

An Optically Isotropic Antiferroelectric Liquid Crystal (OI-AFLC) Display Mode Operating over a Wide Temperature Range using Ternary Bent-Core Liquid Crystal Mixtures

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We report on the synthesis and characterization of bent-core liquid crystal (LC) compounds and the preparation of mixtures that provide an optically isotropic antiferroelectric (OI-AFLC) liquid crystal display mode over a very wide temperature interval and well below room temperature. From the collection of compounds synthesized during this study, we recognized that several ternary mixtures displayed a modulated SmC_aP_A phase down to below -40°C and up to about 100°C on both heating and cooling, as well as optical tilt angles in the transformed state of approximately 45° (optically isotropic state). The materials were fully characterized and their liquid crystal as well as electro-optical properties analyzed by polarized optical microscopy, differential scanning calorimetry, synchrotron X-ray diffraction, dielectric spectroscopy, and electro-optical tests.

Significant improvements of liquid crystal display (LCD) technology over the last decade, including in the development of fast switching liquid crystal (LC) mixtures, new switching modes, optical compensator films, backlights, and driving elec-

tronics, have secured LCDs the lead among display technologies with a $> \$100$ billion market. Described as an industry that is "fast to grow and slow to change",^[1] LCDs are projected to continue as the leading technology, even with the rise of active-matrix organic light-emitting diodes (AM-OLED). Considering the maturity of current commercially available LCD modes that are predominantly based on amorphous silicon thin-film transistor technology (a-Si TFT), current active research largely focuses on the rising need for new display modes (especially transparent LCDs) that can be reversibly switched between optically isotropic and birefringent states featuring excellent gray-scale with sub-millisecond switching times. Blue-phase LCDs were pursued by various academic labs and industry leaders, but have not yet found a commercial breakthrough.^[2] Other recent approaches take advantage of the Kerr effect (a change in birefringence in response to an applied electric field, similar to polymer-stabilized blue-phase LCDs) of nanoencapsulated nematic LC droplets, where an optically isotropic OFF state switches to a birefringent ON state upon application of an electric field.^[3] Considering the advantages (e.g. switching speed) and challenges (zigzag defects) met by surface-stabilized ferroelectric LCs (SS-FLCs) invented by Clark and Lagerwall,^[4] display modes based on bent-core LCs were also the focus of intense investigations.^[5,6] However, high melting points and generally high phase-transition temperatures of bent-core LC compounds have so far thwarted any potential commercial use.

In 2002, Weissflog et al.^[7] and, concurrently, Jákli and co-workers^[8] reported the first optically isotropic smectic bent-core LC material without driving the cell in an applied ac field (i.e. no electro-optic switching) that might be used in an optically isotropic to birefringent switching display mode. Later, for the ester-based bent-core LC material 1,3-phenylene-bis[4-(10-undecenyloxy)benzoyloxy] benzoate (**BC1**,^[9] Figure 1), Jákli and co-workers showed that an applied electric field of $E > 10\text{ V}\mu\text{m}^{-1}$ could transform the birefringent virgin texture to a structure that, after field removal, relaxes to a state that is completely black between crossed polarizers for normal light incidences. This transformed structure could then be reversibly switched to birefringent states, suggesting an orthoconic (i.e. ca. 45° director tilt angle^[10]) anticlinic director structure (Figure 2). Detailed structural and electro-optic studies later verified that the relaxed transformed texture is completely black between crossed polarizers even for oblique incidences (conoscopic images were also black and featureless), indicating

