Heat-driven and electric-field-driven bistable devices using dye-doped nematic liquid crystals

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We have demonstrated memory and rewritable bistable devices based on an anchoring transition of a nematic liquid crystal on a perfluoropolymer surface. Spontaneous orientation changes between planar and homeotropic occur on cooling and heating with a large temperature hysteresis. Photo (heat) addressing is possible from homeotropic to planar using dye-doped samples. For a coumarin dye, photoaddressed images are preserved even after heating up the sample to the isotropic temperature, whereas, for a 4-dicyanomethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran dye the images can be erased by decreasing the temperature out of the thermal hysteresis. Orientation switching also occurs by applying an electric field with a response time of several milliseconds depending on the field strength. © *2010 American Institute of Physics*. [doi:10.1063/1.3446826]

I. INTRODUCTION

The stable orientation of liquid crystal (LC) molecules is facilitated by surfaces of LC cells constructed by parallel plates. Commonly, planar (long axes parallel to the substrate surface) and homeotropic (long axes perpendicular to the substrate surface) alignments are used for various physical measurements and device applications. In the absence of an electric field, LCs with a particular surface condition orient with the minimum elastic energy, typically uniform alignment. Most of LC devices are monostable, that is, LC molecules obtain an unstable orientation under the application of an electric field and switch back to the stable orientation when the electric field is terminated. In these devices, a continuous supply of power is required to maintain the unstable state. By contrast, in bistable LC devices, there are two stable molecular orientations and one of them can be stabilized at a time by external triggering such as a pulsed electric field. Once the desired orientation is obtained no continuous power supply is needed to maintain that orientation. Such bistable devices are useful for electronic devices, particularly for E-book or smart window applications, in which the image has to be displayed for sufficiently long time. One of the well-known examples of the bistable devices is a surface-stabilized ferroelectric LC cell,[1] where molecules tilt right or left in a smectic layer. Since molecules are parallel to surfaces in both states, so that bistability is realized.

For practical bistable LC devices, nematic (N) LCs would be an appropriate candidate in the sense that alignment characteristic is much better, i.e., stable due to their simple structure, than their counterparts. Generally, bistability in nematic-based LC devices can be achieved on various surface conditions; for examples, surfaces exhibiting monostability[2,3] or bistability,[4–6] nonuniform surface alignment patterns,[7–11] or specially treated surfaces that have two-dimensional or three-dimensional micropatterns.[12–17] Bistability being not directly related to surfaces was also proposed and demonstrated.[18–20] Another totally different bistability can be realized by equally stable planar and homotropic alignment. Actually, we recently reported a temperature-driven discontinuous anchoring transition of a nematic LC with a large thermal hysteresis region (bistability) on a commercially available amorphous perfluoropolymer surface.[21] Further we have also proposed and demonstrated a bistable LC device in the dye-doped nematic LC system in which we successfully stabilized bistable states, i.e., planar and homeotropic regions with high resolution by laser-light irradiation.[22] Here we report two different performances of heat-driven bistable devices depending on kinds of dyes doped; i.e., a memory device and a rewritable device. Finally we demonstrate the performance of an electric-field-driven bistable device.

II. EXPERIMENTAL PROCEDURE

The nematic LC, 4′-butyl-4-heptyl-bicyclohexyl-4-carbonitrile (CCN-47) was obtained from Merck Japan Ltd., and used without any further purification. The LC exhibits the following phase transitions: Cr 25.6 °C Sm-A 28.2 °C N 57.3 °C Iso, and possesses a large negative dielectric anisotropy ($\Delta\varepsilon = -5.7$ at 30 °C). Here Cr, Sm-A, and Iso stands for crystal, smectic-A, and isotropic phases. The laser dyes, coumarin 153 (C153) and 4-dicyanomethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM), were purchased from Lambda Physik and Exciton, respectively. Amorphous perfluoropolymer, poly [perfluoro (4-vinyloxy-1-butene)], known as CYTOP (from Asahi Glass Co., Ltd.), was spin coated onto glass substrates and was cured for 30 min at 100 °C. Empty cells were fabricated by using two such glass substrates which were rubbed antiparallel to each other. Polymer beads were used for spacers to make 5 ± 0.3 μm

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thick cells. Then CCN-47 doped with 0.5 wt % C153 or DCM was introduced into the empty cells using capillary action in the isotropic phase.

