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Chiral T-shaped Semiflexible Compound Exhibiting a Wide Temperature Range Blue Phase III

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We have designed a chiral T-shaped compound possessing a flexible spacer, which was found to exhibit a blue phase III with a temperature range of about 30 K including room temperature on cooling. Furthermore, the BPIII changed to a glass phase. Electrooptical switching was observed at all temperatures of the BPIII.

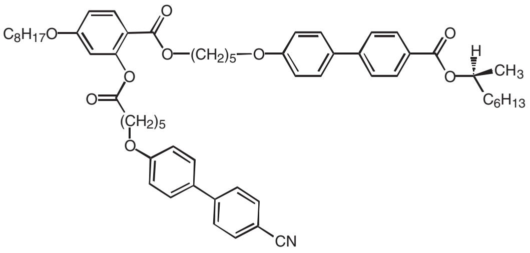

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Figure 1. Molecular structure of compound **1**.

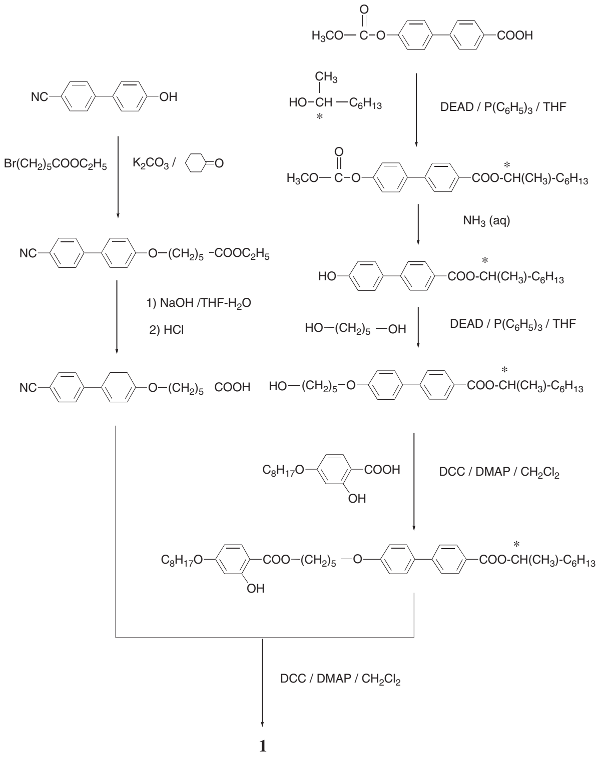

Figure 2. Synthetic scheme of compound **1**.

Blue phases are of particular interest because they have a fluid lattice, the structure of which is stabilized by lattice defects. They are classifiable as blue phase I (BPI), blue phase II (BPII), or blue phase III (BPIII) depending on their double-twist-cylinder packing structure.[1,2] The BPI packing structure is a body-centered cubic structure; that of BPII is a simple cubic structure.[3,4] Theoretical investigations have revealed that BPIII and the isotropic phase have identical symmetry.[5] It is expected that BPIII consists of double twist cylinders with arbitrary orientation.[1,6,7] Blue phases are normally found in a narrow (ca. 1 K) temperature range between the isotropic liquid and a chiral nematic (N*) phase of sufficiently short pitch. Electric field effects in blue phases have been investigated.[1] Blue phases have potential applications as fast light modulators or tunable photonic crystals. However, their narrow temperature range poses a daunting obstacle to their application. Therefore, stabilizing the blue phases has attracted much attention.[8–18]

Recently, we reported an electric field induced phase transition between BPIII and N phases of a chiral T-shaped liquid crystal.[19] Actually, BPIII has a twisted nematic order that exists microscopically, although it appears to be macroscopically isotropic. Furthermore, BPIII has no periodic defects. Therefore, a well black state is obtainable without surface treatment. Then a homogeneous bright state is achieved in the electric field induced N phase. However, some problems remain for application of this technology to display devices: broadening of the temperature range, reduction of the driving voltage, and improvement of the response speed. Herein, we report a chiral T-shaped compound possessing a flexible spacer. The compound was found to exhibit BPIII with a wide temperature range of about 30 K including room temperature.

Molecular structure of the chiral T-shaped compound (*S*)-1-methylheptyl 4′-({4-octyloxy-2-[6-(4-cyanobiphenyl-4′-yloxy)-hexanoyloxy]benzoyloxy}pentyloxy)biphenyl-4-carboxylate (**1**) is presented in Figure 1. Figure 2 shows the scheme of synthesis of compound **1**. The purity of the final compound was checked using elementary analysis. The structure was elucidated using proton nuclear magnetic resonance (^{1}H NMR) spectroscopy.[20]

The phase transition behavior of compound **1** was investigated using polarized optical microscopy (BX-51; Olympus Corp.) equipped with a temperature control unit (LK-600PM; Japan High Tech Co., Ltd.) and differential scanning calorimetry (DSC 6200 calorimeter; Seiko Co., Ltd.). On cooling at a rate of 5 °C min^{-1}, compound **1** showed the following phase sequence: isotropic liquid 24.7 °C (1.0 kJ mol^{-1}) BPIII −8.2 °C glass phase; the melting temperature was 75 °C. The blue phase showed fluidity; it did not appear as platelets that are usually observed in BPI or BPII, thereby indicating that the blue phase is BPIII. The Iso–BPIII transition temperature was independent of the cooling rate. On the cooling at a rate of 0.5 °C min^{-1}, it was 25.2 °C. Compound **1** was found to exhibit BPIII with a

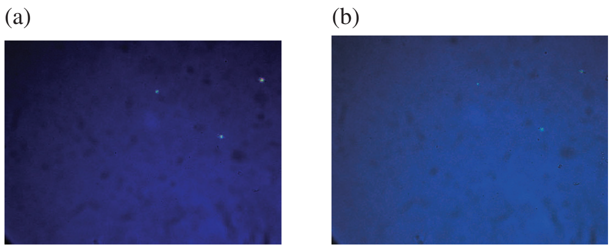

Figure 3. Photomicrographs of (a) the BPIII at 20 °C and (b) the glassy state at −20 °C of compound **1** in an uncovered region on a glass slide.

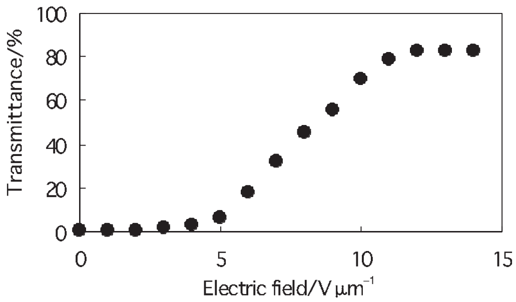

Figure 4. Optical transmittance of compound **1** in the BPIII as a function of an AC field at a frequency of 10 Hz at 19 °C.

temperature range of about 30 K on cooling. The temperature range is the widest among reported chiral compounds. Figure 3 shows photomicrographs of (a) the BPIII at 20 °C and (b) the glass phase at −20 °C. No marked difference in textures was found between those of BPIII and glass phase. The BPIII structure is expected to remain in the glass phase. To our knowledge, the direct BPIII to glass transition has never been reported. The introduction of the flexible spacer to the T-shaped system is thought to disturb the parallel alignment of the mesogens in a single molecule, which can suppress the appearance of the chiral nematic phase. Furthermore, the flexibility is thought to increase the intramolecular twist interaction. The chiral center and a twisted conformation of the two mesogenic moieties via the chiral interaction can produce a biaxial helix to stabilize BPIII.

We investigated electrooptical effects in the BPIII. Optical transmittance, as a function of a square wave of an AC electric field at a frequency of 10 Hz, was observed for a sample contained in the region between comb-type interdigitated electrodes under crossed polarizers. The distance between electrodes was 10 µm; the cell gap was maintained at 12 µm using spacers. Figure 4 portrays the voltage–transmittance curve at 19 °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.

The transmittance without an electric field was 0.7%. A dark state that is macroscopically isotropic is obtainable in BPIII without surface treatment. The transmittance increased concomitantly with the increase of the electric field. With an applied field of 12 V µm^{-1}, the transmittance is 80%.

Switching behavior was observed at all temperatures of the BPIII. Subsequently, we investigated the response speed of the electric field induced phase transition between BPIII and N phases. The response time for the rise process is the time necessary for an increase in the transmittance from the initial state to 90% of the saturated state. That for the decay process is the time necessary for a decrease in the transmittance from the initial state to 10% of the saturated state. The rise time decreased dramatically with increasing electric field, although the decay time was independent of the electric field. The rise and decay times at 22 °C with an AC field of 12 V µm^{-1} at a frequency of 0.1 Hz were 200 and 600 ms, respectively. They lengthen as the temperature decreases. The response times of compound **1** are much longer than those of our previously reported T-shaped compound.[18] The introduction of the flexible spacer might increase the rotational viscosity.

In conclusion, the deigned chiral T-shaped compound was found to exhibit an unusual phase sequence of Iso–BPIII–glass with the widest temperature range of BPIII. The present molecular design stabilizes a chiral hierarchical structure in BPIII.

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