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PAPER

Biphenyl derivative stabilizing blue phases

Yutaro Kogawa,[a] Tetsu Hirose[b] and Atsushi Yoshizawa*[a]

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After preparing a biphenyl derivative possessing two 2,3-difluoro-1,4-diphenylbenzene units, we investigated its phase transition behaviour. It showed a phase sequence of isotropic liquid–nematic phase–anticlinic smectic C phase. A mixture with a chiral additive with a high twisting power exhibited a cubic blue phase and/or an amorphous blue phase III (BPIII). The compound doped with 10 wt% of the chiral additive showed a phase sequence of Iso 85.4 °C BPIII 70.6 °C cubic BP 47.3 °C chiral nematic 37.3 °C unidentified smectic phase. We investigated electro-optical switching in BPIII and in the cubic BP of the mixture. Transmittance without an applied electric field in the BPIII was 0%, whereas that in the cubic BP was 4.6%. Threshold and driving voltages in the BPIII are lower than in the cubic BP. Furthermore, the BPIII exhibits no voltage-induced hysteresis effects on transmittance. Amorphous BPIII has superior potential for use in next-generation displays.

Blue phases are of particular interest because they have a fluid lattice whose structure is stabilized by lattice defects. Believed to consist of double twist cylinders, they are classified into three categories depending on the cylinders' packing structure: blue phase I (BPI), blue phase II (BPII), and blue phase III (BPIII).[1] The packing structure of BPI is a body-centred cubic structure, BPII is a simple cubic structure.[2,3] In contrast, BPIII is expected to consist of double-twisted cylinders with arbitrary orientation.[2,4,5] Usually, blue phases are found in an extremely narrow temperature range (*ca.* 1 K) between the isotropic liquid and the chiral nematic (N*) phase of sufficiently short pitch. Blue phases are potentially useful for application as fast light modulators or tunable photonic crystals, but their narrow temperature range is a critical problem. Therefore stabilizing the blue phases has attracted much attention.[6–18] The most successful approach is polymer stabilization, as reported by Kikuchi *et al.*[6] Specific polymer networks can stabilize the lattice defects of a BPI. The temperature range of the polymer-stabilized BPI is extended to more than 60 K. Fast electro-optical switching with a response time of 10^{-4} s was demonstrated in the polymer-stabilized BPI. Blue phases have several advantages: fast response speed and optical isotropy. Therefore a blue-phase LCD mode using polymer-stabilized BPI was developed in earlier studies.[19–22] However, critical problems such as high operating voltage, hysteresis, residual transmittance, and stability remain as necessary improvements for application to display devices. Particularly, voltage-induced hysteresis affects the accuracy of gray scale control and should therefore be eliminated. This report describes electro-optical switching in an amorphous BPIII.[23] Actually, several groups have investigated BPIII switching,[15,18,24] but no report describes comparison of electro-optical properties between a BP with a cubic structure (cubic BP: BPI or BPII) and amorphous BPIII using a single compound or mixture because no single system exhibits both those blue phases with wide temperature ranges. Elucidation of the influence of the molecular geometry on the stability of blue phases remains in its infancy. A recent report describes that a binaphthyl derivative possessing two 2,3-difluoro-1,4-diphenylbenzene units exhibits a cubic blue phase with a temperature range of about 30 K.[25] Herein a newly designed biphenyl derivative possessing two 2,3-difluoro-1,4-diphenylbenzene units is proposed. It exhibits cubic BP and/or amorphous BPIII in mixtures with a chiral compound. We discuss their mutual differences in electro-optical properties.

Experimental

Materials

Spectroscopic analysis. Purity of the final compound was also checked using elemental analysis (EA 1110; CE Instruments Ltd.). Infrared (IR) spectroscopy (FTS-30; Bio-Rad Laboratories Inc.) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (JNM-ECA500; JEOL) elucidated the structure of the final product.

Preparation of materials. For use in this study, 2,3-difluoro-4-(4-hexylphenyl)-1-(4-hydroxyphenyl)benzene was purchased from Midori Kagaku Co. Ltd.

2,2′-Bis{6-[4-(4-(4-hexylphenyl)-2,3-difluorophenyl)phenyloxycarbonyl]hexyloxy}-1,1-biphenyl (1). To a solution of 2,2′-biphenol (0.37 g, 2.0 mmol) and ethyl 7-bromoheptanoate (1.0 g,

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[a] *Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki, Aomori, 036-8561, Japan. E-mail: ayoshiza@cc.hirosaki-u.ac.jp*
[b] *Tohoku Chemical Corporation, 1-3-1, Kanda, Hirosaki, Aomori, 036-8655, Japan*

4.0 mmol) in cyclohexanone (20 ml) was added potassium carbonate (0.58 g, 3.0 mmol). The reaction mixture was stirred at 140 °C for 8 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified using column chromatography on silica gel with a toluene and ethyl acetate (4 : 1) mixture as the eluent, giving 2,2′-bis[6-(ethyloxycarbonyl)hexyloxy]biphenyl as a colourless liquid; yield 0.87 g (87%).

First, 2,2′-bis[6-(ethyloxycarbonyl)hexyloxy]biphenyl (0.60 g, 1.2 mmol) was added to a solution of NaOH (0.12 g, 3.0 mmol) in an ethanol (30 ml) and water (10 ml) mixture. The resulting solution was refluxed with stirring for 4 h. After removal of the ethanol by evaporation, the residue was acidified using aq. HCl. The solution was extracted with dichloromethane. The organic layers were combined, dried over magnesium sulfate, filtered, and evaporated. The residue was washed with hexane to give 7,7′-(biphenyl-2,2′-diylbisoxy)bisheptanoic acid as a white solid; yield 0.53 g (92%); mp 70.4–71.6 °C.

To a solution of 7,7′-(biphenyl-2,2′-diylbisoxy)bisheptanoic acid (0.18 g, 0.40 mmol) in dichloromethane (30 ml), 2,3-difluoro-4-(4-hexylphenyl)-1-(4-hydroxyphenyl)benzene (0.29 g, 0.80 mmol), *N*,*N*′-dicyclohexylcarbodiimide (0.17 g, 0.80 mmol), and 4-(*N*,*N*-dimethylamino)pyridine (0.009 g, 0.08 mmol) were added. The resulting solution was stirred at room temperature for 20 h. Precipitated materials were removed by filtration. After removal of the solvent by evaporation, the residue was purified using column chromatography on silica gel with dichloromethane as the eluent and then recrystallized with an ethanol and ethyl acetate (1 : 1) mixture, giving the desired product as a white solid; yield 0.30 g (64%); mp 115.0–116.1 °C. ^{1}H NMR (500 MHz, solvent $CDCl_3$, standard TMS) δ/ppm: 7.59 (dd, 4H, Ar-H, $J = 8.6$ Hz, 1.2 Hz), 7.50 (dd, 4H, Ar-H, $J = 8.0$ Hz, 1.2 Hz), 7.29 (d, 4H, Ar-H, $J = 8.6$ Hz), 7.32–7.21 (m, 8H, Ar-H), 7.18 (d, 4H, Ar-H, $J = 8.6$ Hz), 6.998 (t, 1H, Ar-H, $J = 7.5$ Hz), 6.996 (t, 1H, Ar-H, $J = 7.5$ Hz), 6.96 (d, 2H, Ar-H, $J = 8.6$ Hz), 3.94 (t, 4H, $-OCH_2-$, $J = 6.3$ Hz), 2.67 (t, 4H, Ar-CH_2-, $J = 7.7$ Hz), 2.52 (t, 4H, $-OCOCH_2-$, $J = 7.7$ Hz), 1.72–1.33 (m, 32H, aliphatic-H), 0.90 (t, 6H, aliphatic-H, $J = 6.9$ Hz). IR (KBr) ν_{max}/cm^{-1}: 2929, 2855, 1752, 1460, 1209. Elemental anal. calcd for $C_{74}H_{78}O_6F_4$: C 78.01, H 6.90. Found: C 77.94, H 6.87%.

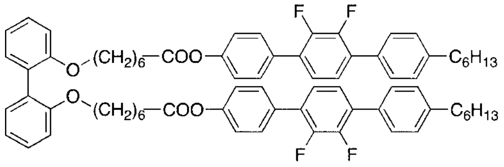
Liquid-crystalline and physical properties. The initial phase assignments and corresponding transition temperatures for the final compound were determined using thermal optical microscopy with a polarizing microscope (BX-51; Olympus Optical Co. Ltd.) equipped with a temperature control unit (LK-600PM; Japan High Tech). The temperatures and enthalpies of transition were investigated using differential scanning calorimetry (DSC, DSC 6200; Seiko Instruments Inc.). Dielectric measurements were performed using an impedance analyzer (Hewlett Packard HP 4284A) with a temperature control unit at a frequency of 1 kHz. Homogeneous and homeotropic configuration cells (5.0 μm) purchased from E.H.C. were used for the measurements.

Optical transmittance as a function of applied electric AC field at 10 Hz was observed for a sample contained in the region between the comb-type interdigitated electrodes under crossed polarizers. 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 distance between the electrodes was 10 μm and the cell gap was maintained at 12 μm by spacers. The cells were kindly supplied by Chisso Petrochemical Corp.

Results and discussion

Liquid crystalline properties

The biphenyl derivative, 2,2′-bis{6-[4-(4-(4-hexylphenyl)-2,3-difluorophenyl)phenyloxycarbonyl]hexyloxy}-1,1-biphenyl (**1**), was prepared as described below through synthesis. 2,2′-Biphenol was treated with ethyl 7-bromoheptanoate in the presence of potassium carbonate. The obtained ester was hydrolyzed to give the corresponding carboxylic acid. The intermediate was treated with 4-(4-(4-hexylphenyl)-2,3-difluorophenyl)phenol in the presence of DCC to give the target compound.



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Phase transition behaviour was investigated using polarized optical microscopy and DSC. On cooling, compound **1** showed the following phase sequence: isotropic liquid 106.1 °C (1.2 kJ mol^{-1}) nematic (N) phase 69.0 °C (0.8 kJ mol^{-1}) anticlinic smectic C (SmCanti) phase −1.4 °C glass. The melting temperature was 113 °C. The SmCanti phase was identified by optical microscopy, *i.e.*, the texture of the homeotropically aligned sample was a schlieren texture that possessed singularities with two ($s = 1/2$) and four ($s = 1$) brushes (Fig. 1). The two-brush singularities were not able to be formed in the synclinic phase, but they can be generated with anticlinic ordering.[26] Dielectric anisotropy of compound **1** in the N phase was obtained as −1.1 at 80 °C.

We investigated the transition behaviour of binary mixtures of compound **1** and a chiral compound ISO-(6OBA)$_2$. The chiral compound possesses high twisting power[27] and is well known to induce blue phases in the mixture with a nematic liquid crystal.[6,10,15,18,28]

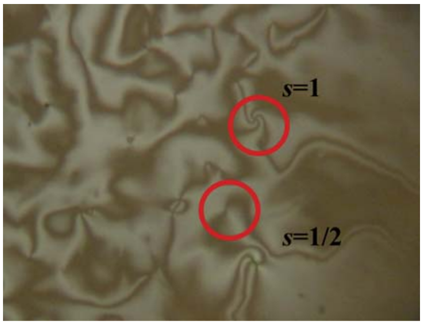
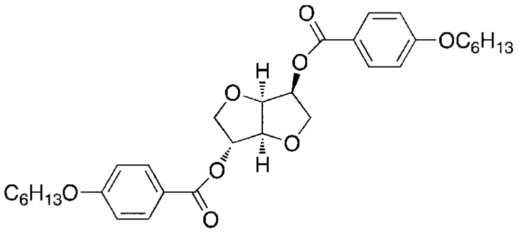


Fig. 1 Photomicrograph of the SmCanti phase of a homeotropically aligned sample of compound **1** at 60 °C.



HTP = 87 μm^{-1}

ISO-(6OBA)$_2$

Fig. 2 shows the binary phase diagram on cooling between ISO-(6OBA)$_2$ and compound **1** obtained using optical microscopy. All mesophases were monotropic. The SmX phase is an unidentified smectic phase. Neither ferroelectric nor antiferroelectric switching was observed in the SmX phase. The cooling rate was 0.1 °C min^{-1} from isotropic liquid to BP; then the cooling rate was changed to 2 °C min^{-1}. For mixtures containing 7–13 wt% of ISO-(6OBA)$_2$, blue phases were found to be induced. In a mixture of ISO-(6OBA)$_2$ (7 wt%) and compound **1** (93 wt%), a platelet texture with various colours which is usually observed in blue phases with a cubic structure appeared at 89.5 °C; then it changed to a typical N* texture at 53.6 °C. In a mixture of ISO-(6OBA)$_2$ (13 wt%) and compound **1** (87 wt%), a blue colour of low birefringence appeared at 69.2 °C. The blue colour phase was clearly observed in uncovered regions of the mixture. The blue phase showed fluidity and did not appear as platelets. These observations indicate that the phase is an amorphous BPIII. When cooled further, the BPIII changed to an N* phase at 43.4 °C. Fig. 3 depicts a DSC thermogram of the mixture on cooling from isotropic liquid. It is particularly interesting that a mixture of ISO-(6OBA)$_2$ (10 wt%) and compound **1** (90 wt%) exhibited both amorphous BPIII and cubic BP. Fig. 4(a) and (b) respectively show textures of BPIII and cubic BP of the mixture. Fig. 5 depicts a DSC thermogram of the mixture on cooling from isotropic liquid. The phase transition temperatures were the following: Iso 85.4 °C BPIII 70.6 °C cubic BP 47.3 °C N* 37.3 °C SmX. No transition enthalpy was detected at the BPIII to cubic BP transition. The temperature ranges of the BPIII and the cubic BP were, respectively, 14.8 K and 23.3 K. Therefore we can investigate electro-optical properties in amorphous BPIII and cubic BP of the single mixture.

Compound **1** can exist in either of two conformations: *cis* or *trans* with respect to the C1–C1′ axis of the biphenyl moiety. Molecular-mechanical calculations using MOPAC-6/PM3 of

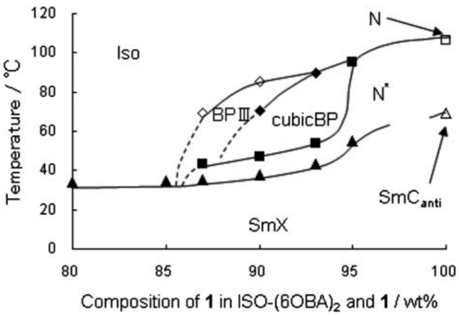


Fig. 2 Binary phase diagram of mixtures of ISO-(6OBA)$_2$ and compound **1**.

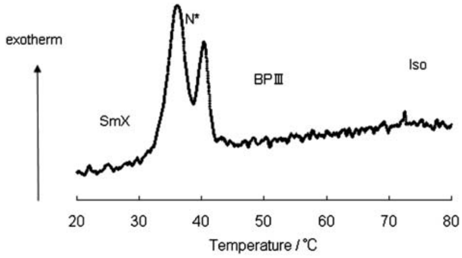


Fig. 3 Cooling DSC thermogram of a mixture of ISO-(6OBA)$_2$ (13 wt%) and compound **1** (87 wt%) at a scanning rate of 1 °C min^{-1}.

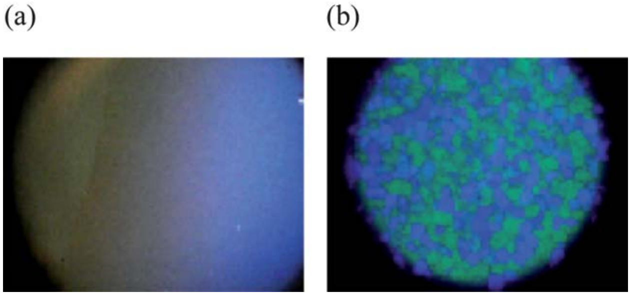


Fig. 4 Photomicrographs of (a) the BPIII at 73.6 °C and (b) the cubic BP at 65.0 °C of a mixture of ISO-(6OBA)$_2$ (10 wt%) and compound **1** (90 wt %).

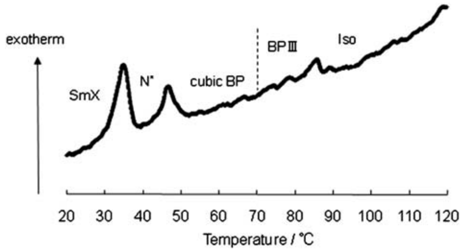


Fig. 5 Cooling DSC thermogram of a mixture of ISO-(6OBA)$_2$ (10 wt%) and compound **1** (90 wt%) at a scanning rate of 1 °C min^{-1}.

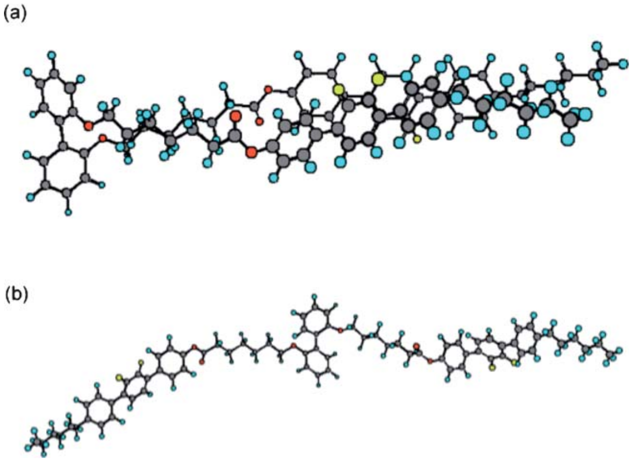


Fig. 6 MOPAC models for compound **1** with (a) *cis* conformation and (b) *trans* conformation.

compound **1** suggest that the *cis* conformation (Fig. 6(a)) is more stable than the *trans* one (Fig. 6(b)). The energy difference between the *cis* and *trans* conformers of compound **1** was estimated to be 43 kJ mol^{-1}. If compound **1** forms the *trans* conformation, then the I–N transition temperature should be much higher than the observed value. For these reasons, we assumed the *cis* conformer for compound **1**. With respect to chiral effects of the binaphthyl derivatives on blue phase stabilization, we made the following interpretation.[25,29] The binaphthyl derivative exists as a cisoid form, which has two helical origins, the asymmetric axis and the twisted conformation of the mesogenic units. Their coexistence is able to stabilize the double-twist structure in the blue phase. In the present system, chiral transfer from ISO-(6OBA)$_2$ to compound **1** *via* core–core interaction can induce twisting of the biphenyl axis, which produces a twist conformation of the two terphenyl mesogenic units, as shown in Fig. 7.[30,31] Therefore compound **1** has two origins for the twisting power: a twist conformation of the biphenyl moiety and that of the mesogenic units, which can stabilize the blue phases.