The texture was observed under a polarizing microscope (Nikon, OPTIPHOT-POL) equipped with a temperature-controlled Mettler-Toledo FP90 hot stage. The cooling and heating rate was ± 2 °C/min. As for light source, we employed a laser diode, LQC405-360C (Newport), whose wavelength (405 nm) matches the absorption peaks of both dyes (C153, DCM) used. For C153-doped and DCM-doped samples, we used 1.2 kW/mm² at 51 °C and 4.2 kW/mm² at 48 °C. For voltage dependent polarizing optical microscopy (POM) images of the switching cell, rectangular voltage with a frequency of 10 kHz was applied.

III. RESULTS AND DISCUSSIONS

In our previous study, we used C153-doped CCN-47. Here we show transmittance of DCM-doped CCN-47 with varying temperature, as shown in Fig. 1. The measurement method is the same as that described in our previous paper.[22] As observed in Fig. 1(a), we confirmed that a DCM-doped sample also exhibits a discontinuous anchoring transition with a considerable width of hysteresis, the same as in C153-doped one. Temperatures in parentheses are for a C153-doped CCN-47 sample. By scanning a focused laser beam on the cells, which was heated from temperatures a little below the upper anchoring transition temperature (50.5 °C for DCM and 53.5 °C for C153), we can record lines if the local heating by laser irradiation exceeds the upper anchoring transition temperature, as shown at the top of Figs. 1(b) and 1(c), for DCM and C153, respectively. Dark background and bright lines correspond to homeotropic and planar orientations, respectively.

Photomicrographs display the temperature dependent evolution of recorded lines for temperature cycles down below the lower anchoring transition temperature. In DCM-doped CCN-47, erasing and rewriting are possible, as shown in Fig. 1(b); i.e., anchoring transition from planar to homeotropic starts to occur at 43 °C, and completed at 41 °C. The homeotropic state obtained at 41 °C was well preserved up to 48 °C during heating process, which made it possible to overwrite another pattern. We could rewrite tiny characters "LC" at 48 °C in the same spot, in which two lines were previously recorded. Thus rewritability is clearly shown; different kinds of patterns were recordable repeatedly using the hysteresis cycle. Totally different performance was obtained in C153-doped sample, as shown in Fig. 1(c). The recorded patterns remained unchanged even at 43 °C, well below the lower anchoring transition temperature, and after heating up to the original temperature 51 °C. Thus, expected anchoring transition from planar to homeotropic state did not occur; the recorded patterns were memorized irrespective of temperature change. Namely, the LC director seems to firmly stick to the surface once the laser-light-induced planar state is stabilized.

To understand the different behavior in DCM-doped and C153-doped samples, texture evolution by raising the temperature up to the isotropic phase was examined. The transi-
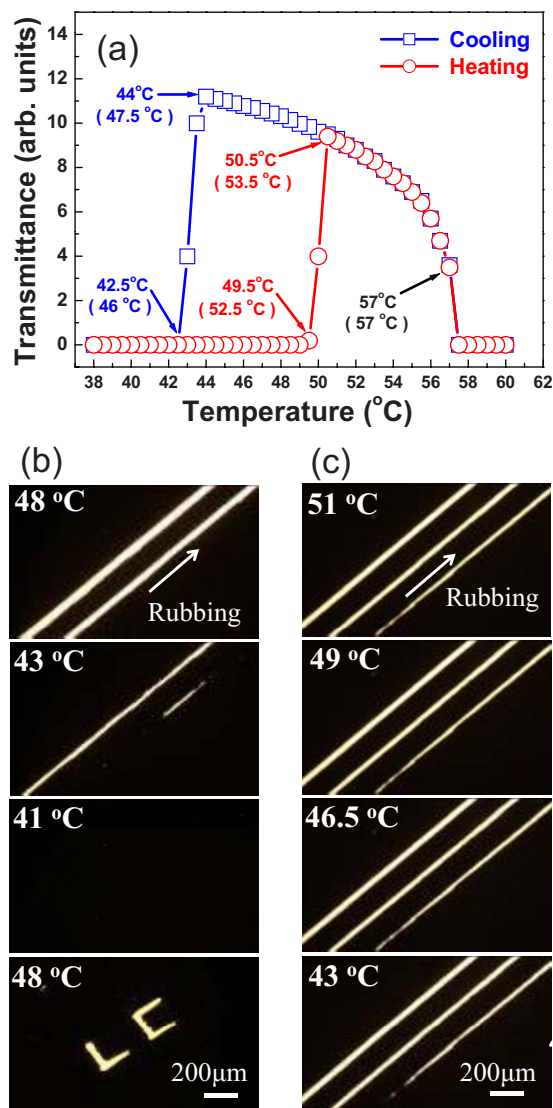

