Supporting Information

Light-regulated molecular diffusion in a liquid crystal network

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Experimental methods

Materials

Di-acrylate **1** is a cross linker that is used to balance the mechanical properties of the polymer. Monomer **2** enhances alignment properties and optimize the elastic properties of the LCN* on light-induced deformation. Nonreactive liquid crystal **3** (5CB) is added to work as porogen for the network. Monomer **1** to **3** were obtained from Merck UK. Chiral component **4** is added to induce the desired chiral-nematic phase where the average molecular orientation describes a helix. It was from BASF. Monomer **5** has the azobenzene unit that provides the photomechanical response to the LCN*. It was custom-synthesized by Syncom (Groningen, Netherlands). Photoinitiator **6** (Irgacure 819) was purchased at Ciba, and chosen as it can be activated by wavelengths 400 nm, preventing premature conversion of azobenzene compound during the photopolymerization process. The mixtures were prepared by dissolving the components in dichloromethane, and subsequently evaporating the solvent under an argon flow.

Sample preparation

The liquid crystal mixture was filled between two glass plates provided with the alignment layers by capillary suction at 85 °C. One glass plate is coated with uniaxially rubbed polyimide AL1051 (JSR Optmer), the other is with uniaxially rubbed polyvinylalcohol (Mw 31000-50000, 87-89% hydrolyzed, from Sigma-Aldrich). The nematic-to-isotropic transition temperature of the LC mixture is 64 °C. To get the desired cholesteric order, the sample was slowly cooled and cured at 42 °C by ultraviolet exposure for 45min with an intensity of 20 mW/cm^2 using a mercury lamp (Exfo Omnicure S2000) equipped with a cutoff filter transmitting light 400 nm (Newport FSQ-GG400 filter). Carefully open the LC cell with a wet razor blade, to get the LCN* film perfectly attached on the PI-coated glass. Leave the LCN*-PI coated glass on 140 °C hot stage for 45 mins, to remove the nonreactive 5CB. Or placing the LCN*-PI coated glass in the absolute ethanol solution at ~45 °C for 15 min can extract 5CB from the film. Finally the

thickness of the final polymer membrane for 5CB and 8CB diffusion measurements is controlled as ~5 μm (after the removal of porogen).

Characterization

The cholesteric film was checked by polarized microscopy (Leica). A LED lamp (Thorlab, M365L2 and M455L3) was used as the light source. UV-vis measurement was performed on UV-3102 PC (Shimadzu). IR absorption test was conducted on a Varian 670 FT-IR spectrometer with slide-on ATR (Ge). SEM was performed on a Jeol 5600. A DSC-Q1000 from TA instruments was used at a rate of 5 °C min^{-1}. The second cycle was used for characterization. The mechanical properties (e.g., storage modulus, T_g) of the LCN* film were measured with a Dynamic Mechanical Thermal Analysis (Q800, TA instrument) with a ramp rate of 3 °C min^{-1}.

UV-vis measurement

To monitor 5CB and 8CB diffusion in the LCN* film, UV-vis transmission test was conducted on the sample over time. Firstly, drop 2 ml of 5CB or 8CB on the LCN* film at 38 °C or 42 °C, respectively, then carefully cover the wet film with a clean glass slide (same size as the film, 3*3 cm^2), and quickly insert the sample into the UV-vis sample holder. Transmission data was collected every 6 minutes. For the diffusion test with polarized light illumination, shine blue light (455 nm, 10 mW/cm^2) directly onto the sample, while the UV light (365 nm) was placed behind a linearly polarizer (10LP-UV, Newport), which is mounted on a rotation stage (from Thorlabs) providing a controllable rotation (both direction and speed). The intensity of UV light on the sample (after passing through the liner polarizer) was set as 100 mW/cm^2. The incident angle of the linearly polarized UV light to the LCN* film was ~10 degree, in order to prevent blocking the light pathway during UV-vis measurements.

Additional data

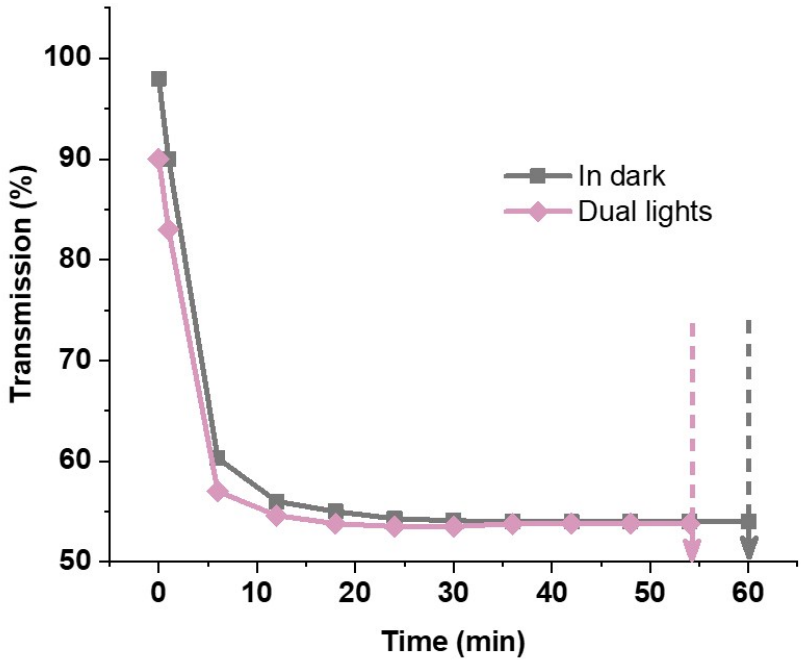

Figure S1. Kinetics of the UV-vis transmission for 5CB diffusion in the LCN* film, which was pretreated with solvent extraction: in dark and with dual lights where linearly polarized UV clockwise rotated in 25 DPS.