Electro-optical studies

We investigated electro-optical properties in the BPIII and the cubic BP of the mixture of ISO-(6OBA)$_2$ (10 wt%) and compound **1** (90 wt%). Optical transmittance, as a function of applied electric AC field at 10 Hz, was observed for a sample contained in the region between comb-type interdigitated electrodes under crossed polarizers. Fig. 8(a) and (b) respectively portray the voltage-dependent transmittance curve in the BPIII at 80 °C and that in the cubic BP at 60 °C. In BPIII (Fig. 8(a)), the transmittance without an electric field was 0%. The transmittance increased concomitantly with the increase of the electric field. With an applied field of 9 V μm^{-1}, the texture showed a homogeneous bright state with a transmittance of 80%. The transmittance decreased with the decrease of the electric field. The backward curve was the same as the forward curve. It is free from both hysteresis and residual transmittance. According to Wu *et al.*,[32] the compact packing in a BP with a cubic lattice structure hinders the formation of the BP structure during the voltage descent process. The absence of a lattice structure in the BPIII produces the hysteresis-free switching. The extinction direction was obtained when the sample with the saturated transmittance was rotated 45°. Transmittance of the dark state was 1.5%. These observations indicate that the electric-field-induced bright state is the N phase. We estimated the response times in rise and decay processes. The rise and decay times were 10 s and 8 s, respectively. Therefore the transmittance change for BPIII shown in Fig. 8(a) is attributed to electric-field-induced phase transition between BPIII and N. There is another possibility that the present electro-optical response is due to reorientation of the local director. In that case, the decay time is thought to be much faster than 1 s. In the cubic BP (Fig. 8(b)), transmittance without an electric field was 4.6%. Although the transmittance increased concomitantly with the increase of the electric field, it did not reach a saturated value with an applied field of 12 V μm^{-1}. Threshold and saturated voltages in the cubic BP were higher than those in the BPIII. We were not able to observe the backward process because the transmittance under an AC field showed time-dependent decay. Such decay was not observed in BPIII. When the sample with the transmittance of 70% was rotated, the texture did not change, indicating that the electric-field-induced bright state is the N* phase. The increase in the transmittance for cubic BP shown in Fig. 8(b) is thought to result from cubic BP to N* phase transition.

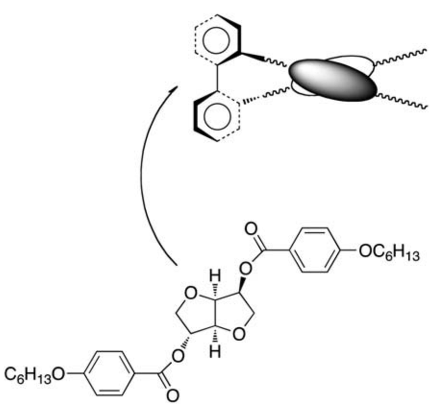


Fig. 7 Schematic model for chirality transfer from a core part of ISO-(6OBA)$_2$ to a biphenyl unit of compound **1**.

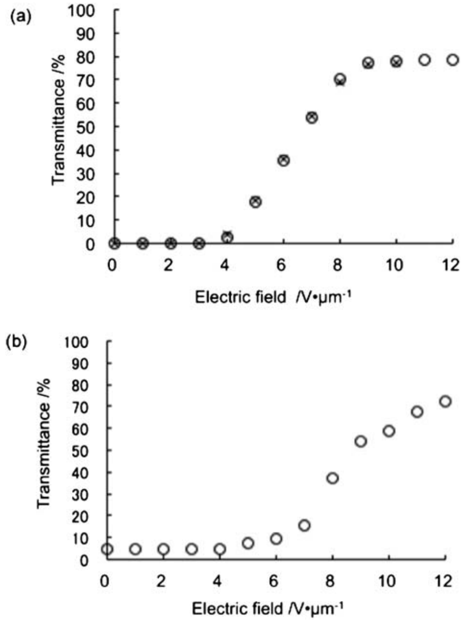


Fig. 8 Optical transmittances of the mixture ISO-(6OBA)$_2$ (10 wt%) and compound **1** (90 wt%) as a function of AC field at a frequency of 10 Hz in (a) BPIII at 80 °C and (b) cubic BP at 60 °C. The ascending and descending cycle is depicted in Fig. 8(a). The only ascending process is shown in Fig. 8(b). Open circles and crosses respectively represent ascending and descending processes.

Time-dependent transmittance under the AC field of 12 V μm^{-1} was observed. The results are portrayed in Fig. 9. In the BPIII at 80 °C (Fig. 9(a)), the transmittance increased with the increase of time, reaching the saturated value. The saturated transmittance did not change with further increase of time. However, in the cubic BP at 60 °C (Fig. 9(b)), the transmittance reached the saturated value of 70%; then it decreased with the increase of time. The transmittance of 1.5% at 30 s is lower than

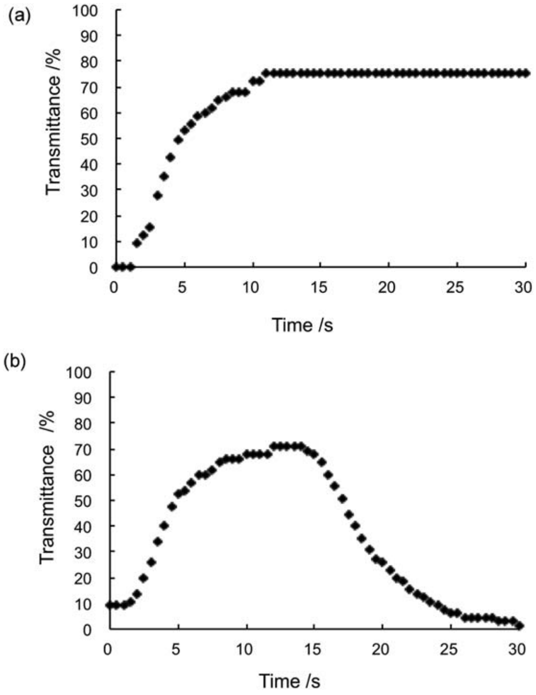


Fig. 9 Optical transmittances of the mixture ISO-$(6OBA)_2$ (10 wt%) and compound **1** (90 wt%) as a function of time under an AC field of 12 V μm^{-1} at a frequency of 10 Hz in (a) BPIII at 80 °C and (b) cubic BP at 60 °C.

that without an electric field. After eliminating the electric field and then re-applying it to the sample, no electro-optical switching occurred. This electro-optical behaviour in the cubic BP occurred under any electric field with a magnitude of 6–12 V μm^{-1}. Phase transition temperatures of the sample after applying electric field were identical to those of the virgin sample. One possible explanation for the unusual decrease in the transmittance is an electric-field-induced phase transition from N* to isotropic liquid. The electro-optical responses in BPIII and cubic BP are reproducible. Therefore the marked difference in the electro-optical response between BPIII and cubic BP is attributed to the difference in the blue phase structure between them. According to earlier studies of electric field effects in cubic blue phases,[1] an increasing electric field initially lengthens the blue phase lattice parameter and causes birefringence. With higher fields, the blue phases may transform between themselves, to the helical phase, and ultimately to the nematic phase. Because BPIII has no lattice structure, we infer that the rise process in BPIII includes two transformations: a double twisted structure to a single twisted structure breaking their cylindrical structure (BPIII to N*) and the single twisted structure to the nematic structure (N* to N). With respect to the cubic BP, short-range correlation due to the lattice structure can remain under the electric field. A double twisted structure might transform to an unstable single twisted structure with the short-range correlation. The activation energy of transition from the electric-field-induced N* state to the isotropic liquid for cubic BP is thought be lower than that from the electric-field-induced N state to the isotropic liquid for BPIII. Further investigation is necessary to clear the mechanism. Amorphous BPIII without three-dimensional order is more stable against an electric field than cubic BP. The instability against the electric field for the cubic BP is one of the reasons to generate the hysteresis of the present cubic BP. The rise time in the BPIII is almost same to that in the cubic BP. In the present system, the response speed is very slow because of the negative dielectric anisotropy of compound **1**. The response time in BPIII can be readily shortened to less than 1 ms at room temperature by using materials with positive dielectric anisotropy.[33]

Conclusions

We designed a new biphenyl derivative possessing 2,3-difluoro-1,4-diphenylbenzene units and found that it exhibits the N and SmCanti phases. A mixture with a chiral additive exhibited a cubic blue phase and/or an amorphous BPIII with a wide temperature range. Comparing the voltage-dependent transmittance in the BPIII and the cubic BP of a single mixture, the BPIII was found to have the following advantages: (1) free from hysteresis, (2) lower transmittance without an electric field, (3) lower threshold and saturated voltages, and (4) higher stability against an electric field. BPIII with the same symmetry as isotropic liquid has favourable characteristics for application to display devices: it is optically isotropic, hysteresis free, and stable in an electric field.

Acknowledgements

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