Supporting information for: Helical naphthopyran dopant for photoresponsive cholesteric liquid crystal

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Materials, methods and instrumentations

Nematic liquid crystal host 5CB was purchased from Tokyo Chemical Industry (Tokyo, Japan). E7 and JC-1041XX were obtained from Daily Polymer Co. and Chisso Petrochemical Co., respectively. Polyimide coating solution (SE-150) was purchased from Nissan Chemical Industries, LTD. Japan. All the solvents and chemicals were purchased from commercial sources and used without further purification.

Helical pitch length was determined by measuring the distance between the Cano lines on the surfaces of the Cano wedge cells (EHC, KCRK-07, tan θ= 0.01858). The relationship between the distances between the Cano lines and the helical pitch is given by the equation P=2Rtanθ in which R is the distance between the Cano lines and θ is the angle between the substrates. Micro glass rods were purchased from Nippon Electric Glass with an average length of 25 μm and average diameter of 5 μm (model PF-50s).

Absorption spectra were recorded using an Agilent 8453 spectrophotometer. CD spectra were recorded using a JASCO J-S720 CD spectrophotometer. Photoisomerization was conducted by using 365 nm (CS-LED3W365, CSE Inc.), 510 nm (CS-KED3W510, CSE Inc.) and white light (Thorlabs OSL1 High-Intensity Fiber Light Source) sources. High pressure liquid chromatography (HPLC) was conducted using a Hitachi Elite La Chrome HPLC system by using CHIRALPAK IA columns (DAICEL Chemical Industries Ltd).

Semi-preparative separation for compound CHR-Hexyl :

• Sample preparation: About 300 mg of compound **CHR-Hexyl** are dissolved in 9 mL of a mixture hexane/dichloromethane (8/2).

• Chromatographic conditions: (*S*,*S*)-Whelk-O1 (250 x 10 mm), hexane / 2-PrOH (95/5) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• Injections: 130 times 70 μL, every 4 minutes.

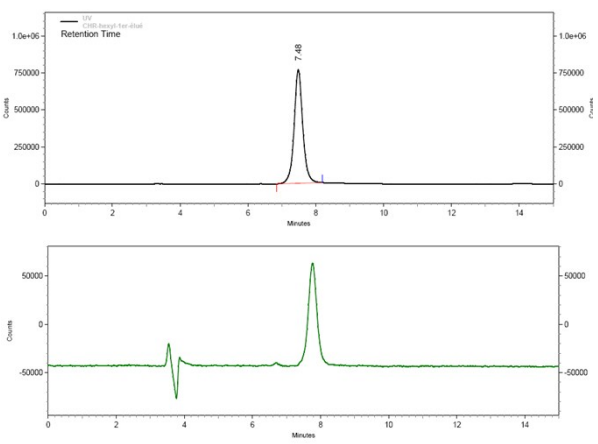
• First fraction: 138mg of the first eluted *P*-enantiomer [(+, polarimeter)-enantiomer)] with ee > 99%,

• Second fraction: 143 mg of the second eluted *M*-enantiomer [(-, polarimeter)-enantiomer)] with ee = 99%

• Chromatograms of the collected fractions:

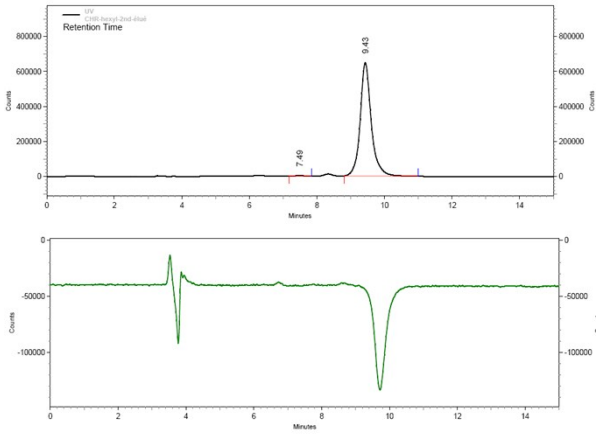
(*S*,*S*)-Whelk-O1

Heptane / 2-PrOH (95/5)



