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Electronic Supplementary Information for

Cascade Energy Transfer Augmented Circular Polarization in Photofluorochromic Cholesteric Texture

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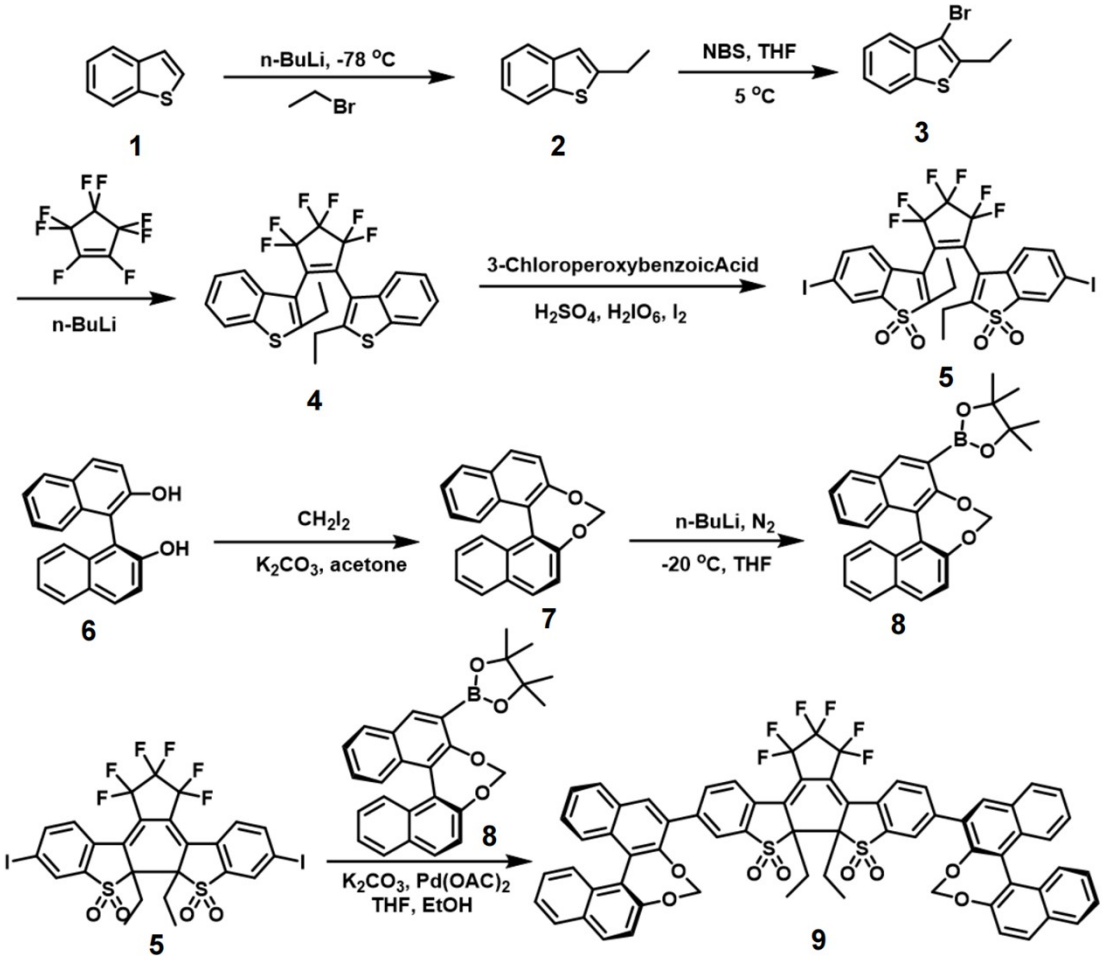
S1. Materials, characterization, and synthesis

Materials: All reagents and solvents were used as received, unless otherwise indicated. Previously reported procedures were used to synthesize 1,2-bis(2-ethyl-6-iodo-1-benzothiophen-1,1-dioxide-3-yl) perfluorocyclopentene (5, DAEI).[1] (±)-1,1'-Bi(2-naphthol) (99.87%) and n-Butyllithium (2.5 M hexane solution) were purchased from Macklin. Diiodomethane (98%) were purchased from aladdin. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (97%) were purchased from Ark Pharm. Palladium (II) Acetate Trimer (analytically pure) and potassium carbonate (analytically pure) Xi Long scientific. Tetrahydrofuran (99.9%, water ≤ 50 ppm). Nematic liquid crystal E7 were purchased from ChengZhi Yonghua Display Material Co., Ltd.

Characterizations: The ^{1}H NMR, ^{19}F NMR spectra were recorded on a Bruker Avance III 400 HD spectrometer. High-resolution mass spectra (HR-MS) were obtained on a Finnigan MAT TSQ 7000 Mass Spectrometer System operated in a MALDI-TOF mode. UV−Vis spectra were recorded in quartz cuvettes on a U-3900 spectrophotometer. Fluorescence spectra were obtained using EDINBURGH FS5 Spectrofluorometer. Fluorescence lifetime measurements were recorded on Edinburg FS5 fluorescence spectrometer using time-correlated single photon counting (TCSPC). Circular Dichroism (CD) spectra were recorded in quartz curettes on a JASCO J-1500 spectrophotometer. CPL measurements were performed with a JASCO CPL-200 spectrometer. In order to keep the detector at the best state and obtain the precise signals, the DV values were monitored to about 0.5 Voltage. Polarizing optical microscopy (POM) was recorded on the Olympus X83 using high-pressure mercury lamp as excitation source for fluorescent images.

Synthetic procedures of *R*-1 and *S*-1:



Scheme S1 Synthesis of *R*(*S*)-1.

Synthesis of 2-ethylbenzo[b]thiophene (2): To a solution of benzo[b]thiophene (5 g, 37 mmol) dissolved in THF (50 mL) was slowly added dropwise (20 mL, 50 mmol) n-BuLi at -78℃. After stirring the mixture at -78 °C for 1 h, slowly add bromoethane (3 mL, 40 mmol). The mixture was warmed naturally from -78°C for 12 h. The whole reaction was carried out under the protection of nitrogen. After the reaction was completed, the reaction was quenched with saturated sodium chloride solution and extracted with petroleum ether 3 times. After the extraction was completed, the combined organic phase was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether) to give compound 2 as a colorless liquid. (84 % yield, 5 g).

^{1}H NMR (400 MHz, *d*-$CDCl_3$) δ 7.79-7.82 (m, 1H), 7.69-7.71 (m, 1H), 7.27-7.37 (m, 2H), 7.04 (d, 1H, *J* = 0.8 Hz), 2,95-3.01 (m, 2H), 1.40-1.44 (t, 3H, *J* = 7.5 Hz).

Synthesis of 3-bromo-2-ethylbenzo[b]thiophene (3): Add KCl to the ice cubes to obtain an environment of about -5°C. At -5 ℃, to a mixed solution of 2-ethylbenzo[b]thiophene (5g, 30.8 mmol) and THF (70 mL) was added NBS (7 g, 59 mmol) in portions, and the mixture was stirred at room temperature for 15 h. The resulting solution was then quenched with saturated sodium thiosulfate solution. The solvent was removed from the cold trap under reduced pressure, and then

the residue was extracted with petroleum ether 3-5 times. The combined organic phase was washed with saturated sodium chloride solution and dried with anhydrous Na_2SO_4. The solution was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (petroleum ether), thereby obtaining almost colorless viscous liquid 3-bromo-2-ethylbenzo[b]thiophene (6.64 g, yield 90 %).

^{1}H NMR (400 MHz, *d*-$CDCl_3$) δ 7.75 (dd, *J* = 10.1, 9.4 Hz, 1H), 7.53-7.44 (m, 1H), 7.39-7.26 (m, 2H), 2.87-2.77 (m, 2H), 1.38-1.27 (m, 3H).

Synthesis of 3,3'-(perfluorocyclopent-1-ene-1,2-diyl) bis(2-ethylbenzo[b]thiophene) (4): To a solution of 3-bromo-2-ethylbenzo[b]thiophene (1 g, 11.8 mmol) dissolved in THF (50 mL) at -78°C was added n-BuLi (10 ml, 25 mmol). After the mixture was stirred at -78°C for 30 min, perfluorocyclopent-1-ene (0.94 mL, 7.08 mmol) was added at this temperature. Warm the reaction naturally from -78 ℃ for 1-2 h. After the reaction was completed, the reaction was quenched with saturated sodium chloride solution and extracted 3 times with petroleum ether. The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue is purified by silica gel column chromatography (petroleum ether). The product in this step is a simple DAE molecule with photochromic properties. The solubility in petroleum ether is very low. The purity of the crystals precipitated during the purification process is high. Clean DAE4 directly with a small amount of petroleum ether several times (20% yield, 460 mg,).

