unless otherwise noted, materials and solvents were purchased from commercial suppliers and were used without further purification. 4-Butyl-4'-hydroxyazobenzene, 1,3-dibromopropane, (*R*)-2,2'-dihydroxy-1,1'-binaphthyl, and (*S*)-2,2'-dihydroxy-1,1'-binaphthyl were purchased from Tokyo Kasei Kogyo Co. Ltd. 1-Bromopropane, potassium carbonate, and 2-butanone were purchased from Kanto Kagaku Co. Ltd. A nematic liquid crystal (LC), ZLI-3282 (mixture of fluorophenylcyclohexane derivatives), was purchased from Merck Ltd. Japan. The compounds synthesized were identified by means of <sup>1</sup>H NMR (JEOL AL400), matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy (PE Biosystems Voyager Elite), and elemental analysis. 2,5-Dihydroxy benzoic acid or 9-nitroanthracene was used as the matrix.

**4-Butyl-4'-(3-bromopropoxy)azobenzene (1).** A mixture of 4-butyl-4'-hydroxyazobenzene (2.0 g, 7.8 mmol), 1,3-dibromopropane (6.4 g, 31 mmol), and potassium carbonate (1.6 g, 12 mmol) in 2-butanone (50 mL) was refluxed for 48 h. The crude product was extracted with ethyl acetate and water and then washed with brine before drying over anhydrous magnesium sulfate. The solvent was evaporated off under reduced pressure, and the solid residue was purified by column chromatography on silica gel (eluents: ethyl acetate:hexane = 1:10) to yield **1** (2.1 g, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ = 0.94 (t, 3H, Ph-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.33–1.43 (m, 2H, Ph-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.55–1.68 (m, 2H, Ph-CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>CH<sub>3</sub>), 2.36 (t, 2H, Ph-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 2.68 (t, 2H, Ph-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.63 (t, 2H, Ph-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 4.19 (t, 2H, Ph-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 7.01 (d, 2H, aromatic rings), 7.29 (d, 2H, aromatic rings), 7.79 (d, 2H aromatic rings), 7.83 (d, 2H, aromatic rings).

**(*R*)-2,2'-Bis[3-(4'-(4-butylphenylazo)phenoxy)propoxy]-1,1'-binaphthyl (RBAC4).** A mixture of **1** (2.0 g, 5.3 mmol), (*R*)-2,2'-dihydroxy-1,1'-binaphthyl (0.69 g, 2.4 mmol), and potassium carbonate (1.1 g, 8.0 mmol) in 2-butanone (50 mL) was refluxed for 48 h. The crude product was extracted with ethyl acetate and water and then washed with brine before drying over anhydrous magnesium sulfate. The solvent was evaporated off under reduced pressure, and the solid residue was purified by column chromatography on silica gel (eluents: toluene/hexane = 5:1). Furthermore, the product was purified by size exclusion chromatography (Shodex K-5001). Eluent was only chloroform at a flow rate of 10 mL min<sup>-1</sup>. The second fraction was collected and evaporated to dryness, to afford **RBAC4** (1.8 g, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ = 0.92 (t, 6H, Ph-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.33–1.42 (m, 4H, Ph-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.60–1.68 (m, 4H, Ph-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.77–1.89 (m, 4H, Ph-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O-binaphthyl), 2.67 (t, 4H, Ph-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.34–3.44 (m, 4H, Ph-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O-binaphthyl), 3.99–4.11 (m, 4H, Ph-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O-binaphthyl), 6.56 (d, 4H, aromatic rings), 7.15 (d, 4H, aromatic rings), 7.30 (d, 6H aromatic rings), 7.38 (d, 2H aromatic rings), 7.78–7.86 (m, 10H, aromatic rings), 7.91 (d, 2H aromatic rings). MALDI-TOF-MS (*m/z*): 875 [M<sup>+</sup>]. Anal. Calcd for C<sub>38</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>: C, 79.60; H, 6.68; N, 6.40. Found: C, 79.70; H, 6.80; N, 6.40.

**(*S*)-2,2'-Bis[3-(4'-(4-butylphenylazo)phenoxy)propoxy]-1,1'-binaphthyl (SBAC4).** **SBAC4** was prepared from **1** in a method similar to that described for **RBAC4**. Yield: 75%. MALDI-TOF-MS (*m/z*): 875 [M<sup>+</sup>]. Anal. Calcd for C<sub>38</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>: C, 79.60; H, 6.68; N, 6.40. Found: C, 79.61; H, 6.74; N, 6.36.

**4-Butyl-4'-propoxyazobenzene (C3OAC4, a model compound of RBAC4 and SBAC4).** A mixture of 4-butyl-4'-hydroxyazobenzene (5.1 g, 20 mmol), 1-bromopropane (2.9 g, 24 mmol), and potassium carbonate (4.1 g, 30 mmol) in acetone (100 mL) was refluxed for 24 h. The crude product was extracted with methylene

chloride and water and then washed with brine before drying over anhydrous magnesium sulfate. The solvent was evaporated off under reduced pressure, and the solid residue was purified by recrystallization (eluent: methanol) to yield the model compound (4.8 g, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ = 0.94 (t, 3H, Ph-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.06 (t, 3H, Ph-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.33–1.41 (m, 2H, Ph-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.60–1.68 (m, 2H, Ph-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.80–1.88 (m, 2H, Ph-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.68 (t, 2H, Ph-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.00 (t, 2H, Ph-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 6.99 (d, 2H, aromatic rings), 7.29 (d, 2H, aromatic rings), 7.79 (d, 2H aromatic rings), 7.88 (d, 2H, aromatic rings). MALDI-TOF-MS (*m/z*): 296 [M<sup>+</sup>]. Anal. Calcd for C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>O: C, 76.99; H, 8.16; N, 9.45. Found: C, 77.01; H, 8.27; N, 9.49.

