Liquid Crystals

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Intrinsic Chirality in a Bent-Core Mesogen Induced by Extrinsic Chiral Structures**

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Chirality has been one of the most attractive subjects in chemistry since Pasteur's famous experiment showing the chirality of tartaric acid.[1] It is particularly interesting that some mesogenic phases of achiral, banana-shaped molecules[2] were found to be spontaneously segregated into two chiral domains.[3,4] Herein we report a simple but efficient method of obtaining a high excess of one handedness of chiral domains in a novel, substituted oxadiazole achiral banana-shaped molecule (Figure 1 a), which exhibits liquid-crystal (LC) polymorphism including both the calamitic (nematic) and undesignated banana smectic phase (B_x phase).[5] From an extrinsically chiral supermolecular structure in the nematic phase,[6] an intrinsically chiral conglomerate with one handedness of the B_x phase could be obtained. Moreover, the preferential chiral handedness can be controlled by the handedness of the twisted configuration.

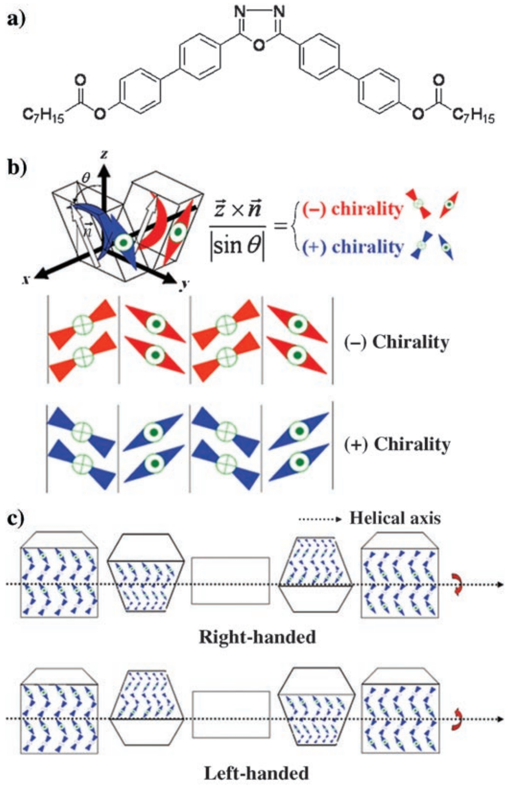

Figure 1. a) The achiral, banana-shaped substituted oxadiazole molecule used. b) Illustration of layer chirality induced by molecular tilting, and layer degeneracy in the B_2 phase of banana-shaped molecules; two layer structures may be observed which correspond to the two possible supermolecular-layer-stacking structures with opposite chirality (in the case of SmC_AP_A structure). c) Two possible TGB structures with opposite helix handedness in the B_4 phase. The tilted version of the TGB structure is drawn, as the present B_x phase is a tilted smectic phase.

Inherent chirality in achiral banana-shaped molecular systems has generated much attention because of a variety of unusual chirality-related phenomena, namely, large optical rotation (OR)[7,8] and chiral nonlinear optical (NLO) effects,[9,10] enhanced twisting power,[11–13] and induced blue phase[14] by doping conventional chiral systems with achiral banana-shaped molecules. Typical phases that exhibit macroscopic chiral separation are the B_2 phase,[7,8,15,16] and the complicated glasslike B_4 phase, as well as analogous uniden-

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tified phases.[3,4,16–18] The spontaneous chirality in the B_2 phase originates from breaking of the symmetry by the tilt of banana-shaped molecule with respect to the layer normal (Figure 1b). In contrast, conformational molecular chirality in the B_4 phase is believed to be nucleated, which results in some helical superstructures such as a twist-grain-boundary (TGB) structure with the helix parallel to the layer (Figure 1c).[17] As the system is achiral, it behaves like a racemic mixture when spontaneous symmetry breaking occurs; spontaneous degeneracy is inevitably formed (Figure 1b,c).[19] So far, the degeneracy has been successfully lifted by at least four methods, namely, by using: 1) chiral molecules;[19] 2) a template for macroscopically chiral structure;[20] 3) chiral surfaces;[21] and 4) circularly polarized light.[22] Herein, we demonstrate a fifth method for breaking this inevitable degeneracy. This method is based on the LC alignment technique twisted configuration field and is simple and efficient.

