

Photo-switchable chiral liquid crystal with optical tristability enabled by a photoresponsive azo-chiral dopant

YU-CHENG HSIAO,¹ KUAN-CHUNG HUANG,² AND WEI LEE^{1,2,*}

¹Institute of Imaging and Biomedical Photonics, College of Photonics, National Chiao Tung University, Guiren Dist., Tainan 71150, Taiwan

²Institute of Photonic System, College of Photonics, National Chiao Tung University, Guiren Dist., Tainan 71150, Taiwan

*wlee@nctu.edu.tw

Abstract: A light-driven tristable chiral-tilted homeotropic nematic (TCHN) cell is demonstrated. The liquid-crystal cell is photo-switchable among the three stable states: the tilted-homeotropic, fingerprint, and the tilted-twist states. The inclusion of a photosensitive chiral bis(azobenzene) compound into a typical nematic liquid crystal makes the resulting material possible to switch from one to another stable state directly and reversibly owing to the photoinduced *trans*–*cis* isomerization of the azo-chiral dopant and, hence, the configurational change of the liquid crystal via the guest–host effect. By further introducing dichroic dyes into the TCHN system, we devised a polarizer-free display and light modulators. The novel TCHN composite material opens up new possible applications in light-driven optical elements and devices.

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OCIS codes: (160.3710) Liquid crystals; (160.1585) Chiral media; (230.3720) Liquid-crystal devices.

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1. Introduction

With the concept of green energy rising rapidly, energy-saving materials have attracted much global attention in recent years. Those electro-optical materials having excellent optical stability do not require constantly applied electric voltage. Based on the stable-state nature, bistable liquid-crystal (LC) devices can be used as e-books or e-papers. There have been several bistable display technologies developed since 1981, including the bistable chiral-tilted homeotropic nematic (BHN) [1,2], bistable cholesteric LCs (CLCs) [3,4], bistable twisted nematic LCs [5–7], zenithal bistable LCs [8], ferroelectric LCs [9], and bistable bend–splay LCs [10]. However, compared with the bistable states in LC modes, tristable or multi-stable LCs have been scarcely reported [11]. Historically, a tristable LC mode was first reported in a ferroelectric LC system in 1988 [12], and the first tristable CLC system was later unraveled by Hsiao *et al* [13]. Nevertheless, the stability of a LC state is very pressure-sensitive and actually vulnerable to stress regardless of the LCs to be bistable or tristable.

Dye-doped LC systems are guest–host systems [14], which function in accordance with the nature of molecular alignment and differential absorption of dichroic dyes. When a light-absorbing dye (as a guest) is doped into a LC (serving as a host), the axis of main absorption is often aligned along the director of LC molecules. The control or extent of light absorption can be realized by an applied electrical field to reorient the LC molecules and, in turn, the axial orientation of main absorption of the dye. White and Taylor suggested that a system of dye-doped, twisted-nematic LC device can absorb light polarized along all axes [15]. Recently, Lee *et al.* have devised a polarizer-free display based on a dye-doped bistable chiral-tilted homeotropic nematic (BHN) system [16]. They show that, by introducing dichroic dyes into a BHN host, a bistable display can be realized. Conventionally, a BHN system possesses two stable states; namely, the tilted-homeotropic (tH) and the tilted-twist (tT) states, operating in the crossed-polarizer scheme as the dark and bright states, respectively [1,2,17]. It comprises a dual-frequency LC (DFLC) doped with a chiral agent, enabling its switch between the bistable tH and tT states [17,18]. A DFCLC exhibits frequency-reversible dielectric anisotropy whose sign is reversed from positive to negative as the frequency goes beyond a temperature-dependent characteristic frequency termed the crossover frequency [19]. The LC director in the tT state takes a 2π twist; a low-frequency voltage pulse imposes an electric torque on the LC molecules and the tendency of vertical alignment of the molecules permits the cell to switch to the tH state. For a BHN device to switch from the tH state to the tT state, a high-frequency pulse is required to induce the backflow effect. The BHN switching is complicated and the successful fabrication is not an

easy task in that the cell parameters, including the rubbing condition for the LC alignment layers, the ratio of the cell gap to the helical pitch, and the pretilt angle of the LC molecules, are all practically critical to its functionality.

