Liquid Crystals

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Circular-Polarization-Induced Enantiomeric Excess in Liquid Crystals of an Achiral, Bent-Shaped Mesogen

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Achiral, bent-shaped mesogens have opened up a new era in liquid-crystal science with respect to polarity and chirality.[1,2] Bent-shaped mesogens are known to segregate into two self-assembling, chiral domains in which the molecules are believed to have chiral conformations.[3] In this sense the system is regarded as a racemate, despite being composed of achiral molecules.[4] Hence, the numbers of the two enantiomers are equivalent and the enantiomeric excess is zero in an unperturbed state. However, the system is not necessarily racemic because an imbalance of chirality can be produced by an external chiral stimulus. At least two methods have been elucidated for this: 1) a small amount of chiral dopant is effective in inducing almost 100% *ee*,[5] and 2) a chiral surface has been successfully used to induce a finite *ee*.[6] Herein we demonstrate another method that does not involve chiral molecular species. Novel, achiral, bent-shaped dimers with photochromic moieties on both side wings form large, chiral domains enantioselectively when the samples are cooled from the conventional anticlinic $\mathrm{SmC_A}$ phase to a low-temperature $\mathrm{B_X}$ phase similar to $\mathrm{B_4}$ while being irradiated with circularly

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polarized light (CPL). The enantioselectivity can be controlled by the handedness of the CPL.

Many chemical and physical systems can occur in two forms that are mirror images of each other. This phenomenon, known as chirality, is found in biological molecular systems because of enantioselective interactions.[7] Thus, the control of chirality is important in science as well as technology,[8–10] and several reactions can proceed enantioselectively if chiral dopants are involved[11] or if an external, chiral bias is present.[7,12,13] One such external bias is irradiation with CPL, and deracemization has been reported in several systems upon CPL irradiation.[14–18] However, the induced *ee* was rather low (a few percent). We demonstrate herein that irradiation with CPL can induce a large imbalance in two chiral domains, leading to large *ee* values in an achiral, bent-shaped mesogenic dimer with azo linkages at both side wings.

We used the bent-core dimer α,ω-bis(4-alkoxyazobenzene-4′-carbonyloxy)alkene (12OAz5AzO12; Figure 1), in which two azobenzene moieties with alkoxy tails are linked by a polymethylene spacer (12 and 5 are the number of carbon atoms in the alkoxy tails and the central spacer, respectively). The detailed synthesis and properties of the homologous molecules have been described elsewhere.[19] This compound shows the following phase sequence: isotropic (108 °C)–SmC$_A$ (94 °C)–B$_X$. The assignment of the higher-temperature phase to the smectic C$_A$ (SmC$_A$) phase[20] was made by texture observations: spherelike textures coalesce into the well-known, fan-shaped texture upon cooling from the isotropic phase. A clear birefringence with Schlieren textures having singularities of $s=1$ and 1/2 was also observed.[21] The actual structure is not the conventional SmC$_A$,[20] but is an interdigitated layer with a periodicity of half a molecular length.[22] The low-temperature B$_X$ phase is a solidlike phase that is considerably different from a crystal in several aspects, like the B$_4$ phase of classical bent-core (banana-shaped) molecules.[23] The most notable feature is that spontaneous chiral segregation occurs in the B$_X$ phase, in which no layer chirality[2] exists because of the nontilted phases. A chiral conformation[3–5] is the origin of this type of chiral domain. In the SmC$_A$ phase, a spontaneous segregation into two chiral domains was not observed.

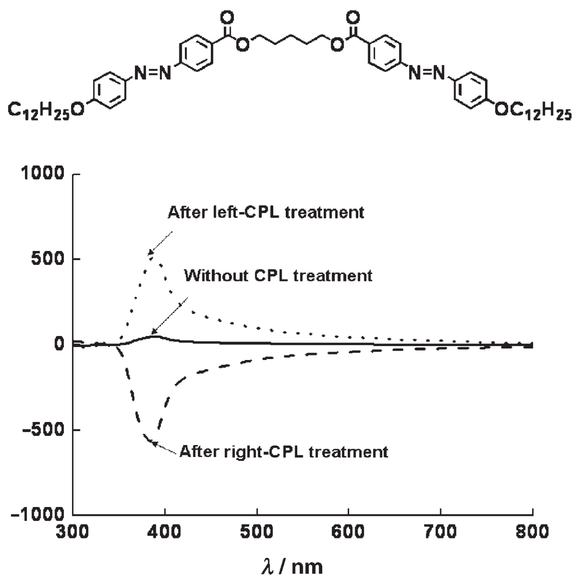

Figure 1. The chemical structure of 12OAz5AzO12 and three typical CD spectra of the B$_X$ phase of achiral, bent-shaped 12OAz5AzO12. The spot size for the CD measurements covers the whole area irradiated by the CPL (10 mm).

