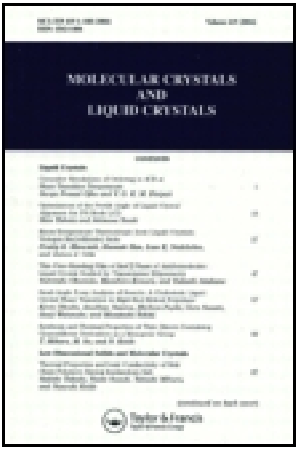

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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# Chirality Induced by Circularly Polarized Light in Liquid Crystalline Twin Dimers with Azo Linkages

Yusuke Hoshino [a], Suk-Won Choi [a], Tatsuya Izumi [a], Yoichi Takanishi [a], Ken Ishikawa [a], Junji Watanabe [a] & Hideo Takezoe [a]

[a] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo, Japan

To cite this article: Yusuke Hoshino, Suk-Won Choi, Tatsuya Izumi, Yoichi Takanishi, Ken Ishikawa, Junji Watanabe & Hideo Takezoe (2007): Chirality Induced by Circularly Polarized Light in Liquid Crystalline Twin Dimers with Azo Linkages, Molecular Crystals and Liquid Crystals, 465:1, 153-163

To link to this article: http://dx.doi.org/10.1080/15421400701205735

*Mol. Cryst. Liq. Cryst.*, Vol. 465, pp. 153–163, 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701205735

# Chirality Induced by Circularly Polarized Light in Liquid Crystalline Twin Dimers with Azo Linkages

**Yusuke Hoshino**
**Suk-Won Choi**
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**Junji Watanabe**
**Hideo Takezoe**
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo, Japan

*Emergence of large circular dichroism (CD) was found in liquid crystal twin dimers with azo linkages, nOAZmAZOn. The compounds with even m are of rod-shape and show the SmA phase, whereas those with odd m are of bent-shape and show the* $SmC_A$ *and* $B_X$ *phases. Right- and left-circular polarized light (CPL) irradiation in the crystal and* $B_X$ *phases induces positive and negative CD, respectively. However, large CD with the opposite sign is induced by decreasing temperature from* $SmC_A$ *to* $B_X$ *under CPL irradiation. Two different mechanisms were discussed.*

**Keywords:** bent-shaped liquid crystal; chirality; circular polarization; twin dimer

## 1. INTRODUCTION

Chirality is one of the most attractive research fields of science. Particularly, chirality control and enantioselectivity have been an important issue in chemistry. In order to produce chiral materials, the uses of chiral molecules and chiral enzymes are indispensable. It is known that chirality can be induced in some achiral systems. Even

This work is partly supported by Grant-in-Aid for Scientific Research (S) (16105003) from the Ministry of Education, Science, Sports and Culture of Japan.

Address correspondence to Hideo Takezoe, Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan. E-mail takezoe.h.aa@m.titech.ac.jp

in this case, however, some chiral stimuli are necessary. One of the conventional methods is the use of circularly polarized light (CPL). This method has been employed to induce chirality in many soft materials such as polymers and liquid crystals [1–9]. The materials have to possess photoisomerizable groups such as azobenzene and stilbene.

Recently we have proposed three methods to control the chirality in achiral bent-core liquid crystal phases, in which spontaneous chiral segregation occurs [10–13]; use of chiral surface [14], CPL [15] and twisted cell geometry [16]. Particularly, the last two methods are quite effective, inducing almost 100% *ee* (enantiomeric excess). In the present study, we focus on the CPL method applied to liquid crystal twin dimers with azo linkages, nOAZmAZOn. We found in a previous work [15] that large circular dichroism (CD) is selectively induced in 12OAZ5AZO12 by decreasing temperature from $\mathrm{SmC_A}$ to $\mathrm{B_X}$ during right- and left-CPL irradiation. In the present study, we extend the measurements to different phases and a different type of mesogens. We found that the irradiation of CPL in the crystal and $\mathrm{B_X}$ phases also induce CD, although the sign of the induced CD is opposite to the previous examples.