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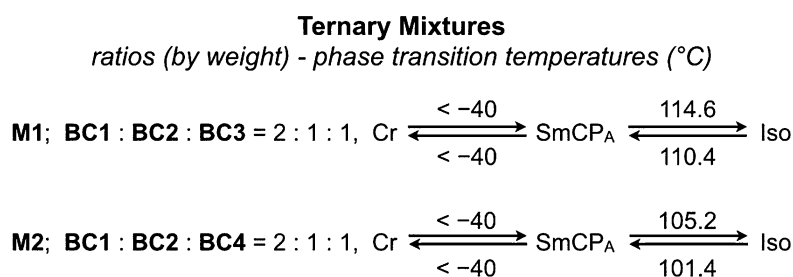
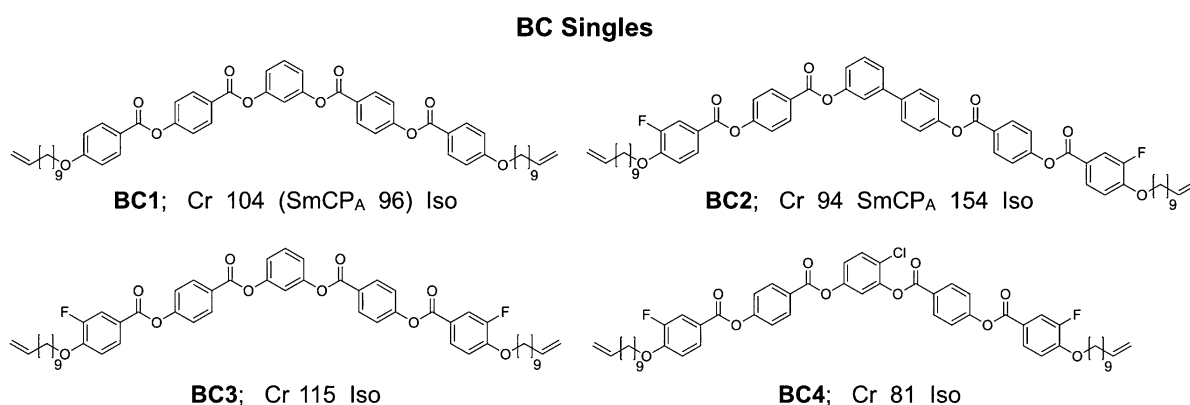


Figure 1. Bent-core compounds used to prepare the ternary bent-core LC mixtures **M1** and **M2**. The parent bent-core LC **BC1** was previously shown to provide ideal tilt (45°) in the SmCP_A phase that serves as the basis for this optically isotropic to birefringent switching mode. The phase-transition temperatures of the single compounds as well as the ternary mixtures are based on DSC measurements (2nd heating run). [Iso = isotropic liquid phase; SmCP_A = antiferroelectric polar smectic-C phase, Cr = crystalline solid phase].

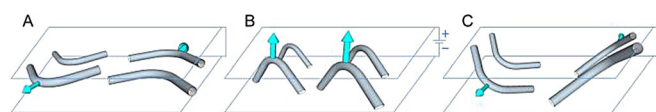


Figure 2. Schematic of the director and layer structure of the OI-AFLC device: A) virgin state, B) ferroelectric transformed state, and C) antiferroelectric ("relaxed") transformed state (no electric field applied) with 45° anticlinic tilt. The device in operation switches between state (B) and (C).

total optical isotropy for any viewing angle.^[11] This is attributed to the nearly 109° opening angle of these specific bent-core molecules. Although the transformed textures in thicker cells (cell gaps > 10 μm) showed small birefringence after a few minutes, indicating a partial relaxation toward the virgin state, the optically isotropic state was surface-stabilized in thinner cells. Electro-optic measurements also revealed that the transmittance was proportional to the applied electric field (i.e. V-shape switching, conveniently allowing for gray-scale devices) below 10 V μm⁻¹, steeply but constantly rising in the applied voltage regime between 10 and 12 V μm⁻¹, and remaining constant at higher fields. The corresponding birefringence increased from Δn = 0 at E = 0 V to Δn ≈ 0.2 at E ≈ 13 V μm⁻¹.^[11] The optically isotropic SmC₃P_A phase is homochiral and shows optical activity as visualized in depolarizing microscopy with slightly uncrossed polarizers.^[11]

The "dark conglomerate" (DC) phase is also optically active and optically isotropic. The DC phase is characterized by a local SmCP structure with short (ca. 20 to 100 nm) smectic

correlation length, indicating a disordered phase structure.^[12] Similar to the SmC₃P_A phase, some materials exhibiting the DC phase also showed field-induced birefringent textures,^[13–17] and several models were established for both structures and switching.^[12,18]

Although the unique electro-optic switching profile of the optically isotropic antiferroelectric LC (OI-AFLC) mode appears suitable for various LCD device architectures (including transparent and reflective LCDs), the proof-of-concept data using **BC1** could only be obtained at temperatures between 95 and 71 °C (the SmCP_A phase range of **BC1** on cooling).^[11] Thus, the challenge has since been to synthesize either single bent-core LC molecules or formulate mixtures of them that exhibit the required SmCP_A phase over a wide temperature range, including room temperature, which additionally satisfy all other structural and electro-optic requirements (tilt, optical isotropy in the transformed state, transmittance vs. applied field response).

