Supporting Information

Light-driven Nanoscale Chiral Molecular Switch: Reversible

Dynamic Full Range Color Phototuning

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1. Materials and methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification. Melting points are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃. Chemical shifts are in δ units (ppm) with the residual solvent peak as the internal standard. The coupling constant (J) is reported in hertz (Hz). NMR splitting patterns are designed as follows: s, singlet; d, doublet; t, triplet; and m, multiplet. Column chromatography was carried out on silica gel (60-200 mesh). Analytical thin layer chromatography (TLC) was performed on commercially coated 60 mesh F₂₅₄ glass plates. Elemental analysis was performed by Robertson Microlet Inc. UV-vis spectrum was taken by a Perkin Elmer Lambda 19 Spectrometer. Mass spectrum was taken by Mass Spectrometry & Proteomics Facility of Ohio State University. Textures, reflected colors and disclination line distance changes were observed by optical microscopy using a Leitz polarizing microscope with temperature controller or Nikon polarizing microscope. The photographs of cells were taken by a camera Canon PowerShot SD 850. UV irradiation was carried out by Xenon light source 100W through a filter at 365nm or a handheld UV lamp with a peak wavelength of 365 nm (UVGL-58, UVP Co.). Visible irradiation was carried out by Xenon light source 100W (Asahi Spectra Inc.) through a filter at 520 nm. Phototuning property of cholesteric LC was examined with an Ocean Optics spectrometer collecting spectra in the dark. The achiral nematic liquid crystal E7 was used in the study, which is a eutectic mixture of LC components commercially designed for display applications.

2. Synthesis of light-driven chiral molecular switch 4

(S)-(-)-1,1'-Binaphthyl-2,2'-diamine **1** (3.5 mmol) was dissolved in a solution of H_2O (17 mL) and concentrated HCl (2.5 mL). The solution was cooled to 0 °C at ice water bath. A solution of sodium nitrite (8.4 mmol) in H_2O (10 mL) was dropped with stirring. The resulting brown yellow suspension was dropped into the solution of Phenol (7.7 mmol) and NaOH (22.6 mmol) in H_2O (15 mL). The suspension was acidified with aqueous HCl and filtered. The precipitate was washed with H_2O and dried to get the crude **2**, which was purified by chromatography on silica gel to give an orange solid. The mixture of the intermediate **2** (1.0 mmol) and PPh₃ (3.0 mmol) was added to a mixture of [4-(4'-propyl-cyclohexyl)- phenyl]

-methanol **3** (2.5 mmol) and diethyl azodicarboxylate (3.0 mmol) in THF under N_2 atmosphere. The resulting mixture was refluxed. The solvents were removed under reduced pressure. The residue was purified by chromatography on silica gel to afford the product as an orange solid **4** in 78 % yields. Satisfactory ¹H NMR, ¹³C NMR, high resolution mass spectrum and elemental analysis were obtained for the new target compound **4**.



Fig. S1 Synthesis of Chiral Molecular Switch **4**; a: NaNO₂, aqueous HCl; b: Phenol, aqueous NaOH; c: PPh₃, diethyl azodicarboxylate

Data for chiral molecular switch **4**: Mp 157-158 °C; ¹H NMR: δ 0.69 (t, J = 7.0 Hz, 6H), 0.74-1.47 (m, 18H), 1.64 (d, J = 10.6 Hz,8 H), 2.24 (t, J = 12.0 Hz, 2H), 4.73 (s, 4H), 6.57 (d, J = 8.8 Hz, 4H), 6.95-7.12 (m, 14H), 7.21-7.30 (m, 4H), 7.73-7.85 (m, 4H), 7.95 (d, J = 8.8 Hz, 2H); ¹³C NMR: δ 14.40, 20.01, 33.51, 34.27, 36.97, 39.68, 44.35, 70.05, 114.45, 114.73, 124.57, 126.54, 126.91, 127.07, 127.59, 127.79, 128.02, 128.96, 133.73, 134.19, 134.25, 136.69, 147.35, 147.91, 148.30, 160.88; Anal.calcd for C₆₄H₆₆N₄O₂: C, 83.26; H, 7.21; N, 6.07. Found: C, 83.33; H, 7.37; N, 6.19; High Resolution MS (M+H) calcd for C₆₄H₆₇N₄O₂: 923.5264, found: 923.5280.

3. Reversibly photoresponsive experiment of light-driven chiral molecular switch 4 in organic solvent



Fig. S2 UV-vis absorption spectra of chiral molecular switch 4 (40 μ M) in CH₂Cl₂ under UV irradiation at 365 nm (6.0 mW/cm²) with 0, 10 s, 20 s, 30 s, 40 s, 50 s, 60 s and 70 s.