**(*R*)-2,2'-Bis[3-(2''-phenoxy)propoxy]-1''-azo-1,1'-binaphthyl ((*R*)-Azo).** (*R*)-Azo was synthesized as previously reported.<sup>13</sup>

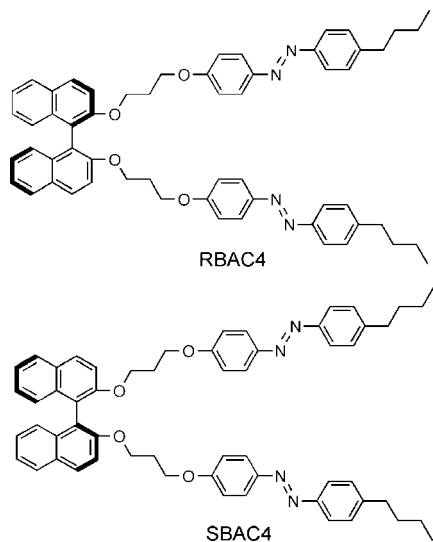
Absorption spectra were measured using a JASCO V-530. CD spectra were obtained using a JASCO J-720. Thermal behavior of the compound was examined on these spectrometers equipped with a JASCO EHC-477. Morphological changes were examined by Mettler hot-stage models (FP-90 and FP-82HT). Samples were irradiated at various wavelengths (365 nm (light intensity: 6 mW cm<sup>-2</sup>), 405 nm (5 mW cm<sup>-2</sup>), and 436 nm (7 mW cm<sup>-2</sup>)) from a 120 W high-pressure mercury lamp (Asahi Spectra REX-120) through glass filters (Asahi Spectra HQBP365, HQBP405, and HQBP436, respectively). Each isomer of the photoresponsive materials at a photostationary state was determined by high-performance liquid chromatography (HPLC; GL Science Inc. SIL100A). Eluents were 1,4-dioxane/hexane = 1:3 at a flow rate of 0.7 mL min<sup>-1</sup>. Their photostationary states were achieved by irradiation of incident light to cause trans-cis photoisomerization of the azobenzene moieties. We checked absorbance of an isosbestic point at 414 nm as the monitoring wavelength.

**Investigation of LC Alignment Behavior in a Wedge Cell.** Chiral compound-doped LC was mixed with ZLI-3282 at various concentrations (3–7 wt %) in a chloroform solution. The solvent was removed under reduced pressure at 40 °C. Thermotropic behavior of LC mixtures was evaluated by differential scanning calorimetry (DSC; Perkin-Elmer DSC7, heating and cooling rate: 3 °C min<sup>-1</sup>). A wedge cell was composed of two glass substrates with rubbed polyimide layers. The thickness of the wedge cell was as follows: one was 10 μm and the other was 550 μm. Samples were filled with the mixture by capillary action at room temperature. Orientation behavior of LC moieties was determined with a polarizing microscope (Nikon E600WPOL) equipped with Mettler hot-stage models and a digital camera (Nikon CoolPix995).

## Results and Discussion

Figure 1 shows chemical structures of **RBAC4** and **SBAC4** used in this study. In the first synthetic step, the intermediate (**1**) was prepared from 4-butyl-4'-hydroxyazobenzene with 4 equiv of 1,3-dibromopropane in 2-butanone. If 1,3-dibromopropane was reacted with (*R*)-2,2'-dihydroxy-1,1'-binaphthyl or (*S*)-2,2'-dihydroxy-1,1'-binaphthyl in the same solvent, binaphthyl derivatives with cyclic structures were obtained.<sup>16</sup> Furthermore, the chiral compounds could not be isolated by column chromatography on silica gel because they exhibited highly viscous oily substances at room temperature. The final compounds were successfully purified by the use of size exclusion chromatography. **RBAC4** and **SBAC4** have the same molecular characteristics except for opposite chirality. Maximum absorption wavelengths, λ<sub>max</sub> (ε M<sup>-1</sup> cm<sup>-1</sup>), of **RBAC4** and

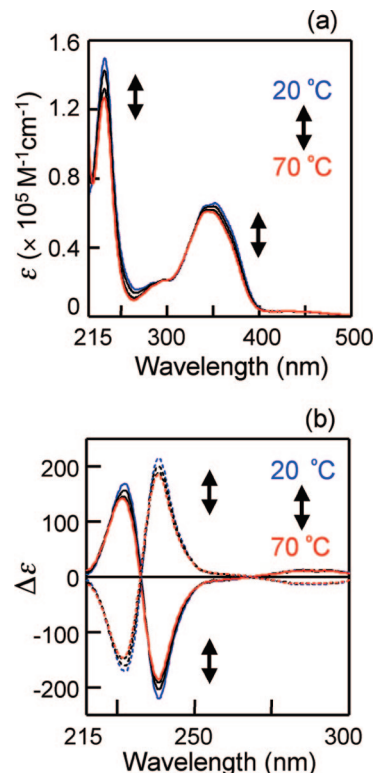




**Figure 1.** Chemical structures of **RBAC4** and **SBAC4** used in this study.

**SBAC4** in 1,4-dioxane were 231 (148 300), 296 (23 000), 341 (48 900), 353 (47 400), and 438 nm (4100). We determined that the  ${}^1B_b$  (231 nm) band corresponds to a long axis of a naphthyl group, while  ${}^1L_a$  (296 nm) corresponds to a short axis of it. On the other hand, the *trans* form of the azobenzene moiety in **RBAC4** exhibited absorption maxima at 353 nm due to a  $\pi-\pi^*$  transition and at 438 nm due to an  $n-\pi^*$  transition. CD spectra of the compound in 1,4-dioxane exhibited symmetrical structures with two exciton couplets: one peak around at 240 nm is due to  ${}^1B_b$  transitions of the two naphthyl moieties and the other peak around at 360 nm is derived from  $\pi-\pi^*$  transitions between two azobenzene moieties, respectively.<sup>17</sup> It also indicates the exciton couplet of azobenzene moieties reflects the same configuration of the binaphthyl moiety and follows the rules of exciton chirality.<sup>18</sup>

