Photonic Bandgap in Achiral Liquid Crystals—A Twist on a Twist

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Achiral mesogenic molecules are shown to be able to spontaneously assemble into liquid crystalline smectic phases having either simple or double-helical structures. At the transition between these phases, the double-helical structure unwinds. As a consequence, in some temperature range, the pitch of the helix becomes comparable to the wavelength of visible light and the selective reflection of light in the visible range is observed. The photonic bandgap phenomenon is reported for achiral liquid crystals.

1. Introduction

A photonic bandgap crystal is a periodic structure through which light may either propagate or not, depending on the energy of the photons. For photonic crystals that operate in the visible part of the spectrum, the wavelengths of interest are from around 350 to 750 nm. The disallowed wavelengths of light are referred to as a photonic bandgap, and the periodicity of the photonic crystal structure must be close to a half of the wavelength of light to be diffracted. The fabrication of a periodic structure on this length scale is highly challenging but offset by a huge application potential, ranging from color changing inks to components for optical computers. In nature, photonic crystals are widespread and responsible for structural colors, such as the iridescent color of opals,[3] animal reflectors found in butterfly wings,[2] or a metallic luster in some beetle shells.[1] In the latter case, it is a liquid crystalline microstructure of the shells that accounts for the photonic band structure. Indeed, the simplest 1D examples of a photonic crystal in soft matter are helical structures of a chiral nematic (cholesteric) and chiral smectic C phase; in both phases, the helical organization is a consequence of the molecular chirality. The chiral intermolecular interactions impose a small twist between the neighboring molecules, leading to a helically modulated structure. If the wavelength of light fits the periodicity of the helix, then the circularly polarized incident light with the same handedness as the helix is reflected while that of the opposite handedness propagates through the structure.[1] Through molecular design, one may vary both the period of the helix, as well as the width of the stopband, which is determined by the ordinary ($n_o$) and extraordinary ($n_e$) refractive indices of the liquid crystal material. Furthermore, the susceptibility of liquid crystalline phases to external fields allows the bandgap to be tuned by electric or magnetic fields, or by temperature, giving the possibility to fabricate devices with readily reconfigurable optical properties.[5] For many decades it was generally believed that intrinsic molecular chirality was a prerequisite to drive the helical structure of a liquid crystalline phase. More recently, however, it was shown that achiral mesogenic molecules may also form helical phases, and this raises an intriguing possibility of fabricating photonic bandgap structures using achiral materials. In this communication, we demonstrate for the first time that this can indeed be achieved. The twist–bend nematic phase, N$_{TB}$, was the first example of a liquid crystalline phase with helices assembled from achiral molecules.[6–9] The N$_{TB}$ phase has a heliconical structure, in which the molecules are tilted at an oblique angle with respect to the helix axis. As the mirror symmetry is spontaneously broken at the transition to the N$_{TB}$ phase, there is an equal probability of the formation of the right- and left-handed helices, and chiral domains are observed in the N$_{TB}$ phase. Electro-optical studies of chiral domains suggested that the director rotates on the cone,[10,11] and the structural characterization of the N$_{TB}$ phase showed that the helical pitch length is

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approximately 8–10 nm.[8–9,12] Upon its discovery, the NTB phase immediately became the hottest topic in the field, and the phase was found in numerous odd-membered liquid crystal dimers (see, for example refs. [13–17]). Unfortunately, in the present context of the photonic bandgap structures, the helical pitch of the NTB phase is very short, and far from the optical range. As also found for solid crystals having a helical structure composed of achiral objects, for example, sodium chlorate, cesium copper chloride, quartz or oligobipyridine complexes (helicates),[18,19] the pitch of the helix in the NTB phase is just a few molecular lengths because it is determined mainly by steric interactions. Recent studies have shown that the lamellar (smectic) analogue of the NTB phase also exists,[20,21] and we termed this the SmCTB phase. For some systems, the SmC_{TB} phase has a simple helical conical arrangement with the molecules changing azimuthal direction of tilt by a constant angle when going from layer to layer, i.e., forming a clock-like structure,[21,22] and the helical pitch being as short as that found for the NTB phase. For other systems, however, the SmC_{TB} structure is more complex, with an additional longer helix with the pitch of the order of tens of smectic layers superimposed on a short helix.[23] Here we present systems, in which the transition between a phase with a single short helix and phase with a double helix takes place. We report on a fascinating observation that upon approaching this transition, the longer helix unwinds, and thus, in a given temperature range, the system exhibits a photonic bandgap for visible light, a phenomenon that has to date been observed exclusively for chiral liquid crystals having helical structures.