UV Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
7.48	13612705	100.00	1.49	0.00	0.00



UV Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
7.49	65450	0.44	1.50	0.00	0.00
9.43	14827117	99.56	2.14	0.00	3.90

Fig. S1 Chromatograms of *P* and *M* of **CHR-Hexyl** obtained by chiral HPLC ((*S*,*S*)-Whelk-O1) using hexane / 2-PrOH (95/5) as eluent at a flow rate of 5 mL/m, and monitored at 254 nm:

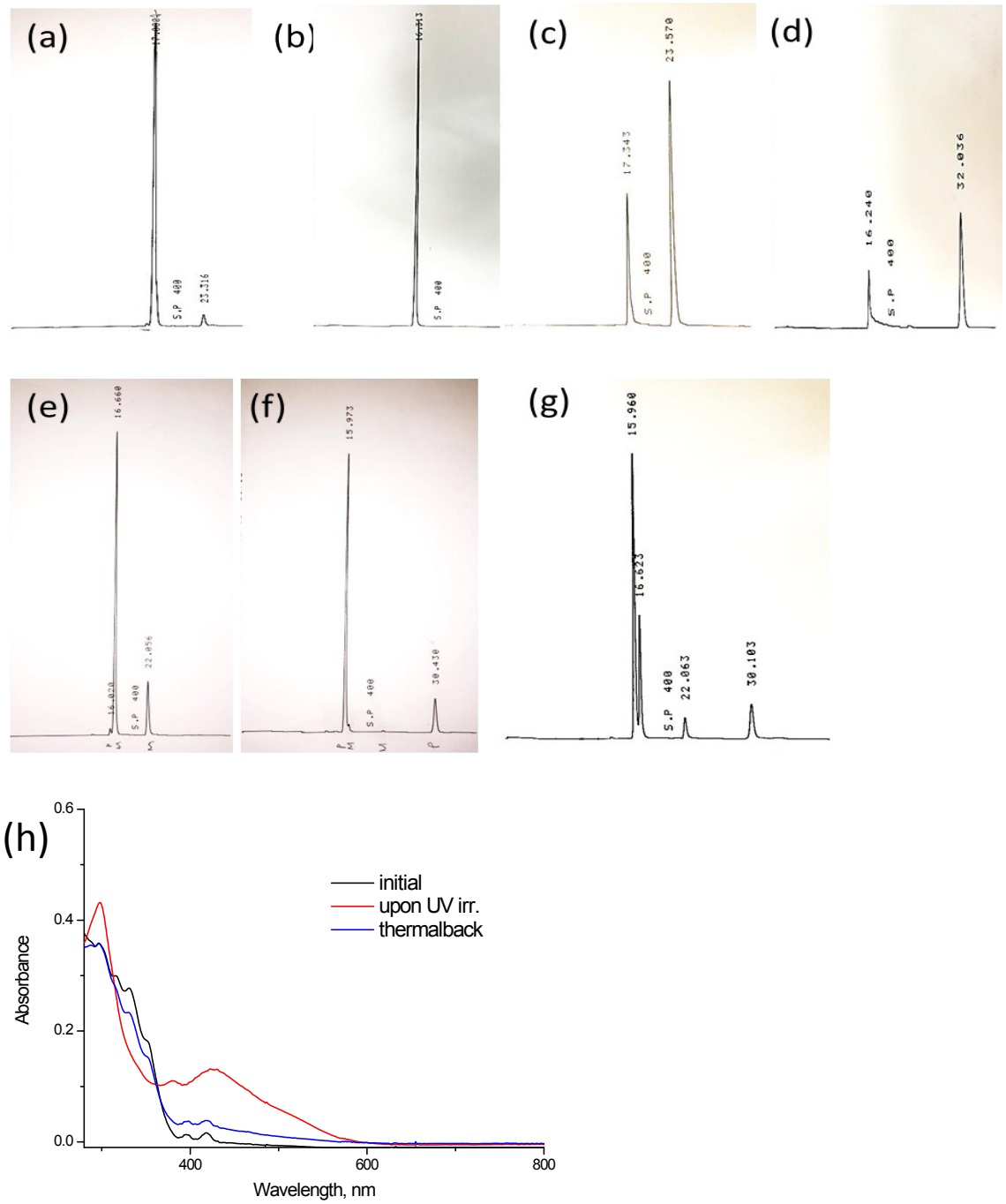


Fig. S2 Chromatograms of *M* and *P* of **CHR-Hexyl** obtained by chiral HPLC using dichloromethane and hexane (1:2) as eluent at a flow rate of 1.0 ml/m, and monitored at 333 nm: Before (a: *M* and b: *P*) and after 365 nm light irradiation for 30 minutes (c: *M* and d: *P*) followed by subsequent overnight thermal relaxation (e: *M*, f: *P*, and g: mixture of *M* and *P*). (h) Absorbance spectra of M in dichloromethane and hexane (1:2) measured before and after UV irradiation followed by thermal relaxation.

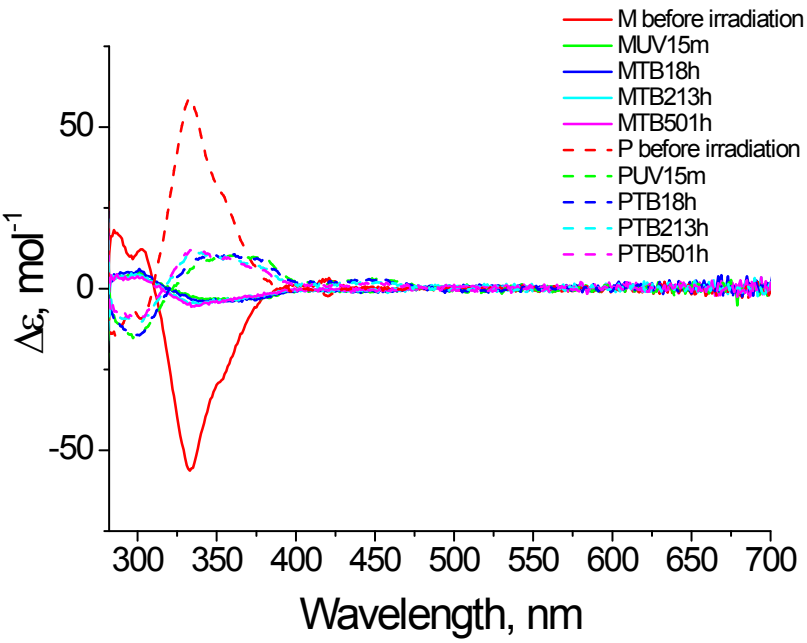


Fig. S3 Thermal back of TT form monitored by CD spectra with CHR-Hexyl solution in toluene (2.5×10^{-5} M) of two enantiomers *M* (solid line) and *P* (dashed line) after UV irradiation for 15 minutes.

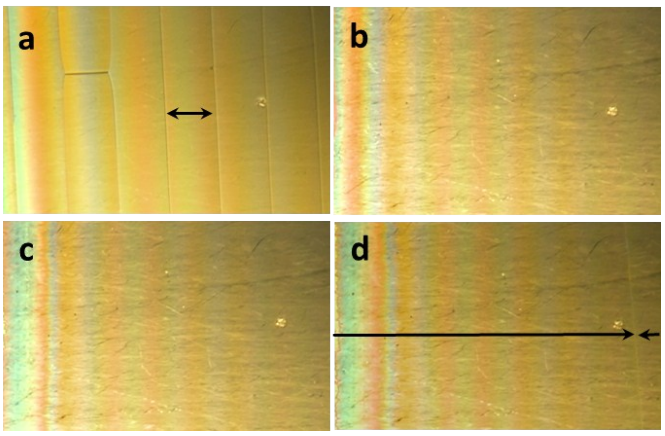


Fig. S4 Cano lines of cholesteric LC containing 0.4 wt% of **CHR-Hexyl** (*M*) in the LC host E7 observed from a wedge cell. Pristine (a) and after sequential irradiation with UV (b) and visible (c) light, and after 48 hrs in darkroom (d) exhibiting pitch lengths of 11.6 µm (a), 80.1 µm (b), 80.1 µm (c) and 69.6 µm (d), respectively. For (b) and (c), Cano's lines moved beyond the recording area due to the low dopant concentration. Although single Cano line is observed for (d), still the entire gap between two Cano lines was beyond the recordable region.

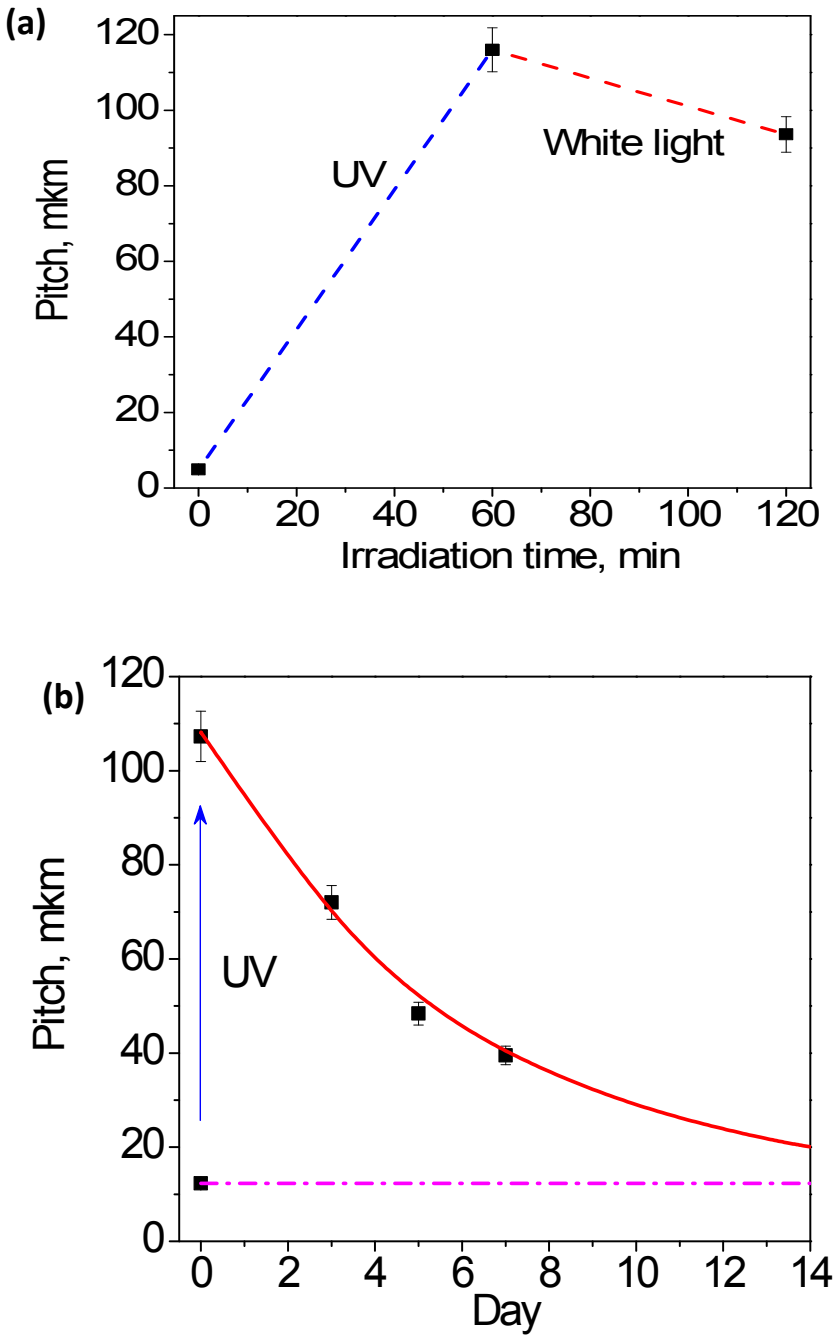


Fig. S5 (a) Cholesteric pitch relaxation (wedge cell, 0.5 wt% in E7) upon white light irradiation, **(b)** relaxation of the pitch with time (wedge cell, 0.2 wt% in E7) in the dark room.

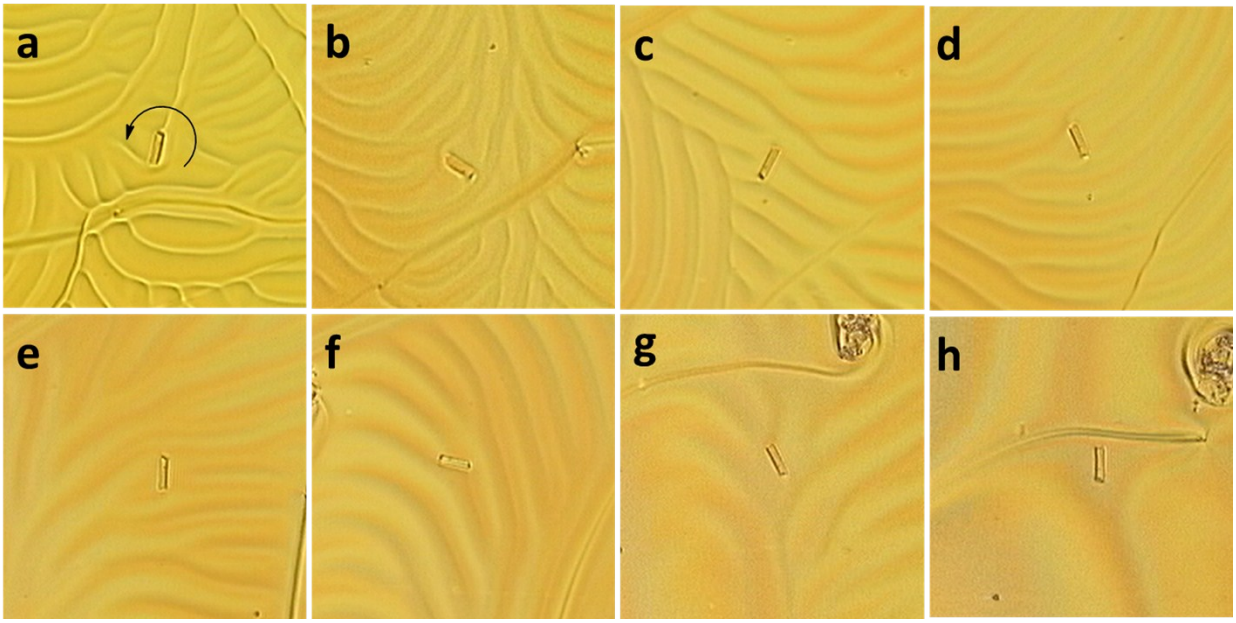


Fig. S6 A 17.5 min UV light irradiation resulted in the anti-clockwise rotational motion of a micro glass rod for 3.5 cycles (1260 °). Images were recorded during the continuous UV light irradiation onto the CLC mixture film (0.6 wt% in E7) from initial (a) to PSS_{365nm}(h).