We measured absorption spectra of **RBAC4** in 1,4-dioxane at various temperatures. It was found that absorbance of the  ${}^1B_b$  band of the binaphthyl moiety and  $\pi-\pi^*$  band of the azobenzene moiety are changed by temperature repeatedly



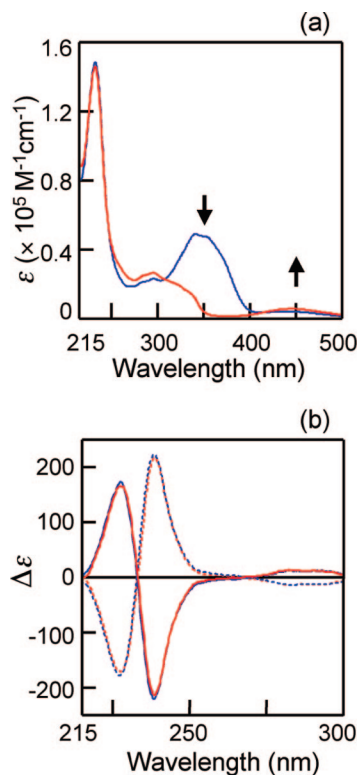
**Figure 2.** Change in absorption spectra of **RBAC4** (a) and CD spectra of **RBAC4** (solid line) and **SBAC4** (dotted line) (b) in 1,4-dioxane at various temperatures.

(Figure 2a). In contrast, isosbestic points of  ${}^1L_a$  and  $n-\pi^*$  bands of the material were observed in the overall spectra. CD spectra also show change in a value of  $\Delta\epsilon$  ( ${}^1B_b$  transitions) of the binaphthyl moiety at 238 nm (Figure 2b). Changes in the values of  $\epsilon_{20^\circ\text{C}} - \epsilon_{70^\circ\text{C}}$  and  $|\Delta\epsilon_{70^\circ\text{C}} - \Delta\epsilon_{20^\circ\text{C}}|$  were 21 800 and 30, respectively. The value is dependent on a dihedral angle between two naphthyl moieties.<sup>14b,17</sup> Furthermore, Rosini et al. calculated the relationship between the value of  $\Delta\epsilon$  and the dihedral angle.<sup>19</sup> We have pointed out that a molecular twisting of the binaphthyl moiety can be observed when the value of  ${}^1B_b$  band is changed.<sup>13</sup> On the basis of these results of the thermal response and the calculation, applied temperature alters the dihedral angle of the chiral materials and the change in the dihedral angle is estimated to be about several degrees.

Irradiation with UV light induced a decrease in the  $\pi-\pi^*$  band and an increase in the  $n-\pi^*$  band (Figure 3a). This indicates that *trans*-*cis* photoisomerization of **RBAC4** takes place in 1,4-dioxane on photoirradiation. Furthermore, the exciton couplet, which is derived from  $\pi-\pi^*$  transitions between two azobenzene moieties, almost disappeared due to *trans*-*cis* photoisomerization of the materials (see Supporting Information). It is also interesting to note that degrees of change in  $\epsilon_{\text{after}} - \epsilon_{\text{before}}$  and  $|\Delta\epsilon_{\text{after}} - \Delta\epsilon_{\text{before}}|$  of  ${}^1B_b$  band are as low as 1% after photoirradiation at 365 nm (Figure 3b). These results indicate the values of  $\epsilon_{\text{after}} - \epsilon_{\text{before}}$  and  $|\Delta\epsilon_{\text{after}} - \Delta\epsilon_{\text{before}}|$  of **RBAC4** and **SBAC4** based on a thermal response are 10–15 times higher than those of the chiral materials based on a photoresponse. Since the material

- (15) For example, (a) Achatz, J.; Fischer, C.; Salbeck, J.; Daub, J. *J. Chem. Soc., Chem. Commun.* **1991**, 504. (b) Kawai, S. H.; Gilat, S. L.; Ponsinet, R.; Lehn, J.-M. *Chem. Eur. J.* **1995**, *1*, 285. (c) Pina, F.; Roque, A.; Melo, M. J.; Maestri, M.; Belladelli, L.; Balzani, V. *Chem. Eur. J.* **1998**, *4*, 1184. (d) Gobbi, L.; Seiler, P.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 674. (e) Raymo, F. M.; Giordani, S. *J. Am. Chem. Soc.* **2001**, *123*, 4651. (f) Goodman, A.; Breinlinger, E.; Ober, M.; Rotello, V. M. *J. Am. Chem. Soc.* **2001**, *123*, 6213. (g) Zhao, W.; Carreira, E. M. *J. Am. Chem. Soc.* **2002**, *124*, 1582. (h) Bergamini, G.; Saudan, C.; Ceroni, P.; Maestri, M.; Balzani, V.; Gorka, M.; Lee, S.-K.; van Heyst, J.; Vögtle, F. *J. Am. Chem. Soc.* **2004**, *126*, 16466. (i) Muramatsu, S.; Kinbara, K.; Taguchi, H.; Ishii, N.; Aida, T. *J. Am. Chem. Soc.* **2006**, *128*, 3764. (j) Ferrer, B.; Rogez, G.; Credi, A.; Ballardini, R.; Gandolfi, M. T.; Balzani, V.; Liu, Y.; Tseng, H.-R.; Stoddart, J. F. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 18411. (k) Andréasson, J.; Straight, S. D.; Bandyopadhyay, S.; Mitchell, R. H.; Moore, T. A.; Moore, A. L.; Gust, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 958. (16) Simpson, J. E.; Daub, G. H.; Hayes, F. N. *J. Org. Chem.* **1973**, *38*, 1771. (17) (a) Di Bari, L.; Pescitelli, G.; Salvadori, P. *J. Am. Chem. Soc.* **1999**, *121*, 7998. (b) Di Bari, L.; Pescitelli, G.; Marchetti, F.; Salvadori, P. *J. Am. Chem. Soc.* **2000**, *122*, 6395. (18) Berova, N.; Nakanishi, K., Eds. *Circular Dichroism, Principles and Applications*; Wiley-VCH: New York, 2000.