2. Results

The materials studied here are dimers, in which two semi-rigid mesogenic units are linked by a flexible chain containing an odd number of atoms. An odd-membered spacer constrains the mesogenic units to be inclined with respect to each other, thus the molecule is bent. This molecular curvature is widely believed to be a prerequisite for the formation of the NTB phase.[24] The focus of this study is the CB6O.m homologues,[25] in which the molecules contain cyanobiphenyl and benzylideneaniline mesogenic units linked by a hexyloxy chain and the length (m) of the terminal alkyl chain is varied (Figure 1A). We will also describe the behavior of CB6O-9 in which the Schiff’s base link has been reversed with respect to that in CB6O.9 (Figure 1A).

The shorter homologues of the CB6O.m series with m < 10 show exclusively nematic (N) and NTB phases, whereas the decyl homologue, CB6O.10, shows an N–NTB–SmCTB phase sequence, and was described in detail previously.[23] For the longer homologues reported here, in the temperature range below the N phase, a sequence of smectic phases was observed (Figure 1, Table S1, Supporting Information). The highest temperature smectic phase observed for the homologues with m ≥ 12, is an optically uniaxial SmA phase which is a nontilted smectic phase, and the layer spacing (d) corresponds to two molecular lengths. This bilayer structure is due to the broken up-down symmetry of the molecules in consecutive layers giving a higher concentration of polar cyano groups in every second layer interface. The layer thickness increases strongly with decreasing temperature in the SmA phase (Figure 2). This is a typical behavior for nonlinear molecules that gradually stop rotating around their long molecular axes on decreasing temperature, and thus the extent of interdigitation of their terminal chains between the layers also decreases.[26]

In homeotropic cells (or surface-free films), the SmA phase appears uniformly black between crossed polarizers, and on cooling to the lower temperature SmX phase, a schlieren texture is observed (Figure 3A, for planar textures, see Figure S1 in the Supporting Information) indicating optical biaxiality.
The difference in the in-plane refractive indices for the light propagating along the layer normal grows continuously from zero at the SmA–SmX phase transition (inset in Figure 3B).

Reducing the temperature further leads to the transition to the SmY phase, at which the homeotropic texture is restored, suggesting that the SmY phase is uniaxial (as will be explained later, the SmY phase is, in fact, a double helix SmC\textsubscript{TB} phase). For the homologues with \( m = 14, 16, \) and \( 18, \) at temperatures below the SmY phase, another lamellar phase (SmZ) is observed, and this exhibits a noncharacteristic, weakly birefringent texture in homeotropic cells. While for the SmA, SmX, and SmY phases only short-range correlations of molecular positions are evidenced by a broad X-ray diffraction signal at high diffraction angles, the SmZ phase exhibits an increased in-plane correlation length typical for hexatic-type smectic phases (Figure S2, Supporting Information). In the SmX and SmY phases, the layer spacing grows monotonically on cooling with nearly the same expansion coefficients, and these are considerably smaller than those in the SmA phase (Figure 2). To check if the biaxiality of the SmX phase is due to the tilting of molecules (a SmC-type phase) or is it a consequence of a hindered molecular rotation in an orthogonal phase (Sm\textsubscript{A\textsubscript{0}} phase), an experiment with chiral doping was performed. In a tilted phase, the chirality of the mixture should induce a helix (i.e., the SmC\textsuperscript{*})

