

Large birefringence smectic-A liquid crystals for high contrast bistable displays

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Abstract: We developed two kinds of bistable smectic-A liquid crystal mixtures. Compared with traditional cyanobiphenyl and cyanoterphenyl derivatives, several changes have been made in molecular design: Isothiocyanato is used as a substitute for cyano to increase the optical anisotropy; fluoro groups are added on 3 and 5 positions of the isothiocyanato substituent terminal phenyl ring to increase both the dielectric anisotropy and eutectic property of the smectic mixture; derivatives of (4-isothiocyanatophenyl) pyridine are introduced to produce a wide smectic range. Thanks to above designs, the final smectic-A mixtures exhibit highly improved properties, such as higher contrast, lower operation voltages and wider temperature range. Based on the developed liquid crystals, electronic tags were also demonstrated, which exhibit reliable performance. This work reveals new insights for tailing liquid crystal molecules with bistability, which is extremely meaningful for the design and fabrication of green display devices.

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1. Introduction

Bistable liquid crystal display (BLCD) has attracted intensive attentions thanks to the feature of power required only in updating images while electrical field unneeded in maintaining off/on states [1–7]. Therefore it is quite suitable for displays that would not be frequently updated, such as electronic signage cards, e-books, and even large electronic billboards. So far, many technologies have been proposed for BLCD. We can classify them according to whether polarizer and backlight are required. One is based on the birefringence induced phase retardation of bistable LCs, such as bistable ferroelectric displays [1], zenithal bistable nematic displays (ZBD) [2] and 360° or 180° bistable twisted nematic (BTN) displays [3, 5]. Their configurations are similar to traditional nematic ones. The other one is based on two distinguished optical states. For instance, transmittance and Bragg wavelength selective reflection states of bistable cholesteric displays [6, 8]; and transmittance and scattering states of polymer dispersed liquid crystal (PDLC) displays [7, 9, 10] or ion-doped smectic-A (SmA) bistable displays [11]. The cell configuration of latter strategy is drastically simplified, thus supplies a light weight, low cost, environment friendly and even flexible way for reliable BLCDs.

Among above approaches, ion-doped smectic-A (SmA) bistable display is especially attractive thanks to its high and uniform transmittance, wavelength insensitivity, no requirement of alignment layers, simple and easy fabrication. Besides energy and resource conservations, it also presents the merits of wide viewing angle and excellent sunlight readability. The bistable SmA LC has two stable states: homeotropic alignment transparent state and random focal-conic arranged scattering state [11]. It can be switched between the two states via specified electric signals [9]. The optical contrast between the two bistable states enables the information display or light-dimming. Few works have been reported on bistable SmA LCs, while most of them are organosiloxane based materials [12, 13]. They exhibit good stability and reliable performance. However, they still suffer from shortages like low optical contrast and high operating voltages (>100 V), which limits both the display quality and device lifetime. Therefore, exploitation of novel bistable SmA LC with improved performance is very meaningful [14].

In this work, we developed two bistable SmA LCs via fusing isothiocyanato-biphenyl, isothiocyanato-terphenyl and (4-isothiocyanatophenyl) pyridine derivatives. Their measured electro-optical properties revealed superiorities of lower operation voltages, higher contrast ratio, wider temperature range over traditional bistable SmA LCs. The electronic tags filled with the new SmA LC exhibit improved electro-optical properties and reliabilities. This work reveals new insights for the design of bistable SmA LCs, which is quite significant for the design and fabrication of the both energy and material efficient displays.

2. Principles and materials

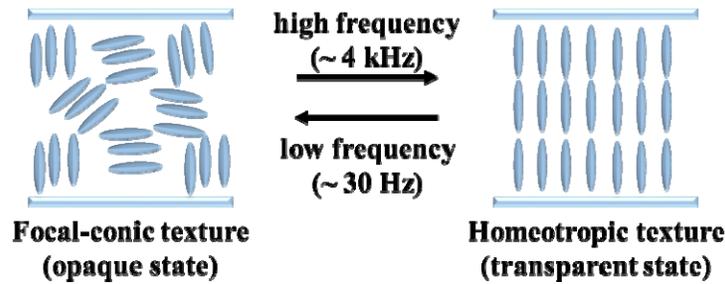
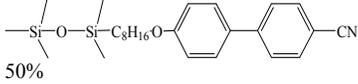
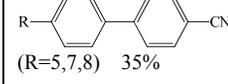
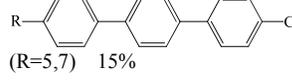
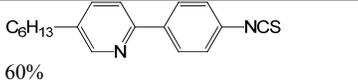
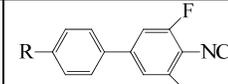
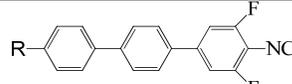
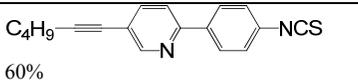
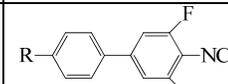
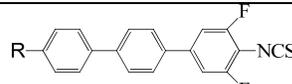