- (19) Rosini, C.; Superchi, S.; Peerlings, H. W. I.; Meijer, E. W. *J. Org. Chem.* **2000**, 61.



**Figure 3.** Change in absorption spectra of **RBAC4** (a) and CD spectra of **RBAC4** (solid line) and **SBAC4** (dotted line) in 1,4-dioxane before (blue) and after irradiation (red) at 365 nm ( $6 \text{ mW cm}^{-2}$ , 30 s) at room temperature.

**Table 1.** Ratio of Trans (t) and Cis (c) Isomers of **RBAC4** at the Photostationary State in 1,4-Dioxane

irradiation wavelength	(t,t)	(t,c)	(c,c)
365 nm	0	0.20	0.80
405 nm	0.25	0.54	0.21
436 nm	0.53	0.40	0.07

possesses two azobenzene moieties, it is assumed that trans,trans (t,t), trans,cis (t,c), and cis,cis (c,c) isomers of the materials observed are based on the ratio of the trans or cis form of azobenzenes. The ratios at the photostationary state were measured by HPLC (Table 1). After photoirradiation in 1,4-dioxane three possible isomers could be obtained. Each fraction at 11.8, 15.3, and 20.7 min was attributable to (t,t), (t,c), and (c,c) isomers, respectively. **RBAC4** shown in Table 1 exhibited effective trans–cis photoisomerization of the azobenzene moieties with no (t,t) isomer when exposed to incident light at 365 nm. On the other hand, some (t,t) isomer of **RBAC4** remained unchanged after photoirradiation at 405 or 436 nm. These results suggest that the materials undergo not only trans–cis isomerization but also cis–trans isomerization of the azobenzene units upon photoirradiation of visible light. We also found **RBAC4** and **SBAC4** do not change their dihedral angle, even though a sufficient amount of the cis form of the azobenzene moiety is produced upon photoirradiation at 365 nm.

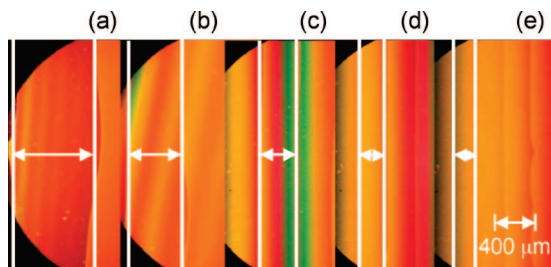
When the materials in 1,4-dioxane were kept in the dark, absorbance was restored because of cis–trans thermal backisomerization. First-order rate constants ( $k$ ) and thermodynamic parameters such as enthalpy of activation ( $\Delta H^\ddagger$ ) and entropy of activation ( $\Delta S^\ddagger$ ) for thermal cis–trans

isomerization of **RBAC4** were determined according to Eyring equations<sup>20</sup> ( $k$  at 308 K:  $3.7 \times 10^{-5} \text{ s}^{-1}$ ;  $\Delta H^\ddagger$ : 21 kcal mol<sup>-1</sup>;  $\Delta S^\ddagger$ :  $-11 \text{ cal mol}^{-1} \text{ K}^{-1}$ , respectively). To compare thermodynamic parameters of **RBAC4** we selected the chiral cyclic material, (**R**)-**Azo**, and **C3OAC4**. **RBAC4** exhibited a large difference in a value of  $\Delta S^\ddagger$  in comparison with (**R**)-**Azo** ( $k$  at 308 K:  $8.1 \times 10^{-6} \text{ s}^{-1}$ ;  $\Delta H^\ddagger$ : 26 kcal mol<sup>-1</sup>;  $\Delta S^\ddagger$ :  $-1.3 \text{ cal mol}^{-1} \text{ K}^{-1}$ ).  $\Delta S^\ddagger$  reflects the difference in a degree of freedom between ground and transition states. Furthermore, a cis form of the cyclic compound has a steric hindrance or a distorted conformation. This difference in molecular shapes of **RBAC4** and (**R**)-**Azo** is due to change in the stabilization of the molecular structure through cis–trans isomerization. On the other hand, thermodynamic parameters of **C3OAC4** ( $k$  at 308 K:  $4.8 \times 10^{-5} \text{ s}^{-1}$ ;  $\Delta H^\ddagger$ : 20 kcal mol<sup>-1</sup>;  $\Delta S^\ddagger$ :  $-13 \text{ cal mol}^{-1} \text{ K}^{-1}$ ) were almost the same as those of **RBAC4**. These results indicate that since two azobenzene moieties in **RBAC4** are attached at both ends of the binaphthyl moiety through alkyl spacers, they can change simply their molecular shapes by cis–trans backisomerization without twisting behavior. It was also clear that **RBAC4** shows a dual molecular response to temperature and light reversibly.