Figure 3. A) Optical textures of the CB6O.14 homologue observed between crossed polarizers in a 3 \( \mu \text{m} \) thick cell with a homeotropic anchoring. B) Temperature dependence of the optical birefringence for green light (\( \lambda = 532 \text{ nm} \)) for CB6O.14, measured in a planar cell (3 \( \mu \text{m} \) thick). The green line is a fit to the critical dependence in the N and SmA phases, with the critical exponents \( \beta \) equal to 0.17 and 0.27, respectively. The inset: the in-plane birefringence of the SmX phase, determined in a cell with homeotropic anchoring.
phase), and therefore, the phase would become optically uniaxial, whereas the structure of the SmA phase should be insensitive to the chirality.\cite{27} For the SmX phase, it was observed that it became optically uniaxial upon chiral doping, and therefore we conclude it is a tilted smectic phase. For the chirally doped material filled in a cell with a homeotropic alignment, all three phases, SmA, SmX* and SmY* are optically uniaxial and practically indistinguishable in the polarized-light optical microscopy observations. Very small changes in birefringence were observed only in cells with planar anchoring for an oblique light transmission. These changes correspond to changes in birefringence observed in the pure compound (Figure 3B). The optical birefringence, \(\Delta n\), measured in the planar cell increases quickly in the nematic phase following a critical behavior \((T - T_c)^\beta\), where \(T_c\) is a clearing temperature and \(\beta\), the critical exponent for the Iso-N phase transition (Figure 3 and Figure S3, Supporting Information). At the N–SmA phase transition, the birefringence grows as the orientational order of the long axes increases due to its coupling to the positional order.\cite{28,29} In the SmX phase, \(\Delta n\) is smaller than expected from the extrapolation of the critical behavior in the SmA phase. At the SmX–SmY transition, the birefringence increases slightly, indicating a weakly first-order transition, but still remains below the value expected from the critical dependence found in the SmA phase (Figure 3 and Figure S3, Supporting Information). By analyzing the departure of the measured birefringence from the extrapolated critical behavior,\cite{10} the tilt of the long molecular axis from the helix axis may be estimated to be not larger than 20°.

Based on the texture changes and the birefringence and calorimetric measurements, the phase diagram for the series was constructed (Figure 1B). From the resonant soft X-ray scattering measurements (RSoXS, an X-ray scattering method sensitive to the spatial variation of the orientation of molecules)\cite{31} performed previously for CB6O.10\cite{23} the phase formed below the N_{TB} phase in this homologue was assigned as a SmC_{TB} phase with a helical four-layer basic crystallographic unit and a longer helix superimposed on it. It is reasonable to expect a similar structure for the SmY phase exhibited by the longer homologues studied here.

The resonant X-ray scattering studies performed for the CB6O.12 homologue, in the temperature range of the SmX phase, revealed only a signal corresponding to the periodicity of four molecular layers (Figure 4), indicating that this phase also has a four-layer repeating unit.

In the nonresonant X-ray diffraction experiments, an electron density modulation with a periodicity of twice the molecular length (a bilayer structure) was detected (Figure 2 and Figure S2, Supporting Information). Thus the four-layer structure observed by RSoXS must be related solely to the modulation of molecular orientation. Upon entering the SmC_{TB}

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure4}
\caption{A,B) Temperature evolution of the resonant X-ray scattering signals for the CB6O.12 homologue observed on heating (A) and cooling (B). C) Scattered intensity versus wavevector (q) measured in a heating run across the SmX–SmC_{TB} phase transition.}
\end{figure}
in the layer thickness at the SmX–SmC TB phase transition

The appearance of these satellites is accompanied by a significant decrease in the intensity of the main signal related to the four-layer periodicity. The satellites are a sign of an additional modulation superimposed on the four-layer structure. Interestingly, the satellites change their position discontinuously with temperature, whereas for the previously studied CB6O.10 homologue, the splitting of the main signal developed continuously with temperature when cooled across the N_{TB}–SmC_{TB} phase transition. For CB6O.12, far from the SmX–SmC_{TB} phase transition, the splitting is 2q_{m} = 0.0232 Å^{-1}, and on heating it decreases discontinuously to 2q_{m} = 0.0155 Å^{-1} and finally, near the SmC_{TB}–SmX phase transition, the splitting jumps to 2q_{m} = 0.0079 Å^{-1}. In cooling scans, the temperature range with the splitting 2q_{m} = 0.0079 Å^{-1} can be either narrow, or absent, due to the overcooling of the SmX phase. What are the possible structures that may account for the observed resonant X-ray scattering patterns? Both the SmX and SmC_{TB} phases have a periodic structure related to molecular orientation with the same basic periodicity of four layers. There are no changes in the layer thickness at the SmX–SmC_{TB} phase transition implying the same magnitude of tilt in both phases. The SmX phase is optically biaxial whereas the SmC_{TB} phase is optically uniaxial, and so a model of the SmC_{TB} phase has to include an averaging of molecular orientations along the layer normal. The biaxial optical properties of the SmX phase suggest a distorted-clock structure of the four-layer helix with the azimuthal direction of the molecules in the consecutive layers being in the sequence 0, δ, π, π+δ (Figure S4, Supporting Information).