In the study, we demonstrate a tristable optical composite—dye-doped tristable chiral-tilted homeotropic nematic (TCHN). The TCHN mode is extended from the technique of BHN mode. We introduced an azo-chiral dye into a typical nematic host to make an energy-saving, photo-switchable, optically tristable device. By further doping dichroic dyes, the TCHN can be employed for polarizer-free displays or other optical elements or devices. In comparison with BHN, TCHN disclosed in this work adopts a common nematic material instead of DFLLC, operates all optically rather than electrically, and it possesses an additional stable state. Moreover, the TCHN is stress-insensitive in stable states.

2. Experiment

Samples of TCHN were composited by doping the left-handed azo-chiral compound Q1-3c-S, also known as ChAD-3C-S, (BEAM) in orange powder form at a concentration of 0.33 wt% into the eutectic nematic host E7 (Merck). The chiral bis(azobenzene) molecule is photo-responsive, having two azo linkages to confer two distinct isomeric conformations—the rod-like *trans* form and the bent *cis* form. The *cis*-form molecule can be stable for several days [15]; however, heating or a high ambient temperature accelerates the isomerization to the *trans* form. The incorporation of the chiral dopant in E7 yields an initial helical twisting power (HTP) of $-42.6 \mu\text{m}^{-1}$ in the dark [20] and a green-light-stabilized HTP of $-30.7 \mu\text{m}^{-1}$ [21]. The concoction was infiltrated in an empty cell with cell gap $d \sim 10 \mu\text{m}$ formed by two identical glass substrates coated with alignment layers. A mixture of two polyimides, 96% of SE150 (planar alignment agent, Nissan) and 4% of AL-8395 (vertical alignment agent, Daily Polymer), led to a desired alignment layer to induce a pretilt angle of LC at 78° from the substrate plane. As a matter of fact, TCHN can be easily prepared as long as the pretilt angle is between 74° and 78° . A resulting sample would exhibit only two stable states (i.e., tT and tH) if the pretilt angle is smaller than 74° , and it is bistable with the absence of the tT state as the pretilt angle goes beyond 78° . To permit the cell to function as a light switch, we introduced dichroic dyes of Blue (AB4), Orange (AZO1), Red (AR1), and Cyan (AC1) (NEMATEL, Germany) to cover the entire visible spectrum at concentrations of 0.7, 0.6, 0.7, and 0.7 wt%, respectively. Compared with our previous study [22], here we succeeded to exclude a yellow dichroic dye thanks to the similar absorption of the chiral azo dye. The transmission spectra were obtained with a high-speed fiber-optic spectrometer (Ocean Optics HR 2000 +) along with a halogen light source (Ocean Optics HL2000). To investigate the photo-optical properties of TCHN exposed to both green and UV light, a green-light LED emitting at wavelength λ of 524 nm was exploited while the UV light was derived from an ultraviolet (UV) LED at $\lambda = 365$ nm. The intensity of green light was fixed at $2.02 \text{ mW}\cdot\text{cm}^{-2}$ throughout the spectral measurement.

3. Results and discussion

Figure 1 schematically depicts the optical switching mechanisms of TCHN and the configurations of the tT, fingerprint (FP), and tH states involved in tristable switching. Obviously, the photo-induced unwinding effect caused by the *trans*-to-*cis* isomerization of the azo-chiral compound exposed to UV light and the winding effect due to the *cis*-to-*trans* isomerization under green-light illumination are in action for direct state transitions among these three stable states. In comparison with the complex, electrical driving scheme for switching a BHN cell between its two stable states—tH and tT, our method by using light illumination for TCHN is very simple in controlling the switching among three stable states. Under UV light illumination at 365 nm, the chiral azo dye isomerizes to the *cis*-form and the HTP drops virtually to null. The substantially weakened helical strength transforms the cell into the tH configuration from the initial, stable tT state. In contrast, exposure to the green

light at 524 nm allows the azo-chiral molecules to recover the *trans*-form, and the system regains the tT configuration. Regarded as a relay-station state, the FP state is an intermediate state between the tH and tT states observable under weak UV or green light illumination. As a result, the pitch in the tT state is *ca.* 10 μm and that in the tH state is virtually infinite with respect to the normal of the substrate plane.