4. Measurement of pitch and helical twisting power

A conventional technique for pitch measurement is Grandjean-Cano wedge method (I. Dierking, *Textures of Liquid Crystals*, Wiley-VCH, Weinheim, 2003). Such wedge cell with an opening angle θ is made by applying two differently sized spacers at each end of the cell (Figure S3). If the alignment of the substrates is planar (the director lies parallel to the surface) and the rubbing directions of the substrates are parallel to one another, the cholesteric LC becomes discrete. Because the value of the pitch is fixed, and the alignment is also fixed, the cholesteric LC arranges itself as in Figure S3. This arrangement produces disclination lines between areas that contain a different number of layers. The difference in thickness between each domain must be p/2 in order to satisfy the alignment boundary condition.



Fig. S3 Schematic illustration of a Grandjean-Cano wedge cell for the pitch measurement of cholesteric LC. Disclination lines are pointed out with arrows and the thickness change between two domains is marked p/2.

The disclination lines of the cholesteric liquid crystal in the wedge cell can be seen through a polarizing optical microscope. The pitch was determined according to the equation $p = 2R \tan \theta$, where R represents the distance between the Grandjean lines and θ is the wedge angle of wedge cells (EHC, KCRK-07, $\tan \theta = 0.0196$). The inverse of pitch proportionally increases with increase in the concentration of a chiral dopant and HTP values is $\beta = (pc)^{-1}$, where β is the helical twisting power, i.e, the ability of the chiral dopant to twist a nematic LC, and c is the concentration of the chiral dopant.

The HTP change of 0.8 wt% **4** in E7 with irradiation time under 365nm and 520 nm is shown in Figure S4. Figure S5 is the reciprocal helical pitch as a function of concentration of **4** in host E7 and the HTP values according to the weight based on weight/weight and mol/mol can be calculated.



Fig. S4 Plot of helical twisting power of 0.8 wt% **4** in LC E7 with different irradiation time upon the light at 365 nm (left); after irradiated by UV light at 365nm for 2 min followed by visible light irradiation at 520 nm (right).



Fig. S5 Reciprocal helical pitch as a function of concentration of chiral switch 4 in LC E7.



5. Thermal relaxation in darkness

Fig. S6 Dark thermal relaxation of 6.5 wt% 4 in LC media E7 in a 5 μ m planar cell after UV irradiation at 365 nm.

6. Phototuning the reflection wavelength back across the entire visible spectrum



Fig. S7 Phototuning of 6.5 wt% **4** in LC media E7 in a 5 μ m planar cell upon visible light at 520 nm (11.0 mW/cm²). It took about 7 s to phototune the reflection light back across the entire visible region, i.e., 780-380 nm (center wavelength).

7. Color driven by light



Fig. S8 The primary blue, green and red colors of a flexible 6.5 μ m thick planar cell (2 inch x 1.5 inch) with 4 wt% **4** in commercially available LC E7 driven by UV irradiation at 365 nm (A), and a glass 5 μ m thick planar cell (1.5 inch x 1.5 inch) with 6 wt% **4** in LC E7 driven by visible light irradiation at 520 nm of the different area of one layer with different time (B right) (the initial cell is the left one which was driven to near infrared region by UV irradiation at 365 nm) were captured at ambient condition. C: Examples of photo-addressed color display (the same cell with B) through different photomask were captured at ambient condition.

8. Measurement of reflection response to a pulse

To measure reflection response to a pulse, the measure procedure was firstly driving the cell to a planar state by applying a high voltage pulse, such as 60 V pulse (100 Hz, 1000 ms). Then a certain voltage pulse was applied to the cell and the reflection of the cell was taken after 3 seconds. Both the incident angle and reflection angle were 22.5°. The reflection light was collected by a battery of lens system and the collection angle was fixed at 2°. The responses of a cell with blue color background before UV irradiation and after UV irradiation at 365 nm for 10 s were shown in Figure S9A. The pulse for achievement of focal conic state can be obtained. For an image recorded in a planar cell through a photomask by 365 nm light irradiation for 10 s, the pattern would be hidden when applying a 30 V pulse, since the LC texture of both unirradiated and irradiated region by UV light were in focal conic state with weak scattering. Therefore the image was hidden.

Figure S9B is an illustration of a reflection response to a pulse of the sample at focal conic state by the similar measure, i.e., driving the cell to a focal conic state by applying a

voltage pulse such as a 35 V pulse (100 Hz, 1000 ms) for the unirradiated cell or applying a voltage pulse such as a 28 V pulse (100 Hz, 1000 ms) for the irradiated cell. Then a certain voltage pulse was applied to the cell. Both unirradiated and irradiated region by UV light were driven back to planar state again when applying a pulse exceed 60 V. The hiding image in the focal conic state was reappeared. Moreover, a positive image can be obtained when applying a 38 V pulse to an image in entire planar state or a 40 V pulse to an image in entire focal conic state. The region irradiated by UV light remained reflective planar state and other un-irradiated region was in focal conic state. Both of two states are stable, which would be recorded indefinitely, as similar as described in the previous report (E. Montbach, N. Venkataraman, I. Shiyanovskaya, T. Schneider, J.W. Doane, L. Green and Q. Li, *SID Digest Tech. Paper*, 919, 2008).



Fig. S9 Reflection response to a pulse of a 5um thick homeotropic cell with 4 wt% **4** in E7. Initial state: plannar state (A); focal conic state (B).