Figure 5. A–D) Models of the double-helical structures formed by changes in the azimuthal direction of molecular tilt in the consecutive layers, with the periodicity of the longer helix being 15 layers (A), 23 layers (B), 46 layers (C), and 100 layers (D). For clarity of the picture, only director projections onto the smectic layers are drawn. In the lower part of the figures the top views of the first four layers of the helix are shown; as the temperature decreases, the system gradually evolves from four layer structure with synclinic and anticlinic interfaces towards a bilayer structure by increasing the ε angle.

(SmY) phase, the symmetric satellites of the resonant signal start to develop and have almost equal intensities (Figure 4). The appearance of these satellites is accompanied by a significant decrease in the intensity of the main signal related to the four-layer periodicity. The satellites are a sign of an additional modulation superimposed on the four-layer structure. Interestingly, the satellites change their position discontinuously with temperature, whereas for the previously studied CB6O.10 homologue, the splitting of the main signal developed continuously with temperature when cooled across the N_{TB}–SmC_{TB} phase transition. For CB6O.12, far from the SmX–SmC_{TB} phase transition, the splitting is 2q_{m} = 0.0232 Å^{-1}, and on heating it decreases discontinuously to 2q_{m} = 0.0155 Å^{-1} and finally, near the SmC_{TB}–SmX phase transition, the splitting jumps to 2q_{m} = 0.0079 Å^{-1}. In cooling scans, the temperature range with the splitting 2q_{m} = 0.0079 Å^{-1} can be either narrow, or absent, due to the overcooling of the SmX phase. What are the possible structures that may account for the observed resonant X-ray scattering patterns? Both the SmX and SmC_{TB} phases have a periodic structure related to molecular orientation with the same basic periodicity of four layers. There are no changes in the layer thickness at the SmX–SmC_{TB} phase transition implying the same magnitude of tilt in both phases. The SmX phase is optically biaxial whereas the SmC_{TB} phase is optically uniaxial, and so a model of the SmC_{TB} phase has to include an averaging of molecular orientations along the layer normal. The biaxial optical properties of the SmX phase suggest a distorted-clock structure of the four-layer helix with the azimuthal direction of the molecules in the consecutive layers being in the sequence 0, δ, π, π+δ (Figure S4, Supporting Information).

a structure analogous to that of the SmC_{S12} phase.[22] In the optically uniaxial SmC_{TB} phase, averaging of the azimuthal tilt directions takes place, which occurs by superimposing an additional azimuthal angle shift, ε, between the consecutive layers, so that the sequence of azimuthal positions of molecules becomes 0, δ+ε, π+2ε, π+δ+3ε (Figure 5 and Figure S4, Supporting Information).

A non-zero value of ε is responsible for the rotation of the four-layer unit cell and the formation of a secondary helix. The pitch of the secondary helix can be calculated from the splitting of the RSoXS signals.[23,33] Far from the phase transition, the pitch of the helix is only about 16 molecular layers. As the temperature increases, the helix elongates to about 23 layers and close to the transition to the SmX phase, it jumps to 46 layers (160 nm). It appears that the helical pitch unwinds upon approaching the transition to the SmX phase, and as we determined previously for the CB6O.10 homologue, such a change of the helical pitch reflects the evolution of the system from a bilayer structure towards four layer with interchanging synclinic and anticlinic interfaces. The discontinuous nature of this process for CB6O.12 might result from surface interactions. The equal intensities of the RSoXS satellite signals observed in the SmC_{TB} phase show that the value of the angle δ is small[23] (a strongly distorted-clock basic four-layer unit, with the consecutive layer interfaces being nearly synclinic and anticlinic). It should be noted that for CB6O.10, in which the SmC_{TB} phase is formed from the N_{TB} phase, a much larger value of δ = 70° was determined (a weakly distorted-clock basic four-layer unit) from the strong asymmetry of the satellite signal intensities.[33]