The *ee* values were determined by circular dichroism (CD) measurements and direct polarizing microscope observations using 2-μm-thick cells. CD measurements were carried out first to confirm that macroscopic chirality occurs in the B$_X$ phase. Figure 1 shows three typical CD spectra observed for the B$_X$ phase after three different treatments. Without CPL irradiation, only a negligible CD signal ($\Delta\varepsilon \leq$ 50 mdeg μm^{-1}) was observed. However, remarkably strong CD signals were observed at about 380 nm after right-CPL or left-CPL irradiation through a 10-mm-diameter aperture for 1 h. These CD signals are due to an induced circular dichroism (CD) and indicate the nucleation of macroscopic chiral domains. A positive intensity is induced by left-CPL, whereas a negative signal is induced by right-CPL. The CD spectra were recorded 10 times after heating the cell to form the isotropic liquid. Without the CPL stimuli, a CD with negligible positive or negative signals was observed, whereas the B$_X$ phase exhibited large CD intensities ($\Delta\varepsilon \geq$ 300 mdeg μm^{-1}) with a negative (positive) sign after right-CPL (left-CPL) irradiation every time. Thus, an intrinsically macroscopic achiral system can be converted into a macroscopic, chiral system by a CPL stimulus.

Next, we directly observed the textures under a polarizing microscope. The existence of chiral domains in the B$_X$ phase was confirmed by a conventional method whereby the two domains become apparent as bright and dark regions when one of the polarizers is rotated clockwise by a small angle ($\theta =$ 5°) with respect to the crossed position. The brightness of the two domains interchanges when the polarizer is rotated counterclockwise. The textures of the cells are shown in Figure 2. In the B$_X$ phase without the CPL stimulus the observed texture exhibits grainy domains segregated into (+) or (−) chiral domains of equal probabilities (Figure 2a), whereas the imbalance between these chiral domains becomes notable upon CPL irradiation (Figures 2b and 2c). Although the texture still includes two opposite chiral domains, an imbalanced domain with a size larger than a few millimeters can be prepared by CPL irradiation. Large, distinct (−) chiral domains with a large, negative CD peak are produced by right-CPL irradiation (Figure 2b), whereas large, distinct (+) chiral domains with a large, positive CD peak are nucleated by left-CPL irradiation (Figure 2c).

We also calculated the value of the induced enantioselectivity in the B$_X$ phase of the 12OAz5AzO12 cell after CPL irradiation. This was done by two methods, namely direct texture observation and CD. Optical microphotographs of B$_X$ were taken of a region including both (+) and (−) chiral domains after irradiation (Figure 3a). The ratio of the (+) and (−) chirality domains was analyzed by using a computer software package (Adobe Photoshop Elements 2.0). Image processing allowed the overall domain to be assigned clearly

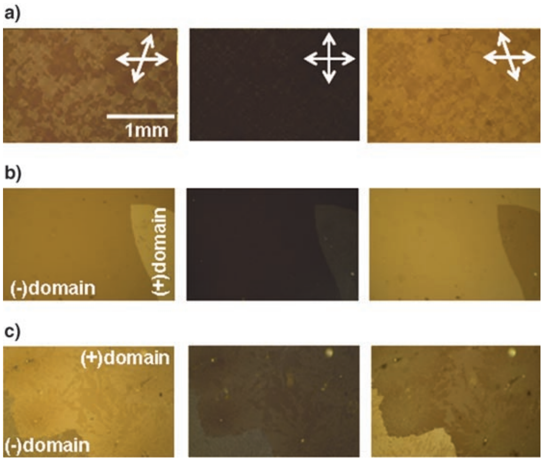

Figure 2. Optical microphotographs of the B$_X$ phase of the achiral 12OAz5AzO12 cell under decrossed and crossed polarizers: a) without CPL treatment, b) after right-CPL treatment, and c) after left-CPL treatment. The arrows indicate the directions of the polarizers.

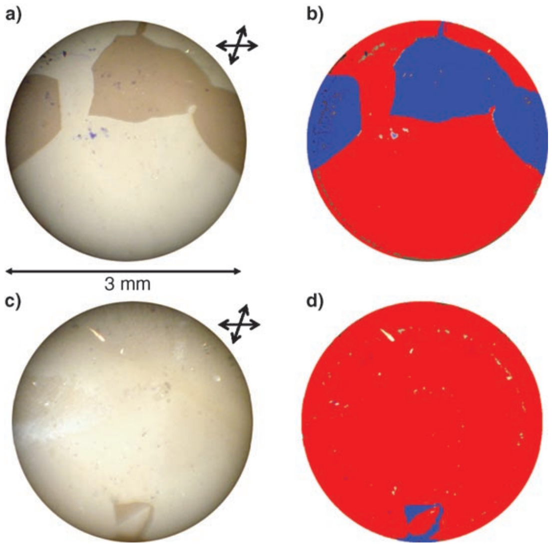

Figure 3. a) An overall view taken with an optical microscope showing the texture of B$_X$ obtained by left-CPL stimuli (30 mW cm^{-2} for 60 minutes) of an area with a diameter of 3 mm where the value of the observed CD intensity is about +1000 mdeg μm^{-1}. b) Image processing allows the overall domain to be divided into two colors (red and blue) indicating the (+) and (−) chiral domains, respectively. c) An almost purely chiral domain 3 mm in diameter and d) its processed image. The arrows indicate the directions of the polarizers.

