Electro-optic properties of high-concentration photochromic dye-doped nematic liquid crystal

Ritsuki Domoto[1], Hao-chun Yang[2], Hsiu-Hui Chen[2], Hiroyuki Yoshida[1]*

* hiroyuki.yoshida@kwansei.ac.jp
[1] School of Engineering, Kwansei Gakuin University, 1 Gakuen Uegahara, Sanda 669-1330, Japan
[2] 1Department of Molecular Science and Engineering, National Taipei University of Technology, Taipei 106, Taiwan

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ABSTRACT

We report the preparation of a high-concentration photochromic dye-doped nematic LC for improved light absorption and electro-optic response. The recently developed diethylcyclopentene derivative dissolves in a commercial nematic LC mixture at a high concentration of 10 wt%, enabling a thin cell to be used for sufficient coloration, thereby improving the response time.

1 Introduction

The property that a material absorbs light of a specific wavelength, alters its molecular structure, and reversibly transitions between two states with different colors and physical properties is called photochromism [1]. Photochromic dyes are classified into T or P-type depending on whether they return to the original structure thermally or by absorbing photons. T-type dyes have been commercialized in lenses that can adjust their color in response to environmental stimuli. While P-type dyes have yet to find commercial success, they possess an attractive possibility of realizing devices with actively tunable coloration properties. LCs are an attractive medium in which to embed such functional molecules, as the optical properties become tunable also by an electric field, via field-induced molecular reorientation.

Despite their unique properties, photochromic dye-doped LCs typically suffer from low absorbance that originates from the poor solubility for the dye in the host. Increasing film thickness to enhance absorbance leads to a trade-off in LC device performance: an increase in response speed proportional to the square of thickness [2].

In this study, we report the preparation of a high-concentration photochromic dye-doped nematic LC containing a diethylcyclopentene derivative at a weight ratio of 10%. The higher dye content leads to sufficient hue even when a LC cell as thin as 2 um is used, enabling visible color switching with response times on the order of 10 ms.

2 Experiment

The molecular structure of the diethylcyclopentene derivative dye, BIPH-PH-OC8 is shown in Fig. 1 [3]. The dye possesses a diethylcyclopentene core which switches between the transparent, open ('deactivated') and colored, closed ('activated') forms by irradiation of ultraviolet or visible light. Interestingly, the dye shows high miscibility with a standard nematic phase, possibly as a result of the asymmetry introduced by the side chains. The dye was mixed with a nematic LC mixture, MLC-2140 (Merck) at a concentration of 89.9wt% : 10.1wt%. MLC-2140 was selected because its high birefringence and dielectric anisotropy, which is advantageous for device applications.

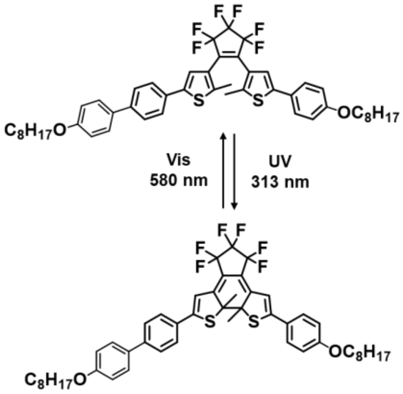


Fig. 1 Molecular strucutre of BIPH-PH-OC8 in the open (deactivated) and closed (activated) forms

We measured the photochromic reaction efficiency and the static and dynamic electro-optic characteristics of the dye-doped LC sample. All measurements were made in ITO-coated, glass cells with anti-parallel rubbing treatment (EHC).