Careful optical observation of the SmC_{TB} phase of CB6O.12 (and also of the longer homologues) reveals that very close to the transition to the SmX phase there is a narrow temperature range in which the secondary helix is much longer than the one determined from the RSoXS studies, and comparable to optical wavelengths. In homeotropic cells, in a range smaller than 0.1 K, selective reflection colors appear covering the whole optical spectrum (Figure 6A).

As this temperature range is very narrow, it was not possible to follow the helix unwinding using a spectroscopic method. Therefore, we decided to make several small modifications to the molecular structure, searching for materials that would have a similar phase sequence but a broader range of temperature over which the optical bandgap may be observed. One of these structural changes was to reverse the direction of the imine link in the mesogenic unit (compound CB6O-9, Figure 1). The phase sequence found for CB6O.9 was N–N_{TB}–SmX–SmC_{TB} (Table S1 and Figures S5–S7, Supporting Information), and at the SmC_{TB}–SmX phase transition the selective reflection of visible light was observed over an increased temperature range of 0.5 K. Spectroscopic measurements performed as a function of temperature clearly show the critical unwinding of the helix on approaching the SmX phase (Figure 6B,C). To ensure that the effect is not related to surface-induced structure or defects, the observations were also performed for freely suspended films, and similar results were found. In order to eliminate the possibility that the selective light reflection is due to the rotation of layers (i.e., that the SmC_{TB} phase is a type of TGB phase[34]), atomic force microscopy (AFM) studies were performed as a function of temperature, which showed that the orientation of
the smectic layers is only weakly affected by the SmX–SmCTB phase transition (Figure S8, Supporting Information). This confirms that the helix must be formed by a change in the azimuthal orientation of the molecules within the layers. The chiral nature of the phase is reflected also by the presence of the strong circular dichroism signal recorded in the temperature range of the SmCTB phase, the signal sign is positive or negative depending on predominance of the right- or left-handed helix in the tested area (Figure S9, Supporting Information).

3. Conclusion

Although helical structures formed by achiral materials are not particularly unusual among solid crystals, in soft matter they are observed much less frequently. Recently, such structures were reported for liquid crystalline phases without or with a limited positional order, composed of bent mesogens. However, in crystals as well as in the twist–bend nematic phase, the pitch of the helix is in the range of a few to several nanometers, and far from the optical range. In the analogous twist–bend smectic phase, the molecular organization can be more complex, and our results show that the helix locks to four molecular lengths but is distorted from the ideal clock structure due to the interlayer interactions that force molecules in the neighboring layers to tilt but stay in the same plane (“all-in-one-plane”, synclinic, or anticlinic structures). For the materials studied here, the transition between the distorted-clock four-layer structure (SmX) and a phase with a more complex molecular arrangement, in which a longer helix is superimposed on the four-layer repeating unit (SmCTB) was found. Such a structure can be viewed as an intermediate stage between a four layer and bilayer structure. The pitch of the longer helix is temperature dependent, because the four-layer clock-like structure (favored at higher temperature) evolves gradually towards a bilayer, nearly anticlinic arrangement of molecules in the neighboring layers favored at lower temperature. In the temperature range close to the transition to the SmX phase, the secondary helix unwinds and its pitch becomes comparable to the optical wavelength. This leads to the well-known phenomenon of the selective reflection of light with an energy bandgap in the visible range. This effect, although common for chiral liquid crystal phases, is reported here for the first time for achiral mesogens. It should be noted, however, that whereas in the case of helical LC structures made from chiral molecules the handedness of the helix is unique, defined by the configuration of chiral center in molecules, the helical structures in the here reported compounds are formed spontaneously and thus their twisting sense is degenerated. The photonic bandgap for chiral compounds thus appears for one type of circular polarization of light, while for the SmCTB phase a selective reflection is expected for both types of circular polarization of light. In the case of a statistical distribution of right- and left-handed domains each circular polarization is extinguished only partially.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
