Vibrational Circular Dichroism Spectroscopic Study on Circularly Polarized Light-induced Chiral Domains in the B4 Phase of a Bent Mesogen

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In this work, we report vibrational circular dichroism (VCD) spectra in chiral domains induced by circularly polarized light (CPL) irradiation to the achiral bent-core liquid-crystalline B4 phase.
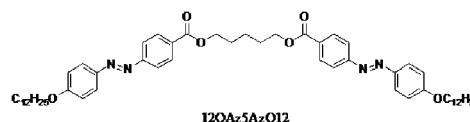

Chart 1.

The emergence of chirality has been reported at the early stage of the discovery of bent-core liquid crystals.[1,2] Since the molecules do not have a chiral carbon, the presence of chiral phases has been fascinating chemists and physicists in the field of liquid crystals.[3–7] Thus, chirality in bent-core molecular systems is an arguably important topic to be studied. The most typical chiral phase is the complicated glass-like B4 phase[1–3] and analogous unidentified phases. Optical microscopy reveals two segregated chiral microdomains showing optical rotatory power of opposite senses;[8] The two domains become apparent as bright and dark regions when one of the polarizers is rotated clockwise by a small angle with respect to the crossed position. The brightness of the two domains interchanges when the polarizer is rotated counterclockwise. Although the structure of the B4 phase has not been fully elucidated yet, the chiral origin of the B4 phase has been regarded as the twisted conformation of the molecules, which is attested by nuclear magnetic resonance measurements and molecular calculations.[4] Moreover, inherent chirality in the B4 phase of achiral bent-core molecular systems has generated much attention[1,2] because of various unusual chirality-related phenomena such as chiral nonlinear optical effects.[6] Particularly, large chiral Pockels constant[6] observed in the B4 phase is nearly equal to that of $LiNbO_3$, which allows promising electrooptic applications if large uniform chiral domains could be obtained.[7]

Recently, we have proposed several methods[8–10] to control the chirality and to enlarge the chiral domain size in achiral bent-core liquid crystal phases; use of chiral surface,[8] circularly polarized light (CPL),[9] and twisted cell geometry.[10] Among them, the CPL-irradiation method has been widely employed to induce and control the chirality in many soft materials such as polymers and liquid crystals,[11] which possess photoisomerizable groups.

Here, we focus on the B4 phase stabilized by CPL irradiation of a bent-shaped dimer with azobenzene linkages to elucidate the molecular conformation, which is not completely clear and still preliminary. For the purpose, we adopted vibrational circular dichroism (VCD) spectroscopy, which is a relatively new but powerful technique to obtain conformational information of molecular chirality and chiral supramolecular organization.[12,13] By comparing VCD spectra with simulated ones using various possible molecular conformations, we expected to have the knowledge for conformational information of molecular chirality and chiral supramolecular organization in the B4 phase.

The material used was a bent-shaped dimer with azobenzene linkages in both end chains, 12OAz5AzO12 (Chart 1).[14] This molecule exhibits the SmC_A and B4 phases on cooling; Isotropic (108 °C)–SmC_A (94 °C)–B4. The CPL-irradiation technique[9] was adopted to control the chirality and enlarge the domain size for fabricating cells with either (+) or (−) chirality. The CPL-irradiation technique is as follow: By cooling the cell from SmC_A to B4 under CPL irradiation, one of the chiral domains relevant to the CPL becomes large and attains a size of several millimeters. Opposite CPL stabilizes the opposite chirality.

We fabricated sandwich-cells of about 2-μm thick using CaF_2 substrates without alignment treatments such as alignment layer coating or rubbing. The detailed conditions for fabricating cells and irradiation were described in ref 10. CD and VCD measurements were made using JASCO J-720WI and JASCO FVS-4000 at room temperature, respectively.

Figure 1a shows the photomicrographs for large (+) and (−) domains of the B4 phases, stabilized by L-CPL (upper) and R-CPL (lower) treatment, under decrossed polarizers. Relatively large domains up to a size of 2–3 mm were obtained. As shown in Figure 1b, (+) and (−) domains showing opposite signs of optical rotation give large CD peaks with opposite signs of dichroic ratio in a UV–vis light region, which indicates that a macroscopic chiral structure exists. The observed CD signals from (+) and (−) domains are mirror images, indicating that chiral structures of mirror images were produced with L- and R-CPL irradiation.[9] Such intrinsically chiral structures can originate from twisted conformation and chiral assemblies of such molecules.