Fig. 1. Schematic representation of the operational principle of the bistable SmA displays.

The operational principle of bistable SmA display, which can be switched between two distinct states via applying specified electric signals [9], is schematically illustrated in Fig. 1. When applying a low frequency (e.g. 30 Hz) electric field, the LC converts to a turbulent light-scattering state. The mechanism is similar to the molecular motion occurring in nematic dynamic scattering named Carr-Helfrich nematic turbulence [11]. The organic ions (here 0.05% N-Hexadecyltrimethylammonium Chloride is added) mixed in the smectic LCs are excited by low frequency alternating current (AC), and tend to move and disturb the close-packed plane of smectic layers randomly, thus focal conic (FC) texture is generated through electrohydrodynamic instability (EHDI) and the opaque state forms. On application of a high frequency (e.g. 4 kHz) electric field, homeotropic (HT) texture is generated because of the dielectric re-orientation of the smectic LC molecules, which have positive dielectric anisotropy. Thus the transparent state forms. It should be noted that both two textures can persist after the field removed. Through electrically switching at different frequencies, the materials can be switched between two stable optical states: the transparent state (HT texture) and the opaque state (FC texture).

Table 1. The molecular structures, compound names and composition weight of three kinds of SmA LCs.

1	 50%	 (R=5,7,8) 35%	 (R=5,7) 15%
	4'-((8-(1,1,3,3,3-pentamethyldisiloxanyl)octyl)oxy)-[1,1'-biphenyl]-4-carbonitrile	4-alkyl-4-cyanobiphenyl	4-alkyl-4-cyanoterphenyl
2	 60%	 (R=5,7,8) 25%	 (R=5,7) 15%
	5-hexyl-2-(4-isothiocyanatophenyl)pyridine	3,5-difluoro-4-isothiocyanato-4'-alkyl-1,1'-biphenyl	3,5-difluoro-4-isothiocyanato-4''-alkyl-1,1':4',1''-terphenyl
3	 60%	 (R=5,7,8) 25%	 (R=5,7) 15%
	5-(hex-1-yn-1-yl)-2-(4-isothiocyanatophenyl)pyridine	3,5-difluoro-4-isothiocyanato-4'-alkyl-1,1'-biphenyl	3,5-difluoro-4-isothiocyanato-4''-alkyl-1,1':4',1''-terphenyl

Since the scattering is induced by the refractive index difference among adjacent domains, high birefringence (Δn) SmA materials will lead to stronger scattering and correspondingly better display quality could be obtained. Then high birefringence SmA materials are needed. High birefringence could be achieved by extending the conjunction length by adding multiple bonds or aromatic rings in the rigid core [15]. However, there are several problems arising with highly conjugated LC compounds such as high melting temperature, increased viscosity and reduced UV stability. Fortunately, isothiocyanato (NCS) groups supply higher birefringence while are less viscous than cyano (CN) ones. Besides, NCS compounds tend to exist in smectic phases. Thereby, we developed two kinds of bistable SmA LC mixtures (Table 1 materials 2 & 3) with NCS as a substitute for CN in traditional cyanobiphenyl and cyanoterphenyl derivatives (Table 1 material 1) to increase the optical anisotropy. Fluoro atoms are added on 3 and 5 positions of the isothiocyanato substituent terminal phenyl ring to increase both the dielectric anisotropy and eutectic property of the smectic mixture. The introduction of fluoro groups facilitates the reduction of V_{th} and could decrease the viscosity of the LC mixture thus leading to a lower melting point [16]. Derivatives of (4-isothiocyanatophenyl) pyridine are also introduced for a wide smectic range.