Jákli et al. reported multiple attempts to address this challenge, but each mixture or compound failed to satisfy at least one of the critically required parameters (see the Supporting Information for chemical structures). First, a binary mixture of bent-core LCs featuring molecules similar to **BC1**, with one component having a Schiff-base and a second component, cinnamic ester side arms (mixture I, see Figure S1), provided a much wider temperature range, almost down to room temperature on cooling (Iso 130 °C SmCP 25 °C Cr), but the tilt angle was much too low (tilt angle: 35°).^[5] A second binary mixture formulated by using a bent-core LC (structurally similar

to **BC1**) and 40 wt% of a rod-like nematic phenylbenzoate LC derivative (mixture **II**, see Figure S1) lowered the crystallization temperature on cooling even further (phase sequence of that mixture on cooling: Iso 84 °C N 68 °C SmCP_A 16 °C Cr), but again failed to display a sufficiently high enough tilt (tilt angle: 30°).^[19] A single-component bent-core compound (**III** in Figure S1) reported in 2004 formed the desired SmCP_A phase over an astonishingly wide temperature interval of 121 °C, including room temperature (22 °C SmCP_A, 143 °C Iso on heating),^[20] but did not provide the optically isotropic state, as it required fields that were too high for switching and contained (similar to mixture **I** above) the chemically and thermally comparatively unstable Schiff-base segments,^[21] rendering these materials unsuitable for practical LCD devices.

To further address this challenge and deliver a material suitable for practical OI-AFLC mode devices, we report the synthesis and characterization of bent-core LC compounds structurally related to **BC1**, which (in mixtures with **BC1**) provide the desired SmCP_A phase over a very wide temperature interval and well below room temperature, a 45° tilt angle, as well as the OI-AFLC electro-optic response. From the large collection of compounds synthesized during this study (several others will be reported separately), we recognized that several ternary mixtures of **BC1** doped with two specific compounds displayed the SmCP_A phase to below -40 °C on both heating and cooling as well as optical tilt angles in the transformed state of approximately 45° (optically isotropic). The design strategy for these compounds was to remain as structurally close to **BC1** as possible, particularly focusing on retaining structural elements that support the formation of the SmCP_A phase and the optical tilt angle. Additional phase-stabilizing elements, such as fluoro substituents in the outermost aromatic ring, were also introduced for all three compounds **BC2–BC4** (Figure 1). Last, but not least, two derivatives are non-symmetric (**BC2** and **BC4** lack mirror or C₂ rotational symmetry through the central benzene ring), which should help lower the phase-transition temperatures in mixtures with **BC1**. Detailed synthetic information and characterization data of **BC1–BC4** are described in the Supporting Information. Actually, only **BC1** and **BC2** form the SmCP_A phase; **BC1** (as reported previously) only forms the SmCP_A phase on cooling, whereas **BC2** forms the SmCP_A phase on both heating and cooling. The magnitude of the polarization of both materials is in the range of 300–400 nC cm⁻². The antiferroelectric polarization current peaks for **BC2** are shown in Figure S6. **BC3** and **BC4** are not liquid crystalline. All compounds were fully characterized and checked carefully for purity as detailed in the Supporting Information.

The first set of experiments to verify if a particular additive to **BC1** would lower the melting point (freezing point depression, formation of an eutectic) was done using temperature-controlled polarized optical microscopy (POM) studies (using crossed linear polarizers and plain glass slides) of contact preparations between **BC1** and all other bent-core compounds (see Figures S7–S9). When the textural features in the contact zone between the two compounds indicated a SmCP_A phase stabilization, a wider SmCP_A temperature range, and a lower freezing point, binary mixtures with uniform concentration indicated by

the contact preparation were prepared. Of the various compositions investigated, the 1:1 (by weight) mixtures appeared to be the most insightful. As summarized in Table S1, all three bent-core binary mixtures (**BC1/BC2**, **BC1/BC3**, and **BC1/BC4**) appeared to form exclusively the SmCP_A phase with Iso/SmCP_A phase-transition temperatures on cooling ranging from 128 °C (for **BC1/BC2**) to 86 °C (for **BC1/BC4**), and with SmCP_A/Cr phase-transition temperatures in all three cases at around 20 °C on cooling. Considering the molecular structures of **BC2**, **BC3**, and **BC4**, the 1:1 binary mixtures followed the expected trend in phase-transition temperatures (particularly of the clearing point) with the highest molecular weight derivative **BC2** (featuring the central 3,4'-biphenyl core^[22]) giving rise to the highest, and the non-symmetric **BC4** (with respect to **BC3**) the lowest Iso/SmCP_A phase-transition temperature.

Once **BC2–BC4** were selected as the three most promising candidates, we started formulating ternary mixtures. Among the various compositions, the 2:1:1 ratios between **BC1** and two other bent-core compounds were found to be the most successful. **BC2** was initially chosen as the constant ingredient for the two ternary mixtures reported here, because **BC2** itself forms the SmCP_A phase over a relatively large 60 °C temperature interval. The third component was then varied, either by using **BC3** or **BC4**.

Both ternary mixtures **M1** and **M2** were prepared in a similar way to the binary mixtures, using a common organic solvent and subsequent solvent evaporation (see Section 4 in the Supporting Information). **M1** and **M2** were first characterized by complementary thermal analysis methods, that is, temperature-dependent POM and differential scanning calorimetry (DSC). Each method confirmed that **M1** and **M2** form the SmCP_A phase on both heating and cooling over a >140 °C temperature interval, ranging from about 105 °C (**M2**)–115 °C (**M1**) to well below -40 °C for both mixtures (see Section 5 in the Supporting Information). Even prolonged storage in a -30 °C freezer did not lead to any crystallization of either of these two mixtures.

Next, we tested their ability to assume the transformed state after cooling cells (rubbed polyimide, 4–6 μm cell gap) filled with either **M1** or **M2** while applying an electric field of $E > 10 \text{ V } \mu\text{m}^{-1}$. As shown in Figure 3 a–c, at zero field both **M1** and **M2** show completely dark, optically isotropic states in support of the required 45° tilt angle. On the studied films, no apparent optical activity could be detected under oppositely uncrossed polarizers.

We also performed synchrotron small-angle X-ray diffraction measurements (SAXD) on one of the mixtures (**M1**, see Figure 4). The peak position at $q \approx 0.17 \text{ \AA}^{-1}$ gives the layer spacing $d \approx 3.7 \text{ nm}$. Comparing this with the average size of the molecules, $L_{\text{ave}} \approx 5.3\text{--}5.5 \text{ nm}$, the tilt angle can be estimated to be 46–47°, which is very close to the 45° that is needed (though not necessarily enough) for optical isotropy of the SmCP_A phase. We note that, at low temperatures, there is an additional minor peak at $q \approx 0.14\text{--}0.15 \text{ \AA}^{-1}$. This, together with the short (ca. 30 nm) correlation length of the smectic layers (see Figure 4), indicates a frustrated and modulated layer structure, resembling that of the DC phase.^[12–18] Future TEM experi-

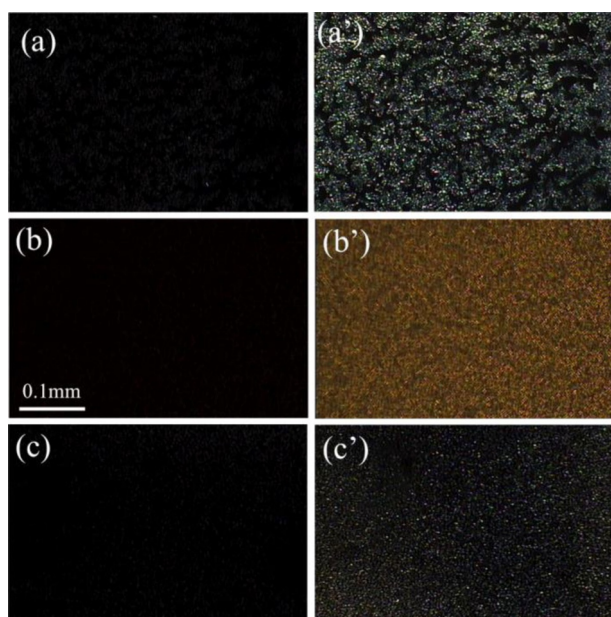


Figure 3. Polarized optical microscopy images of the ternary bent-core LC mixtures **M1** and **M2** in 2 μm cells with rubbed polyimide alignment layers promoting planar anchoring: a) **M1** at 12 °C and $E=0$, a') **M1** at 12 °C and $E=20 \text{ V}\mu\text{m}^{-1}$ ($f=170 \text{ mHz}$), b) **M2** at 75 °C and $E=0$, b') **M2** at 75 °C and $E=20 \text{ V}\mu\text{m}^{-1}$ ($f=60 \text{ Hz}$), c) **M2** at -1 °C and $E=0$, and c') **M2** at -1 °C and $E=30 \text{ V}\mu\text{m}^{-1}$ ($f=49 \text{ mHz}$).

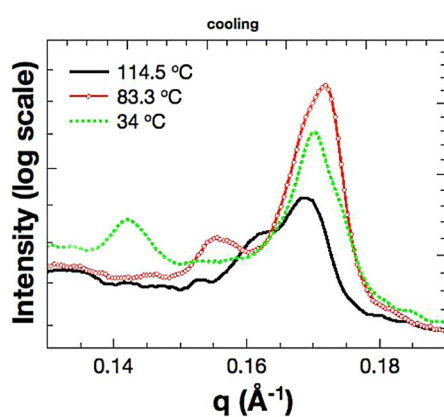


Figure 4. SAXD intensity in logarithmic scale versus wave number q in \AA^{-1} of the SmCP_A phase of the mixture **M1** at various temperatures on cooling from the isotropic liquid phase.

ments are planned to verify the precise nanostructure of the studied materials.

Finally, we evaluated the temperature-dependent electro-optic response of these mixtures in planar cells. Driving the cells with an applied electric field resulted in the formation of birefringent textures, as shown in Figure 3 a'–c', similar to neat **BC1** reported earlier. Most importantly, switching was observed at temperatures well below room temperature, as seen in Figures 3 a' and 3 c', although the birefringence is much smaller than at elevated temperatures (see Figure S11 for **M2**). The switching time strongly increases at lower temperatures; at 75 °C, however, it is well below 1 ms, as shown in Figure S11, where the time dependence of the transmitted intensity of

a 3 μm thick cell of **M2** is shown the instant a square wave voltage of 10 V amplitude and 67 Hz frequency is applied. The switching time at and below room temperature is in the range of 0.1–1 s, indicating that the materials are highly viscous at these temperatures. This increase in viscosity is also seen in the dielectric spectra of **BC2**, **M1**, and **M2** (Figure 5). At high temperatures, the magnitude of the low-frequency dielectric constants are over 30, which is typical for antiferroelectric bent-core materials.^[23] The relaxation frequencies are in the range of (or over) 10 kHz at high temperatures, in agreement with the high switching speeds observed well above room temperature, and below 100 Hz at or below room temperature, again in accordance with the observed slower switching at lower temperatures.

Overall, we have been successful in synthesizing a series of structurally related phenylbenzoate-based bent-core LCs and generating mixtures that display the desired SmCP_A phase over a very large temperature interval, from well below room temperature (–40 °C) to +100 °C, and with the optimal tilt angle of 45° that is suitable for the optically isotropic antiferroelectric LC mode. This breakthrough, with respect to temperature interval and tilt angle, was achieved with mixtures containing only three components. These ternary SmCP_A mixtures show

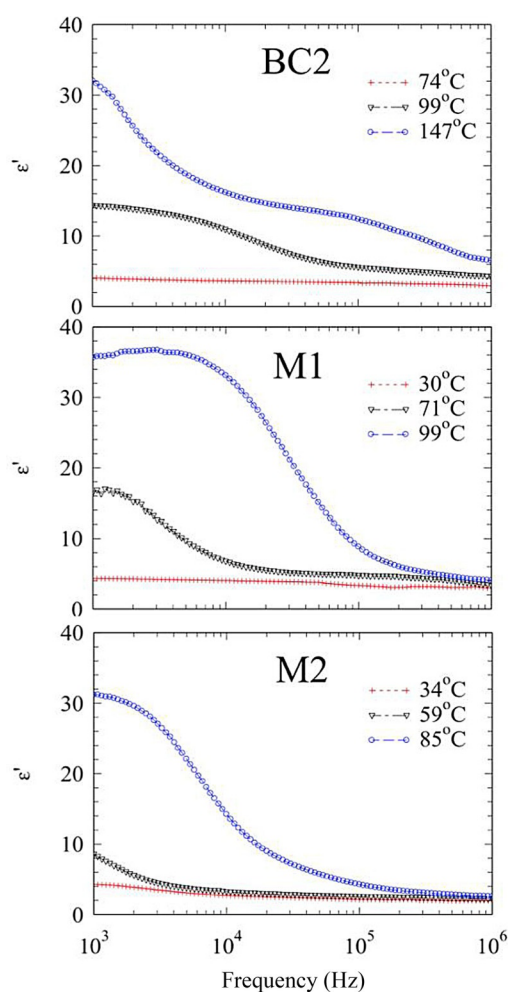


Figure 5. Frequency dependence of the dielectric constant at different temperatures: **BC2** (top), **M1** (middle), and **M2** (bottom).

sub-millisecond switching times at elevated temperatures, but an increase in viscosity currently limits the switching speed at room temperature to around 100 ms. To increase the switching speeds at or below room temperature, a further decrease in the clearing point of the materials is needed. To achieve this, we are currently testing four-, five- and even more-component mixtures common for LC mixtures used in nematic LCD technologies.

Experimental Section

Synthesis and Characterization of Bent-Core Compounds

Experimental details related to the synthesis of **BC1–BC4** and their precursors are provided in the Supporting Information.

Methods

POM images were taken on Olympus BX-53 and BX-60 microscopes equipped with either Linkam LTS420E or INSTEC STC200D + LN2-P heating/cooling stages. Phase-transition temperatures were determined by using a PerkinElmer Pyris 1 differential scanning calorimeter at a constant heating and cooling rate of 10 Kmin⁻¹, reporting data from the second heating and cooling run, respectively. SAXD was carried out on beamline 7.3.3 of the Advanced Light Source of Lawrence Berkeley National Lab^[24] (10 keV incident beam energy, 1.24 Å wavelength, utilizing a Pilatus 2 M detector). The materials were filled into 1 mm diameter quartz X-ray capillary tubes, which were then mounted into a custom-built aluminum cassette that allowed X-ray detection with ±13.5° angular range. The cassette fits into a standard hot stage (Instec model HCS402) that allowed temperature control with ±0.1 °C precision. The stage also included two cylindrical neodymium iron boron magnets that supplied a magnetic induction of $B=1.5$ T perpendicular to the incident X-ray beam. The analyses proceeded in Igor Pro software with the Nika package.^[25] Dielectric spectroscopy measurements were carried out by using a Schlumberger 1260 impedance/gain-phase analyzer in the frequency range of 200 Hz to 1 MHz with a measuring voltage of 0.1 V (RMS). The material was investigated in custom-made 5 μm thick cells with ITO electrodes (area 5 × 5 mm²). Prior to the measurements, the samples were cooled to the Sm_CA_PA phase while strong (20 Vμm⁻¹) electric fields were applied to arrange the smectic layers along the electric fields. After this treatment, dielectric measurements were carried out only in the smectic phase. Electro-optic measurements were carried out by placing a biased photodetector (detection limit being 1 μs) in the eyepiece of an Olympus BX-60 polarizing microscope and applying square wave electric fields with an HP 33120A arbitrary waveform generator as well as a FLC F20AD voltage amplifier. The optical signal was recorded by using a MSO X-3024A KEYSIGHT digital oscilloscope.

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Conflict of Interest

The authors declare no conflict of interest.

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