Figures 2a and 2b show infrared (IR) and VCD spectra in the B4 phase after the CPL treatment. The IR peaks are assigned as listed in Table 1. As shown in Figure 2b, relatively strong VCD signals were observed at vibration bands of (1) C=O stretching of ester (1714 cm^{-1}), (2) C–O stretching of ester (1279 cm^{-1}), and (3) combined C–O stretching of ester and C–N stretching of azobenzene (1246 cm^{-1}). Namely, distinct VCD signals were observed at the vibration bands related to central ester groups of the dimer molecule used. This result strongly supports that the bent-shaped molecules in the B4 phase possess axial chirality (twisted conformation) due to central ester groups of molecules. It is also notable that the VCD signals for the (+) and (−) domains are almost mirror images apart from its signal intensity. Thus, opposite chiral conformations and/or chiral assemblies
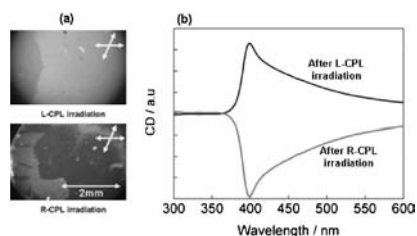
Figure 1. (a) Photomicrographs under decrossed polarizations after L-CPL (upper) and R-CPL (lower) irradiation. (b) CD spectra for the large (+) and (−) domains of the B4 phases stabilized by L-CPL (black) and R-CPL treatment (gray), respectively.
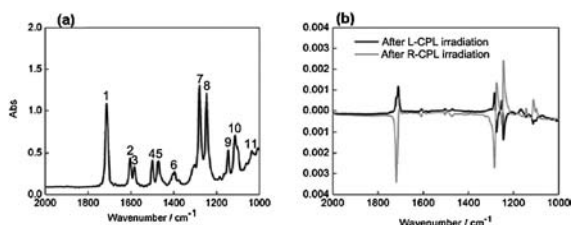

Figure 2. (a) Observed IR spectrum and (b) VCD spectra in the B4 phases stabilized by L-CPL (black) and R-CPL (gray) treatment.

Figure 3. (a) Calculated molecular conformation optimized by density functional theory calculation. (b) VCD spectrum calculated using the molecular geometry shown in (a).

Table 1. List of IR peaks and their assignment

Peak	Position /cm^{-1}	Assignment
1	1714	C=O stretching of ester
2	1605	N=N stretching, phenyl ring stretching of azobenzene
3	1585	phenyl ring stretching of azobenzene
4	1501	N=N stretching, phenyl ring stretching of azobenzene
5	1473	N=N stretching of azobenzene, CH$_2$ scissor of terminal group
6	1397	N=N stretching, phenyl ring deformation of azobenzene
7	1279	C–O stretching of ester
8	1246	C–O stretching of ester, C–N stretching of azobenzene
9	1147	Aromatic CH in-plane deformation of azobenzene
10	1115	C–O stretching of ester, phenyl ring deformation of azobenzene
11	1036	C–O stretching of terminal group

are stabilized by L- and R-CPL light irradiation.

For the purpose of detailed discussion on the molecular conformation, VCD spectra were simulated in the dimer molecule, which was simplified by replacing the alkoxy tails with methoxy groups. First, the molecular geometry of the dimer model was optimized by density functional theory calculation (B3LYP/6-31G(d,p)).[15] Then, VCD spectra were calculated under the optimized geometries.[16] Figure 3a illustrates one of the optimized molecular geometries with a twisted C_2 symmetry. The VCD spectra calculated using this molecular geometry is shown in Figure 3b. Although overall agreement is not obtained, we can find some important agreements by comparing the experimental (Figure 2b) and calculated (Figure 3b) VCD spectra: (1) The VCD structure of the first derivative of the absorption peak 7, i.e., C–O stretching of ester, is remarkably well simulated by the calculation. (2) The small VCD peaks around the absorption peaks 9 and 10 also show good agreement. On the contrary, experimental large VCD peaks related to the absorption peaks 1 and 8 could not be obtained or very small by calculation. We continued the calculations for various torsional angles of bonds in the molecular model close to the optimized structures without success particularly for the peak 1. The experiments were made in the B4 phase, in which molecules sit under strong intermolecular interaction, whereas the calculated spectrum was based on a single molecule. This difference may make the complete agreement impossible. In other words, the experimental VCD spectra are due to the twisted conformation of molecules forming chiral molecular assemblies. Although perfect agreement was not obtained, the present work indicates that VCD spectra are quite useful to identify the chiral molecular structure.