## 2. EXPERIMENTAL

The compounds used were $\alpha,\omega$-bis(4-alkoxyazobenzene-4′-carbonyloxy) alkenes, in which two azobenzene moieties with alkoxy tails are linked by a polymethylene spacer. A rod-shaped molecule 8OAZ4AZO8 and a bent-shaped molecule 12OAZ5AZO12 shown in Figure 1 were used. The detailed synthesis and properties of the homologous molecules were described elsewhere [17]. These compounds show the following phase sequence, respectively; isotropic-(168°C)-N-(146°C)-SmA-(145°C)-Cryst and isotropic-(108°C)-$\mathrm{SmC_A}$-(94°C)-$\mathrm{B_X}$. Actual

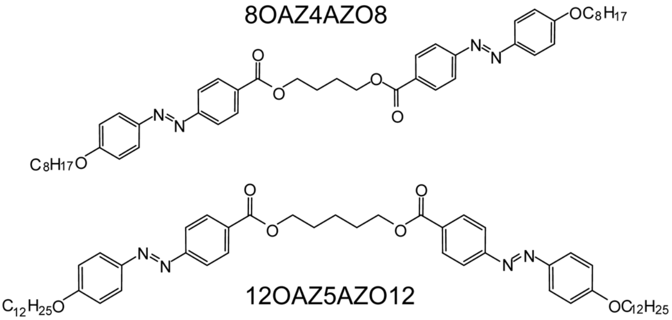

**FIGURE 1** Chemical structures of twin dimers used.

structure of $SmC_A$ is not the conventional $SmC_A$ [18], but is of an interdigited layer with a periodicity of half a molecular length [19]. The low temperature phase $B_X$ phase is a solid-like phase, but is considerably different from a crystal in several aspects like the $B_4$ phase in the classic bent-core (banana shaped) molecules [13,20]. The notable feature is that spontaneous chiral segregation occurs in the $B_X$ phase [10–13], in which no layer chirality [21] exists because of the nontilted phases. A conformational chiral structure [12,13,22,23] is the origin of this type of chiral domain. In the $SmC_A$ phase and the crystal phase, the spontaneous segregation into two chiral domains was not observed.

The materials were sandwiched between two quartz substrates without surface treatment. The cell thickness was about 2 µm. Irradiation was performed with a Mercury lamp after passing through a Fresnel's rhomb and an aperture of $10\,\mathrm{mm}^{\phi}$ to obtain CPL. The irradiated light wavelength was 365 nm, which corresponds to the absorption wavelength of the *trans* form of nOAzmAzOn. The intensity of the irradiation light was $30\,\mathrm{mW/cm^2}$. The light was incident on the cell directly through the aperture.

The imbalance between the two chiral domains was evaluated by means of circular dichroism (CD) spectroscopic analysis (JASCO J-720WI) and direct observation of the texture under a polarizing microscope (Nikon, OPTIPHOT-POL). All evaluations were carried out at room temperature (RT) and atmospheric pressure.

## 3. EXPERIMENTAL RESULTS

Let us first show the results in the rod-like twin dimer 8OAZ4AZO8. The cell was irradiated with right- and left-CPL (R-CPL and L-CPL) at RT. The CD spectra are shown in Figure 2. Before irradiation, the CD signal was negligible. After R- and L-CPL irradiation for several hours, positive and negative CD signals were induced at about 370 nm, respectively. We also confirmed that no CD was generated by the irradiation of non-polarized light. No texture change was observed, even when the CD signal was induced by the CPL irradiation.

In order to confirm that the CD signal originates from chiral structure and not from birefringence, CD spectra were measured at various cell rotation angles about the cell surface normal. As shown in Figure 3, the spectra showed essentially no change. This certifies that the CD signal truly originates from some chiral structures. The induction of chiral structure was very slow, as shown in Figure 4. After 9 hours irradiation, the CD signal continued to increase and saturation tendency was not observed in this time range.

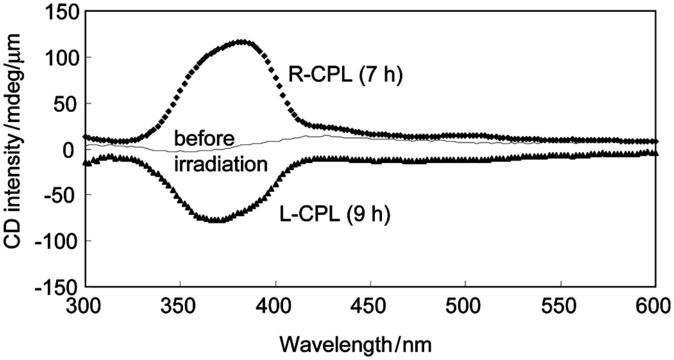

**FIGURE 2** CD spectra induced by R- and L-CPL irradiation at RT in 8OAZ4AZO8.

The same experiments were performed in the bent-shaped dimer 12OAZ5AZO12. The CD spectra after L-CPL irradiation at RT are shown in Figure 5. Negative signals at about 400 nm were observed and tended to saturate after 1 hour irradiation. The saturation of the CD signal occured in a shorter time interval of light irradiation compared with the rod-shaped dimer 8OAZ4AZO8. Another difference between bend- and rod-shaped dimers is the peak position and the shape of the CD spectra. The reason is not known at present.

In order to examine the stability of the chiral structure, the CD spectra were measured using a cell after irradiation. No signal change was observed after several hours, but slight decrease of the signal was detected after keeping the cell in a dark condition at RT for one day.

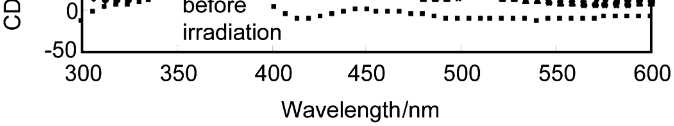

**FIGURE 3** CD spectra as a function of cell rotation angle about the cell surface normal.

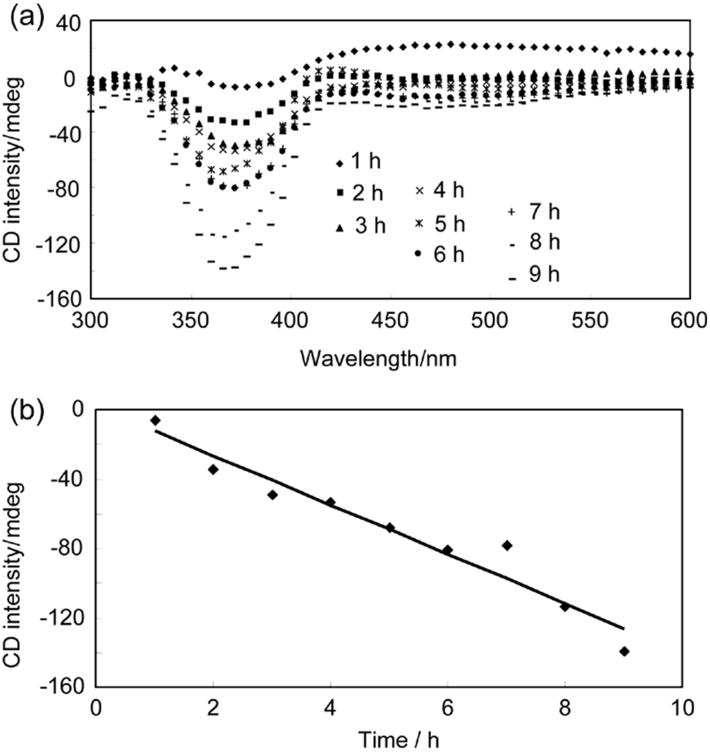

**FIGURE 4** (a) CD spectra induced by L-CPL irradiation at RT in 8OAZ4AZO8 for various irradiation times. (b) CD intensity as a function of irradiation time.

