DOI: 10.1002/adma.200700903

Electro-Optical Switching in a Blue Phase III Exhibited by a Chiral Liquid Crystal Oligomer**

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Investigation of chirality in liquid crystals is an exciting area of liquid crystal science. Perhaps frustrated phases induced by chirality are the most interesting phenomena. Blue phase (BP), twist grain boundary (TGB) phase and smectic Q (SmQ) phase have been observed and structure-property correlations investigated.[1] Blue phases are of particular interest because they have a fluid lattice whose structure is stabilized by lattice defects. Appearance of blue phases results from the competition between the chiral twisting force and the tendency of molecules to pack in ways such that they fill space uniformly. Blue phases are believed to consist of double twist cylinders, and are therefore classifiable into three categories depending on the double-twist-cylinder packing structure: blue phase I (BPI), blue phase II (BPII) and blue phase III (BPIII).[2,3] The BPI packing structure is a body-centered cubic structure; that of BPII is simple cubic structure.[4,5] On the other hand, theory indicates that BPIII and the isotropic phase have identical symmetry.[6] It can be expected that BPIII consists of double twist cylinders with arbitrary orientation.[2,7,8] Usually, blue phases are found in a very narrow temperature range (ca. 1 K) between the isotropic liquid and the chiral nematic (N*) phase of sufficiently short pitch, except in a few cases where a SmA to BP transition has been observed.[9–13] Electric field effects in blue phases have been investigated. The applied field can engender three distinct transformations: a local reorientation of the molecules, distortion of the lattice (electrostriction), and phase transition to lower symmetry phases.[14–20] Recently blue phases are recognized to offer the potential for applications as fast light modulators or tunable photonic crystals, but their narrow temperature range is a daunting obstacle to their application. Kikuchi et al. reported polymer-stabilized blue phases for which the temperature range is extended to more than 60 K. They demonstrated fast electro-optical switching for the stabilized BPI.[21,22] Switching with the speed of 10^{-4} s is attributed to the local reorientation of molecules by an electro-optic Kerr effect. The field-induced birefringence arose from the regions between the defect or disclination lines. Coles et al. reported that eutectic mixtures of three homologues of symmetric dimer doped with a small quantity of a highly twisting chiral additive show BPI of a very wide temperature range; moreover, the BPI shows a wide color range of reflected color switching in 10^{-2} s by applied electric fields because of electrostriction.[23] On the other hand, an electric-field-induced phase transition in BPI and BPII necessitates higher applied voltages and shows slow switching of more than few seconds. Recently we reported that chiral compounds possessing molecular biaxiality can stabilize BPIII.[24] We report here a fast electric-field-induced phase transition in amorphous BPIII exhibited by a newly designed chiral liquid crystalline molecule. Switching caused by the phase transition between BPIII and N can supply not only a pronounced black state but also a homogeneous bright state.

We introduced a polar group into our previously reported chiral T-shaped molecule in order to couple the molecule with an electric field. Figure 1 depicts the molecular structure of the chiral liquid crystal. Its purity was confirmed by elemental analyses. The structure was elucidated using IR and ^{1}H NMR.

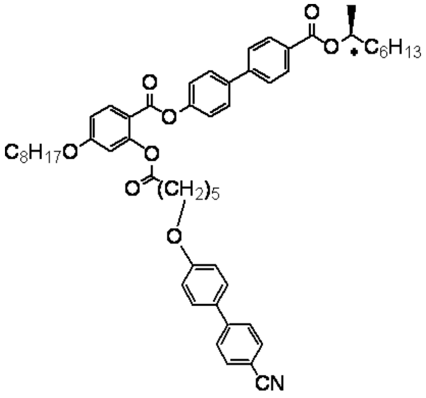

Figure 1. Molecular structure of compound 1.

On cooling, compound **1** showed the following phase sequence: isotropic liquid 49 °C (0.4 kJ mol^{-1}) BPIII 41 °C (0.4 kJ mol^{-1}) N* –10 °C glass phase; the melting temperature was 61 °C. The cooling rate was 0.1 °C min^{-1} from the isotropic phase to 47 °C. The blue colored phase showed fluidity and it

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[**] The authors thank Chisso Petrochemical Corporation for providing the cells. We thank Dr Yasuhiro Haseba of Chisso Petrochemical Corporation of for helpful discussions. This work was partially supported by Research for Promoting Technological Seeds, JST and a Grant for Priority Research Designated by the President of Hirosaki University.

did not appear as platelets, which phenomenon is usually observed in BPI or BPII, thereby indicating that the blue phase is BPIII. Compound **1** was found to exhibit BPIII with a relatively wide temperature range. Coupling between the molecular biaxiality and chirality is thought to produce a stable double twist structure of the blue phase.

Then, we investigated electro-optical effects in the BPIII. Optical transmittance, as a function of the AC field at a frequency of 10 Hz, was observed for a sample in the region between the comb-type interdigitated electrodes under crossed polarizers. The distance between electrodes was 10 µm and the cell gap was maintained at 10 µm using spacers. Figure 2a shows the cell geometry and Figure 2b shows the voltage-transmittance curve at 47 °C. Transmittance with 100 % was calibrated by that of the cell under parallel polarizers. Transmittance with 0 % was calibrated by that of the cell under crossed polarizers. Figure 3a shows an optical texture at 47 °C without an electric filed. The transmittance is 0.85 %. A dark state is obtainable in the BPIII that is macroscopically isotropic. Figure 3b shows that with an applied field of 8.2 V µm^{-1} and the transmittance is 55 %. An extinction direction was observed when the sample was rotated 45° anticlockwise as shown in Figure 3c, indicating that the applied electric field induces the BPIII to N phase transition. The induced N phase shows a homogeneous bright state. A local reorientation of the molecules or distortion of the lattice in blue phases is thought to be difficult to achieve a homogeneous bright state.

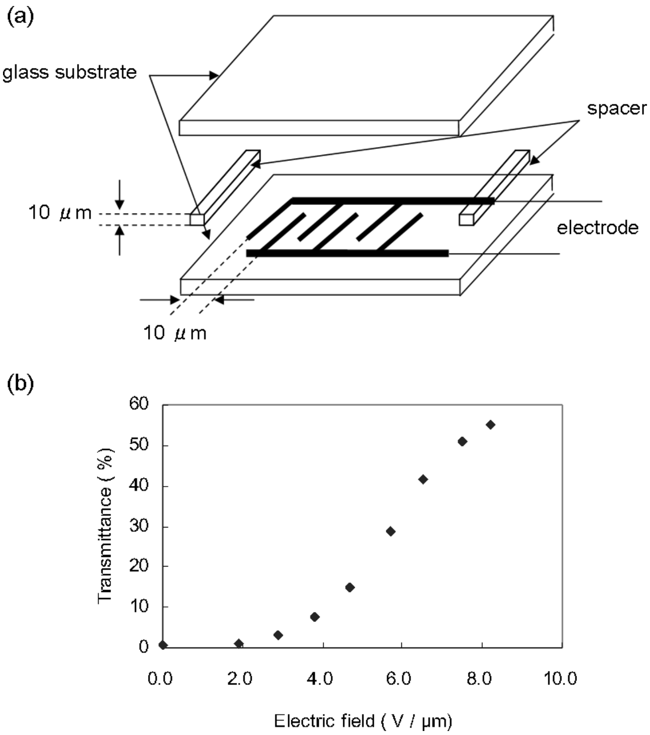

Figure 2. a) Cell geometry for measurements of the electro-optical effect; b) optical transmittance as a function of an AC field at a frequency of 10 Hz at 47 °C.

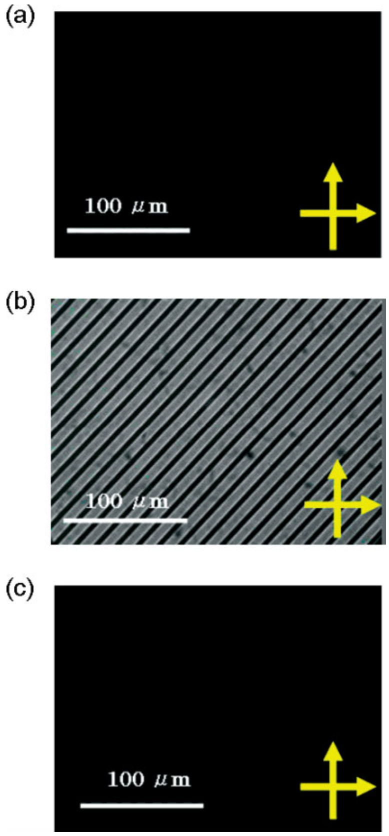

Figure 3. a) Optical texture of compound **1** in the BPIII at 47 °C; b) that with an electric filed of 8.2 V µm^{-1}, which was set at 45° to the polarizing axes of both polarizers; c) that for which the sample was rotated with 45° anticlockwise from (b).

Switching behavior was not observed in the N* phase below the BPIII of compound **1** with the applied AC field up to 8.2 V µm^{-1}. This is explainable in terms of high rotational viscosity of the liquid crystal in the N* phase. Reorientation of the molecules in the BPIII is much faster than that in the N* phase.

We investigated the response speed of the electric-field-induced phase transition between BPIII and N phases. Figure 4 shows an applied driving voltage wave and its corresponding optical transmittance. The response time for the rise is defined as $\tau_{0\text{–}90}$, which is the time for increase in the transmittance from the initial state to 90 % of the saturated state. That for the decay is defined as $\tau_{100\text{–}10}$, which is the time for decrease in the transmittance from the initial state to 10 % of the saturated state (see also Fig. 4).

Figure 5a shows the electric-field dependence of the response times for the rise and decay processes at 47 °C. The rise time was found to decrease dramatically with increasing the electric field, whereas the decay time is independent of the electric field. Figure 5b shows the temperature dependence of response times for the rise and decay processes with an AC field of 8.2 V µm^{-1} at 10 Hz. Both the rise and decay times are about 8 ms at 47 °C. The rise time does not depend on the temperature, indicating that the rise process

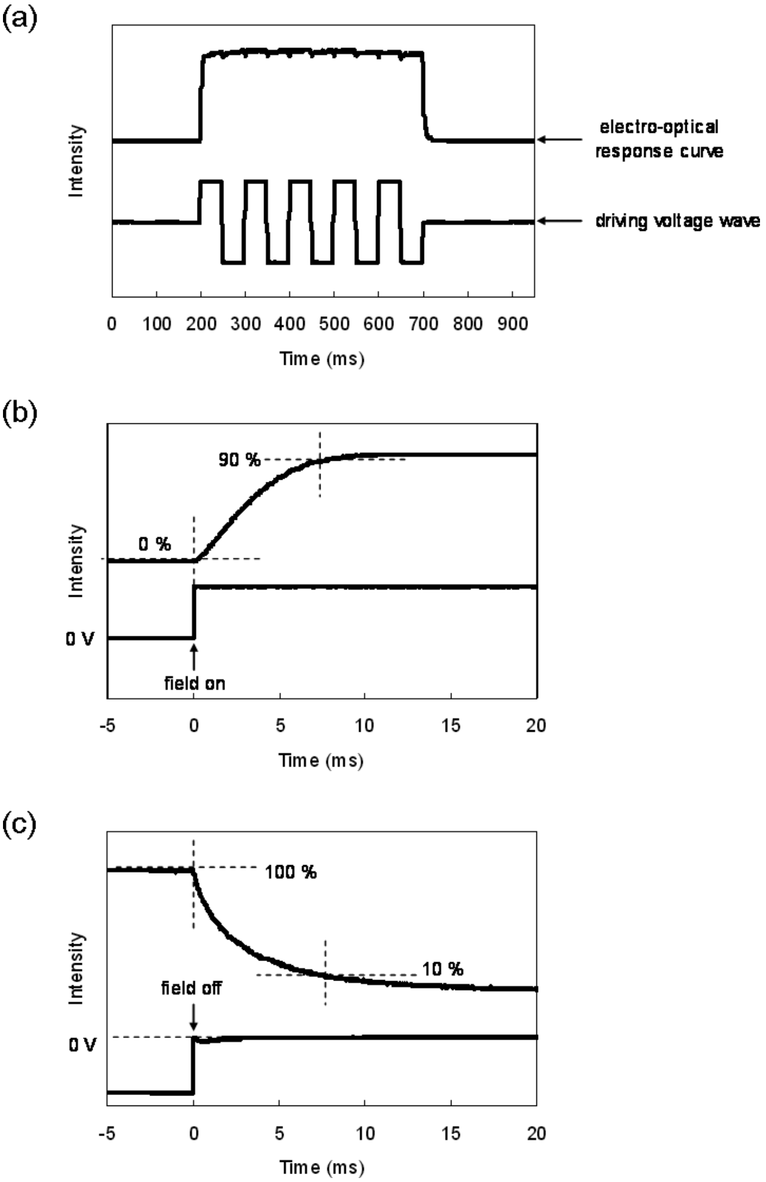

Figure 4. a) Electro-optical response curves of compound **1** in the BPIII at 47 °C. Expansions, the rise process (b) and the decay process (c), are shown for clarity.

occurs cooperatively. However, the decay time lengthens with decreasing temperature. The increase of the decay time with decreasing temperature is explainable by temperature dependence of the rotational viscosity. The activation energy is estimated from the Arrhenius plot to be about 483 kJ mol^{-1}.

An electric-field-induced phase transition in BPI or BPII generally shows a switching with a response time of the order of seconds. This slow response is attributed to a three-dimensional cubic structure of BPI or BPII. On the other hand, BPIII has an amorphous structure consisting of double twist cylinders with arbitrary orientation. Therefore, the phase transition in BPIII might be much faster than that in BPI or BPII. Recently, Yelamaggad reported that bent-core molecules with a chiral center show a wide temperature range of BPIII.[25] However, no electro-optical switching in the BPIII has ever been reported.

Actually, BPIII has a twisted nematic order which exists microscopically, although it appears to be macroscopically isotropic. The applied electric field amplifies the nm-scale order of the twisted organization in the BPIII to the µm-scale order of the anisotropic nematic organization with a response time of an order of 10^{-2} s, which induces a marked change in the birefringence. The rise time is dependent on the electric field strength. Therefore, the response speed might be increased considerably with an appropriate design for the electric field. Furthermore, a well black state is obtainable in BPIII without surface treatment and a homogeneous bright state has been achieved in the electric-field induced N phase. They are great advantages for liquid crystal displays. Surface treatment, e.g., a rubbing process, cannot achieve perfect alignment of liquid crystalline molecules for a pronounced black state and needs high manufacturing costs. Furthermore, reported electro-optical effects in blue phases, e.g., a local reorientation of the molecules or distortion of the lattice, seem to be difficult to produce a high transmittance with a relatively low voltage.

In conclusion, we report here the fast electric-field induced phase transition from BPIII to N of a newly designed polar chiral liquid crystal possessing molecular biaxiality. The applied field amplifies the nm-scale order of the twisted nematic organization in the BPIII to the µm-scale order of the nematic organization with a response time of the order of 10^{-2} s. The present nanotechnology can offer fast switching between a well black state of the BPIII and a homogeneous bright state of the induced N phase without surface treatment, and it can extend liquid crystal science to novel photonics applications.

Experimental

Preparation of Materials: *(S)-1-Methylheptyl 4′-{4-octyloxy-2-[6-(4-cyanobiphenyl-4′-yloxy)hexanoyloxy]benzoyloxy}biphenyl-4-carboxylate (**1**)*: To a solution of 4-cyano-4′-hydroxybiphenyl (0.83 g, 6.0 mmol) and ethyl 6-bromohexanoate (1.3 g, 6.0 mmol) in acetone (60 mL) was added potassium carbonate (0.8 g, 6.0 mmol). The reaction mixture was stirred under reflux for 8 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with a toluene-ethyl acetate (9:1) mixture as the eluent, and recrystallized from ethanol. The intermediate product, ethyl 6-(4-cyanobiphenyl-4′-yloxy)hexanoate, was obtained. Yield: 0.62 g (30 %).

Subsequently, ethyl 6-(4-cyanobiphenyl-4′-yloxy)hexanoate (0.56 g, 1.7 mmol) was added to a sodium hydroxide solution (10 mL, 3 N).

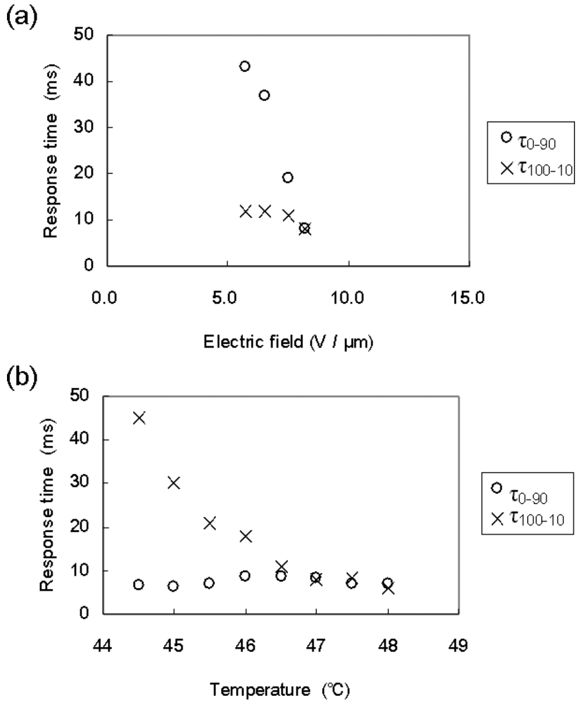

Figure 5. a) Electric-field dependence of the response times for the rise and decay processes of compound **1** at 47 °C; b) temperature dependence of response times for the rise and decay processes with an AC field of 8.2 V μm^{-1}.

Then THF was added until a homogeneous suspension was formed. The reaction mixture was stirred at room temperature for 4 days. After completion of hydrolysis, the suspension was neutralized with a solution of hydrochloric acid (5 N) at 0 °C. The crude product was filtered off and washed with diethyl ether and water, 6-(4-cyanobiphenyl-4′-yloxy)hexanoic acid was obtained. Yield: 0.50 g (96 %).

(*S*)-1-Methylheptyl 4′-(2-hydroxy-4-octyloxybenzoyloxy)biphenyl-4-carboxylate was prepared using our reported method [24]. To a solution of 6-(4-cyanobiphenyl-4′-yloxy)hexanoic acid (0.12 g, 0.4 mmol) in dichloromethane (18 mL), (*S*)-1-methylheptyl 4′-(2-hydroxy-4-octyloxybenzoyloxy)biphenyl-4-carboxylate (0.17 g, 0.3 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.083 g, 0.4 mmol), and 4-(*N*,*N*-dimethylamino)pyridine (5 mg, 0.04 mmol) were added. The resulting solution was stirred at room temperature for 18 h. Precipitated materials were removed by filtration. After removal of the solvent by evaporation, the residue was purified by column chromatography on silica gel with a toluene-ethyl acetate (15:1) mixture as the eluent. Recrystallization from ethanol gave the desired product. Yield: 0.10 g (37 %). ^{1}H NMR (JNM-A400; JEOL, 400 MHz, solvent CDCl$_3$, standard TMS) δ_H/ppm: 8.20(d, 1H, Ar–*H*, $J = 9.3$ Hz), 8.09(d, 2H, Ar–*H*, $J = 8.3$ Hz), 7.68(d, 2H, Ar–*H*, $J = 8.3$ Hz), 7.64–7.60(m, 6H, Ar–*H*), 7.48(d, 2H, Ar–*H*, $J = 8.7$ Hz), 7.25(d, 2H, Ar–*H*, $J = 7.3$ Hz), 6.94(d, 2H, Ar–*H*, $J = 8.8$ Hz), 6.88(dd, 1H, Ar–*H*, $J = 8.0$ Hz, 2.4 Hz), 6.66(d, 1H, Ar–*H*, $J = 2.4$ Hz), 5.21–5.13(m, 1H, –C**H*(CH$_3$)), 4.03(t, 2H, –OC*H*$_2$, $J = 6.6$ Hz), 3.97(t, 2H, –OC*H*$_2$, $J = 6.4$ Hz), 2.66(t, 2H, –OCOC*H*$_2$–, $J = 7.6$ Hz), 1.83–1.29(m, 27H, aliphatic *H*), 0.89(t, 3H, –C*H*$_3$, $J = 6.6$ Hz), 0.88(t, 3H, –C*H*$_3$, $J = 6.8$ Hz); IR (FTS-30; Bio-Rad Laboratories Inc., KBr) ν_{max}/cm^{-1}: 2930, 2858, 2225, 1737, 1607, 1495, 1253, 1133. Elemental anal. (EA. 1110; CE Instruments Ltd.) Calcd. for $C_{55}H_{63}NO_8$: C 76.27, H 7.33, N 1.62. Found: C 76.15, H 7.75, N 1.68.

Physical Properties: The initial phase assignments and corresponding transition temperatures for the final compound were determined using thermal optical microscopy using a polarizing microscope (BX-51; Olympus Optical Co. Ltd.) equipped with a temperature control unit (LK-600PM; Japan High Tech). The temperatures and enthalpies of transition were investigated using differential scanning calorimetry (DSC, DSC 6200; Seiko Instruments Inc.). Optical transmittance, as a function of applied electric AC field of 10 Hz, was observed for a sample contained in the region between the comb-type interdigitated electrodes under crossed polarizers. The distance between the electrodes was 10 μm and the cell gap was maintained at 10 μm by spacers. The cells were kindly supplied by Chisso Petrochemical Corporation.

Received: April 16, 2007
Revised: June 2, 2007

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