

## Supporting Information

### **Photoswitchable and Thermally Stable Axially Chiral Dithienylperfluorocyclopentene Dopant with High Helical Twisting Power**

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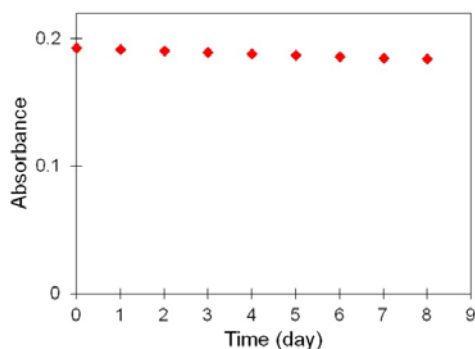
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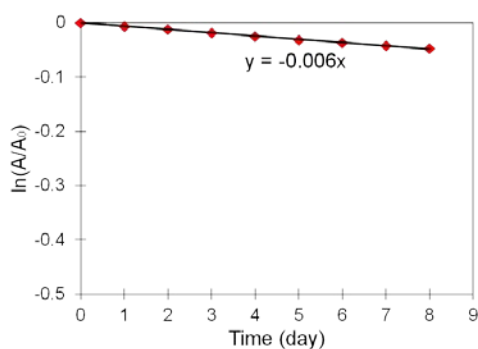
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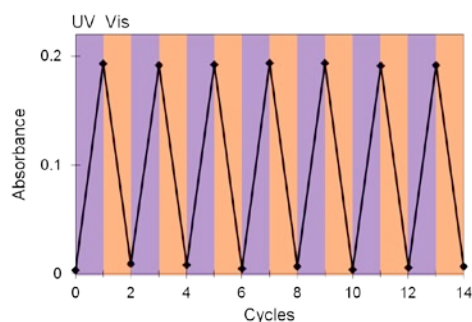
## 1. Thermal stability, photoisomerization and CD spectra of (*R,R*)-1 in organic solvent



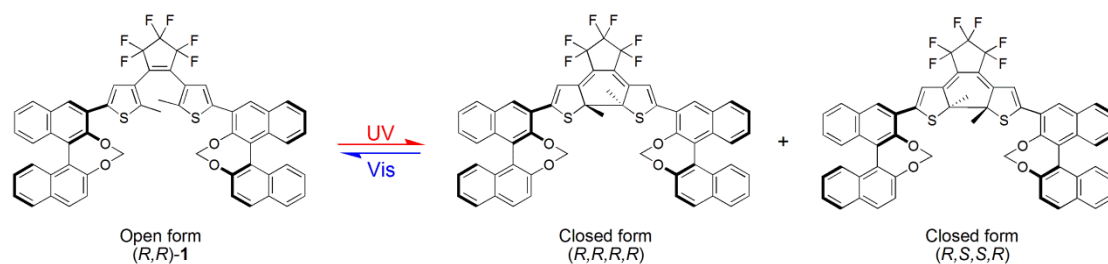
**Figure S1.** Thermal stability of closed-ring isomers (*R,R*)-1 in hexane monitored by the absorbance at 612 nm in dark from the irradiated state.



**Figure S2.** Thermal stability of closed-ring isomer of (*R,R*)-1 in hexane monitored by the absorbance (*A*) at 612 nm in dark starting from the  $PSS_{310nm}$  ( $A_0$ ). Plot of  $\ln(A/A_0)$  versus time shows the first order kinetics of the thermal relaxation. The half-life was calculated by  $t_{1/2} = \ln 2/0.006$ .

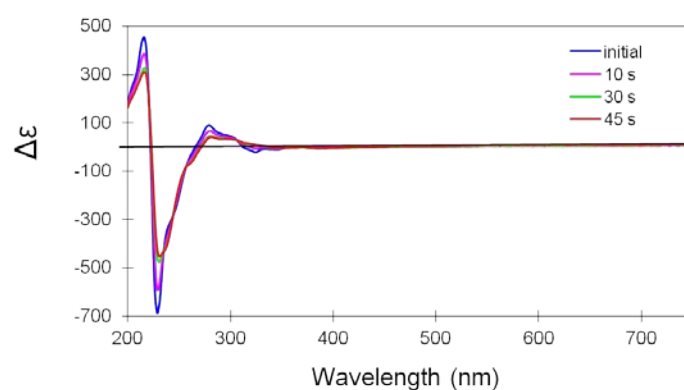


**Fig S3.** Cyclical absorbance of compound (*R,R*)-1 in hexane at 612 nm as the solution is repeatedly irradiated with UV light (310 nm) and visible light (630 nm).



**Figure S4.** Photoisomerization of  $(R,R)$ -1.

The open form of diarylethene molecules may exist as *anti*-parallel and parallel conformation isomers, and they can exchange even at room temperature. The photocyclization reaction can only occur in *anti*-parallel isomers upon UV light irradiation. The photocyclization will generate two new chiral centers with the configuration of  $(S,S)$  or  $(R,R)$ , and thus form two diastereomers in closed form of  $(R,R)$ -1. However, no Cotton effect was observed in the visible region around 612 nm corresponding to the absorption band of the closed form, indicating no diastereoselective photoisomerization occurred. The chiroptical properties of  $(R,R)$ -1 are still mainly attributed to the binaphthyl units.

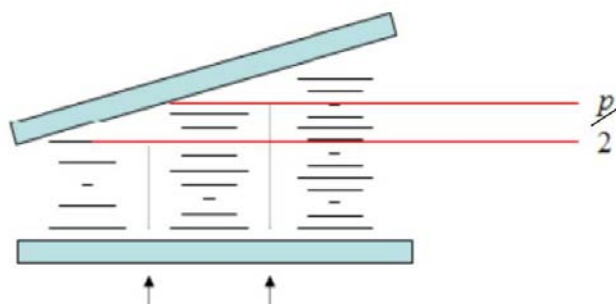


**Figure S5.** CD spectra changes of  $(R,R)$ -1 (10  $\mu\text{M}$  in hexane) upon UV irradiation at 310 nm for different time.