Recently, it was found that oxadiazole-based molecules[23] show an interesting polymorphism in which the banana mesophase is formed in a lower temperature region than well-known calamitic phases (i.e., nematic, SmA, and SmC phases).[5] Such a polymorphism including both banana and calamitic mesophases is attributed to a bend angle of oxadiazole cores (135°) which is a little larger than that of the classic banana-shaped molecules based on a resorcinol core (120°).[24]

We prepared the banana-shaped compound 2,5-bis(*p*-nonaloyloxybiphenyl)-1,3,4-oxadiazole (Figure 1a). The detailed syntheses and properties of homologous molecules are described elsewhere.[5] Polymorphism is clearly observed for this compound, with the calamitic phase (conventional nematic phase) in a higher temperature region and the undesignated banana smectic phase (B_x phase) in a lower temperature region (phase transition: isotropic-(266 °C)-nematic-(252 °C)-B_x-(193 °C)-cryst.). The B_x phase has a layered structure in which the molecules are packed in a liquidlike manner and are tilted with respect to the layer by 28°. It is thus similar to the well-known banana smectic B_2 phase in classic banana-shaped molecules, but is completely different from the typical B_2 phase. The most striking feature of this phase is a spontaneous chiral segregation that exhibits a transparent texture exactly like that of the typical B_4 phase. Thus, the B_x phase has the characteristics of not only the B_2 but also B_4 phases.

First, we confirmed good alignment in the nematic phase by alignment techniques such as homogeneous and twisted nematic (TN) treatment. Next, the clockwise- or counterclockwise-TN cells were cooled down to form the B_x phase at a rate of $-1\,°\mathrm{C\,min^{-1}}$. Figure 2a–d shows the textures observed with slightly (=10°) decrossed polarizers at twist angles of $\alpha = 0°$, $\alpha = -60°$, $-80°$ (corresponding to a counterclockwise, right-handed twist), and $\alpha = 80°$ (corresponding to a clockwise, left-handed twist), respectively. The two chiral domains become apparent as bright and dark regions, and the brightness of the two domains interchanges when the polarizer is decrossed in the opposite direction. For $\alpha = 0°$, a large-scale heterogeneity caused by the degeneracy of the chiral structure was seen clearly (Figure 2a). Heterogeneity was also observed in cells with $\alpha < |40°|$. In contrast, the degeneracy is lifted by means of the twisted configuration with $\alpha > |50°|$ and almost complete symmetry breaking is observed in cells with $\alpha = -60°$ and $-80°$, if appropriate chiral domains are chosen (Figure 2b,c). In a cell with $\alpha = 80°$, the predominant domain was reversed with respect to that of the cell with $\alpha = -80°$ (Figure 2d). This indicates that a preferentially chiral conglomerate with one handedness can be regulated selectively by the twisted handedness (right-handed or left-handed twist) of the fabricated cell.

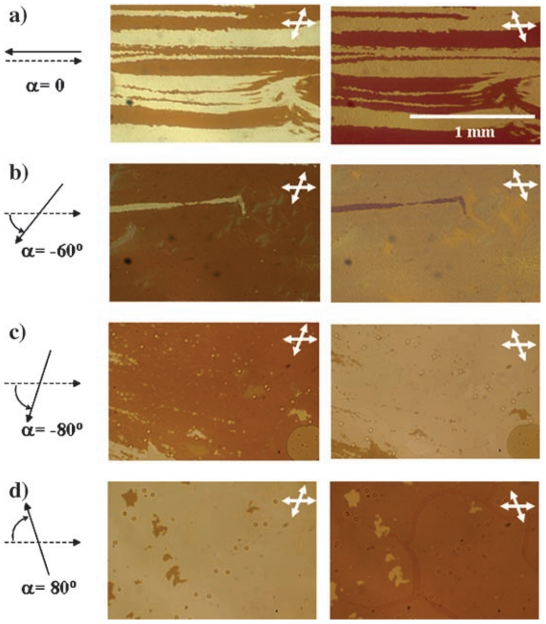

Figure 2. Polarizing optical microphotographs of the banana B_x phases in cells with several twisted configuration treatments. Twist angles were chosen to be a) $\alpha = 0°$, b) $\alpha = -60°$, c) $\alpha = -80°$, and d) $\alpha = 80°$.

Circular dichroism (CD) measurements were carried out to confirm the occurrence of intrinsic chirality in the B_x phase. Figure 3 shows typical CD spectra observed in the B_x phase of cells with several twist angles. The CD measurements were repeated after several cycles of heating the cell to form the nematic phase and then cooling to form the B_x phase. In the B_x phase with $\alpha < |40°|$, a CD spectrum with negligible positive or negative signals was observed and the CD intensity was almost zero as a result of two chiral domains with

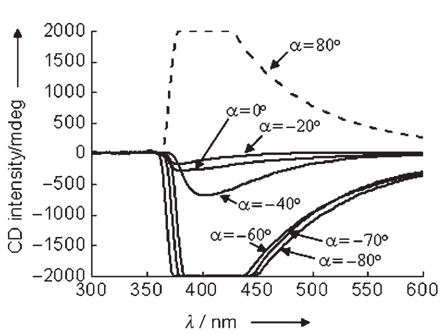

Figure 3. Typical CD spectra of the B_x phase in cells with several twist angles ($\alpha = 0°$, $-60°$, $-80°$, and 80°).