3. Results and discussion

The measured physical properties of the above materials are listed in Table 2. Material 1 is a traditional bistable SmA LC acting as a reference. Their transformation points are characterized by differential scanning calorimetry. The clearing points are 53.3 °C, 64.9 °C and 72.7 °C subsequently. The melting points measured in the temperature dropping process are usually lower than true values due to supercooling, therefore $<-40^{\circ}\text{C}$ is presented instead of their accurate values in Table 2. The three materials can be used at low temperature, while the extended SmA ranges of material 2 & 3 mean that they are suitable for usage and storage at high temperature as well. Material 2 & 3 possess higher birefringence as expected. Since the conjunction length of material 3 is further extended compared to material 2, it exhibits the largest birefringence to 0.3342. Two reasons could be considered. For rod-like rigid materials, the longer the rigid structure is, the higher the birefringence is. The second is attributed to its higher T_c . From the equation $\Delta n_0(1-T/T_c)^\beta$, a higher T_c is helpful to enhance the birefringence since the molecular structure is similar. Thanks to above molecular designs, the final SmA mixtures exhibit highly improved properties.

Table 2. The physical properties of the three materials and their response time of FC-HT (4 kHz) and EHDI (30 Hz) transitions at 100 V.

SmA mixtures	1	2	3
$T_c(^{\circ}\text{C})$	53.3	64.9	72.7
$T_m(^{\circ}\text{C})$	<-40	<-40	<-40
Δn	0.1768	0.3113	0.3342
FC-HT(ms)	6	4.25	7
EHDI(ms)	367	333	333
$V_{th}(\text{V})$	66	48	51
$V_{sat}(\text{V})$	75	61	70

Unlike the traditional laser based set-up which used a monochromatic coherent laser with the diameter of 1 mm [7, 9], here a microscope system (Fig. 2(a)) was utilized not only to observe the textures, but also to carry out the electro-optical measurements at the same region simultaneously. A tungsten halogen lamp provided collimated white light, the light transmitted through the sample and then recorded by a charge-coupled device (CCD) through objective lens. The transmittance is calculated using a specified program. This setup recorded large-area average transmittance in the whole visible range. Figure 2(b) and 2(c) show the

formation of HT textures and FC textures respectively. The HT textures were uniformly converted from FC textures when applying a 4 kHz AC signal. Because the LC has a positive $\Delta\epsilon$, and the LC directors were reoriented continuously till parallel (or anti-parallel) to the applied field along with the voltage increasing. Correspondingly a higher transmittance state was observed under the microscope. When a 30 Hz AC signal was applied, the FC textures (dark areas) firstly occurred at the electrode boundaries and spread slowly across the electrode area along the applied voltages. After the cell was driven fully into a scattering state, vortices with similar size were uniformly dispersed and a dark state was observed.

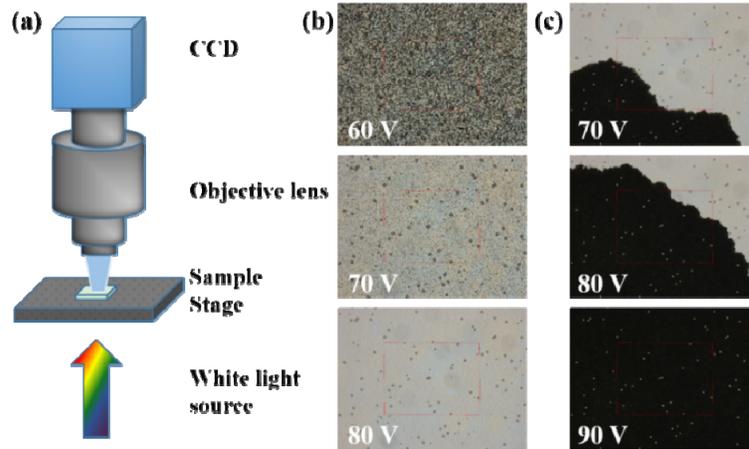


Fig. 2. (a) Experimental set-up for electro-optical measurements. Photographs of the textures taken with parallel polarizers: (b) Formation of HT textures. (c) Formation of FC textures.