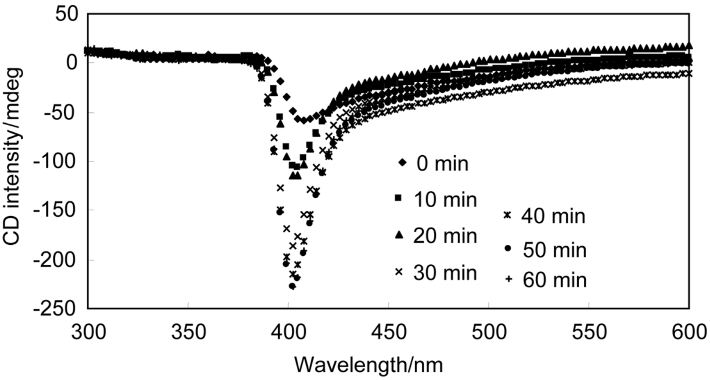

**FIGURE 5** CD spectra induced by L-CPL irradiation at RT in 12OAZ5AZO12.

To examine the repeatability, additional R- and L-CPL irradiation was made on cells with negative and positive CD signals, respectively. Slight decrease of CD signals by a factor of 10% was observed after irradiation for about 10 min, but further decrease was not observed in both cases. In this way, R- and L-CPL irradiation promotes the changes toward positive and negative sides in the CD signals, respectively. However, it was impossible to switch over the chirality to the opposite sense.

To control the enantioselectivity more drastically in this system, a hot (103°C) cell in the $\mathrm{SmC_A}$ phase was irradiated with R- or L-CPL for 1 h. Then, keeping on irradiation, the cell was allowed to cool to 80°C, which is lower than $\mathrm{SmC_A}$-$\mathrm{B_X}$ phase transition temperature, by fast cooling of more than 10°C/min. After this procedure, drastic change in the chiral structure was observed. As shown in the textures shown in Figure 6, spontaneous chiral segregation is clearly observed

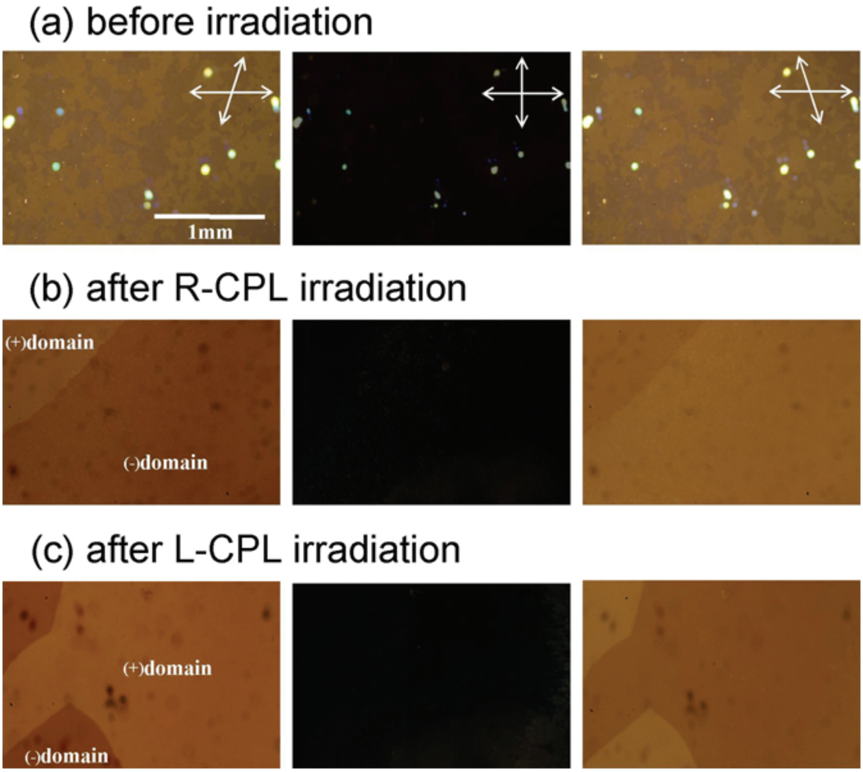

**FIGURE 6** Optical photomicrographs before and after R- and L-CPL irradiation through the phase changes from $\mathrm{SmC_A}$ to $\mathrm{B_X}$ in 12OAZ5AZO12. (See COLOR PLATE XIII)