## 2. Measurement of pitch and helical twisting power

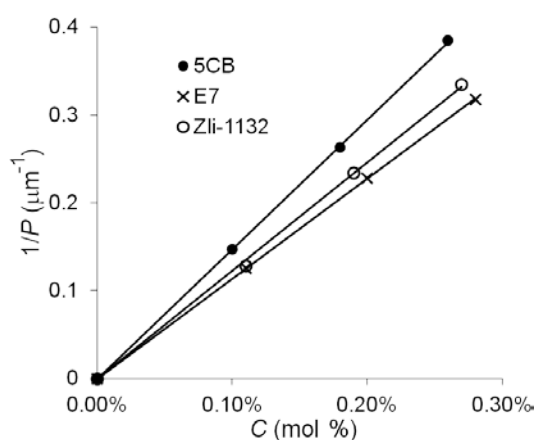
A conventional technique for pitch measurement is Grandjean-Cano wedge method. Such wedge cell with an opening angle  $\theta$  is made by applying two differently sized spacers at each end of the cell (Figure S6). If the alignment of the substrates is planar (the director lies parallel to the surface) 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 S6. 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.

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  $\theta$  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 value is  $\beta_M = 1/(PC)$ , where  $\beta_M$  is the helical twisting power, *i.e.*, the ability of the chiral dopant to twist a nematic LC, and  $C$  is the molar concentration of the chiral dopant.



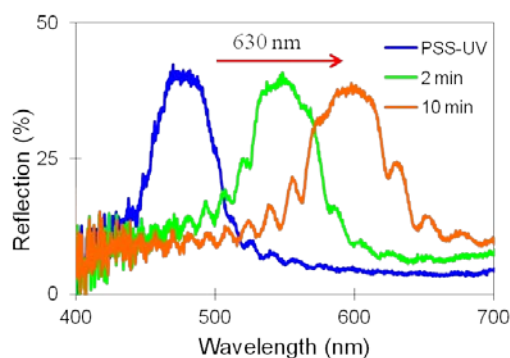
**Figure S6.** Schematic illustration of a Grandjean-Cano wedge cell for the pitch measurement of cholesteric LC. Disclination lines are pointed out with arrows and the thickness change between two domains is marked as  $P/2$ .

The chiral nematic liquid crystal was prepared by weighing appropriate amount of host liquid crystal and the dopant into a vial followed by mixing them with the addition of a few drops of dichloromethane. After evaporation of the solvent under reduced pressure, the mixture was loaded into the wedge cell by capillary action at room temperature. The pitch was then determined by measuring the intervals of Cano's lines appearing on the surfaces of wedge-type liquid crystalline cells. Three different concentrations were used by this method for each sample, and the HTP were determined by plotting  $1/P$  ( $\mu\text{m}^{-1}$ ) against concentration of the dopant  $C$  (mol%) according to the equation  $\beta = 1/(PC)$ .

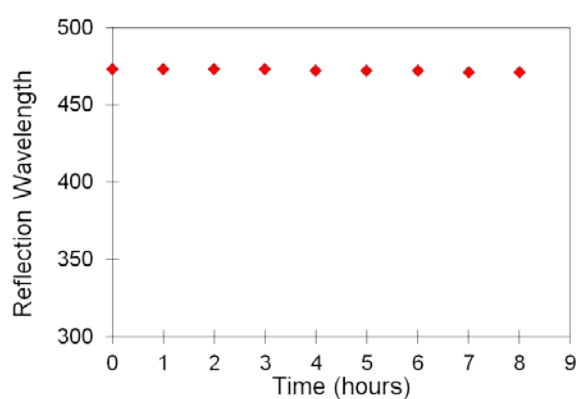


**Figure S7.** Plots of reciprocal helical pitch ( $1/P$ ) as a function of doping concentrations of  $(R,R)$ -1 in different LC hosts. The slopes of the trendlines are determined as HTPs.

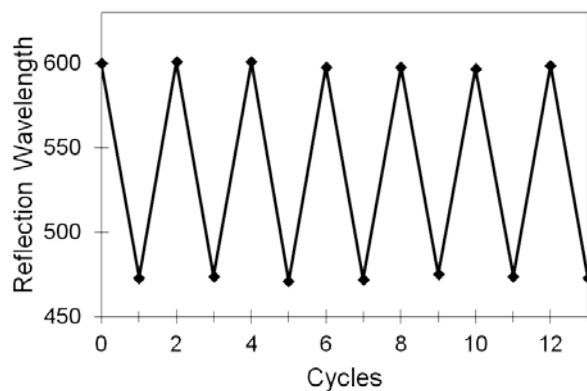
### 3. Reflection spectra, thermal stability and fatigue resistance of $(R,R)$ -1 in liquid crystals



**Figure S8.** The reflection spectra changes of 1.80 mol% of (*R,R*)-**1** in 5CB from PSS<sub>310nm</sub> upon visible light irradiation at 630 nm.



**Figure S9.** Thermal stability of 1.80 mol% of (*R,R*)-**1** in 5CB monitored by the reflection wavelength at the PSS<sub>310nm</sub>.



**Figure S10.** Cyclical reflection wavelength of 1.80 mol% of (*R,R*)-**1** in 5CB as the cell was repeatedly irradiated with UV light (310 nm) and visible light (630 nm).

#### 4. Copies of NMR spectra:

