Supplementary Information for

Photomodulated Tri-Color-Changing Artificial Flowers

Bo Zuo, Meng Wang, Bao-Ping Lin and Hong Yang*

*School of Chemistry and Chemical Engineering, Jiangsu Province Hi-Tech Key Laboratory for Bio-medical Research, Jiangsu Key Laboratory for Science and Application of Molecular Ferroelectrics, State Key Laboratory of Bioelectronics, Southeast University, Nanjing, 211189, China.

Correspondence and requests for materials should be addressed to H.Y. (email: yangh@seu.edu.cn).

General Considerations. Platinum-divinyltetramethyldisiloxane complex and 4-dimethylaminopyridine (DMAP) were purchased from Aladdin Inc. Polymethylhydrosiloxanes (HMS-993, M.W. 2200-2400) were purchased from Gelest Inc. Organic dyestuffs (Green 575, Blue 623, Red 306, Yellow 110) were commercially available products bought from Kelly Chemical Corporation. 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran (compound **11**, Supplementary Figure 14) was bought from Heowns Biochem LLC. Toluene and CH_2Cl_2 were redistilled from sodium benzophenone ketyl under nitrogen. Other chemical reagents were used without further purification. All non-aqueous reactions were conducted in oven-dried glasswares, under a dry nitrogen atmosphere.

Ultraviolet and visible spectra (UV-vis) were recorded with a UV-2600 ultraviolet-visible spectrophotometer (UV/VIS spectrometer) (Shimadzu Co., LTD). The scanning electron microscope (SEM) images were recorded on an Inspect F50 S3 field emission scanning electron microscope (FEI-SEM, America). A TA Q100 instrument (New Castle, DE) was used to record differential scanning calorimetry (DSC) spectra under nitrogen purge at a heating rate of 10 °C/min, to measure the phase transition temperatures of the samples. New chemical compounds routinely characterized by NMR spectroscopy. ^{1}H NMR spectra were recorded at a Bruker HW500 MHz spectrometer (AVANCE AV-500), using $CDCl_3$ (internal reference 7.26 ppm) as solvent. The mass spectra were obtained from Waters Micromass Q-TOF micro system mass spectrometer. Polarized optical microscopy (POM) observations of the LCE samples were performed

on an Olympus BX53P microscope with a Mettler PF82HT hot stage. The images were captured by using a Microvision MV-DC200 digital camera with a Phenix Phmias 2008 Cs Ver2.2 software. All the UV-responsive, NIR-responsive and visible light-responsive experiments were performed by using either a LP-20A UV lamp (5 $mW \cdot cm^{-2}$, λ = 365 nm; LUYOR Corporation), a 808 nm semiconductor laser source (0.83 $W.cm^{-2}$, Center wavelength: 808 ± 3 nm, Nanjing Latron Laser Company, China) or a 520 nm laser source (44 $mW.cm^{-2}$, Output power: 500 mW, Center wavelength: 520 ± 5 nm, Changchun Laser Optoelectronics Technology Co., Ltd., China).

Synthesis of (±)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline]-5',8-diol (compound 8).

The synthetic intermediates of each step were prepared according to the literature procedures and the compound **8** (a dark powder) was used directly without further purification as described in the literature.[S1]

Synthesis of SP1 (compound 10, Figure S8).

To a 100 mL round-bottom Schlenk flask was added compound **8** (1.42 g, 4.01 mmol, 1.0 equiv.) and dimethylaminopyridine (1.47 g, 12.03 mmol, 3.0 equiv.). After purging the airtight system with nitrogen gas, 50 mL of dichloromethane was added into the Schlenk flask, followed by a dropwise addition of 10-undecylenoyl chloride (1.87 g, 9.22 mmol, 2.3 equiv.) in 5.0 mL dichloromethane at 0 ^{o}C. The reaction mixture was stirred at 0 ^{o}C

for 16 h, concentrated *via* rotovap, diluted by 100 mL of diethyl ether and further filtered off the precipitates. The organic solution was concentrated and purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1:15 v/v) to provide a yellow solid product (0.81 g, 1.18 mmol, 29.4 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.81 (d, □ = 5.0 Hz, 1H), 6.97 (d, □ = 10.0 Hz, 1H), 6.84 (m, 1H), 6.79 (s, 1H), 6.47 (d, □ = 5.0 Hz, 1H), 5.91 (d, □ = 10.0 Hz, 1H), 5.81 (m, 2H), 5.02 (s, 1H), 4.98 (s, 1H), 4.95 (d, □ = 10.0 Hz, 2H), 2.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.59, 171.04, 151.02, 145.09, 144.42, 140.15, 139.09, 137.69, 137.17, 128.44, 120.96, 120.12, 119.90, 119.33, 119.14, 115.36, 114.19, 114.16, 107.58, 107.26, 51.82.

Synthesis of SP2 (compound 12, Figure S12).

To a 50 mL round-bottom Schlenk flask was added compound **11** (0.20 g, 0.57 mmol, 1.0 equiv.) and dimethylaminopyridine (0.21 g, 1.70 mmol, 3.0 equiv.). After purging the airtight system with nitrogen gas, 30 mL of dichloromethane was added into the Schlenk flask, followed by a dropwise addition of 10-undecylenoyl chloride (0.26 g, 1.31 mmol, 2.3 equiv.) in 5.0 mL dichloromethane at 0 ^{o}C. The reaction mixture was stirred at 0 ^{o}C for 16 h, concentrated *via* rotovap, diluted by 50 mL of diethyl ether and further filtered off the precipitates. The organic solution was concentrated and purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1:15 v/v) to provide a yellow solid product (0.13 g, 0.25 mmol, 44.2 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (m, 2H), 7.24 (t, □ = 5.0 Hz, 1H), 7.12 (d, □ = 10.0 Hz, 1H), 6.95 (m, 2H), 6.81 (d, □ = 10.0

Hz, 1H), 6.74 (d, □ = 10.0 Hz, 1H), 5.92 (d, □ = 15.0 Hz, 1H), 5.85 (m, 1H), 5.05 (d, □ = 15.0 Hz, 1H), 4.99 (d, □ = 10.0 Hz, 1H), 4.28 (m, 2H), 3.51 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.57, 159.42, 146.70, 141.16, 139.13, 135.69, 128.27, 127.83, 125.95, 122.74, 121.84, 121.79, 119.92, 118.46, 115.55, 114.15, 106.76, 106.51, 62.28, 52.85, 42.45, 34.18.

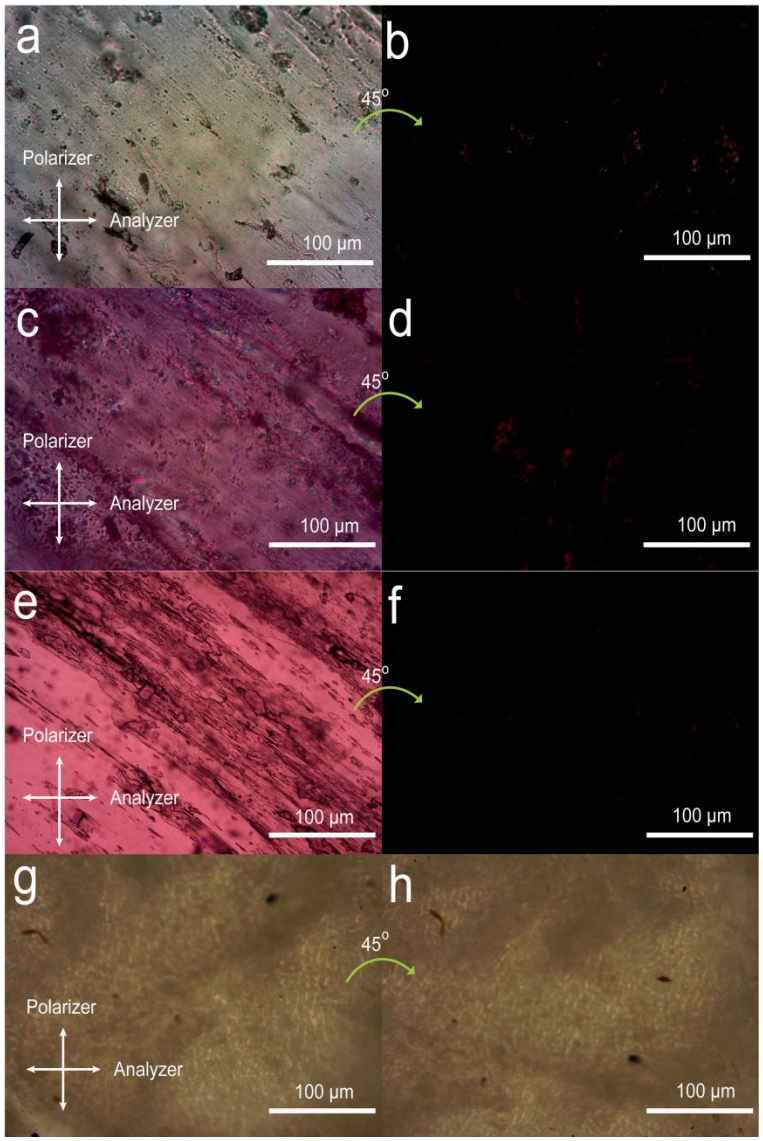

Figure S1. POM images of (a,b) LCE1 and (c,d) LCE2 and (e,f) LCE3 and (g,h) LCE0 recorded at room temperature.

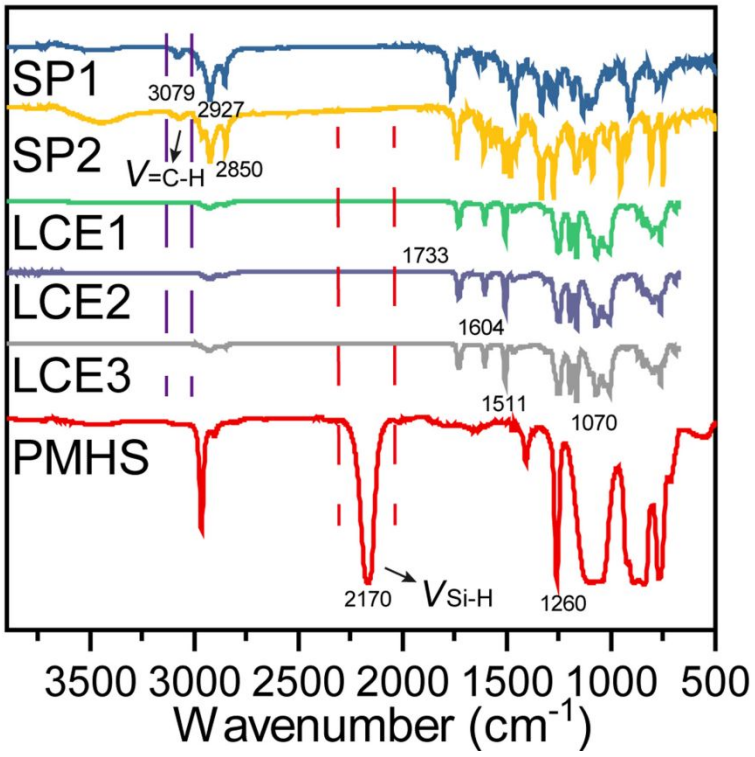

Figure S2. FT-IR spectra of monomers (SP1, SP2), LCE samples (LCE1, LCE2, LCE3) and the starting polymer PMHS.