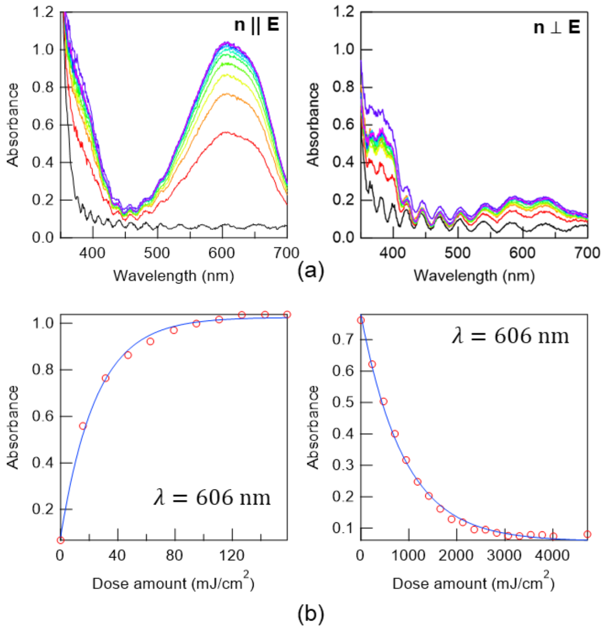
3 Results and Discussions

3.1 Photochromic reaction efficiency

The photochromic reaction efficiency was characterized at 30°C using cells with nominal thickness of 2 um. The dose dependence of the polarized absorbance spectrum was measured upon irradiating light with wavelengths of approx. 365 and 590 nm, both with intensities approx. 8 mW/cm^2, to activate and deactivate the dye, respectively. The polarization of the excitation light was parallel to the director, and the absorbance parallel and perpendicular to the director were measured.

Figure 2 shows the evolution in the absorbance spectrum caused by the photochromic reaction, measured with the light polarization (**E**) parallel and perpendicular to the director (**n**). Starting from the transparent, deactivated state plotted in black, the absorbance grows approximately at 380 nm and 600 nm, leading to the appearance of blue hue. The sample shows clear linear dichroism with the dichroic ratio reaching 5.66 at 606 nm.

Figure 2(b) shows the dose dependence of the absorbance at 606 nm for the activation and deactivation processes, respectively. The difference in the initial absorbance is caused by the difference in cell-gap. Both processes can be described by a monoexponential curve $A(t) = A_0 \exp(-kt)$, where k is the reaction rate and t is time. In the prepared material, the activation process was more efficient than the deactivation process, with $k_{activation}$ ~ 25 mJ/cm^2 and $k_{deactivation}$ ~ 900 mJ/cm^2.



(a)

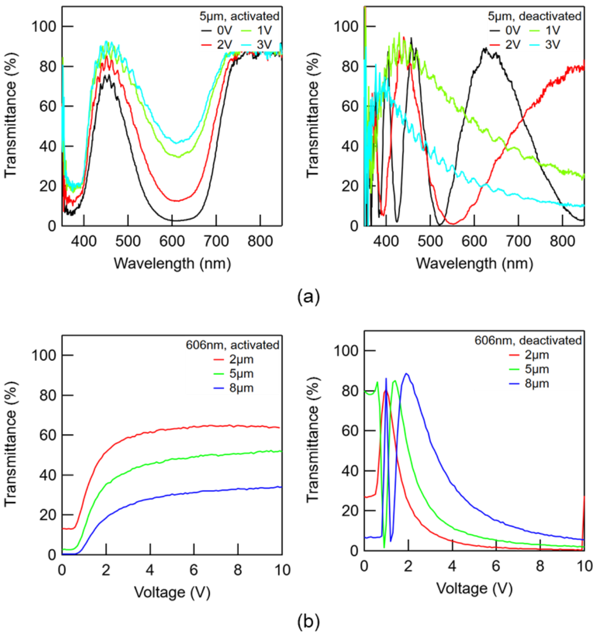
(b)

Fig. 2 (a) Evolution in absorbance spectra parallel and perpendicular to the director for the activation process. (b) Dose dependence of the absorbance at λ = 606 nm for the activation and deactivation processes.

3.2 Static and dynamic electro-optic properties

The static and dynamic electro-optic properties were characterized at 30°C using devices with cell-gaps of approximately 2, 5 and 8 μm. Static properties were measured on a micro-spectroscopy setup built on a polarizing optical microscope. White light from a halogen lamp was polarized by passing through a polarizer and incident on the sample. For characterization of the colored (activated) samples, the transmittance was measured at different applied voltages on the sample, with the polarization aligned parallel to the LC director. For the deactivated (transparent) samples, the sample was placed at 45° between crossed polarizers and the voltage dependence of the polarized transmittance was measured.

Figure 3 (a) shows the voltage dependence of the transmittance spectrum for the 5 μm sample in the colored and transparent forms. In both forms, a change in transmittance occurs due to molecular reorientation. Figure 3 (b) compares the transmittance at 606 nm for devices with different thicknesses. For all samples, the threshold was approximately at 0.5 - 0.6 V, similar to pure MLC-2140 (V_{th} = 0.5). The insignificant change in threshold voltage despite the relatively high doping concentration of 10 wt% is attributed to the large dielectric anisotropy of MLC-2140. The dye-doped LC device thus operates in two modes, that either allows tuning of transmitted light intensity (activated state) or the light phase (deactivated state).



(a)

(b)

Fig. 3 (a) Voltage dependence of transmittance spectra of the 5 um device in the activated and deactivated states. (b) Voltage dependence of transmittance at 606 nm in the same cell.

Figure 4 shows characteristic response curves of the dye-doped samples in the 2 um cell for an applied voltage of 6 V. The response of pure MLC-2140 filled in a 2 um thick cell is also shown for comparison. The response times are similar for all samples, implying that photochromic dye doping has small impact on the electro-optic transient response. Importantly, the high content of the dye leads to clear hue being visible even in cells that are only 2 um thick; this leads to a fast color switching with response times ~ 20 ms, which is limited by the free relaxation response of the LC director. We believe further improvement to be possible by optimization of dye concentration and cell gap.

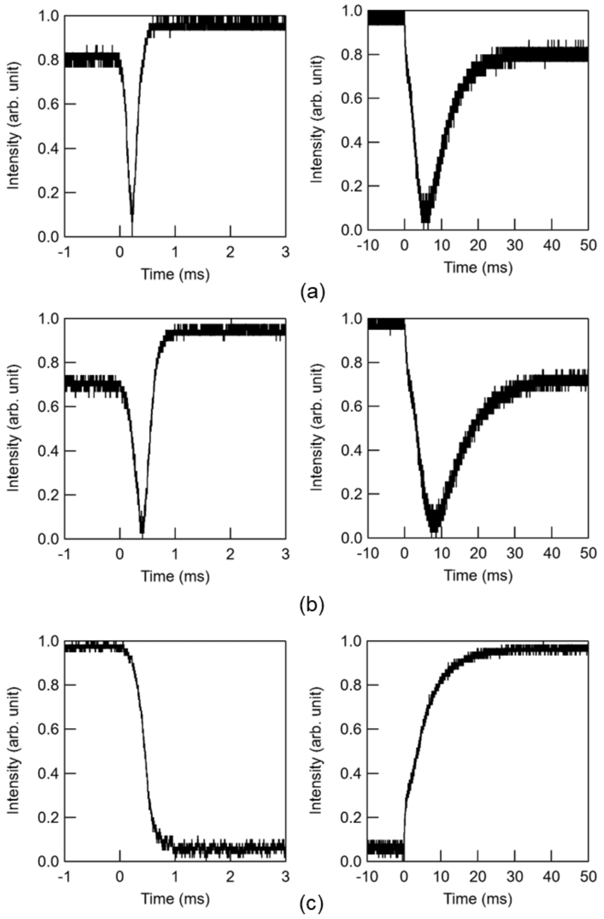


Fig. 4 (a) Rise and fall response curves of pure MLC-2140 for applied voltage of 6 V. (b) Same response curves for the dye-doped sample in the deactivated state

4 Conclusions

We developed a high concentration guest-host LC system containing a P-type photochromic dye. Because of the high content of the dye, sufficient coloration reaching absorbance values of ~ 1 can be achieved using cells as thin as 2 μm, enabling fast switching with ~ 20 ms response times, limited by the free relaxation of the LC director in the cell. On the other hand, in the deactivated state, the sample shows high transmittance, operating as a phase modulator. The dual mode device enabled by LC soluble photochromic dyes may lead to smart windows with new or improved functionalities.

Acknowledgements

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References

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