In conclusion, we found that large VCD signals appeared at the molecular vibration bands related to ester groups of the dimer molecule. These results indicate the bent-shaped molecules in the B4 phase possess twisted conformation due to central ester groups of molecules. According to the comparison between the experimental and calculated VCD spectra, we can conclude that
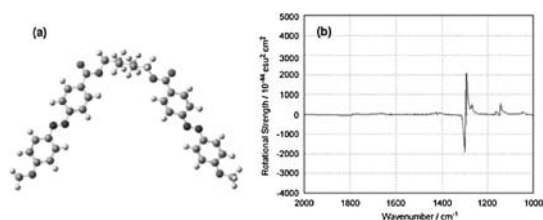
not only the conformation of azobenzene linkage but also that of central core are harmonized with their preferential twisted conformation in bent-shaped molecules with azobenzene moieties.

References
1   H. Takezoe, Y. Takanishi, *Jpn. J. Appl. Phys.* **2006**, *45*, 597.
2   R. A. Reddy, C. Tschierske, *J. Mater. Chem.* **2006**, *16*, 907.
3   D. M. Walba, L. Eshdat, E. Körblova, R. K. Shoemaker, *Cryst. Growth Des.* **2005**, *5*, 2091.
4   J. Thisayukta, H. Takezoe, J. Watanabe, *Jpn. J. Appl. Phys.* **2001**, *40*, 3277.
5   J. Thisayukta, H. Niwano, H. Takezoe, J. Watanabe, *J. Mater. Chem.* **2001**, *11*, 2717.
6   a) F. Araoka, Y. Takanishi, H. Takezoe, A. Kim, B. Park, J. W. Wu, *J. Opt. Soc. Am. B* **2003**, *20*, 314. b) F. Araoka, N. Y. Ha, Y. Kinoshita, B. Park, J. W. Wu, H. Takezoe, *Phys. Rev. Lett.* **2005**, *94*, 137801.
7   Y. Takanishi, G. J. Shin, J. C. Jung, S.-W. Choi, K. Ishikawa, J. Watanabe, H. Takezoe, P. Toledano, *J. Mater. Chem.* **2005**, *15*, 4020.
8   K. Shiromo, D. A. Sahade, T. Oda, T. Nihira, Y. Takanishi, K. Ishikawa, H. Takezoe, *Angew. Chem., Int. Ed.* **2005**, *44*, 1948.
9   S.-W. Choi, T. Izumi, Y. Hoshino, Y. Takanishi, K. Ishikawa, J. Watanabe, H. Takezoe, *Angew. Chem., Int. Ed.* **2006**, *45*, 1382.
10 S.-W. Choi, S. Kang, Y. Takanishi, K. Ishikawa, J. Watanabe, H. Takezoe, *Angew. Chem., Int. Ed.* **2006**, *45*, 6503.
11 a) D. Hore, Y. Wu, A. Natansohn, P. Rochon. *J. Appl. Phys.* **2003**, *94*, 2162. b) S.-W. Choi, T. Fukuda, Y. Takanishi, K. Ishikawa, H. Takezoe, *Jpn. J. Appl. Phys.* **2006**, *45*, 447. c) S.-W. Choi, N. Y. Ha, K. Shiromo, N. V. S. Rao, M. K. Paul, T. Toyooka, S. Nishimura, J. W. Wu, B. Park, Y. Takanishi, K. Ishikawa, H. Takezoe, *Phys. Rev. E* **2006**, *73*, 021702. d) S.-W. Choi, S. Kawauchi, N. Y. Ha, H. Takezoe, *Phys. Chem. Chem. Phys.* **2007**, DOI:10.1039/b702835k.
12 V. Setnička, M. Urbanová, P. Bouř, V. Král, K. Volka, *J. Phys. Chem. A* **2001**, *105*, 8931.
13 G. Tian, G. Zhu, X. Yang, Q. Fang, M. Xue, J. Sun, Y. Wei, S. Qiu, *Chem. Commun.* **2005**, 1396.
14 T. Izumi, S. Kang, T. Niori, Y. Takanishi, H. Takezoe, J. Watanabe, *Jpn. J. Appl. Phys.* **2006**, *45*, 1506.
15 M. J. Frisch, et al, Gaussian 03, Revision C.02, Gaussian, Inc., Pittsburgh PA, 2003.
16 J. R. Cheeseman, M. J. Frisch, F. J. Devlin, P. J. Stephens, *Chem. Phys. Lett.* **1996**, *252*, 211.