Figure 2 shows three photos taken with the four letters “NCTU” printed on a piece of paper underneath a dye-doped TCHN cell. Three different extents of transparency are illustrated in the three corresponding TCHN states. The tH state with LC molecules oriented practically normal to the substrates appeared transparent for unpolarized light. This can be easily understood because the major absorption axis of dichroic dye molecules is virtually oriented along the light propagation direction in the tH state. On the other hand, the dye molecules incurred considerable absorption due to the twist configuration in the tT state where the long axis of absorption of the dichroic dyes became approximately parallel to the field vibration directions of unpolarized light, giving a dark state for the dye-doped TCHN. Moreover, the FP state manifesting a stable scattering state is also demonstrated in TCHN. Figure 3 displays the optical textures of the tristable tT, FP, and tH states observed under a polarizing optical microscope (POM) in the transmission mode with crossed polarizers. One can see that the tH texture with LC and dye molecules oriented almost vertically produced the dark state under crossed polarizers. The tT state exhibited a bright optical texture with some rubbing traces. The FP texture involves the lying helix of chiral nematic molecules owing to the rubbing on the mixed homeotropic–homogeneous alignment layers to impose the 78° LC pretilt. Here the FP structure characterized by a grating constant of *ca.* 22 μm induced strong light scattering.

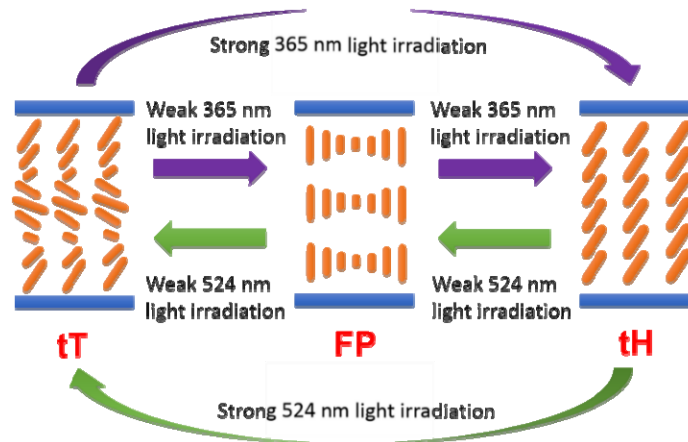


Fig. 1. Photo-switching mechanisms and configurations of TCHN molecules in the tilted-twist (tT), fingerprint (FP), and tilted-homeotropic (tH) states.

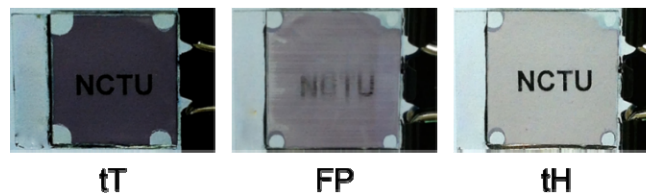


Fig. 2. A dye-doped TCHN sample atop a piece of paper with the letters NCTU printed on it. No modification with any photographic or image processing software is applied to the photographs of the TCHN in three different stable states.

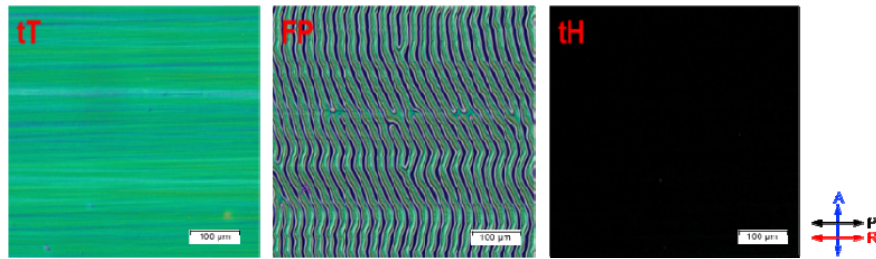


Fig. 3. Optical textures in three stable states observed under a POM equipped with crossed polarizers. The arrows to the right indicate the transmission axes of the polarizer (P) and analyzer (A) as well as the rubbing direction (R).