to two colors—red and blue—corresponding to the (+) and (−) chiral domains, respectively (Figure 3b). A ratio of 70:30 (i.e., 40% *ee*) can be easily obtained by counting the number of red and blue pixels. If we choose appropriate chiral domains, such as those shown in Figures 3c and 3d, we find domains with almost 100% *ee*. The CD intensity of these homochiral domains exceeds the detection limit of our CD instrument (>2000 mdeg). Thus, we can conclude that a remarkably large *ee* values can be induced by CPL. Optimization of the irradiation and cell conditions should produce a homochiral domain in the whole of the irradiated area of this system.

This is the first report of a large *ee* value being attained and visualized and where macroscopic chirality is controllable in achiral, bent-shaped molecular systems by irradiation with CPL. However, a basic question arises: How can CPL stimuli, particularly exposure of a higher-temperature, liquid-crystalline SmC$_A$ phase, give rise to enantioselectivity in a B$_X$ phase with two chiral domains and induce a large *ee* value in achiral, bent-shaped 12OAz5AzO12 molecules? CPL is a chiral electromagnetic radiation that is theoretically able to induce enantioselective conversion.[13] Three types of asymmetric photoreactions are known to be effected by CPL irradiation: 1) preferential photodestruction, in which one of the enantiomers of a racemate is preferentially destroyed and the remaining enantiomer is therefore enriched,[14] 2) photoresolution, namely a deracemization of photochemically interconvertible enantiomers,[15,16] and 3) asymmetric photosynthesis, namely an enantioselective photochemical formation of an optically active compound from a prochiral starting material.[17,18] However, the *ee* values in these cases are very low (a few percent at most),[13] except for the photodestructive reaction.[14]

Bent-shaped molecules like the one used here can be regarded as racemic mixtures rather than as an achiral system because of their spontaneous segregation into chiral domains. Therefore, our asymmetric photoreaction by CPL irradiation can be seen as a kind of photoresolution. Furthermore, this chirality is not inherent in phases formed from bent-shaped molecules and can be switched easily to the opposite by changing the external chiral stimulus; chiral *S* and *R* conformers cannot be interchanged. In this sense, the present enantioselectivity is unique.

The higher-temperature, liquid-crystalline SmC$_A$ phase is a fluid phase in which two axially twisted conformers interchange such that the system is either achiral or racemic. Photochromic azobenzenes have been utilized extensively in supramolecular chemistry, catalysis, and materials science because of their efficient, reversible *trans–cis* photoisomerization, which leads to large changes in molecular geometry.[24] It is well known that rod-like, azo-containing molecules tend to reorient under linearly polarized light irradiation to the direction perpendicular to the polarization.[25] The same scenario may apply here: preferential conversion into a particular chiral conformation could occur under CPL irradiation because of a finite CD (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 takes place, meaning that a large imbalance of optical purity and high *ee* are induced by CPL irradiation. This CPL-induced enantioselectivity is observed only in systems containing azobenzene bonds, thus photochromic *trans–cis* isomerization is most important for this phenomenon. It is also notable that the enantioselectivity induced in the B$_X$ phase can be maintained for several months at least at room temperature.

In conclusion, we have succeeded in obtaining a large imbalance in the two chiral domains and inducing large *ee* values in a B$_X$ phase that is similar to the B$_4$ phase in classical bent-core (banana-shaped) molecules using circularly polarized light. This technique opens up the possibility of enantioselectively converting an achiral molecular system into a chiral system for practical use in functional materials. Our future goals include enantioselective syntheses in a chiral domain to provide a new method of photopolymerization in the B_X phase with high *ee* values that may lead to chiral films for chiral segregation.

Experimental Section

Sandwich cells were fabricated from fused-quartz slides without alignment treatments such as coating with an alignment layer or rubbing. The dimensions and thickness of the cell were about $1.2 \times 1.2\,\mathrm{cm}^2$ and 2 μm, respectively. Irradiation was performed with light from a Mercury lamp after passing it through a Fresnel rhomb and an aperture with a diameter of 10 mm to produce circular polarization. Irradiation was performed at the absorption wavelength of *trans*-12OAz5AzO12 (365 nm; intensity $30\,\mathrm{mW\,cm^{-2}}$). The temperature was adjusted within $\pm 2\,^{\circ}\mathrm{C}$ by a temperature control unit (Chino, DB1150). Better enantioselectivity control was achieved by irradiation of a heated cell (103 °C) in the $\mathrm{SmC_A}$ phase with right- or left-CPL for 1 h. Then, while maintaining the irradiation, the cell was allowed to cool to 80 °C, which is below the $\mathrm{SmC_A}$–$\mathrm{B_X}$ phase-transition temperature, at more than $10\,\mathrm{K\,min^{-1}}$.

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 and atmospheric pressure.

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