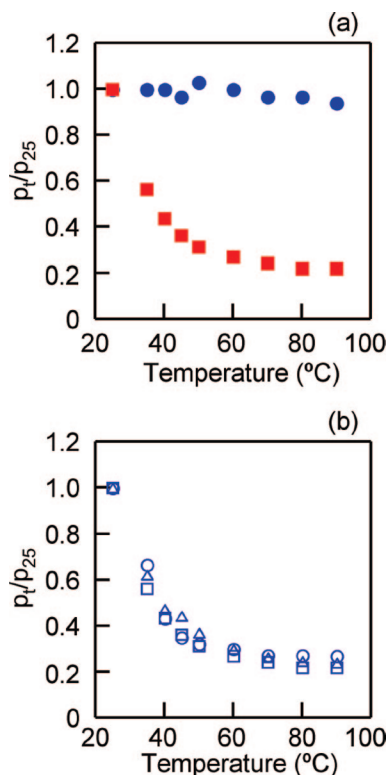
**RBAC4** was added to a N LC host (ZLI-3282, N to isotropic (I) phase transition temperature on cooling: 112 °C) at various concentrations of 3–7 wt % to induce a chiral N phase with a right-handed helical structure. The LC mixtures exhibited a stable chiral N phase in a wide temperature range, because DSC thermograms showed only one peak corresponding to the LC to I phase transition temperatures ( $T_{\text{LC-I}}$ ) on heating and cooling, and no LC to crystalline phase transition peaks were observed to  $-30 \text{ }^\circ\text{C}$ . We also found that  $T_{\text{LC-I}}$  decreases with increasing the concentrations of **RBAC4** (3 wt %: 111 °C, 5 wt %: 109 °C, 7 wt %: 105 °C, respectively). This may be interpreted in terms of the assumption that **RBAC4** acts as a plasticizer, because the material exhibits no LC properties with a low melting point of 17 °C. We checked thermo- and photoreversible behavior of **RBAC4** in the LC host by using the Grandjean–Cano method.<sup>21</sup> The sample was put into a wedge cell, which had been coated with polyimide and rubbed to align LC moieties. The length of a helical pitch at 25 °C was estimated to be 32  $\mu\text{m}$  at a concentration of 7 wt % (see Supporting Information). It was found that pitch length of the mixture decreases with increasing temperature (Figure 4). The maximum degree of change in pitch length was 78% at 90 °C, and this behavior was independent of the concentration of **RBAC4** (Figure 5). These results suggest that change in the helical pitch of the LC is derived from its molecular shape of the (t,t) isomer of **RBAC4**. As mentioned above, **RBAC4** changes its dihedral angle by temperature (Figure 2). Change in the dihedral angle of the dopant would affect the phase structure of the chiral LC, because the molecular shape of the chiral dopant is crucial for the induction of the chiral N phase. If a temperature-dependence of the helical pitch is monitored in the chiral N phase, a

(20) Eyring, H. *Chem. Rev.* **1935**, *17*, 65.

(21) (a) Grandjean, F. *C. R. Acad. Sci.* **1921**, *172*, 71. (b) Cano, R. *Bull. Soc. Fr. Mineral Cristallogr.* **1968**, *91*, 20.



**Figure 4.** Polarizing micrographs of liquid-crystalline textures observed in a wedge cell at various temperatures. (a) 25 °C, (b) 35 °C, (c) 40 °C, (d) 60 °C, and (e) 90 °C.

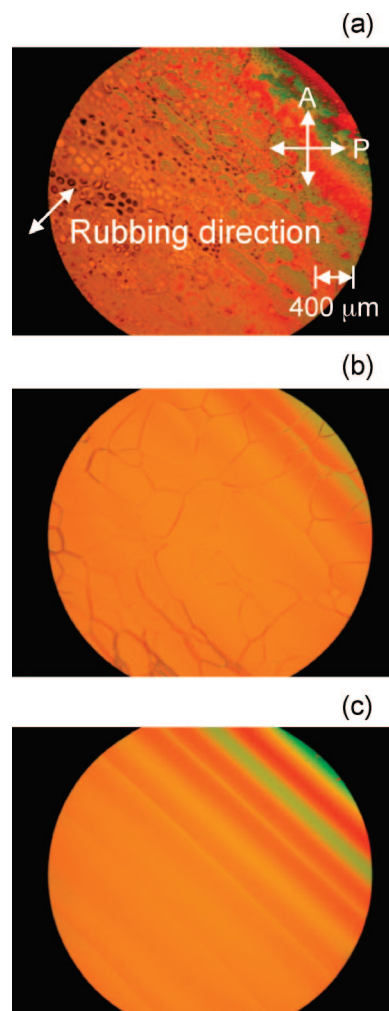


**Figure 5.** (a) Normalized helical pitch length ( $p_t/p_{25}$ ) of a chiral nematic phase doped with **RBAC4** (square) and **(R)-azo** (circle) as a function of temperature.  $p_{25}$  and  $p_t$  are length of the helical pitch at 25 °C and temperature  $t$ , respectively. (b)  $p_t/p_{25}$  of **RBAC4**-doped liquid crystals as a function of temperature at various concentrations of 3 wt % (circle), 5 wt % (triangle), and 7 wt % (square), respectively.

plot of the helical pitch against temperature is found to be almost linear,<sup>22</sup> and  $dp/dT$ , where  $p$  and  $T$  denote helical pitch length and temperature, can be determined from experimental data.<sup>23</sup> It was clear that the **RBAC4**-doped sample shows specific and nonlinear responses in their self-organizing LC structures (Figure 5). Change in helical pitch length is fully reversible, and no LC phase transition occurred in the

(22) For example, (a) Bobrovsky, A. Y.; Boiko, N. I.; Shibaev, V. P. *Adv. Mater.* **1999**, *11*, 1025. (b) Ruslim, C.; Ichimura, K. *J. Phys. Chem. B* **2000**, *104*, 6529. (c) Popova, E. L.; Rozenberg, V. I.; Starikova, Z. A.; Keuker-Baumann, S.; Kitzerow, H.-S.; Hopf, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3411. (d) Thisayukta, J.; Niwano, H.; Takezoe, H.; Watanabe, J. *J. Am. Chem. Soc.* **2002**, *124*, 3354. (e) Geng, J.; Dong, C.; Zhang, L.; Ma, Z.; Shi, L.; Cao, H.; Yang, H. *Appl. Phys. Lett.* **2006**, *89*, 081130. (f) Januszko, A.; Kaszynski, P.; Drzewinski, W. *J. Mater. Chem.* **2006**, *16*, 452.

(23) (a) Demus, D.; Goodby, J.; Gray, G. W.; Spiess, H.-W.; Vill, V. *Handbook of Liquid Crystals*; Wiley-VCH: Weinheim, Germany, 1998; Vol. 2A, Low Molecular Weight Liquid Crystals I, p 365. (b) Baessler, H.; Labes, M. M. *J. Chem. Phys.* **1970**, *52*, 631. (c) Voss, J.; Sackmann, E. *Z. Naturforsch.* **1973**, *28a*, 1496.



**Figure 6.** Polarizing micrographs of liquid-crystalline textures observed in a wedge cell after photoirradiation at 365 nm (a), 405 nm (b), and 436 nm (c) at 50 °C. P: polarizer, A: analyzer.

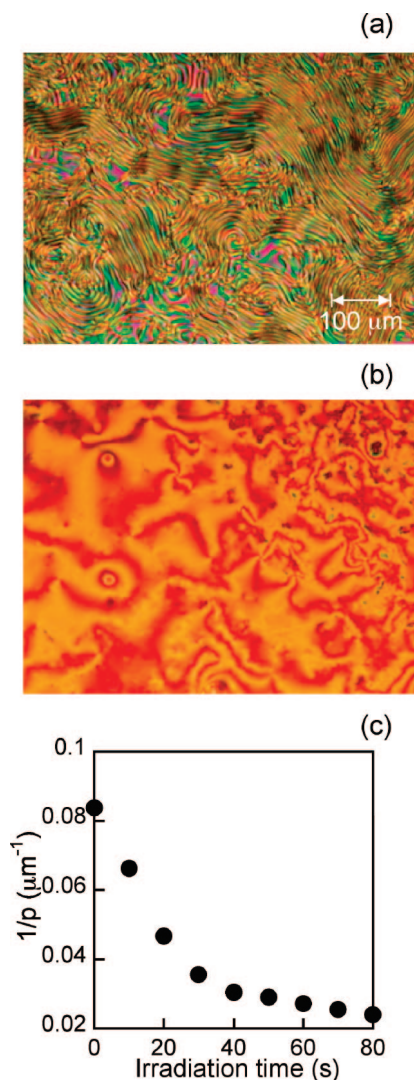
temperature range from 25 to 90 °C. Furthermore, the chiral N LC exhibited the same helical pitch length at a certain temperature while keeping its LC helical structure without any substantial changes around this temperature. We also investigated an the effect of a molecular structure of **(R)-Azo** dispersed in the same LC host at the highest concentration of 1 wt % ( $T_{LC-I}$ : 110 °C, length of a helical pitch: 10  $\mu\text{m}$ ). However, the LC mixture exhibited little change in length of the helical pitch at various temperatures. We found that **(R)-Azo** in the LC phase shows no response to temperature and  $dp/dT \sim 0$ . This indicates no modulation of the LC helical structure can be ascribed to suppression of the molecular twisting motion of **(R)-Azo** due to its cyclic structure in the wide temperature range. The large difference in the molecular shape gives rise to a significant change in the orientation behavior of the chiral N LC; especially, modulation of the helical pitch of the **RBAC4**-doped LC can be carried out stepwise.

Next, we evaluated photoresponsive behavior of the chiral N LC in the wedge cell upon photoirradiation at various wavelengths. Before photoirradiation Grandjean–Cano lines were observed with a polarizing microscope, indicating that the LC moieties aligned parallel to the rubbing direction. Figure 6 shows polarizing optical micrographs of the LC



textures at the photostationary state. It was found the LC samples exhibit differently responsive behavior by incident light with different wavelengths. On the other hand, a recovery of an initial state could be achieved after *cis*–*trans* backisomerization. When the LC mixtures were irradiated with UV light at 365 nm, the Grandjean–Cano lines disappeared after *trans*–*cis* photoisomerization (Figure 6a). It is assumed that the helical structure of the chiral N LC disappears and change in the LC structure occurs. After photoirradiation at 405 nm the orientation of the LC mixture became disordered through the *trans*–*cis* photoisomerization process, and then distorted structures of the Grandjean–Cano lines were obtained by change in the LC alignment (Figure 6b). In contrast, photoirradiation at 436 nm brought about an increase in helical pitch length of the LC with uniformity of the helical alignment (Figure 6c). The degree of change in the helical pitch of the **RBAC4**-doped LC after photoirradiation was about 60%. These results suggest that change in the orientation of the LCs depends on ratios of both isomers of azobenzenes in **RBAC4**, and the *cis* isomer of the azobenzene unit tends to destabilize the phase structure of the LC mixture.