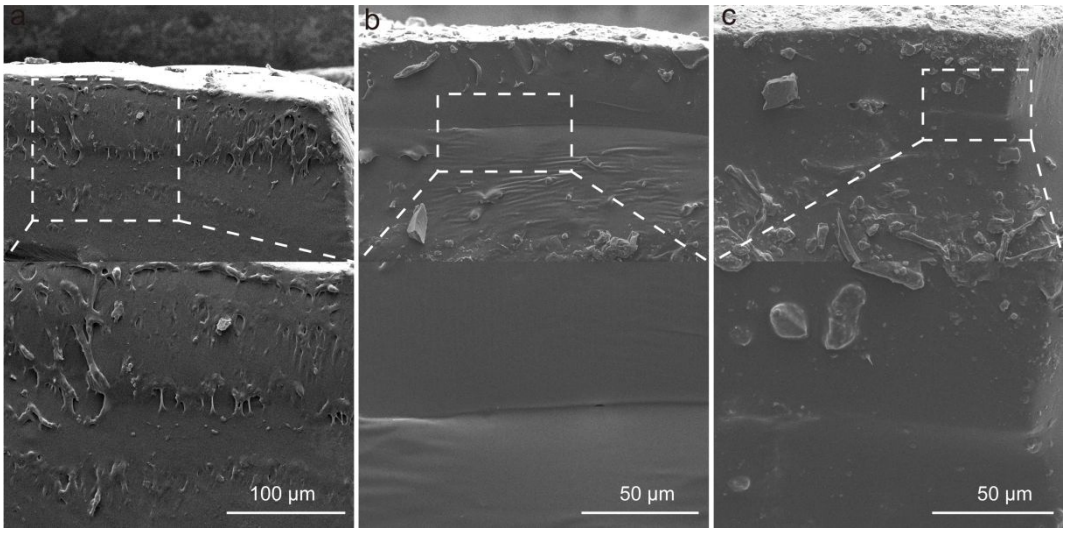

Figure S3. SEM images of the cross-sectional areas of the bilayered (a) LCE1B, (b) LCE2B and (c) LCE3B.

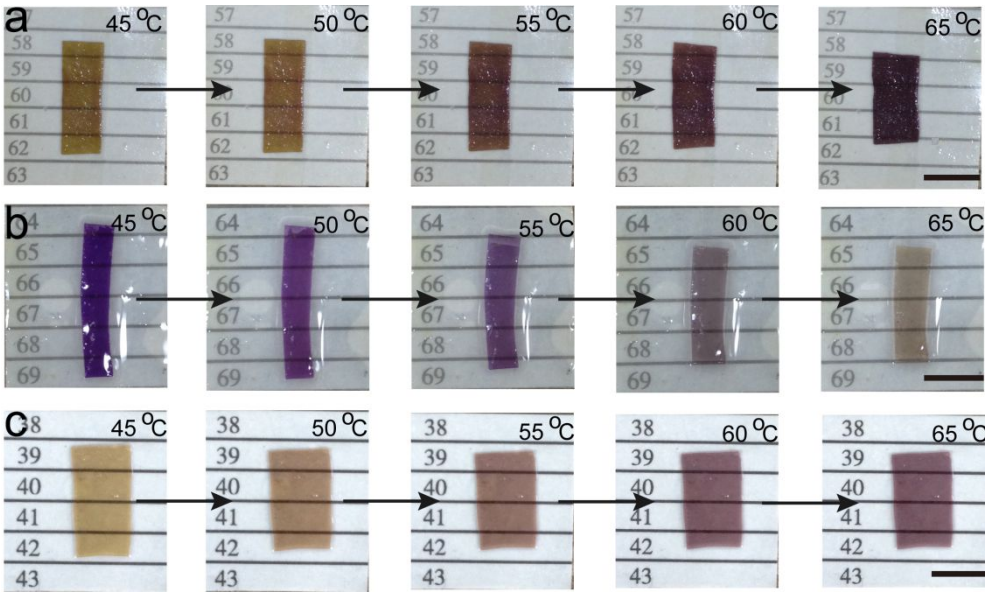

Figure S4. Thermo-chromic responses of (a) LCE1, (b) LCE2 and (c) LCE3 films at 45, 50, 55, 60 and 65 °C. Scale bar = 8 mm.