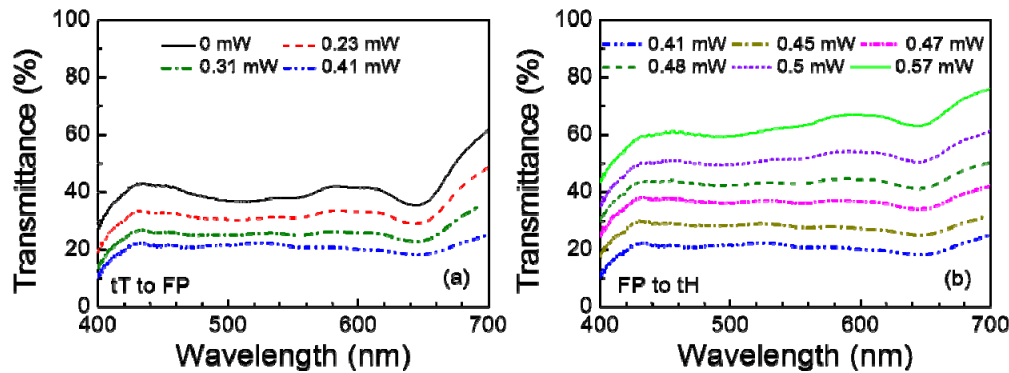


Fig. 4. Transmission spectra of TCHN in the (a) tT-to-FP and (b) FP-to-tH state transitions under various UV exposure conditions. Each legend indicates the corresponding UV power per unit area in cm^2 for a 6-s duration of irradiation to ensure the measurement in the steady state.

Figure 4(a) shows the transmission spectra of the tT-to-FP state transitions for a dichroic-dye-doped TCHN cell in various UV illumination conditions (as labeled by the legends). To facilitate the observation, the cell was constantly exposed to green-light irradiation at $2.02 \text{ mW}\cdot\text{cm}^{-2}$. In the initial tT state well sustained by the green light, the twist-oriented dichroic molecules are almost followed by the polarization rotation of light so that the absorption is strong. The effect of UV exposure was remarkably monitored upon unblocking the UV light and it took merely a few seconds for the LC configuration to reach the steady state. Increasing UV intensity up to $\sim 0.4 \text{ mW}\cdot\text{cm}^{-2}$ gave rise to the state transferring to the light-scattering FP structure, thereby lowering the transmittance as shown in Fig. 4(a). Figure 4(b) presents the transmission spectra from 400 to 700 nm of the FP-to-tH state transitions. With further increasing illumination intensity of UV light, the tH state was recovered until an even higher transmittance was reached when the LC molecules were fully unwound by the intense UV light ($\sim 0.6 \text{ mW}\cdot\text{cm}^{-2}$ in this study). Note that the wide-range flat transmittance in the initial tT state is caused by the mixed dyes to absorb the visible light evenly at various wavelengths. In addition, the spectral change in the reversed sequence (tH \rightarrow FP \rightarrow tT) yielded quite the same spectra.

According to Beer's law, the transmittance is given by $T = \exp(-acd)$, where a , c , and d are the effective absorption coefficient, the concentration of dye molecules, and the absorptive path length, respectively. The absorbance of the dye-doped TCHN is proportional to the concentration of dichroic dye molecules. A relatively heavy loading of dichroic dyes can enhance the contrast ratio defined as the ratio of the transmittance (or, precisely, luminance) of the brightest state to that of the darkest state that the dye-doped system can produce. However, the tradeoff is that the transmittance of the bright tH state is reduced accordingly. In this study transmittance of $\sim 60\%$ was obtained when the LC cell was switched

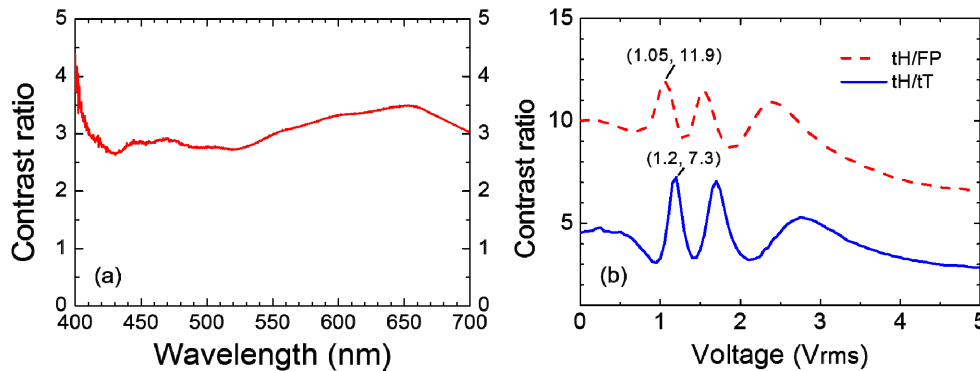


Fig. 5. (a) Contrast ratio of the TCHN device deduced from the transmittance ratio of tH to FP with data retrieved from Fig. 4(b) and 4(b) the reflective contrast ratios of tH to tT and tH to FP at 632.8 nm varying with the applied voltage across a supplementary planar-alignment E7 cell of 5.5 μm in thickness as a phase retarder.

to the tH state. Also note that the FP state, rather than the tT state, results in the lowest transmittance due to its strong scattering effect. The all-optical switching exhibits a satisfactory contrast ratio, defined as the ratio of the transmittance in the tH state to that in the FP state. The contrast ratio is about 4.5:1 at $\lambda = 400$ nm and *ca.* 3:1 at $\lambda = 550$ nm as shown in Fig. 5(a), which is comparable to that of a typical guest–host LC display; i.e., 5:1 [14]. The contrast ratio of the dye-doped TCHN is primarily limited by the dichroic ratios of the dyes used and likely imperfect adiabatic following. However, this problem can be solved by simply adding a supplementary retarder based on our previous work [16]. Figure 5(b) delineates the reflective contrast ratios of the tristable device at various applied voltages V across an additional E7 cell as a variable phase retarder (see Ref. 16 for detailed information about the corresponding electro-optical measurement at $\lambda = 632.8$ nm). One can see from Fig. 5(b) that the contrast ratio was promoted up to $\sim 12:1$ at $V = \sim 1$ V_{rms}. This means that the contrast ratio of the dye-doped TCHN, once in combination with a suitable retarder or wave plate, can reach a value of 2.4 times higher (than that of a typical guest–host LC system).

In comparison with its well-known counterpart—bistable or tristable CLCs, the most advantageous feature of TCHN is the mechanical stability. Our test with hard press on a dye-doped TCHN cell by a pen in the tT and tH states showed that the disturbed LC reverts to the original state quickly after removal of the stress. As such, the TCHN device is of stress-resistance based on the light-driven azo-chiral system. We found that it takes a couple of seconds to regain the tT state whereas the tH state can be recuperated immediately (< 1 s) after removal of stress. The stability of each stable state is about several weeks.

4. Conclusions

We succeeded in contriving the light-driven TCHN mode enabling direct and reversible switching among three optically stable states. In comparison with its previous counterpart; namely, BHN with the stable tH and tT states, TCHN possesses an extra stable state (FP), simply demands a typical nematic host (say, E7 in this study), which is more commercially available and thus much inexpensive than a DF LC (say, MLC-2048 of Merck) as used in BHN, and can be controlled with a straightforward approach rather than a complex mechanism for DF driving. Moreover, the fabrication of a TCHN cell is of comparative ease, less crucial in terms of the rubbing condition, the cell-gap-to-pitch-length ratio and the pretilt angle dictated by the aligning layers. With a photo-responsive chiral bis(azobenzene) compound incorporated for functionality, the photo-switching of TCHN is easily regulated by two distinct visible light sources (wavelengths of 365 and 524 nm in this study) to induce the desired state transition. By further doping dichroic dyes into the TCHN system, the resulting cell becomes a polarizer-free device, holding great promise for applications as an optical

switch, a light modulator or a display. The TCHN cell particularly boasts its feature to be able to preserve its stable state after a mechanical stimulus, which outperforms the CLC counterpart. It is worth reminding that this work is concerned with a new LC mode invented in 2004 instead of the well-documented CLC [11], a historically known LC mode. Moreover, we emphasize the pressure-insensitive characteristic which has not been proposed by Wang *et al.* [11]. The concept developed in this study can be potentially applied to optically rewritable displays [23] or displays with memorized grayscale levels [24].

Funding

Ministry of Science and Technology (MOST), Taiwan, (104-2112-M-009-008-MY3).