opposite chiral structures coexisting with equal probability. In contrast, an enormous CD signal was observed around 400 nm in the twisted cells with $\alpha > |60°|$. The CD intensity of nearly perfect degeneracy-breaking domains exceeded the range of our CD instrument (i.e., >2000 mdeg). To evaluate the CD intensity per unit μm, we assembled thinner cells (2 μm and 4 μm) with $\alpha = -80°$, which gave CD intensities of about 1000 mdeg and 2000 mdeg, respectively, at about 400 nm. The CD intensity is proportional to the cell thickness in the range 2–6 μm, (500 mdeg μm^{-1}) owing to the intrinsically chiral conglomerate, and a CD intensity of about 3000 mdeg is expected in a 6-μm-thick cell. However, the critical twist angle (between 50° and 60° in our case for 6-μm-thick cells) becomes larger for thicker cells.

These CD signals result from an induced circular dichroism (ICD) in the wavelength region in which the compound exhibits an absorption band, which indicates that a macroscopic chiral structure exists. The observed CD signals from oppositely twisted geometries are perfect mirror images (Figure 3), which indicates that mirror-image chiral structures were produced by twisted cell configurations of opposite handedness. The CD signal intensity obtained is comparable to that obtained from theoretical predictions,[7,8] which indicates the existence of an intrinsically chiral conglomerate with one handedness.

The fundamental difference between the nematic phase and the B_x phase of a compound is that, in the nematic phase, if the molecules are in a geometrically chiral configuration (i.e., TN structure), the structure is regarded as extrinsically chiral,[6] as it results from only the influences of surface treatment. In this case, a CD signal due to birefringence is observed. In contrast, the B_x phase is known to exhibit spontaneous symmetry breaking, and a huge CD signal due to intrinsic chirality is observed. The origin for this intrinsic chirality could be: 1) the tilt of the bent molecules within the layers,[15] 2) twist conformation of molecules[11,19] and so on, thus leading to the TGB-like model structure; the blocks of B_2 layers are twisted about the axis parallel to the layer plane.[3–4,25] In any event, such intrinsically chiral conglomerates originate from molecular axial chirality or chiral assemblies of such molecules.

Why can twisting give rise to degeneracy breaking in the B_x phase of the achiral banana-shaped compound? We can draw equal-energy minima for generating two possible chiral conglomerates in the B_x phase.[19] The clockwise (left-handed) or counterclockwise (right-handed) twisted field is considered to be the origin of the symmetry breaking. Moreover, this degeneracy-breaking is observed only in systems exhibiting polymorphism between the calamitic and banana phases, thus a well-developed TN configuration plays a key role in this phenomenon. If the banana-shaped molecules are incorporated into a well-developed TN configuration, that is, under a degeneracy-breaking field, then upon cooling down to form the B_x phase, chiral interactions are formed between the extrinsically chiral configuration and intrinsically chiral segregation of banana-shaped molecules. Thus, this preference triggers and accelerates a preferential formation of one of the two possible chiral conglomerates and is fixed when the system is brought into the B_x phase. Although, this phenomenon is the first example of a macroscopic geometric chiral perturbation biasing the formation of one handedness of an LC conglomerate, several similar phenomena[26–28] have been reported in the solid or solution state. Particularly, Ribo et al.[26] reported that achiral diprotonated porphyrins, which self-associate in aqueous solution, lead to spontaneous chiral symmetry breaking by vortex motion during the aggregation process. This chiral vortex is analogous to the twisted nematic geometry of the LC cell in our case.

In conclusion, under the degeneracy-breaking field, we demonstrated a preferential formation of LC conglomerate with one handedness in the B_x phase of an oxadiazole-based banana-shaped molecule, which exhibits liquid-crystal polymorphism involving both the calamitic and banana phases. The collective net chirality and orientation of the molecules into a single-handed domain of the B_x phase is the origin of the optical activity and CD behavior observed. The homochiral films obtained by achiral molecules open up the possibility for a wide range of practical applications, such as chiral separation and enzyme adsorption through chiral molecular recognition.

Experimental Section

We fabricated well-aligned cells by using inorganic (diamond-like carbon (DLC)) films with low-energy ion beams impinging at a glancing angle.[29] The DLC films were used for TN cells, as the used compound showed a high transition temperature from the nematic phase to the B_x phase (>250 °C) and rubbed-organic polyimide films show poorer thermal stability than the DLC film. The nominal cell thickness was maintained by columnar spacers (5–6 μm in height) made by photolithography.

Degeneracy breaking was evaluated by means of direct texture observation under a polarizing microscope (Nikon, OPTIPHOT-POL) with uncrossed polarizer combinations and circular dichroism (CD) spectroscopic analysis (JASCO J-720WI).

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