The electro-optical measurements were also carried out. Square waveforms of 30 Hz were used for HT-FC transition while 4 kHz pulses were used for the reverse. In the static-response measurements, the voltage was increased by a step of 1 V. The cell was driven to saturated scattering state first and then applied with high frequency electric field each time to avoid the cumulative effect. The EO performances at high frequency were shown in Fig. 3(a). The three materials all have excellent transparent states, while materials 2 & 3 have improve scattering states. The optical contrast ratio (CR, T_{HT}/T_{FC}) are 5.8, 8.23 and 8.57 for materials 1, 2 and 3 respectively. The threshold voltage V_{th} and saturation voltage V_{sat} for FC-HT transition were calculated from the curves in Fig. 3(a) and listed in Table 2. The V_{th} of materials 2 and 3 were reduced as expected. The static-response of the HT-FC transition was measured as well, and large variations were found among different measurements since the scattering regions appeared randomly each time even the same voltage was applied. From the results, the HT-FC transition occurs typically in the voltage range of 50 V to 60 V, which decrease over material 1. However, due to the uncertainty, the voltage dependent transmittance curves could not reveal the HT-FC transition behavior faithfully. Therefore, the accurate values of V_{th} and V_{sat} for HT-FC transition could not be achieved either.

The response times for FC-HT transition and EHDI were determined at the 90% change in transmission when the cell was driven by an electric field. Here we used a novel strategy for the measurement. Taking the FC-HT transition as an example: firstly, 90% transmittance is recorded as a reference; secondly, the saturated scattering state is fixed as the initial state for each measurement; thirdly, signals of different durations are attempted to match the 90% change, thus the response time of the FC-HT transition is achieved. The response time for EHDI transition could be determined similarly. Exact values measured at 100 V are shown in Table 2. The developed SmA materials response faster than the traditional one, especially in the EHDI transitions.

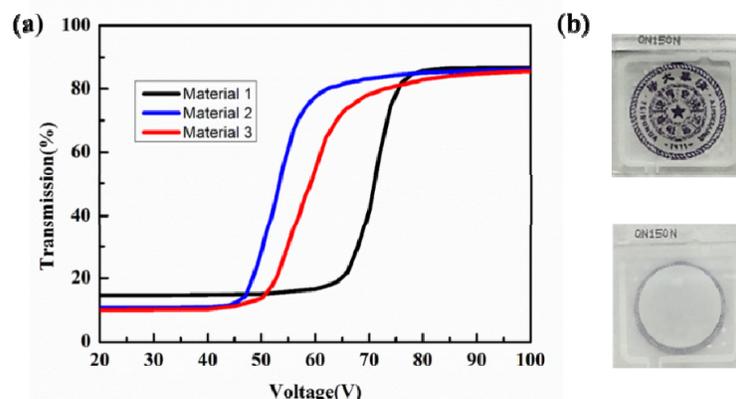


Fig. 3. (a) The static-response curve of FC-HT transition at 4 kHz for different SmA LCs. (b) Pictures of transparent and opaque states of single pixel cell filled with material 3.

Photos of a single pixel cell filled with material 3 reveals good transparent and opaque states after different signals applied (Fig. 3(b)). No voltage is needed to maintain the states. As presented, the static homeotropic texture has very good transparency, whereas the focal conic scattering texture offers good opacity. Figure 4(a) and 4(b) are the photos of electronic tags filled with material 1 and material 3. Comparing the two samples, we can see the display quality is drastically improved due to the higher contrast ratio induced by larger Δn .

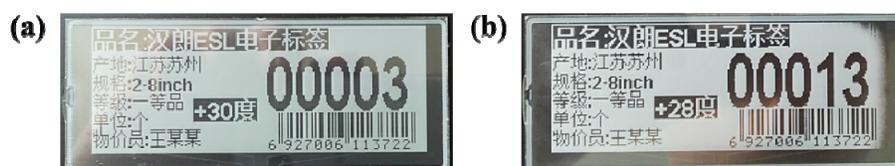


Fig. 4. Photos of electronic tags filled with (a) material 1 and (b) material 3.

4. Conclusion

We have developed two new high birefringence SmA LCs by introducing NCS and 3,5-difluoro groups. Lower operation voltage of 45 V~60 V for either the EDHI transition or the FC-HT transition is achieved. The optical contrast ratio was substantially increased and high quality bistable display devices were demonstrated. The work reveals new insights for tailoring liquid crystal molecules with bistability, which is extremely meaningful for the design and fabrication of green display devices.

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