Principle of Elevator-type diffusion

Figure S2 schematically represents the mechanism of the transport of free volume through the film as enhanced by rotating polarized light. The linearly polarizer is placed between the UV light and the LCN* sample, only the azobenzene, aligning with the linearly polarizer, is activated by the UV irradiation. More importantly, when the linearly polarizer rotates, azobenzene in different regions is excited respectively. So the free volume created by excitation of azobenzene moves along with the rotation of the linearly polarizer. The diffusion can be facilitated by the formation of free volume in the network.Tthe area, where free volume forms, as an “elevator” to transport the diffusing component in

the LCN*. When the “elevator” moves along with the helical axis twisting of LCN*, which is clockwise, enhancement of the diffusion is obtained.

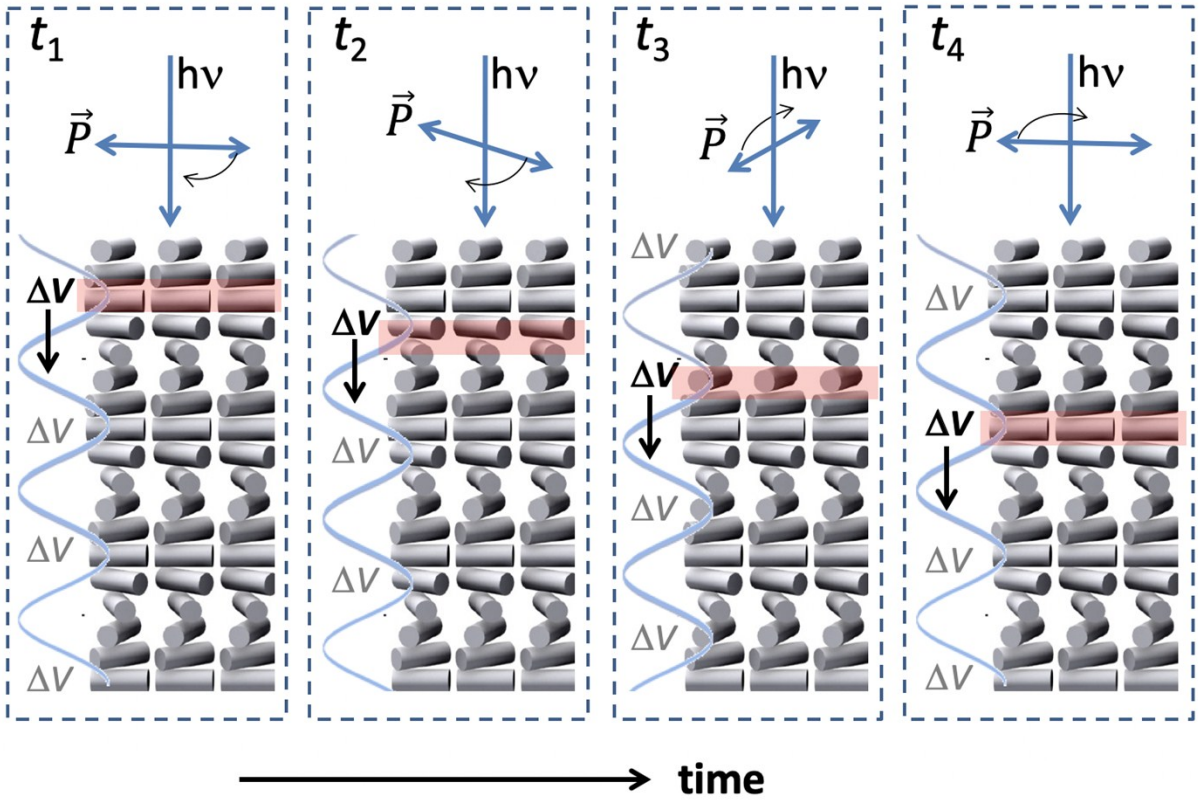

Figure S2. Schematic representation of the transport of localized free volume (ΔV) through a chiral-nematic membrane. The polarization of the activating UV light rotates continuously. Polarized light selectively excites the dichroic trigger molecules that are aligned parallel to the polarization and creates local free volume on periodic locations. The free-volume packets transfer through the film by the rotation of the polarization of the light source. In this figure the rods resemble the local director of an ensemble of molecules. The pitch of the chiral-nematic helix is chosen such that while traveling through the medium the light remains close to plane polarized but rotates slightly through the optical activity of the chiral molecules inducing the helix.