FIG. 1. (Color online) (a) Temperature dependence of transmittance showing anchoring transition in DCM-doped CCN-47. Note the existence of temperature hysteresis (bistability) with a wide temperature range. C153-doped CCN-47 exhibits the similar behavior with slightly different anchoring transition temperatures, which are given in parentheses. (b) POM images showing a rewritable bistable device using DCM-doped CCN-47; i.e., cooled from 48 to 41 °C, then heated up to 48 °C and rewrote LC. (c) POM images showing a memory bistable device using C153-doped CCN-47; i.e., cooled from 51 to 43 °C. Heating from 43 to 51 °C exhibited the same textures.

tions from homeotropic to planar alignment occurred at 50.8 °C. As expected, the textures of DCM-doped CCN-47 were very uniform without any trace of stripes when heated up to 55 °C, as observed in Fig. 2(a). The uniform texture was maintained even after cooled down to 44 °C from isotropic (60 °C). With further decreasing temperature below 44 °C, the anchoring transition to homeotropic alignment (dark part) was initiated at 43.9 °C and was completed with further decreasing temperature. By contrast, in C153-doped sample, homeotropic orientation indicated by dark region began to turn into planar (53.7 °C). However, an afterimage recorded at 51 °C was preserved even at 56 °C, as shown in Fig. 2(b). The afterimage could not be erased even after heating up the cell to the isotropic phase, and reappeared when
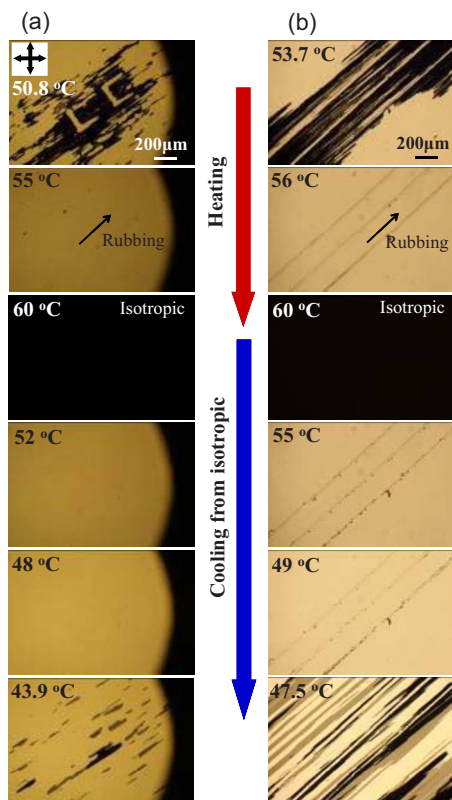
FIG. 2. (Color online) POM images of LC textures as observed above upper anchoring transition temperature in (a) DCM-doped sample and (b) C153-doped sample.
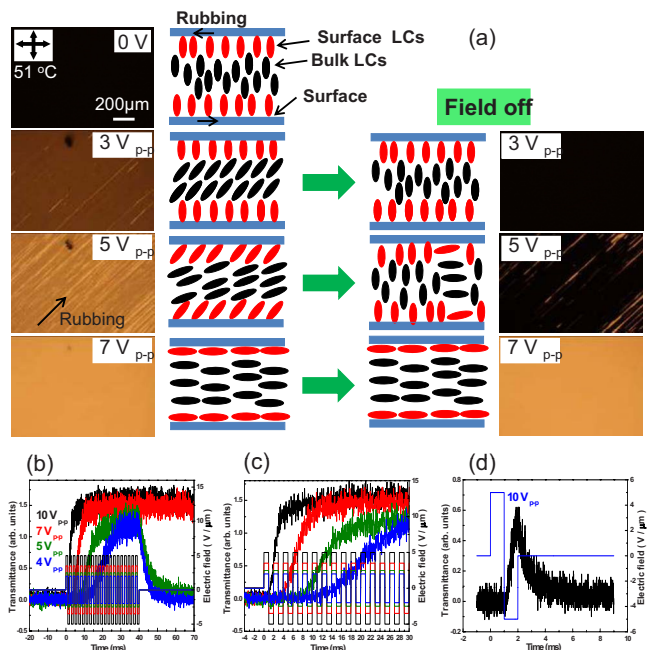

FIG. 3. (Color online) (a) Schematic illustration of the electric-field-induced LC molecule reorientation by application of an electric field (middle) and POM images of LC textures during (left) and after (right) the application of an electric field at 51 °C. (b) Electro-optical response curves of an LC cell by application of a single bunch of rectangular voltage of 10, 7, 5, and 4 V_{p-p} (from left to right) during 40 ms. (c) The rise process in the electro-optical response in an enlarged time scale. (d) The response by applying a single rectangular reverse pulse of 10 V_{p-p}.

the sample was cooled down to the nematic phase (55 °C) and even down to 49 °C. When the temperature of the sample was brought to close to the lower transition temperature (47.5 °C), the planar alignment changed into homeotropic one only at the background part. The texture evolutions with further decreasing temperature below 47.5 °C exactly followed the situations as already described in Fig. 1(c). As inferred from Fig. 2(b), dye adsorption to the surface is most likely to be responsible for temperature-insensitive permanent planar orientation in C153-doped samples. Actually dye aggregation at the surface has been reported earlier.[23,24] However, DCM has no contribution to the surface but acts as a heat source for the recording process.