by decrossing the analyzer with respect to the polarizer. Clockwise and anticlockwise rotations of the analyser give opposite contrast for two chiral domains; namely bright and dark domains interchange by the opposite analyser rotation. Before CPL irradiation (Fig. 6(a)), nucleated chiral domains were very small and the ratio of positive and negative domains was equal. Here positive and negative domains mean those exhibiting positive and negative CD signals, respectively.

Two important observations after CPL irradiation must be made in Figure 6; (1) The size of the chiral domains becomes remarkably large: (2) R- and L-CPL irradiations promote the enlargement of negative and positive chiral domains, respectively. Note that the signs of chirality induced by R- and L-CPL are opposite to those in the previous chirality induction process, i.e., CPL irradiation in the crystal and $B_X$ phases at RT.

Next, CD measurements were conducted in the cells before and after the above CPL irradiation process. As mentioned above, chiral segregation spontaneously occurs, but the ratio of the positive and negative domains is approximately 50:50 without irradiatioin. Hence no CD signal was observed, as shown in Figure 7. Large CD signals at about 380 nm were induced by CPL irradiation. Note that positive and negative signals were induced by L- and R-CPL, respectively. Thus, the chirality induction ability is very efficient in the present treatment. Sometimes, whole the aperture area for the CD measurements (3 mm in diameter) became a single chiral domain and showed a CD signal of

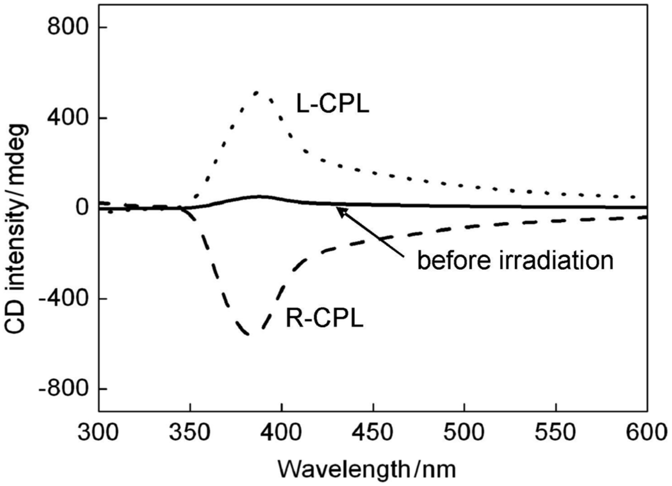

**FIGURE 7** CD spectra induced by R- and L-CPL irradiation through the phase changes from $SmC_A$ to $B_X$ in 12OAZ5AZO12.

500 mdeg/μm [15]. In this way, we can obtain chiral films of 100% *ee* and the chirality is selectively chosen by R- and L-CPL. It is also notable that the induced enantioselectivity in the $B_X$ phase can be maintained constant at least for several months at RT.

## 4. DISCUSSION

It is clear that there are two mechanisms in the induction of chiral domains. The chirality induction by CPL has been reported in various soft material systems [1–9]. In all the examples, R- and L-CPL induce positive and negative CD signals, respectively. The phenomenon was explained by chiral momentum transfer from light wave to material systems, inducing precession of the chromophores with a sense of rotation consistent with the sense of the CPL [24–26]. Therefore, R- or L-CPL induces R- or L-chiral structure, which gives positive or negative CD signal, respectively. Photoisomerization assists to produce free volumes in the bulk, which makes the structural changes easier. The first example in the present study, i.e., CPL irradiation in the crystal and $B_X$ phases at RT, is based on this mechanism, which is schematically illustrated in Figure 8.

What is the mechanism for the induction of opposite chiral structures in the second example? In this case, the irradiation was made in the $SmC_A$ phase, which is a fluid phase and electric-field-induced switching is possible. Therefore, trans-cis photoisomerization and cis-trans thermal relaxation processes efficiently occur and are

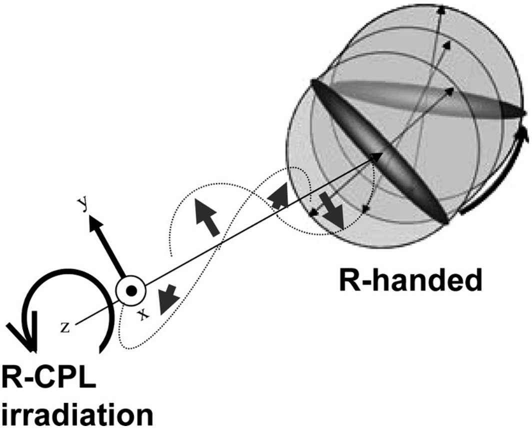

**FIGURE 8** Mechanism of the chirality induction by CPL irradiation at RT in 8OAZ4AZO8.

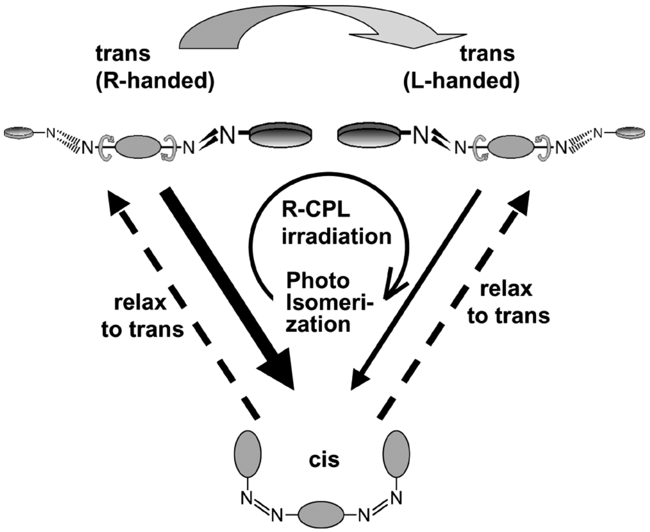

**FIGURE 9** Mechanism of the chirality induction by CPL irradiation through the phase changes from $SmC_A$ to $B_X$ in 12OAZ5AZO12.

repeated frequently. In such condition under continuous CPL irradiation, we can suggest a mechanism schematically illustrated in Figure 9. It is well known that azo-containing molecules tend to reorient under linearly polarized light irradiation to the direction perpendicular to the polarization [27–29]. The same scenario may work: Preferential conversion to a particular chiral conformation could occur under CPL irradiation because of a finite CD, i.e., absorption difference between two chiral conformations. This preference triggers and accelerates the conversion and is fixed when the system is brought into the $B_X$ phase, where spontaneous chiral resolution inherently occurs. In this way, a large imbalance of optical purity and high *ee* are induced by CPL irradiation and the induced chirality is opposite to CPL.

## 5. CONCLUSION

Induced chirality by CPL was studied in two liquid crystalline twin dimers. In rod-shaped dimer (8OAZ4AZO8), CPL irradiation at RT induced chirality of the same sign as that of the chirality of CPL used. The same phenomenon was observed in bent-shaped dimer (12OAZ5AZO12), if the CPL irradiation was made at RT ($B_X$ phase).

On the contrary, large and opposite chirality was induced by the temperature change from $SmC_A$ to $B_X$ under CPL irradiation. Two different mechanisms were discussed for these chirality induction phenomena.

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