^{1}H NMR (400 MHz, d-$CDCl_3$) δ 7.69 (dd, *J* = 17.9, 8.0 Hz, 3H), 7.60 (ddd, *J* = 15.3, 6.2, 3.8 Hz, 1H), 7.41-7.35 (m, 1H), 7.32-7.27 (m, 1H), 7.20-7.15 (m, 1H), 2.92 (dt, *J* = 15.0, 7.5 Hz, 1H), 2.80-2.66 (m, 2H), 2.44 (dq, *J* = 15.0, 7.5 Hz, 1H), 1.51 (s, 1H), 1.33-1.25 (m, 2H), 0.84-0.75 (m, 4H).

Synthesis of 1,2-bis(2-ethyl-6-iodo-1-benzothiophen-1,1-dioxide-3-yl) perfluorocyclopentene (5, DAEI): A mixture of 4 (1.0 g, 2 mmol) and 70% 3-chloroperoxybenzoic acid (2.9 g, 11.8 mmol) was dissolved in DCM (50 mL) and stirred at room temperature for 24 h. The solution was washed with saturated Na_2SO_4 solution. The organic layer was separated, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (n-hexane: ethyl acetate = 4:1) to obtain DAE5 (790 mg, 1.4 mmol) as a white or light-yellow solid. The closed ring isomer of the product in this step emits green fluorescence under 365 nm ultraviolet light. (1.0 g, crude).

Place the sulfonated DAE5 (500 mg, crude) in concentrated H_2SO_4 cooled by liquid nitrogen, stir for 20 min in an ice-salt bath, and then add H_2IO_6 (0.6 g, 2 mmol) and I_2 (1.2 g), 4.7 mmol), react for 4 h. The reaction solution was neutralized with sodium carbonate under ice water conditions, and then extracted with ethyl acetate. The organic phase was washed with sodium thiosulfate solution to remove residual iodine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography. Get DAEI (ethyl acetate: petroleum ether = 1:10).

^{1}H NMR (400 MHz, d-$CDCl_3$) δ 8.09 (t, *J* = 1.8 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.1 Hz, 1H), 7.68 (d, *J* = 6.9 Hz, 1H), 7.65 – 7.54 (m, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 2.60 (ddq, *J* = 44.7, 15.2, 7.6 Hz, 3H), 2.38 (dq, J = 15.1, 7.6 Hz, 1H), 1.40 (t, *J* = 7.6 Hz, 2H), 1.26 (t, J = 7.1 Hz, 1H), 1.05 (t, J = 7.6 Hz, 3H).

Synthesis of (*R*/*S*)-2,2'-Methylenedioxy-1,1'-binaphthyl, (7): At 65 ℃, (*R/S*)-BINOL (5 g, 17.5 mmol), CH_2I_2 (4.25 mL, 53 mmol) and K_2CO_3 (24 g, 174 mmol) were added to acetone (80 mL) and stirred for 12 h. The reaction mixture solution was connected to a cold trap and removed under reduced pressure. After adding $CHCl_3$, the organic layer was separated and washed with saturated brine (twice). After drying with anhydrous Na_2SO_4, the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether: chloroform = 1:1) to obtain a colorless powder. (63 % yield, 3.3 g).

^{1}H NMR (400 MHz, *d*-$CDCl_3$) δ 7.96 (dd, *J* = 17.6, 8.4 Hz, 4H), 7.59-7.39 (m, 6H), 7.36-7.26 (m, 2H), 5.69 (s, 2H).

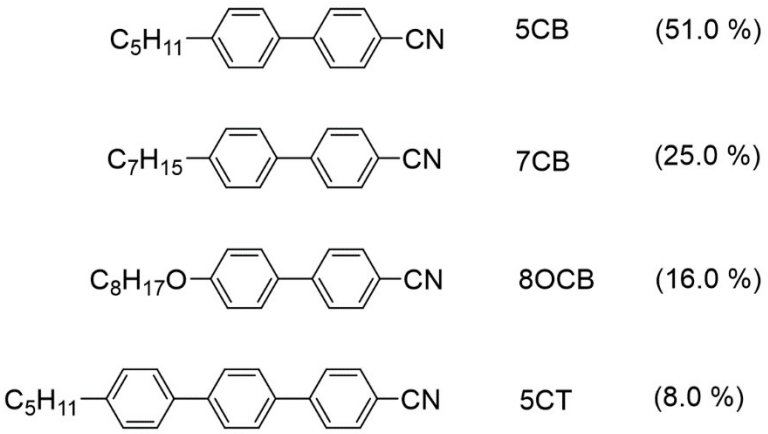
Synthesis of (*R*/*S*)-2-(dinaphtho[2,1-d:1',2'-f][1,3]dioxepin-2-yl)-4,4,5,5-tetramethyl-1,3,2-Dioxaborolane, (8): To ethyl (*R/S*)-2,2'-Methylenedioxy-1,1'-binaphthyl (3.3 g, 11 mmol) in THF (60 mL) was added dropwise n-BuLi (4.4 ml, 11 mmol) under nitrogen protection at -20°C. The reaction was maintained at this temperature and stirred for 30 min, and then 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.2 g, 22 mmol) was added dropwise. The reaction mixture was naturally warmed to room temperature and then stirred for another 3 h. The reaction was quenched with saturated NaCl solution and extracted with dichloromethane (DCM). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by column chromatography (dichloromethane: petroleum ether=1:1, gradually increasing the ratio to pure dichloromethane) to obtain a colorless solid boric acid pinna Alcohol ester binaphthyl ether. (73% yield, 3.4 g).

^{1}H NMR (400 MHz, *d*-$CDCl_3$) δ 8.46 (s, 1H), 7.94-7.79 (m, 3H), 7.51-7.40 (m, 3H), 7.34 (q, *J* = 7.4 Hz, 2H), 7.27-7.17 (m, 2H), 5.80-5.66 (m, 2H), 1.33 (d, *J* = 5.7 Hz, 12H).

Synthesis of *R*(*S*)-1 (9): Add DAEI (0.1 g, 0.12 mmol), (*R/S*)-2-(dinaphtho[2,1-d:1',2'-f][1,3]dioxepin-2-yl)-4,4,5,5-tetramethyl-1,3,2- Dioxaborolane (0.126 g, 0.3 mmol), K_2CO_3 (0.05 g), and $Pd(OAC)_2$ (0.003 g). Add 1.5 mL of THF and 1 mL of EtOH to a 10 mL Shrek bottle, stir for 30 min, add 0.1 mL of water dropwise to it until the phases separate, and stir for 1 h. The reaction solution was extracted with ethyl acetate, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The obtained residue was purified by silica gel column chromatography (ethyl acetate: petroleum ether = 1:20) to obtain (*R/S*)-1. (14% yield, 20 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 7.28 (m, 26H), 7.18 (s, 1H), 5.60 (d, 1H), 5.42 (s, 2H), 4.31 (t, 1H), 3.22 (dd, 2H), 2.48 – 2.24 (m, 2H), 1.78 – 1.39 (m, 4H), 0.96 (t, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.16 (ddd, 2F), -113.78 (dt, 2F), -131.80 (dd, 2F). MS (Maldi) calcd for $C_{68}H_{42}F_6O_8S_2$+Na $(M+Na)^+$: 1175.2, found: 1175.5 (Figure S13-S16).

Preparation of *R*(*S*)-1 toluene solution: The sample used for the detection of absorption and fluorescence is selected *R*(*S*)-**1** toluene solution in 1cm x1cm (optical path 1cm) cuvette. The samples used for the detection of CD and CPL choose *R*(*S*)-**1** toluene solution (10^{-4} mol/L), 1 cm x 1 mm (optical path 1mm) cuvette.



Scheme S2 Composition of nematic liquid crystal E7

Preparation of *R*(*S*)-1/E7 N*-LCs for tests: The 0.5 wt% chiral dopant and achiral nematic liquid crystal E7 were co-dissolved in the toluene solvent. Then the mixture was slightly heated for half an hour to evaporate toluene. The N*-LCs samples were injected into flat liquid crystal cell after the solvent was completely evaporated.

S2. Supplementary Figures and Tables

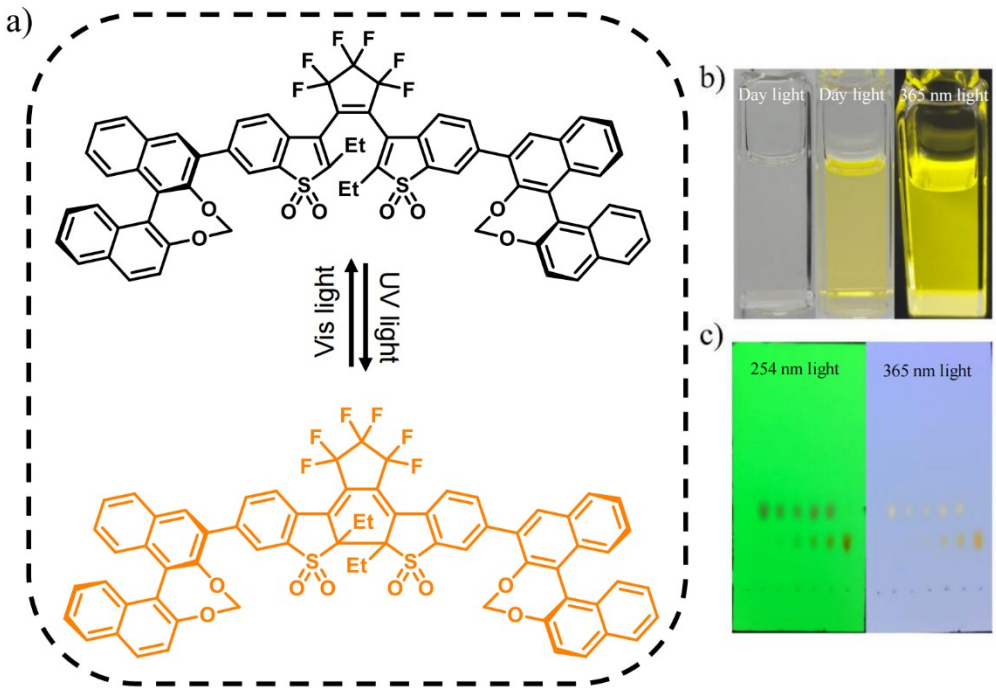


Figure S1 a) The two isomers of *R*-1 under UV/Vis light. b) Photographs of two isomers of *R*-1 in toluene under day light and *R*-1-C under UV 365 nm lamp. c) Thin layer chromatography in the Process of molecules transitioning from an Open-Ring State to a Closed-Ring State (under UV 254/365 nm lamp).

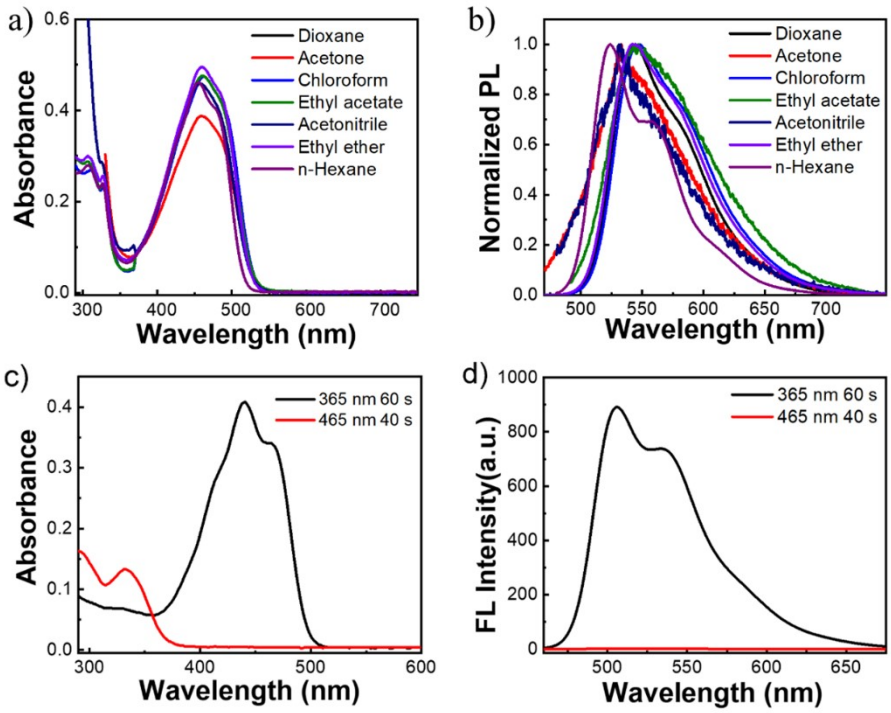


Figure S2 a) Absorption spectra of *R*-1-C in different solvents (1 x 10^{-5} mol/L). b) emission spectra. c) Absorption spectra, d) emission spectrum of DAEI in toluene solution (1x10^{-5} mol/L) (DAEI-O is the red line and DAEI-C is the black line).

Table S1. Photophysical properties of *R*-**1**-C in different solvents

Solvent	λ_{Abs} (nm)	λ_F (nm)	Φ_{PL} (%)	Lifetime (ns)
Toluene	460	545	87.57	2.63
n-hexane	455	524	96.71	2.64
Dioxane	460	545	79.31	2.95
Acetone	459	532		
Chloroform	462	548		
Ethyl acetate	460	460		
Ether	458	544		
Acetonitrile	460	531		

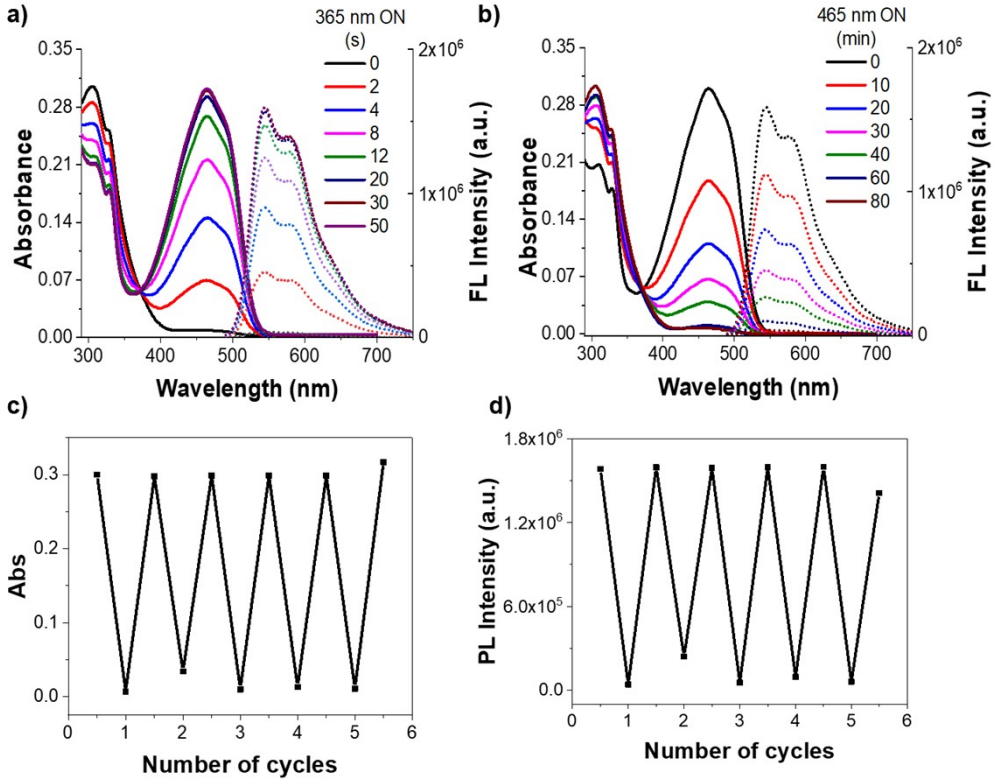


Figure S3 a) Absorption and fluorescence spectral changes of *R*-**1**-O in toluene under the irradiation of 365 nm light. b) Absorption and fluorescence spectral changes of *R*-**1**-C in toluene (10^{-5} mol/L) under the irradiation of 465 nm light. Photoswitching of *R*-1 in toluene monitored at c) 465 nm (absorption spectra) and d) 545 nm (fluorescence spectra) by alternating irradiation of UV 365 nm light and 465 nm light.

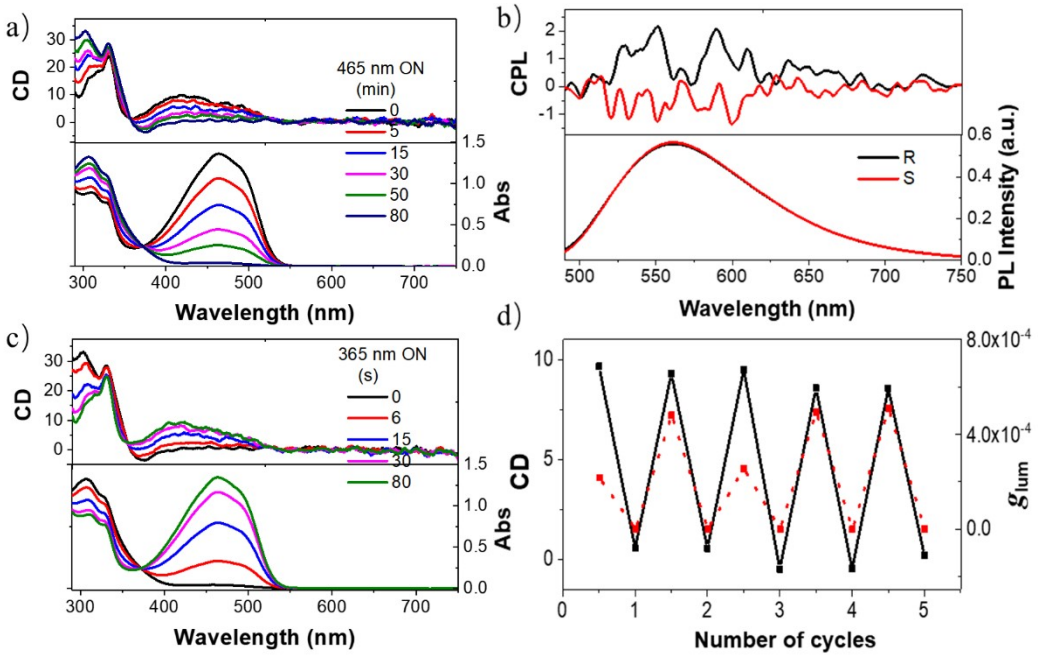


Figure S4 a) CD spectral changes of *R*-**1**-C in toluene (10^{-5}mol/L) under the irradiation of 465 nm light. b) CPL spectral of *R*-**1**-C in toluene. c) CD spectral changes of *R*-**1**-O in toluene (10^{-5} mol/L) under the irradiation of 365 nm light. d) CD signal (black solid line) of *R*-**1** in toluene monitored at 420 nm and g_{lum} (red dashed line) at 545 nm by alternating irradiation of UV 365 nm light and 465 nm light.

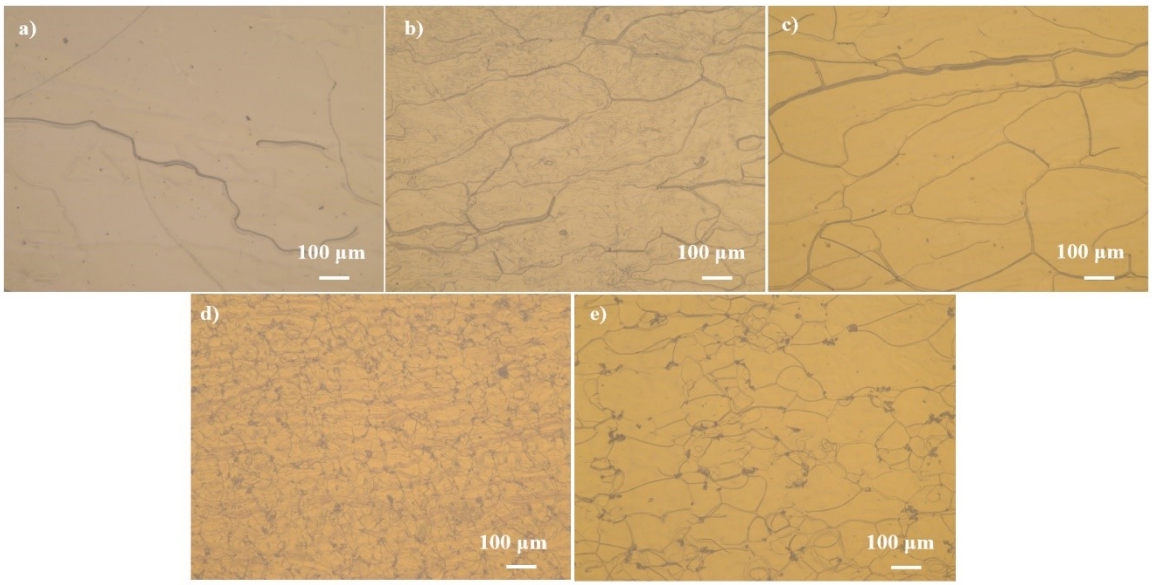


Figure S5 a) POM images of a) N*-LC including 0.25 wt% *R*-**1**-C, b) N*-LC including 0.5 wt% *R*-**1**-C, c) N*-LC including 0.75 wt% *R*-**1**-C, d) N*-LC including 1 wt% *R*-**1**-C, e) N*-LC including 0.5 wt% *R*-**1**-C.

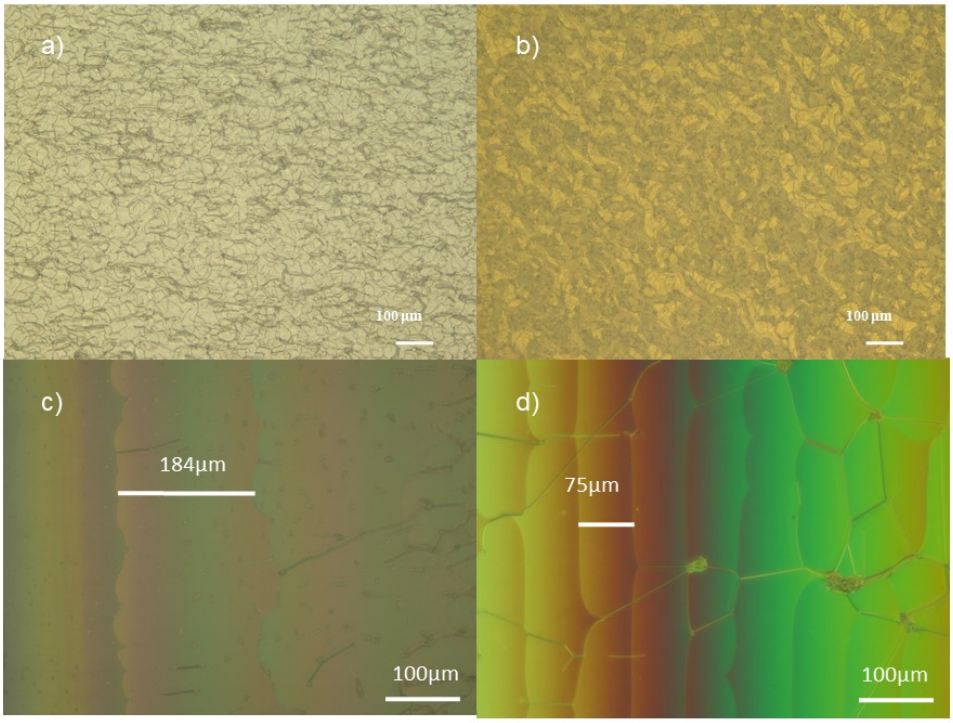


Figure S6 POM images of a) N*-LC including 0.5 wt% *R*-1-O, b) N*-LC including 0.5 wt% *R*-**1**-C in liquid crystal cell cells at room temperature. POM images of c) N*-LC including 0.5 wt% *R*-**1**-O, d) N*-LC including 0.5 wt% *R*-**1**-C in wedge cells at room temperature.

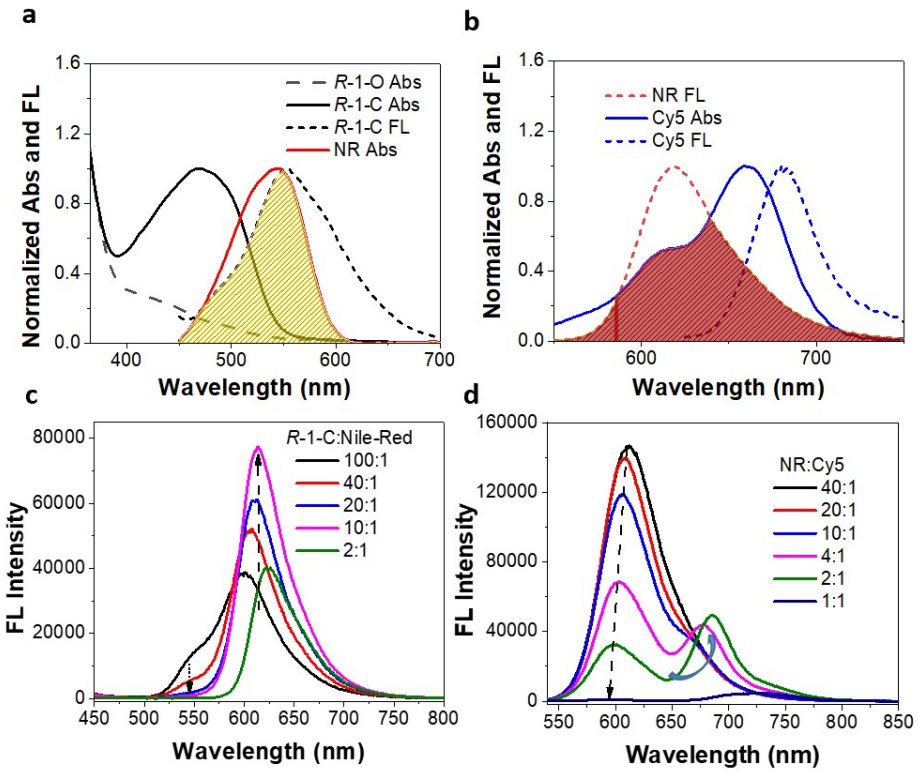


Figure S7 (a and b) Normalized absorption and emission spectra of the *R*-**1**-O, *R*-**1**-C, NR, and Cy5. (c) Fluorescence spectra of *R*-**1**-C/NR cholesteric texture in the presence of different amount of NR (λ_{ex} = 360 nm). (d) Fluorescence spectra of NR/Cy5 doped into E7 in the presence of different amount of Cy5 (λ_{ex} = 550 nm).

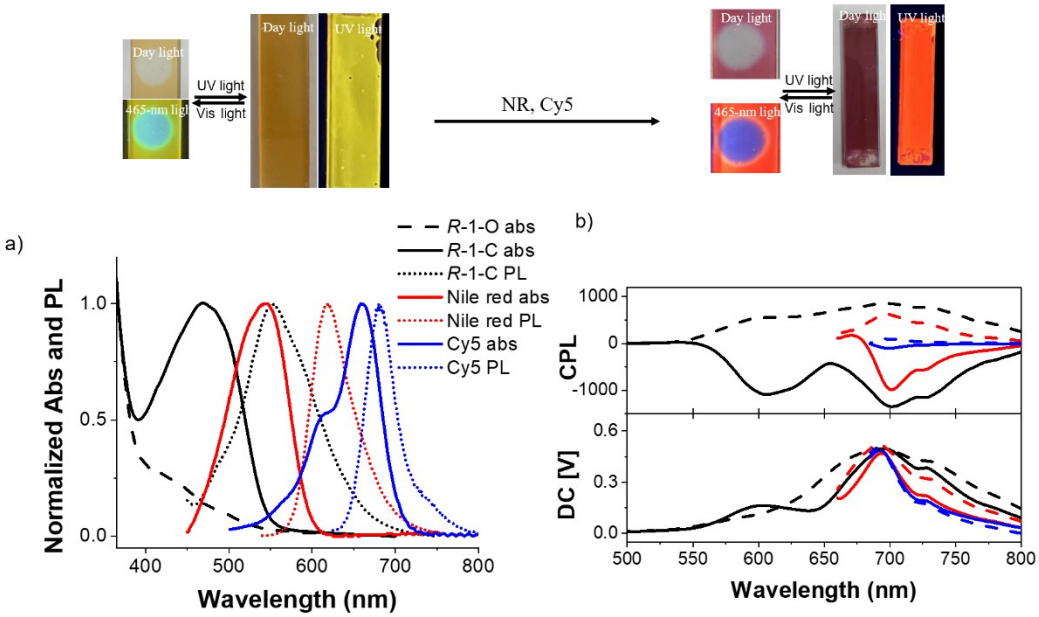


Figure S8 a) UV/Vis and emission spectra of the different chromophore in liquid crystal Normalized absorption (solid line) and emission (dashed line) spectra of R-**1** (black line), NR (red line) and Cy5 (blue line). b) CPL spectra of *R*(*S*)-1-C/NR/Cy5 excited by 360 nm (black line), 550 nm (red line), 625 nm (blue line).

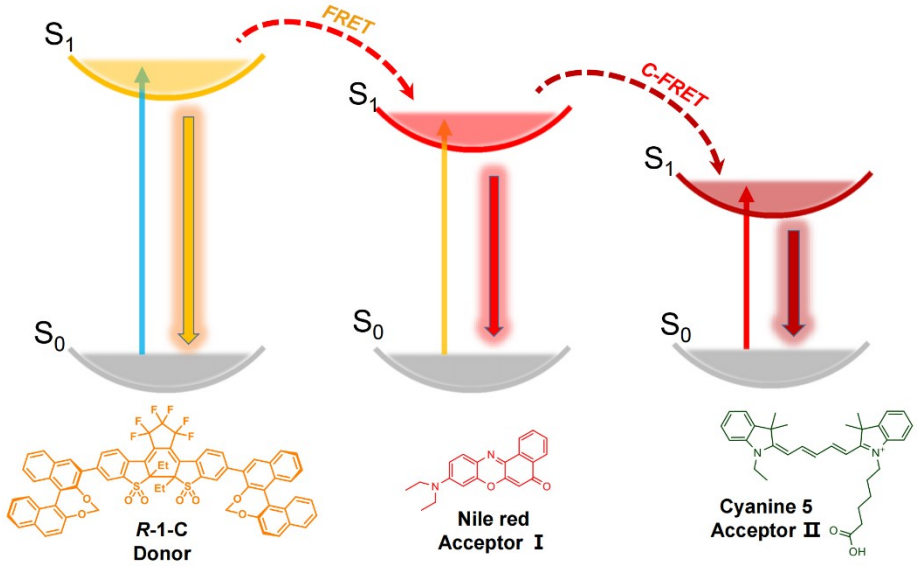


Figure S9 Illustration of the process of sequential C-FRET.

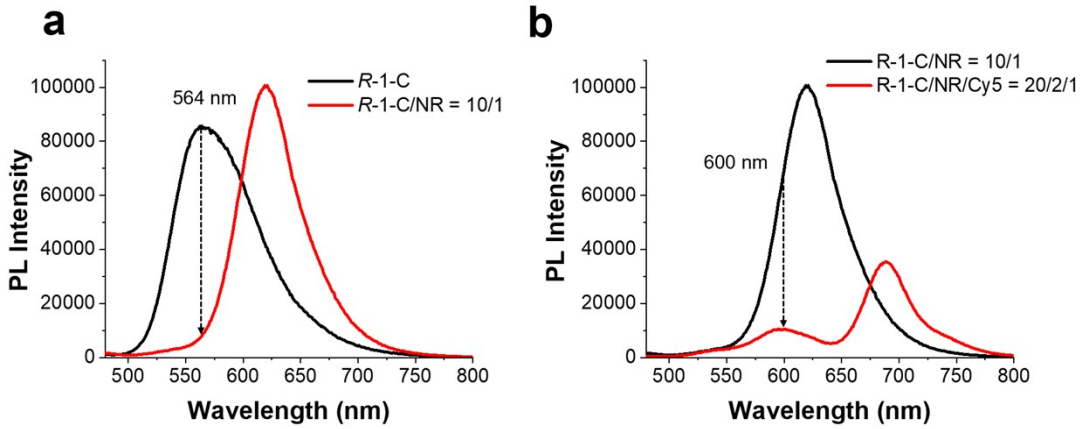
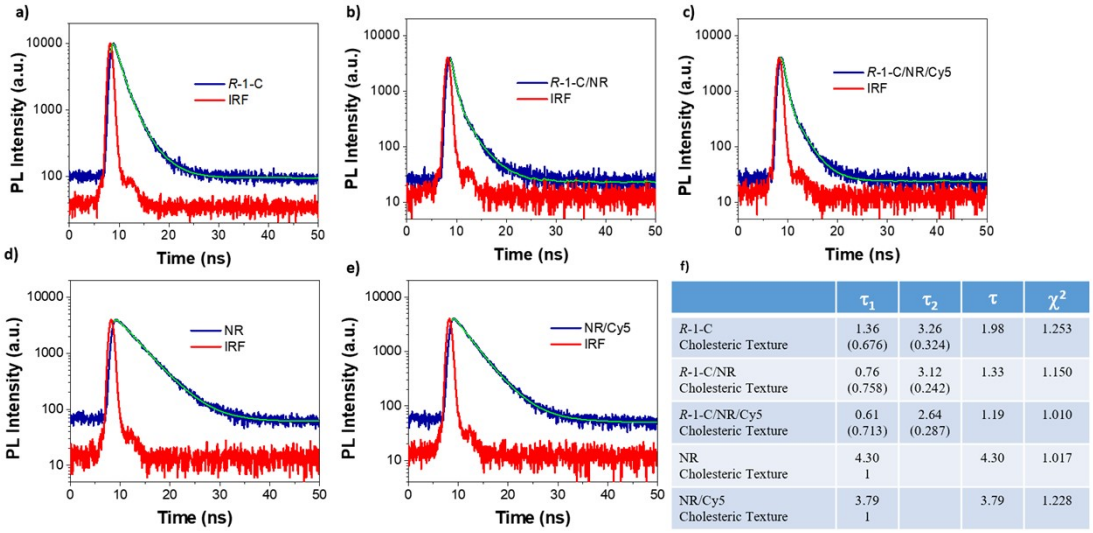


Figure S10 Energy transfer investigations in cholesteric phase a) The fluorescence emission spectra in the presence and absence of NR. b) The fluorescence emission spectra in the presence and absence of Cy5.

According to the definition of energy transfer efficiency $\Phi_{ET} = 1\text{-}I_{DA}/I_D$, where I_{DA} and I_D are the fluorescence intensities of the donor in the presence and absence of the acceptor. The Φ_{ET} of different combinations are calculated as follows:

Combination and ratio	Spectral analysis method	Fluorescent lifetime analysis
R-1-C/NR	Φ_{ET} = 90.8 %	Φ_{ET} = 32.5 %
R-1-C/NR/Cy5	Φ_{ET} = 85.0 %	Φ_{ET} = 11.9 %

In addition, the energy transfer efficiency can be calculated by analyzing the fluorescence lifetime ($\Phi_{ET} = 1\text{-}\tau_{DA}/\tau_D$). The energy transfer efficiency calculated by the lifetime in figure S11 is shown in the table above.



	τ_1	τ_2	τ	χ^2
R-1-C Cholesteric Texture	1.36 (0.676)	3.26 (0.324)	1.98	1.253
R-1-C/NR Cholesteric Texture	0.76 (0.758)	3.12 (0.242)	1.33	1.150
R-1-C/NR/Cy5 Cholesteric Texture	0.61 (0.713)	2.64 (0.287)	1.19	1.010
NR Cholesteric Texture	4.30 1		4.30	1.017
NR/Cy5 Cholesteric Texture	3.79 1		3.79	1.228

Figure S11 Emission decay curves of the cholesteric texture. a), b) and c), *R*-1-C/E7, R-1-C/NR/E7 and R-1-C/NR/Cy5/E7 monitored at 550 nm. d) and e), NR/E7 and NR/Cy5/E7 monitored at 700 nm. λ_{ex} = 365 nm, IRF represents instrument response function.

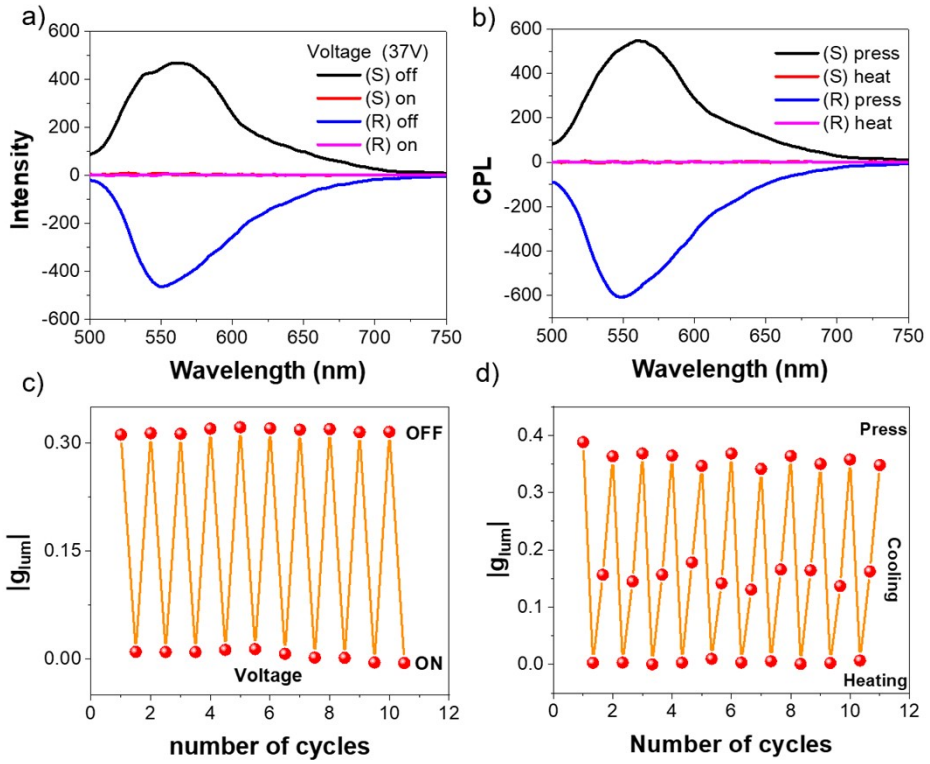


Figure S12 a) CPL spectra of N*-LCs including 0.5 wt% *R*(*S*)-**1**-C/E7 with the electric field "off" and "on", respectively. b) CPL spectra of N*-LCs including 0.5 wt% *R*(*S*)-**1**-C/E7 under heating and pressing, respectively. c) The CPL g_{lum} value of N*-LC including 0.5 wt% *R*(*S*)-**1**-C/E7 repeated electric field "off" and "on" cycles. d) The CPL glum value of N*-LC including 0.5 wt% *R*(*S*)-**1**-C/E7 repeated heat and mechanical force.

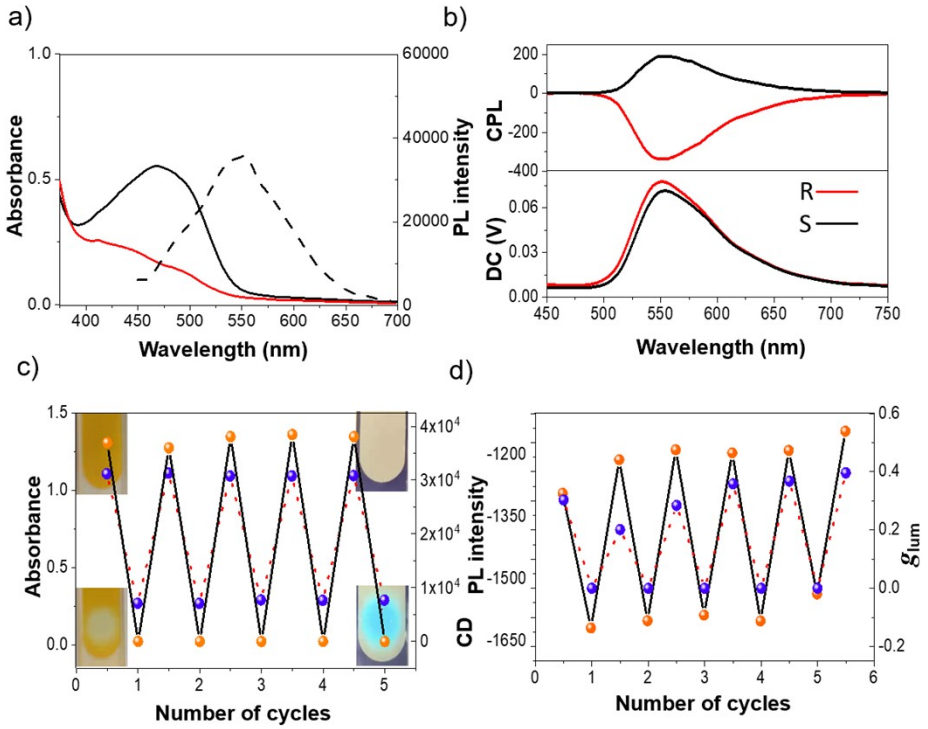


Figure S13 a) Absorption spectra (black line is *R*(*S*)-**1**-C, red line is *R*(*S*)-**1**-O) and emission spectrum (excited at 360 nm) of *R*(*S*)-**1**/E7 (0.5 wt %). b) CPL spectra of *R*(*S*)-**1**/E7 (0.5 wt%, λ_{ex} = 360 nm, $|g_{lum}|$ = 0.3). c) Absorbance of *R*(*S*)-**1**/E7 (0.5 wt %) monitored at 465 nm (black line) PL intensity monitored at 545 nm by alternating irradiation of UV 365 nm light and 465 nm light (red line). d) CD signal of *R*(*S*)-**1**/E7 (0.25 wt %) monitored at 465 nm (black line) and g_{lum} of *R*(*S*)-**1**/E7 (0.5 wt %) monitored at 545 nm by alternating irradiation of UV 365 nm light and 465 nm light (red line).

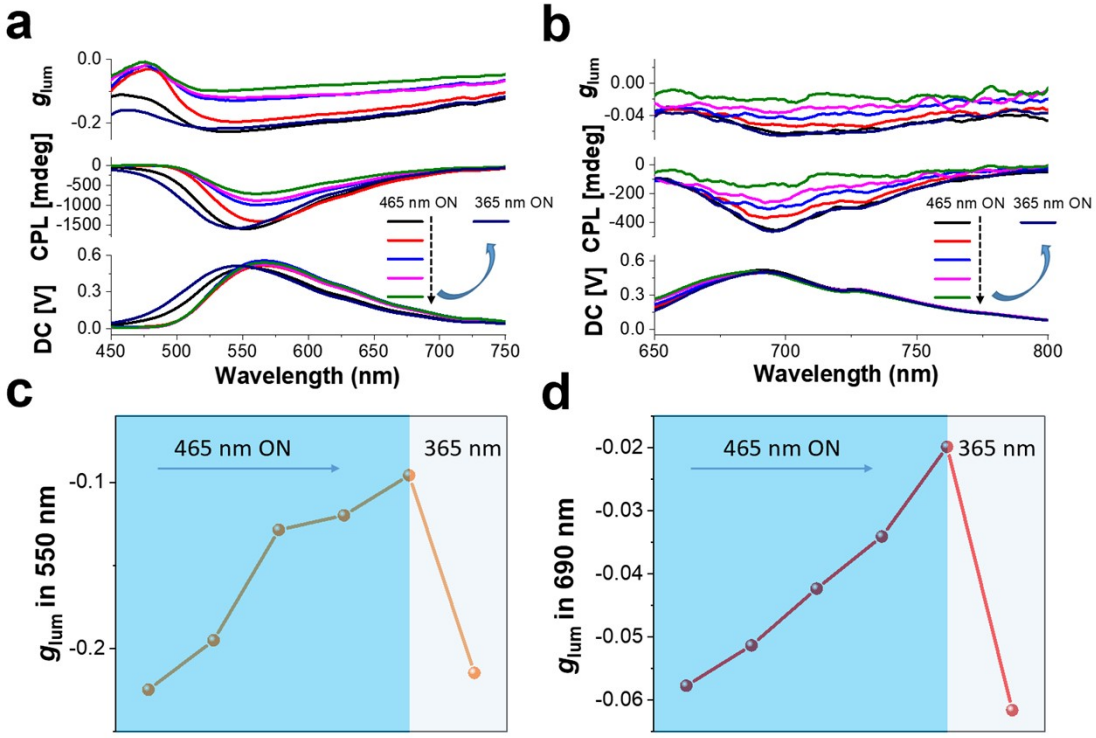


Figure S14 a) CPL and g_{lum} values of *R*-1/E7 during the cycloreversion process under 465 nm LED light (λ_{ex} = 465 nm) and cyclization under 365 nm light (λ_{ex} = 360 nm). b) CPL and g_{lum} values *R*-1/NR/Cy5/E7 during the cycloreversion process under 465 nm LED light (λ_{ex} = 600 nm) and cyclization under 365 nm light (λ_{ex} = 600 nm).

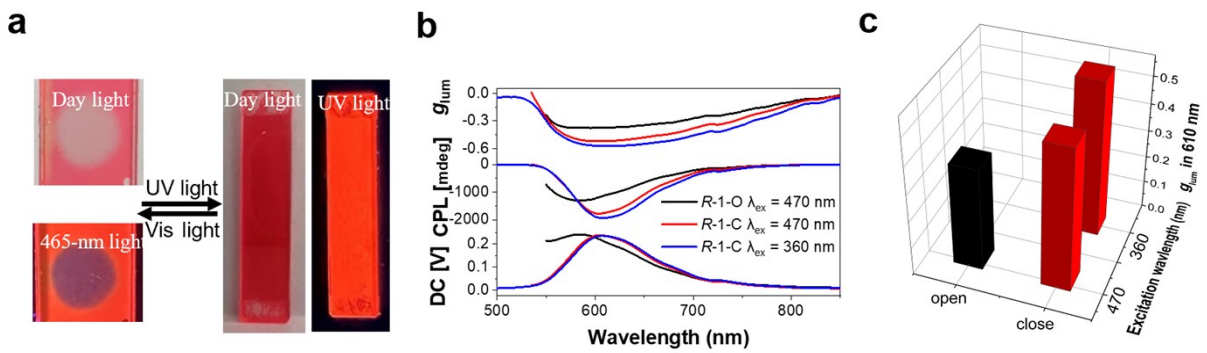


Figure S15 (a) Photographs of *R*-**1**-C/NR/E7 (left) and *R*-**1**-O/NR/E7 (right) under day light and UV 365 nm lamp, respectively. (b) CPL spectra of *R*(*S*)-**1**-O-NR-Cy5 (λ_{ex} = 470 nm) and *R*(*S*)-**1**-C-NR-Cy5 (λ_{ex} = 360 nm and λ_{ex} = 470 nm) cholesteric texture. (c) 3D Column diagrams of g_{lum} values obtained by irradiation of donor *R*-1 in open-ring state/closed-ring state or acceptor NR.

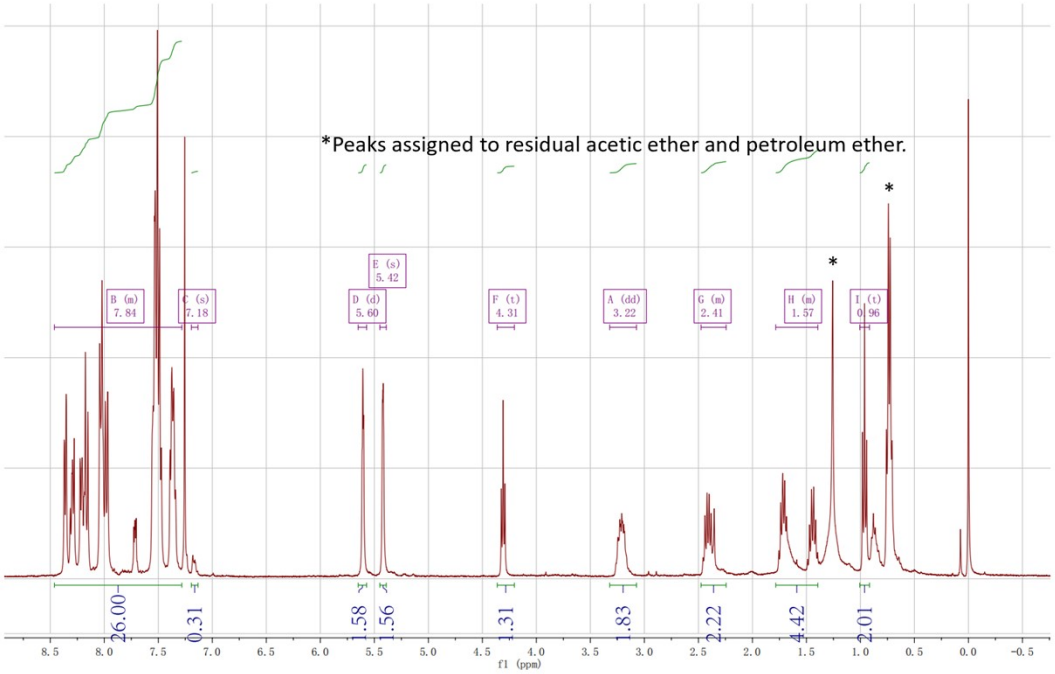


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) of *R*-1

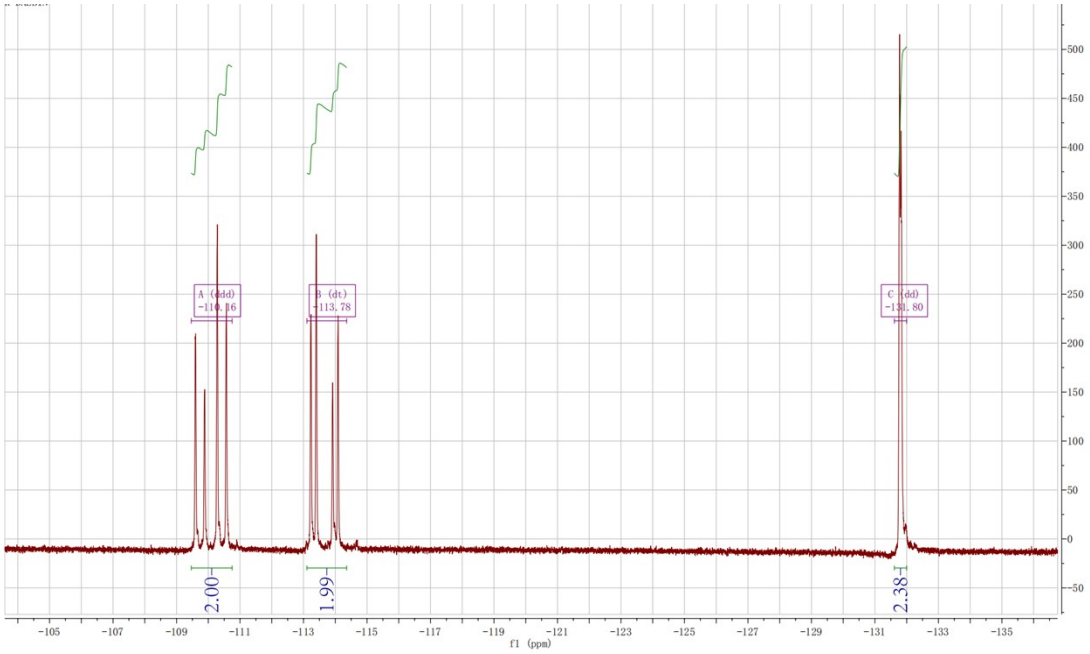


Figure S17. ^{19}F NMR (376 MHz, $CDCl_3$) of *R*-1.

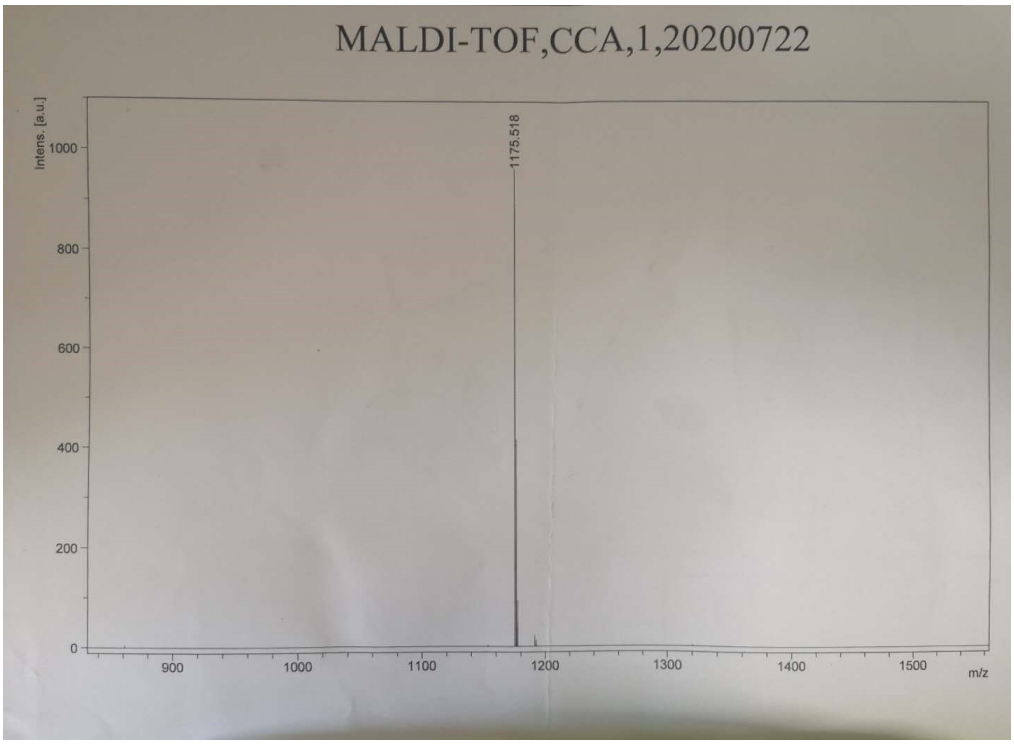


Figure S18. Mass spectrometry of *R*-1.

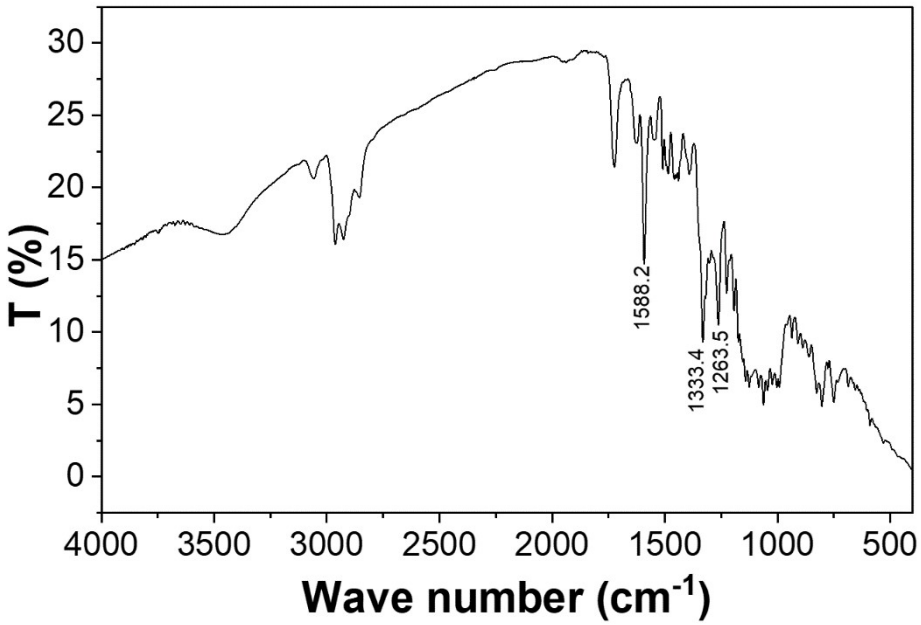


Figure S19. FTIR spectra of *R*-1.

References

1 S. Y. Lin, S. S. Zeng, Z. Y. Li, Q. Y. Fan, and J. B. Guo, *ACS Appl. Mater. Interfacesm,* 2022, **14**, 30362-30370.