So far we have discussed heat-induced switching of the LC molecular orientation. The orientation change can be achieved from homeotropic to planar by applying an electric field between substrate surfaces, since the LC director is forced to be perpendicular to the field because of negative dielectric anisotropy, as schematically shown in the middle of Fig. 3(a). Since molecules are homeotropically anchored to surfaces, the field-induced orientation change first occurs in bulk at a field (3 V_{p-p}) for the Frederiks transition. However, this distortion is so small as not to influence the deviation of surface molecules from vertical direction. With further increasing voltage (5 V_{p-p}), the distortion of the bulk molecules as well as the surface molecules becomes larger. When switched off, most of the bulk molecules return to homeotropic state, so do the surface molecules by elastic torque. However, some of the surface molecules stay in pla-

nar state due to nonuniformity of the cell surface. All of the surface molecules eventually become stabilized as planar state at 7 V_{p-p} being applied and removed.

The situation described above was actually realized using a C153-doped sample, as shown in both sides of Fig. 3(a). In the absence of a field, the equilibrium texture of the cell at 51 °C was homeotropic. When a voltage exceeding the Frederiks transition is applied to the cell (3 V_{p-p}), the bulk LC molecules started to reorient with the director perpendicular to the field. When the field is turned off, they relax back to the original (homeotropic) state. With 5 V_{p-p} being applied, the bulk molecules are more deviated from the vertical direction, which results in higher birefringence. When the field is removed, the majority of the homogeneous state relaxes into homeotropic, whereas a tiny minority does not. Above 7 V_{p-p}, presumably being capable of overcoming the energy barrier between two stable states, surface anchoring state also changed so that back switching did not occur. In this way, all the experimental observation is consistent to the cartoons illustrated in the middle of Fig. 3(a).

Figures 3(b) and 3(c) show transmittance changes in field-induced anchoring transitions in long and short time ranges, respectively. Here we applied a bunch of ac rectangular voltage (1 ms pulse duration (500 Hz), 40 ms bunch duration). The transmittance changed from dark to bright under 7 and 10 V_{p-p}, whereas it increased first and decreased back under 4 and 5 V_{p-p} [Fig. 3(b)], being consistent with the results shown in Fig. 3(a). With increasing voltage, an induction period becomes shorter and the transmittance rise becomes faster, that is more clearly seen in Fig. 3(c). At

10 V$_{p-p}$, a fast rise in the range of 1 ms is followed by a slow process. The fast process is also seen at 5 V$_{p-p}$, although it is not very fast because of a low voltage but about 10 ms. These switching behaviors suggest that the fast and slow components are due to the molecular reorientation in the bulk and at the surfaces, respectively. To confirm this, we applied a single rectangular reverse pulse of 10 V$_{p-p}$. We found that fast switching occurred transiently but returned back to the original dark state, as shown in Fig. 3(d). This can be possible only when the surface orientation remains unchanged. After application of 10 V$_{p-p}$ to a small electrode region, perfect planar alignment was realized as a bright region in a dark homeotropic region (not shown). The image was kept for a long time showing memory effect. In addition, the planar region was reproducible; i.e., the bright region disappeared as the temperature decreased out of the bistable region and it appeared again by applying 10 V$_{p-p}$ within the hysteresis region.

IV. CONCLUSIONS

We have demonstrated the performance of bistable devices based on the anchoring transition in dye-doped CCN-47 on amorphous perfluoropolymer. Three types of devices were demonstrated, namely, heat- (light-) driven memory and rewritable devices, and electric-field-driven rewritable devices. In heat-induced switching, the temperature evolution of the planar regions was highly related to the dyes chosen. For DCM-doped samples, rewritable devices are possible, whereas C153-doped samples provide memory devices. The planar regions can be memorized in C153-doped samples because of adsorption of dyes and associated surface modification. In an electric field-induced switching, 7 V$_{p-p}$ was high enough to induce full reorientation, although the application of a low voltage such as 5 V$_{p-p}$ reoriented the molecules only in the bulk.

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