One can see that **RBAC4** should undergo mainly a photochemical process, because the compound changes its molecular shape upon photoirradiation without change in the dihedral angle of the binaphthyl moiety as shown in Figure 3. It has been demonstrated that reversible modulation of the LC helical structure is induced by a photochemical reaction of a small amount of the incorporated photoresponsive moieties. However, irradiation of the LC mixture at 365 nm led to disappearance of the helical structure. We checked bright and dark views alternately every 45° by rotating the optical texture after photoirradiation at 365 nm with respect to the plane of polarization under polarizing microscopic observation. The irradiated site still remains anisotropic as evidenced by birefringence. Figure 7a,b shows change in optical textures of the **RBAC4**-doped LC at the concentration of 7 wt % before and after photoirradiation at 365 nm. When the LC mixture was heated at 50 °C on a glass substrate, fingerprint textures were observed with a polarizing optical microscope, indicating that the sample shows the chiral N phase (Figure 7a). During photoirradiation at 365 nm, the fingerprint textures diminished and typical Schlieren textures of the N phase were observed (Figure 7b). Upon irradiation of the resulting phase with visible light, the initial chiral N phase reverted. Figure 7c shows change in  $1/p$  of the LC mixture upon continuous UV irradiation at 50 °C. Length of a helical pitch was estimated to be 12  $\mu\text{m}$  before UV irradiation. The chiral N mixture was irradiated with UV light at 365 nm, which caused increase in pitch length of the LC phase and almost disappearance of the fingerprint texture on a time scale of 90 s. These results indicate change in the optical textures is due to destabilization of the helical structure by *trans*–*cis* photoisomerization of **RBAC4**.<sup>24</sup> The *trans* form of the azobenzenes has a rod-like shape, which stabilizes the phase structure of the LC phase, while the *cis* form is bent and tends to destabilize the phase structure of

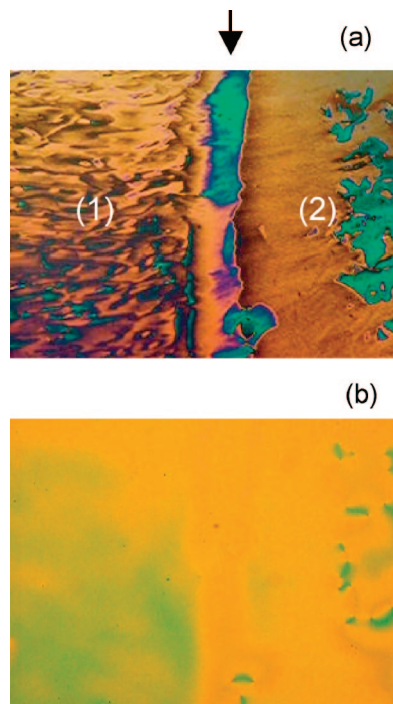


**Figure 7.** Change in the optical textures of **RBAC4**-doped liquid crystals at the concentration of 7 wt % before (a) and after photoirradiation (b) at 365 nm (6 mW/cm<sup>2</sup>, 120 s) at 50 °C. (c)  $1/p$  of the liquid-crystalline mixture as a function of irradiation time at 50 °C upon continuous irradiation at 365 nm.

the mixture.<sup>2d</sup> We also checked a photoinduced change in the LC structure by means of the contact method.<sup>25</sup> The method is one of the most typical techniques for determination of phase structures of LCs. When the miscibility of each material with the same LC phases is observed, a continuous LC texture occurs. However, when these LC phases are different, a narrow band of an interface is observed. Before photoirradiation the discontinuous band of the interface was observed with a polarizing microscope, because each LC showed the chiral N and N phases (Figure 8a). Irradiation of the sample with UV light at 365 nm led to the disappearance of the band (Figure 8b). These results suggest that *trans*–*cis* isomerization of **RBAC4** in the chiral N phase on photoirradiation at 365 nm results in change in an alignment of the LC moieties to the N phase (Figures 7 and 8). For example, Kurihara et al. demonstrated experimentally change in helical pitch length of LCs doped with

(24) If a chiral N phase shows infinite length of a helical pitch, the phase is equal to a N phase.

(25) Gray, G. W.; McDonnell, D. G. *Mol. Cryst. Liq. Cryst. (Lett.)* **1977**, *34*, 211.



**Figure 8.** Optical micrographs of **RBAC4**-doped liquid crystals (1) and host nematic liquid crystals (2) before (a) and after photoirradiation (b) at 365 nm ( $6 \text{ mW cm}^{-2}$ , 90 s) at  $50^\circ\text{C}$ . Arrow in the figure indicates interface between chiral nematic and nematic liquid crystals.

chiral azobenzenes upon trans–cis photoisomerization.<sup>11f,26</sup> To control the helical pitch they prepared mixtures of nematic LCs, chiral materials with no photoresponsive segments, and the chiral azobenzenes and the resulting composites showed a variety of specific characteristics arising from the differences in conditions in the sample preparation. Photoirradiation of the chiral N LCs containing the chiral azobenzenes resulted in change in helical pitch length due to trans–cis photoisomerization at various concentrations. They concluded this photoinduced modulation is due to the bent shape (*cis* isomer) of the chiral azobenzene as a guest molecule. Feringa et al. also have reported chiral diarylethene derivatives for photoswitching between chiral N and N phases.<sup>27</sup> Diarylethenes are a class of photochromic molecules that show high thermal stability of both isomers.<sup>28</sup> The chiral material was dispersed in a N LC at a concentration of 0.7 wt % to produce a chiral N phase. The mixture was irradiated with UV light at 300 nm, which caused increase in helical pitch length of the chiral N phase and appearance of a N phase. The initial chiral N phase was reverted with visible light. Before irradiation a open-ring form isomer of the diarylethene was effective to induce the helical structure of the chiral N phase. On the other hand, the mixture was exposed to UV light to exhibit isomerization from the open-ring form to a closed-ring form. This reversible change was interpreted in terms of a stability of the helical structure arising from the molecular shape of the photoresponsive chiral dopant. In our

system, two azobenzene moieties were incorporated into the binaphthyl moiety, and the resulting material was found to exhibit three different types of isomers, (t,t), (t,c), and (c,c), after photoirradiation. The (t,t) isomer of **RBAC4** is effective to induce the helical structure of the chiral N phase. In contrast, the (t,c) and (c,c) isomers have a steric hindrance and a bent shape due to the *cis* form in the terminal groups according to the results of MOPAC.<sup>29</sup> This difference in molecular shapes of the isomers can give rise to change in the stabilization of the LC helical structure through trans–cis photoisomerization. We found that change in the optical textures is due to large increase in pitch length of the chiral N phase because of destabilization of the helical structure, thus the Schlieren textures of the N phase occur by trans–cis photoisomerization of **RBAC4** (Figure 7). We also demonstrated that the chiral material acts as a phototrigger to induce the deformation of the self-organizing helical structure, depending on ratios of the isomers of the azobenzene moieties.

In this work, we did not try to optimize characteristics such as an ability of an induced helical structure (helical twisting power, HTP). HTP is defined as a value of  $\beta$  according to the following equation:  $\beta = 1/pc$ , where  $p$  and  $c$  are helical pitch length and concentration of a chiral dopant, respectively. The maximum value of  $\beta$  of **RBAC4** was  $+2.0$ .<sup>30</sup> Binaphthyl derivatives are regarded as promising chiral dopants due to stable configuration. Gottarelli and Spada et al. have demonstrated that bridged or open forms of the binaphthyl derivatives act as chiral dopants to induce the chiral N phase when added to N LCs.<sup>31</sup> They also investigated the relationship between the values of  $\beta$  and chemical structures of these chiral dopants. It was clear that the value of the bridged form is much larger than that of the open form, and dihedral angles of the bridged and open forms are about  $55^\circ$  and  $90^\circ$ , respectively. For example, the  $\beta$  values of the bridged form of 2,2'-methylenedioxy-1,1'-binaphthyl<sup>31a</sup> and the open form of 2,2'-dimethoxy-1,1'-binaphthyl<sup>31b</sup> in the same LC host are  $+85$  and  $+1.5$ . Since the bridged form is a rigid or restricted structure, the resulting molecule shows the larger value of  $\beta$ . On the other hand, **RBAC4** and **SBAC4** can be classified as the open forms, and the dihedral angle of the materials is about  $90^\circ$  according to the results of the calculation. The values of  $\beta$  and the dihedral angle of our materials are almost the same as those of 2,2'-dimethoxy-1,1'-binaphthyl. This is due to the introduction of the azobenzene unit in the terminal group, which cannot strongly affect the  $\beta$  value of the material. However, photoirradiation of the **RBAC4**-doped system caused trans–cis isomerization of the guest molecule and resulted in the photomodulation of the chiral N phase. Since there are many

(29) Stewart, J. J. P. *Int. J. Quantum Chem.* **1996**, *58*, 133.

(30) A positive value of  $\beta$  indicates that a chiral N phase has a right-handed helical sense.

(31) (a) Gottarelli, G.; Hibert, M.; Samori, B.; Solladié, G.; Zimmermann, R. *J. Am. Chem. Soc.* **1983**, *105*, 7318. (b) Gottarelli, G.; Spada, G. P.; Bartsch, R.; Solladié, G.; Zimmermann, R. *J. Org. Chem.* **1986**, *51*, 589. (c) Rosini, C.; Franzini, L.; Salvadori, P.; Spada, G. P. *J. Org. Chem.* **1992**, *57*, 6820. (d) Bandini, M.; Casolari, S.; Cozzi, P. G.; Proni, G.; Schmohel, E.; Spada, G. P.; Tagliavini, E.; Umani-Ronchi, A. *Eur. J. Org. Chem.* **2000**, 491. (e) Pieraccini, S.; Ferrarini, A.; Fuji, K.; Gottarelli, G.; Lena, S.; Tsubaki, K.; Spada, G. P. *Chem. Eur. J.* **2006**, *12*, 1121.

(26) (a) Kurihara, S.; Nomiyama, S.; Nonaka, T. *Chem. Mater.* **2000**, *12*, 9. (b) Kurihara, S.; Nomiyama, S.; Nonaka, T. *Chem. Mater.* **2001**, *13*, 1992. (c) Alam, M. Z.; Yoshioka, T.; Ogata, T.; Nonaka, T.; Kurihara, S. *Chem. Eur. J.* **2007**, *13*, 2641.

(27) Denekamp, C.; Feringa, B. L. *Adv. Mater.* **1998**, *10*, 1080.

(28) Irie, M. *Chem. Rev.* **2000**, *100*, 1685.



other photochromic moieties, which can be connected with the binaphthyl unit, we expect new multifunctional materials with good performance to be further developed in this line of molecular design. Furthermore, **RBAC4** and **SBAC4** exhibit dual molecular motions; especially, thermal change in the dihedral angle of the binaphthyl unit in the LC host is a novel and interesting phenomenon. A further detailed investigation in the LC host is now in progress.

### Conclusions

In conclusion, we investigated photo- and thermoresponsive behavior of the chiral materials containing azobenzene and binaphthyl moieties. It was clear that **RBAC4** and **SBAC4** show reversible change in the dihedral angle of the binaphthyl moiety at various temperatures. In contrast, no change in the twisting angle of the materials during trans–cis photoisomerization was observed. We found the materials are a novel type of multistable materials, which show dual response to temperature and light. Furthermore, the induced helical structure of the chiral N phase could be controlled by external fields. Helical pitch length of the chiral N LC decreased with increasing temperature, and the degree of

reversible change in the helical pitch is 78%. The thermal modulation of the helical structure was derived from change in the dihedral angle of the binaphthyl moiety. On the other hand, the LC helical structure disappeared by means of trans–cis isomerization of the azobenzene moiety, resulting in photoswitching between chiral N and N phases. The photoinduced modulation of the LC helical structure was derived from a bent shape of *cis* isomer of the azobenzene moiety in the chiral dopant. We hope that these materials will make it possible to fabricate multistable and multifunctional LC devices driven by external stimuli.

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**Supporting Information Available:** Experimental and analytical details and spectral and kinetic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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